1st Spanish National Conference on Advances in Materials Recycling and Eco – Energy
Madrid, 12-13 November 2009
S03-5

CEMENTED MATRICES USED IN THE STORAGE OF LOW AND MEDIUM RADIOACTIVE WASTE: SPANISH EXPERIENCE

S. Goñi[1], M.S. Hernández[1] y A. Guerrero[1]

[1]Instituto de Ciencias de la Construcción "Eduardo Torroja" (ICCET) Consejo Superior de Investigaciones Científicas (CSIC). 28033 Madrid, Spain

---

Abstract

Within RECIMAT 09 supply that takes into account scientific and technological sectors in relation to different types of wastes, including radioactive, the objective of this work is to present a small part of an extensive research program supported by ENRESA (the official agency for the management of radioactive wastes in Spain). Cement based materials are being used generally as a solidification systems of wastes, and particularly, in the case of Spain, for low and medium radioactive wastes management in El Cabril repository (Córdoba). One of the aims of this investigation is to study the durability of some cement materials used in this repository, like compact cement matrices formed by ordinary Portland cement (OPC) and Boiling Water Reactor (BWR) simulated sulphate liquid waste: A (0,68 M) and B (2,05 M), as well as the pozzolanic backfilling mortars of the repository concrete containers. Leaching test of the matrices by means of the American National Standard (ANSI/ANS-16.1.19869); Köch-Steinegger durability test and ASTM C452-88 standardized test with the backfilling mortar of the repository are the most important tests carried out with these cement based materials. To accelerate the attack process, all testing processes have been performed at 40º C.

Keywords: radioactive liquid waste, cement based-materials, durability.

INTRODUCTION

The risk of radioactive wastes is due above all to the long time they need to eliminate the radioactivity levels and to become stable wastes. That is why their management is so important. It is based on stabilisation and solidification (1) processes, being afterwards stored for a long term, where the isolation from the biosphere can be ensured.

In the stabilization/solidification systems, for the immobilization and solidification of low and medium radioactive wastes (LRW and MRW), different kinds of cementitious materials have been employed; the ordinary Portland cement (OPC) is the most frequently used (2, 3), because it presents a lot of advantages.

In Spain, the storage place for low and medium level radioactive wastes was designed to ensure their confining during 300 years, which is the time calculated to exhaust their radioactive emission levels. This storage, called "El Cabril", is situated in the mountains of Cordoba. It is constituted, mainly; by three superpose engineering barriers of isolation (Fig. 1).

Figure 1. Storage Place Design for Low and Medium Level Radioactive Wastes

In the first one, is where the cement plays the most important role as a waste confining material. In one hand, on the immobilization matrices the cement is an inner part of them, mixed with the wastes; in other hand, in the storage container, as a part of a specific mortar, named "Backfilling Mortar". This mortar will immobilize the wastes in the container.

According to the recommendations of Scientific European Committees, one can say that although the main objective of the matrix is to immobilize the radioactive species, however the great amount of non radioactive material, that the wastes take gets, they can interact with the concrete, altering the durability of the group. Based on this, the studies that here shown up, they allow us to evaluate if the matrices and design immobilization system is durable against the attack of sulphate ions, ions of great aggressiveness for the cement-based materials.

EXPERIMENTAL

As raw materials we are used:

- CEM I-35 Ordinary Portland Cement.
- Backfilling Mortar: pozzolanic Portland cement type IV-35A, sand, additive and water.
- Aggressive dissolution with different sulphate ions concentrations: 0,68M for dissolution A and y, 2,05M for dissolution B.

