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STUDY OF COMMERCIAL CHEMICAL ADDITIVES FOR CEMENTATION OF RADIOACTIVE WASTE

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ABSTRACT

In this research it has been studied the effects of chemical additives (admixtures) in the cementation process of radioactive wastes, which are used to improve the properties of waste cementation process, both of the paste and of the solidified product. However there are a large variety of these materials that are frequently changed or taken out of the market, then it is essential to know the commercially available materials and their effects. The tests were carried out with a solution simulating the evaporator concentrate waste coming from PWR nuclear reactors. It was cemented using two formulations, A and B, incorporating higher or lower amount of waste, respectively. It was added chemical admixtures from two manufacturers (S and H), which were: accelerators, set retarders and superplasticizers. The experiments were organized by a factorial design 23. The measured parameters were the viscosity, the setting time, the paste and product density and the compressive strength. In this study we performed comparative analyzes of the results of compressive strength at age of 28 and 90 days and between the densities of the samples at the same ages.The compressive strength test at age of 28 days is considered a parameter essential issues related to security handling, transport and storage of cemented waste product. The results showed that the addition of accelerators improved the compressive strength of the cemented product, but presented lower values density products.

1. INTRODUCTION

The nuclear-power is responsible for about 17% of world electricity needs. This percentage tends to increase with the construction of new plants, mainly in developing countries (China, India and others). It is a clean energy supply that does not emit gases responsible for the increase of global warming neither other toxic products. Nuclear power plants occupy relatively small areas and can be installed close to the consumer centers which, reducing the cost of energy distribution. Additionally they are independent on climatic factors for their operation [1].

Nuclear power plant operation generates different in wastes that are classified as radioactive wastes when they have contaminants in amounts that may bring potential negative impact on human health and the environment and, them, should be properly managed. The treatment consists of volume reduction, followed by solidification and / or packaging and to repository, aiming to ensure the protection of human being and the environment of possible negative impacts. The reduction of the waste generation and its secure storage are targets of nuclear industry [2].

In Brazil, there are currently two nuclear power plant with PWRs (Pressurized Water Reactor), which use enriched uranium and light water as coolant. Most of the wastes generated by these facilities are classified as intermediate level of radiation and this liquid ones should be solidified, using cement or other material, in order to prevent or hinder the release of contaminants from the waste to the environment during storage, transport and disposal, and also to ensure stability and the durability. In view of the multi-barrier concept for the repository, the final waste product is the considered the first barrier having the function of retaining radioactive contaminants [3].

The cemented waste product should meet three basic acceptance criteria to ensure safe handling in subsequent stages of the radioactive waste management until to disposal in repositories, which are: permeability, stability and mechanical strength. These criteria can be evaluated by measuring some parameters of the pastes: the density, the viscosity and the setting time, and the product compressive strength. [4].

In PWRs the fission reaction are controlled by adding boric acid to the primary circuit water and by inserting control rods in the reactor vessel, both absorb neutrons and consequently the reactions are controlled in the required levels. The waste generated by this operation is water with boron, which is treated in the evaporator to reduce the volume, producing the concentrate with approximately 12.5% of boric acid, being and that constitutes the largest volume of liquid waste generated in nuclear power plants with PWRs [5].

To cementing these wastes is not simple, due to the acidity of the wastes and the action of borate ion on the cement that retards its setting time strongly. To improve the process conditions and the physical and chemical properties of the waste product are used chemical and minerals additives. The cementation of radioactive waste using different chemical additives is in continues development, in order to improve the characteristics of the cemented waste product to meet the increasing quality requirements set by the standards. The additive industry development requires constant updating, once new products come on the market, but these cannot be used indiscriminately, needing some experiments to evaluate their effects on the waste product [6].

The main objective of this paper was to verify the performance of commercial chemical additives (accelerators, set retarders and superplasticizers) in the cementation process of the concentrate from the evaporator by comparing the results of density and compressive strength test of specimens at age of 28 days and 90 days. The compressive strength test at age of 28 days is considered a key safe parameter related to the handling, transport and storage of cemented waste product.