The study methodology carries out for the study of cemented matrices used for storage of LLW and MLW, keeps in mind, among others, the following tests:

- Leaching Attack: is one of the best methods to evaluate the efficiency of a material as a waste immobilization system. In this work, a matrix has being tested, in which the simulated liquid wastes is evaporator concentrate solutions synthesized in the laboratory: Boiling Water Reactor (BWR). Matrix was fabricated by mixing the BWR solutions with a kind of ordinary Portland cement. The leaching test was the ANSI/ANS-16.1-1986 (*4)*.
- Durability Test or microstructural Stability of a specific backfilling mortar versus the chemicals attack of a specific simulated radioactive liquid wastes (SRLW), mixture of sulphate, chloride and borate. The study was carried out according to the ***Köch-Steinegger*** (6) test at 40ºC during a period of 365 days
- Study about the Dimensional Stability of a specific backfilling mortar, which is used in the concrete containers for the storage. To determine the dimensional stability, specifically, the expansion associated to the sulphate attack coming from cemented-based matrices (5), a Standarized Test, the "ASTM C452-88" has been used (7). In this case two modifications have been made to the test, always simulating drastic conditions for the mortar attack: Substitution of the water by aggressive solutions: simulated sulphate liquid waste: A (0,68 M in sulphate ions) and B (2,05 M in sulphate ions).

To continue, here are some of the results obtained in the Institute Construction Sciences "Eduardo Torroja", with these kinds of experiments

RESULTS AND DISCUSSION

1. *Leaching Test: Efficiency of Ceemnted Matrices and Characterization*

In this work, a matrix, type BWR, has been investigated by mean of the leaching process to evaluate, in general, the capability of migration of any ionic species, radioactive or no, to the inside of confining matrices. The experiment was carried up at two temperatures: 20ºC and 40ºC, to study the process in a quick way.

It has been employed the ANSI/ANS-16.1-1986. This test gives, in a short period of time enough data, which treated with an adequate mathematical way, permit to obtain a series of parameters characteristics for every matrix. From them it is possible to obtain a classification of the material that indicates its efficiency to confine a specific ion. That efficiency is determined by the "Leachability Index" (L).

As far as the leachability index "*L*" is concerned, it is a normalization factor, which is related to the specific material tested:

$$L = \log (\beta / D_e)$$

where β is a defined constant (1.0 cm^2/s). "*L*" also depends on the leaching conditions and the leachant renewal schedule. The mean leachability index (*L*) is used to catalogue the efficiency of a matrix material to solidify a waste, being the value of 6 the threshold to accept a given matrix as adequate for the immobilization of nuclear wastes.

Following the specifications of ANSI/ANS-16.1-1986, the leachant utilized was demineralized water. The leachate was replaced periodically after intervals of static leaching, for cumulative leach times of 0,08d; 0,3d; 1d; 2d; 3d; 4d; 5d; 19d; 47d and 90 days, being the rate of a function of the leachant renewal frequency.

A different leach times, we are analysed the follows ions: Na^+, K^+, Cs^+, Cl^-, Ca^{2+} y SO_4^{2-} in each leachate.

Other important parameter, is the effective diffusion coefficient (*D*e), which together the mean leachability index (L) for each leaching interval are given in Table 1, for the matrix studied at two temperatures.

Table 1. Leaching Test Results

Ion	L		D_e	
	20ºC	40ºC	20ºC	40ºC
Cs^+	6,8	6,7	1,7E-07	2,0E-07
Na^+	7,3	6,8	5,5E-08	1,7E-07
K^+	7,2	6,2	7,2E-08	6,3E-07
Cl^-	7,4	6,7	4,5E-08	1,8E-07
Ca^{2+}	9,1	8,9	1,2E-09	2,0E-09
SO_4^{2-}	9,5	8,9	2,4E-10	1,1E-09

The mean leachability index (L) for Ca^{2+} y SO_4^{2-} ions are higher that the rest of the ions. This result is similar to the value of D_e. In all the cases, the mean leachability index (*L*), are higher that 6, consequently, this matrix at 20ºC and 40ºC, can be catalogued as efficient materials for immobilizing cesium and others ions from nuclear wastes.

2. *Durability Test: Koch-Steinegger Test*

The present work deals with the durability of a backfilling pozzolanic cement mortar, in a specific simulated radioactive liquid waste, with high content in sulphate ions. The study was carried out at 40ºC during a period of 365 days.