2. EXPERIMENTAL

2.1. Materials

Cement. It was used Portland cement CP V-ARI a high-early-strength cement whose the main characteristic is to provide high compressive strength values at an early period, usually a week or less. The development of high early strength is achieved by using a different dosage of limestone and clay in the production of clinker, as well as by the finer grinding of the cement, so that, when reacting with water, it faster reaches high resistances.

Microsilica. It is a by-product of silicon metal, iron silicon and other iron alloys, and it consists of very fine particles of silica, forming a fine powder whose colors vary according to its origin. It used in the proportion of 10% related to the weight of cement, here called dry mixture.

Accelerators. They reduces the setting time of the cement mixtures (paste, mortar and concrete), which normally cause an increase in the compressive strength at low temperatures and reduce demolding time

Set retarders. They slow the hydration process of the cement mixtures, and consequently the setting time, maintaining the workability at high temperatures, increasing the compressive strength at older ages and expanding the application time.

Superplasticizers. They provide high resistance to the cemented products in the early ages (24 hours), making the mixture more fluid with high workability. Due to the reduction of the capillarity, the cemented product becomes more waterproof, durable and resistant.

Simulated waste. It was prepared a solution to simulate the concentrate from the evaporation process. The concentration of boric acid in the solution was approximately 12.5%.

Formulations. It was prepared two formulations of the pastes (A and B). The Formulation A contains the lowest quantity of cement and the greaterst quantity of waste, contrasting the Formulation B, which contains more cement and less waste.

Manufacturers. Two manufacturers of these chemical additives were selected for this work (S and H).

Dejar dos líneas libres antes y solo una después de cada título secundario. Ellos deberán estar alineados a la izquierda y numerados como se ilustra en este ejemplo.

2.2. Experimental Planning

The chemical additives (accelerators, set retarders and superplasticizers) were separately tested. For each one the experiments were organized by planning factorial 2^3 with replicates. The variables (or factors) studied were: manufacturers (H and S), quantities (the minimum and maximum ones specified by the manufacturers) and formulations of the pastes (A and B). The factors were evaluated at two levels: low (-) and high (+). Generally, when the factor is quantitative, the level below was that of lowest value, while the high level was the highest value. In the case of qualitative factors such as the manufacturer, they were chosen arbitrarily.

The experiments were randomly performed so that the effects of external factors did not influence the evaluation of the results. Admixtures called “Blank” were prepared without any additive, also in duplicate. A total of 52 batches were carried out, included the blank mixtures and eight experiments in duplicate of each admixtures under conditions as homogeneous as possible. The experiments were organized according to Table 1.

Table 1. Planning factorial 2^3 for the experiments with chemical additives.

Test	Variable		
	Formulation*	Quantity additive	Manufacturer**
1	-	-	-
2	-	-	+
3	-	+	-
4	-	+	+
5	+	-	-
6	+	-	+
7	+	+	-
8	+	+	+

* A (-) B (+)
** S (-) H (+)

2.3. Preparation of the Cement Pastes and Samples

It was prepared two formulations of the pastes (A and B). The Formulation A contains a lower quantity of cement and greater quantity of waste, contrasting the Formulation B, which contains more cement and less waste.

The dry mixture was prepared with Portland cement CP V-ARI and microsilica in the proportion of 10% of the cement weight. Then the simulated waste is neutralized with calcium hydroxide and mixed with the dry mixture. During the mixture process the admixture was added, producing homogeneous pastes. After that the samples were molded in metal cylinders (diameter of 5cm and 10cm in height), illustrated in Figure 1. For each batch eight (08) samples were molded. Were also made eight samples in metallic molds with 5cm in diameter and 10cm in height, for testing of compressive strength at ages of 28 and 90 days and the density of the samples.

Figure 1. Mixer and cement paste containing simulated waste and chemical additive

2.4. Tests

2.4.1. Determination of compressive strength

This test consists of subjecting the sample to the growing tension, continuing until its deformation or break, it is one of the most important mechanical characteristics (Figure 2). It is related to the degree of compression and the stiffness of the product. Therefore, products that are less minimum porous and more homogeneous, cracks and fissures tend to present more resistance to compression. The product must be resistant to impacts that may occur, especially during handling and transport [7].

The compressive strength test was performed in accordance of the Brazilian standard NBR 7215 [8]. For this test were used cylindrical specimens, with 5 cm in diameter and 10 cm height, with age of 28 and 90 days.

Figure 2. Tests compression strength.

2.4.2. Determination of density

Density is the ratio of mass to volume occupied. The density of the product is related to its stiffness. The more dense the product, it present less porosity, being therefore more resistant. The minimum acceptable density will depend on the type of product that will be disposed [9]. The density is calculated according to equation 1:

$$\rho = \frac{1,27 \times m}{D^2 \times H} \times 10^3 \qquad (1)$$

with: (ρ) density of sample (kg / m³); (m) mass of sample (g); (D) average diameter measurement of the sample (cm); (H) average height of the sample (cm);

3. RESULTS

The results are presented and analyzed separately for each type of additive, using the statistical software MINITAB ®.

3.1. Results using Superplasticizer

The results obtained from compressive strength and density with at age of 28 and 90 days test in products with superplasticizer are shown in Table 2.

Table 2. Superplasticizer - Result of compressive strength and density with at age of 28 and 90 days.

Tests	Variable*			Superplasticizer			
	F	Q	M	RC** 28 days (Mpa)	Density 28 days (g.mL^{-1})	RC** 90 days (Mpa)	Density 90 days (g.mL^{-1})
Blank A (-)				14,73 ± 0,31	1,63 ± 0,07	14,85 ± 0,02	1,62 ± 1,70
1	-	-	-	14,80 ± 0,02	1,60 ± 3,11	17,94 ± 0,29	1,57 ± 5,16
2	-	-	+	14,89 ± 0,18	1,63 ± 4,45	17,00 ± 0,38	1,61 ± 0,64
3	-	+	-	13,00 ± 0,14	1,62 ± 3,11	12,92 ± 0,05	1,62 ± 3,61
4	-	+	+	15,5 ±0,05	1,64 ± 0,35	16,67 ± 0,53	1,63 ± 0,57
Blank B (+)				24,28 ± 0,14	1,69 ± 2,05	22,82 ± 0,02	1,65 ± 4,38
5	+	-	-	7,14 ± 0,29	1,68 ± 0,85	6,74 ± 0,12	1,67 ± 0,07
6	+	-	+	18,38 ± 0,20	1,67 ±0,49	16,64 ± 0,10	1,63 ± 0,78
7	+	+	-	14,83 ± 0,43	1,64 ± 0,85	18,40 ± 0,60	1,64 ± 1,98
8	+	+	+	18,52 ± 0,06	1,69 ±0,49	18,08 ± 0,72	1,66 ±0,85

* F: Formulation; Q: Quantity; M: Manufacturer;
** RC: compressive strength

For the samples of age of 28 days and 90 days the higher compressive strength and density were obtained using the formulation B. The highest value of compressive strength was obtained by the Blank with formulation B and the lowest value was obtained with formulation B with less quantity the superplasticizer of manufacturer S.

The Formulation B (+) showed very significant effect on the density at age of 28 days and 90 days (Figure 7). The addition of superplasticizer of the Manufacturer H (+) resulted in higher values of density at age of 28 days and 90 days. A quantity of superplasticizer was not significant in the density of the samples with at age of 28 days, but at age of 90 days higher density were obtained with the addition of a larger amount of superplasticizer.