The backfilling mortar was prepared at a sand to cement ratio of 1.75 and de-ionized water to cement ratio of 0.4. an organic additive was used at an additive to cement ratio of 0.012. After mixing, different portions were molded into 1x1x6 cm prisms specimens and compacted by vibration. After curing period, gropus of 6 samples were immersed in the simulated radioactive liquid wastes (SRLW) with high amount of sulphate ions. The samples were stored in sealed plastic bottles at the temperature of 40ºC for 365 days (Fig. 2).

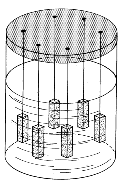

Figure 2. Disposal of Köch-Steinegger Test

Similar of six samples were stored in de-ionized water as reference.The durability was evaluated from the changes in flexural strength of the backfilling mortars after the immersion in the SRLW compared with those obtained in similar samples immersed in de-ionized water.

According to the Köch-Steineggger test, the criterion to classify a material as durable in a specific aggressive medium is that the relative strength of a aggressive-solution-stored samples to water-stored ones should be higher than 0.7-0.8, In all the cases the relative strength is above the aforementioned threshold (Fig. 3b).

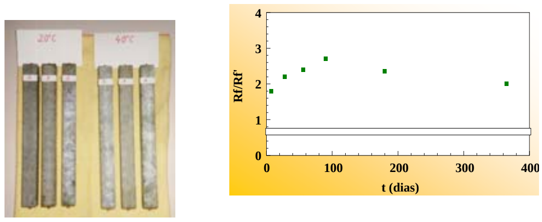

Figure 3. Mechanical Strength and Corrosion Index versus time.

The samples immersed in the SRLW for 7 days had a flexural strength value considerable higher than that of samples immersed in de-ionized water, progressively increasing during 90 days of immersion. The flexural strength starts decreasing thereafter, but never reaches the values of the mortar in de-ionized water.

This results shown that this backfilling pozzolanic cement mortar has a good durability in this media at 40ºC during a period of 1 year.

3. *Dimensional Stability:* Standarized Test, the "ASTM C452-88".

This test was carried out during 1 year at 40ºC. So the expansion value was obtained by the methodology of the standard test ASTM C452-88, in three tpes of probes: some of them made with the backfilling mortar mix with water, other mixed with sulphate solution A and the others mixed with sulphate solution B. The accuracy of measure, done in four prismatic specimens of: 25,4x25,4x287 mm dimensions, was 0.001mm. (Fig. 4). The first measure, which will be the reference, was taken immediately after demolding the specimens. The following measures were obtained daily during the first 90 days and later every week until finishing the test. In this study we were carried out a modification to the ASTM, since established cycles of temperature to better study the behaviour of mortar. The cycle here presented is: 40ºC-20ºC-40ºC .

According to the consulted standarized date, the accepted expansion values are, at 14 days, around 0.02-0.04%, although in some concretes exposed to the effect ot alkaline sulphate, is even allowed a expansion value of 01-0.2% (8,9).

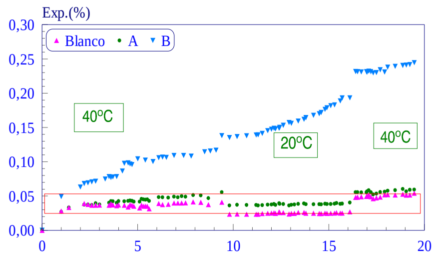

Figure 5. Relative Expansion versus time in the cycle: 40ºC-20ºC-40ºC

In Figure 5, it can be seen the expansion associated to the specimens fabricated with backfilling mortar with sulphate solution A (0.68M) and sulphate solution B (2.05M). The most important results are:

1. 40ºC: The stability is reach at 5days for the 3 samples. From this days, the sample A and the reference, do not experiments important expansion; however, in the case of sample B, this continues the expansion during 25 days, starting from those which it is stabilized in values around 0.1%. The rate of expansion, in the case of sample B, is 1,3 times higher that the sample A and the reference.
2. 40-20ºC: In this part of the cycle, it is observed a decreased of the expansion in the case of sample A and reference. However, the sample B, continues the expansion until 225 days, where it begins an stabilization plateau, around 0.2%.
3. 40-20-40ºC: It can be confirm the reversibility of the relative expansion in the case of sample A and referenda, reaches values around of 0,04%. The sample B, has an expansible growing profile, in values of 0,2-0,25%.

Therefore, the sample B exceeds the maximum value of 0,2%, allowed in attack by alkaline sulphates, according to some authors (12, 13). The expansion in the other two samples A and reference, it is very below this limit, toward 0,04%. This would suppose a better behaviour of these 2 materials in front of the expansion that B.

CONCLUSIONS

1. In all the cases, the mean leachability index (*L*), are higher that 6, consequently, this matrix at 20ºC and 40ºC, can be catalogued as efficient materials for immobilizing ions from nuclear wastes.
2. The results of durability shown that this backfilling pozzolanic cement mortar has a good durability in this media at 40ºC during a period of 1 year and in all the cases the relative strength is above the aforementioned threshold (0.7-0.8) at 56 days
3. Backfilling mortar can be considered as a dimensionally stable material when in mixed with a solution of (0,68M SO_4^{2-}); its relative expansion reaches values accepted by the standards test, between 0,04%. But in the case of a solution with a high amount of sulphate this mortar reaches higher values of expansion.

REFERENCES

1. Arce, R; Domínguez, R.; Mennini, S.; Morales, G.; Moreno, S.; Sainz, J.A. y Santa Olalla, J.; (1996), “El Medio Ambiente en España”, Cuadernos EOI. Escuela de Organización Industrial. Ediciones Mundi Prensa, ISBN 84-7114-615-0.
2. Glasser, F.P., Rahman, A.A.; Crawford, R.W.; McCulloch, C.E. and Angus, M.J. (1984), “Immobilization of Leaching Mechanisms of Radwastes in Cement-Matrices”, DOE, U.K. Report, Nº DOE/RW/84050.
3. Macphee, D.E. and Glasser, F.P., (1993), “Immobilization Science of Cement Systems”, Mat. Res. Soc. Bull. XVIII, pp. 66-71.
4. ANSI-ANS-16.1.1986, (1986), American National Standards Institute, “Measurement of the Leachability of Solidified Low-Level Radioactive Waste by a Short-Term Test Procedure”, American Nuclear Society, 555 North Kensington Avenue, Labrange Park, IL 60525.
5. Guerrero, A., (1997), “Confinamiento de Residuos: Estabilidad Microestructural de los Materiales Cementicios frente a los Iones Sulfato de las Matrices Inmovilizadoras de Residuos de Media y Baja Radiactividad”. Tesis Doctoral. Universidad Autónoma de Madrid.
6. Köch, A. and Steinegger, H. (1960). “A Rapid Test for Cements for Their Behaviour under Sulphate Attack”. Zement-Kalk-Gips, vol. 7, pp. 317-324.
7. Norma ASTM C452-88 (1986). “Standard Test Method for Potential Expansion of Portland Cement Mortars Exposed to Sulfate”, vol, 04.01 ASTM.
8. Norma ASTM C-1012-84 (1985). “Standard Test Method for Length Change of Hydraulic Cement Mortars Exposed to a Mixed Sodium and Magnesium Sulfate Solution”, vol, 04.01 ASTM.
9. Talero, R. (1989). “Los Cementos Portland de Moderada Resistencia Sulfática. Métodos Acelerados de Ensayos para Determinarla. Bases para su Caracterización y Control”. Monografía nº 399. IETcc.CSIC.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support by ENRESA (Empresa Nacional de Residuos, Sociedad Anónima) (Spain).