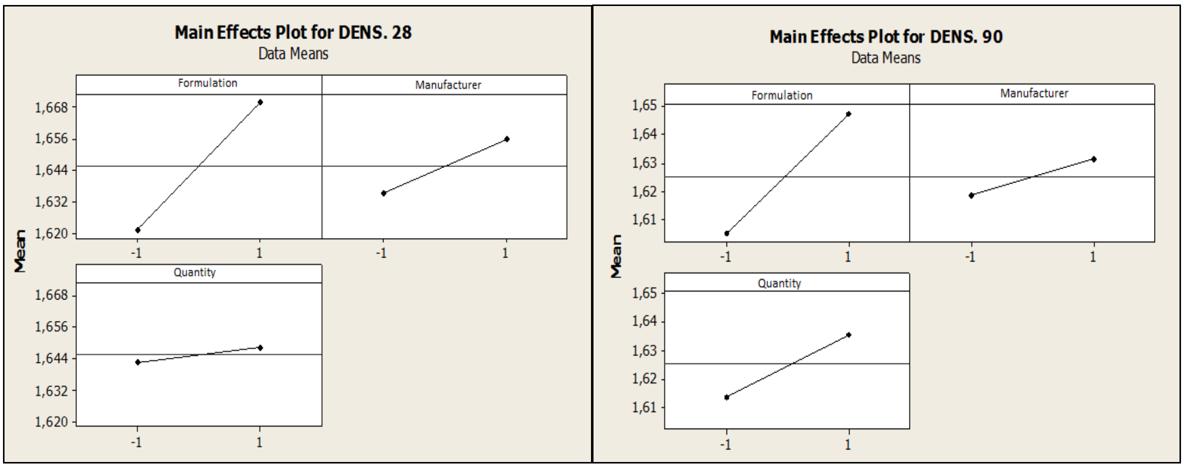

Figure 7. Superplasticizer - Effect of each variable (factor) in density at age of 28 days and 90 days.

The studies to analyze the effect of the superplasticizer on the compressive strength at age of 28 days and 90 days are represented in the Figure 8. In the samples, which containing the largest quantity of superplasticizer from the manufacturer H, there was a positive effect on the compressive strength. The formulation did not effect on the compressive strength at age of 28 days. However, for samples at age of 90 days, the highest values the compressive strength were obtained using the Formulation B (+).

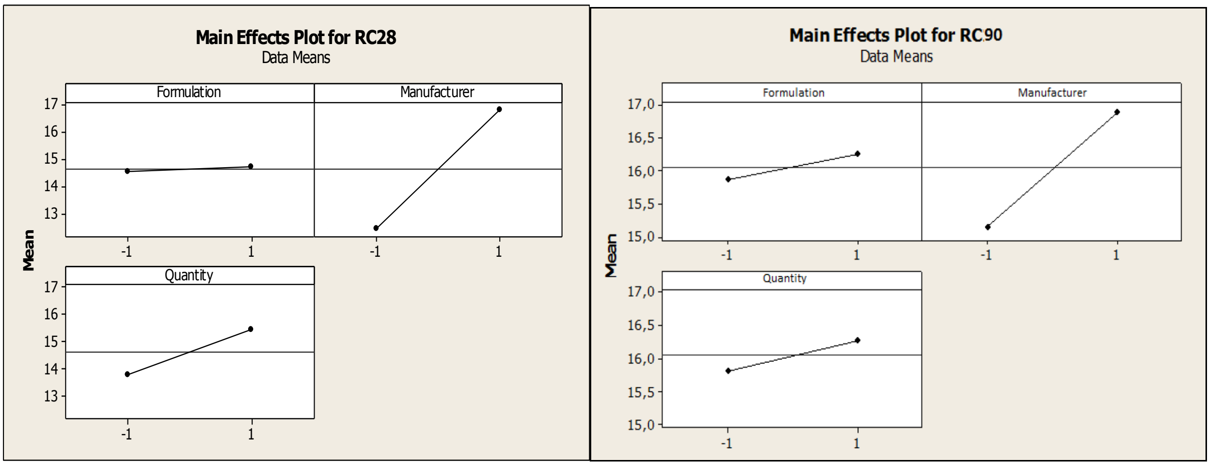

Figure 8. Superplasticizer - Effect of each variable (factor) in compressive strength at age of 28 and 90 days.

3.2. Results using set retarders

The results obtained of compressive strength and density with at age of 28 and 90 days test in products with set retarders are shown in Table 3.

Table 3. Set retarders - Results of compressive strength and density with at age of 28 and 90 days.

Tests	Variable*			Set retarders			
	F	Q	M	RC** 28 days (Mpa)	Density 28 days (g.mL^{-1})	RC** 90 days (Mpa)	Density 90 days (g.mL^{-1})
Blank A (-)				14,73 ± 0,31	1,63 ± 0,07	14,85 ± 0,02	1,62 ± 1,70
1	-	-	-	14,24 ± 0,12	1,61 ± 2,12	20,35 ± 0,00	1,58 ± 4,74
2	-	-	+	12,45 ± 0,02	1,61 ± 5,02	18,12 ± 0,41	1,60 ± 3,82
3	-	+	-	13,22 ± 0,10	1,64 ± 0,99	14,69 ± 0,07	1,62 ± 0,57
4	-	+	+	10,15 ± 0,04	1,60 ± 1,20	20,60 ± 0,00	1,64 ± 0,00
Blank B (+)				24,28 ± 0,14	1,69 ± 2,05	22,82 ± 0,02	1,65 ± 4,38
5	+	-	-	18,02 ± 0,58	1,65 ± 1,70	15,39 ± 0,95	1,61 ± 1,46
6	+	-	+	12,90 ± 0,35	1,68 ± 0,42	16,10 ± 0,65	1,58 ± 0,00
7	+	+	-	14,67 ± 0,07	1,64 ± 3,68	19,72 ± 0,73	1,62 ± 3,54
8	+	+	+	16,05 ± 0,05	1,66 ± 0,71	14,27 ±0,08	1,65 ± 0,57

* F: Formulation; Q: Quantity; M: Manufacturer;
** RC: compressive strength

For the samples at age of 28 days the lowest values of both density and compressive strength were obtained by using Formulation A (-) with higher amounts of set retarders from the manufacturer H (+), being this value lower than those for the Blanks. The highest values were obtained using the formulation B Blank (+).

The highest values compressive strength at age of 90 days, were also obtained with the blank test using formulation B and the smallest value using formulation B with the highest amount of retarder of the manufacturer H (+), the highest density at age of 90 days was obtained in the same situation. The lowest density value of 90 days was observed using formulation B with the smallest amount of retarder of manufacturer H. In general the addition of retarders has adversely affected the quantity of the products.

3.3. Results using Accelerators

The results of the test, compressive strength and density, in products prepared with accelerators are presented in Table 4.

The highest values of compression strength at age of 28 days were obtained using formulation B with a greater quantity of accelerator of manufacturer S (-) and the smallest value using the formulation A with the least amount of accelerator manufacturer H (+). This is because the formulation B contain higher amount of cement. The density values presented the same tendency.

The greatest results of compressive strength and density at age of 90 days were obtained with Blank products prepared with the formulation B. The lowest compressive strength was obtained with formulation B, the lowest amount of accelerator of manufacturer S, while the smallest density value was obtained using the formulation A with the largest amount of accelerator manufacturer H.

Table 4. Accelerators - Result of compressive strength and density with at age of 28 and 90 days

Tests	Variable*			Accelerators			
	F	Q	M	RC** 28 days (Mpa)	Density 28 days (g.mL^{-1})	RC** 90 days (Mpa)	Density 90 days (g.mL^{-1})
Blank A (-)				14,73 ± 0,31	1,63 ± 0,07	14,85 ± 0,02	1,62 ± 1,70
1	-	-	-	17,00 ±0,18	1,59 ± 3,32	20,67 ± 0,19	1,57 ± 2,62
2	-	-	+	14,59 ± 0,28	1,61 ± 1,77	16,06 ± 0,38	1,59 ± 1,34
3	-	+	-	17,33 ± 0,16	1,6 ± 1,91	15,96 ± 0,41	1,57 ± 3,68
4	-	+	+	15,58 ± 0,18	1,6 ± 0,14	14,47 ± 0,42	1,56 ± 2,47
Blank B (+)				24,28 ± 0,14	1,69 ± 2,05	22,82 ± 0,02	1,65 ± 4,38
5	+	-	-	19,09 ± 0,21	1,65 ± 0,28	13,23 ± 0,04	1,62 ± 0,99
6	+	-	+	20,52 ± 0,42	1,66 ± 0,28	18,49 ± 0,67	1,63 ± 1,56
7	+	+	-	25,49 ± 0,15	1,63 ± 0,64	16,26 ± 0,49	1,61 ± 2,19
8	+	+	+	15,09 ± 0,66	1,62 ± 4,17	15,9 ± 0,04	1,61 ± 4,24

* F: Formulation; Q: Quantity; M: Manufacturer;
** RC: compressive strength

The use of the accelerator presented lower values the densities ate age of 28 days for the two formulations. The density at age of 90 days was higher with the addition of superplasticizer, for both formulations (A and B).

4. CONCLUSIONS

This paper studied the influence of chemical additives in the process of cementing waste concentrate evaporator, from PWR. Chemical additives were tested: set retarder, accelerator and superplasticizer from two different manufacturers (S and H). Two cementation formulations, A and B, are used; being A more efficient than B, since higher amount of waste is incorporated generating a lower number of packages, consequently lower costs and decrease of the volume to be stored.

Higher values of densities were obtained using the additive superplasticizer, since better workability, thereby reducing the number and the size of pores.

The standard CNEN-NN-6.09 establishes acceptance criteria for disposal of radioactive wastes with low and intermediate radiation level, in which the compressive strength for products at age of 28 days must be greater than or equal to 10 MPa. Then all the products were approved in this parameter, with the exception of test number 5 (lower quantity SF Manufacturer S) [10].

The use of superplasticizer allows the cementation using simpler mixture systems and less expensive. In addition the pastes are more homogeneous, and the products have higher quality. In general, the use of superplasticizer showed better results.

Some results were not expected, in accordance of the manufacturer specification. The first hypothesis is that these chemical additives, typically prepared for use in the construction industry, when used associated with the wastes, reacted differently with the cement. The second hypothesis is that the quantities specified by the manufacturer may be above or below the values required for the expected effects.

Analyzing the data obtained in order to continue the study important to perform further tests with lower, intermediate and higher amounts of chemical additives than the range specified by each manufacturer by this way can select those that provide the best products and make an economic evaluation of their use.

The industries of chemical additives produce a multitude of products for cement and concrete, changing their formulas and details of additives, for this reason it is essential maintain these studies.

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6. REFERENCES

1. “ELETRONUCLEAR: Panorama da energia nuclear no mundo,” http://www.eletronuclear.gov.br (2014).

2. COMISSÃO NACIONAL DE ENERGIA NUCLEAR. *Glossário de Segurança Nuclear.* CNEN. Rio de Janeiro, Brasil, 2011.

3. TELLO, C. C. O. *Efetividade das bentonitas na retenção de césio em produtos de rejeitos cimentados*. Tese (Doutorado em Engenharia Química), Faculdade de Engenharia Química, Universidade Estadual de Campinas, Campinas, Brasil, 2001.

4. FREIRE, C. B.; TELLO, C. C. O. Repositórios. Revista Brasileira de Pesquisa e Desenvolvimento. *Research and Development Brazilian Journal*. v. 9, n. 3, 2007.

5. 3. ALVES, L. J. L. *Seleção de uma formulação para tratamento de rejeitos de reator do tipo PWR por cimentação*. Dissertação de Mestrado do programa de Pós-graduação em Ciências e Técnicas Nucleares da Escola de Engenharia da Universidade Federal de Minas Gerais, Belo Horizonte, Brasil, 2001.

6. INTERNATIONAL ATOMIC ENERGY AGENCY. *Improved cement solidification of low and intermediate level radioactive waste.* Vienna: IAEA, Aug. 1993. 110p. (Technical reports series, 350).

7. DINIZ, P. S. *Estudo do ensaio de resistência à compressão para rejeitos tóxicos / radioativos tratados por cimentação, visando à qualificação / certificação de ensaios.* 1999, Tese (Mestrado em Ciências e técnicas Nucleares), Escola de Engenharia, Departamento de Engenharia nuclear, Universidade Federal de Minas Gerais, Belo Horizonte, Brasil, 1999.

8. ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. *ABNT-NBR 7215. Cimento Portland: Determinação da Resistência à compressão*.Rio de Janeiro, Brasil, 1996.

9. INTERNATIONAL ATOMIC ENERGY AGENCY. *Characterization of radioactive waste forms and packages*. Vienna: IAEA, 1987. 138p. (Technical reports series, 383).

10. COMISSÃO NACIONAL DE ENERGIA NUCLEAR. *Critérios de aceitação para deposição de rejeitos radioativos de baixo e médio nível de radiação*. CNEN-NN-6.09, Rio de Janeiro, Brasil, 2002.