

Application of Electrical Fields in the Study of Concretes with respect to the Transport of Several Ionic Species Present in Radioactive Wastes: Characterisation and Decontamination.

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ABSTRACT

Cement based matrices are being increasingly used to confine toxic and radioactive wastes; therefore, determination of the diffusion coefficients of ionic contaminants becomes of strategic importance in order to characterise the system in relation to the release of ionic components of wastes. In this paper, a summary of the determination of steady-state diffusion coefficients of Cs, Sr, Co and Fe through concrete, as well as the extraction of these ions from cementitious matrixes, by an accelerated procedure based in the application of electrical fields (migration experiments), is presented. As a result, the application of electrical fields to contaminated structures arises as a new technique to extract radioactive ionic species from concrete, which allows the management of initially radioactive wastes as conventional ones, after declassification. This method of decontamination has been patented by ENRESA (Spanish Company for the Management of Radioactive Wastes) in association with the IETcc.

INTRODUCTION

Environmental compatibility of man-made materials will be an important issue of this century. This problem will be at stake in particular in the case of storage nuclear wastes. The cement-based systems are being increasingly used in the confinement of this kind of wastes due to several reasons. Among other, technology of cement has been experienced for long time and processing can be automatic, primary materials are cheap, composition is controlled independently of the source, the final matrix can be modified by adding mineral additions (fly ash, silica fume, blast furnace slags) in order to increase the confining ability, liquid wastes can be managed and it is not flammable. But the mainly reason arise from the own nature of cement that provides, in most of cases, chemical as well as physical immobilisation [1]. Prediction of the release rate of ionic wastes through the cement, determined by the diffusion coefficient of each species, is thus very important in the characterisation of the system in order to assure the confining ability of the system.

On the other hand, providing that the service life of nuclear power plants have to finish after a specified amount of years, it arises the need of managing a quite large volume of radioactive contaminated concrete, which, in most cases, was not taken into account when dimensioned the low and medium activity repository. Therefore, it would be of a great interest the decontamination of these structures in order to declassify the wastes as radioactive and manage them as conventional ones.

These two aims (characterisation and decontamination), can be considered by studying the movement of ions through concrete under the application of an electrical field.

Concerning the determination of diffusion coefficients, a large amount of research have been done to calculate diffusion coefficient of Cs⁺ in cement matrices, not only from leaching tests [2-7] but as well, from cell diffusion experiments [8-12]. More scarce are the work carried out about other contaminant ions [3,5,6,10,13,14,15]. All these referenced studies were based in natural diffusion tests, whose main disadvantage is that it is very time consuming and it is necessary a long time to obtain reliable data. Shortening of testing time to characterise concrete resistance to transport of several ions is the main improvement of the use of migration tests to calculate diffusion coefficients. At present, this method of acceleration is being used by a increasingly number of authors [16-28] but only applied to chloride ions. Recently, the authors presented results of steady-state diffusion coefficients of Cs, Sr, Co and Fe (that are common elements contained in low and medium level radioactive wastes), through concrete, which had been calculated by migration experiments, and their validation with natural diffusion tests [29]. A summary of the procedure and results will also be given in this paper.

Concerning the decontamination of concretes, the extraction of ions by application of electrical fields has been applied to the case of chloride ions. Chloride removal in concrete was first investigated in the seventies [30-31], and since then, the application of electrical fields to concrete, as non-destructive repair methods, has been increasingly used. However, no

references to the extraction of other contaminant ions has been reported in literature. In this paper, results of extraction of Cs^+ , Sr^{++} , Co^{++} and Fe^{+++} , in laboratory experiments are given, which qualify this method to be used in real structures.

EXPERIMENTAL

Materials

In order to determine the diffusion coefficient of Cs^+ , Sr^{++} , Co^{++} and Fe^{+++} in an accelerated way, specimens of concrete with a water/cement ratio of 0.4 were cast. They were demoulded after 24 hours of being cast and were cured during 28 days under water. Then, they were stored until testing time in a $Ca(OH)_2$ saturated solution.

In order to perform the decontamination experiments, mortar specimens of 75 mm diameter and 30 mm height were cast, and they were allowed to cure for 28 days in a chamber with a relative humidity of 95% before testing. The casting solution was 0.001 M in Cs^+ , Sr^{++} , Co^{++} and Fe^{+++} , added in the form of the chloride salt of the corresponding cation. The resulting concentration was (in percentage with respect to the total dry sample) of $1.077E-3$ for Cs^+ , $8.555E-4$ for Sr^{++} , $5.333E-4$ for Co^{++} and $3.888E-4$ for Fe^{+++} . The chemical analysis of the cement employed is shown in table 1 while table 2 contains the mix proportion of the concrete and mortar fabricated.

Table 1. Chemical analysis of the cement used

Parameter (%)											
L.I.	I.R.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Free CaO	Cl ⁻	Na ₂ O	K ₂ O
3.45	1.97	19.37	6.12	3.13	62.86	1.78	3.23	1.28	0.013	0.18	1.00

Table 2. Mix proportion of the matrixes fabricated

	Cement (Kg/m ³)	Sand (Kg/m ³)	Coarse Aggregate (Kg/m ³)	Ratio (w/c)	Casting solution
Concrete	380	771	1177	0.4	Water
	Ratio Cement/Sand	-----	-----	Ratio (w/c)	Casting solution
Mortar	1/3	-----	-----	0.5	0.001 M in Cs^+ , Sr^{++} , Co^{++} and Fe^{+++}

Techniques and Procedures

The arrangement and procedure used for the calculation of the diffusion coefficients through concrete by migration tests and in natural conditions was described extensively in [29]. Therefore, not all of the details will be reported here.

In order to decontaminate the mortar specimens, the device used was a migration cell, that is shown schematically in figure 1. The 30 mm thick disc was introduced between the two chambers (of about 350 cm³ each) were cathode (graphite) and anode (activated titanium) were placed, and both compartments were filled with distilled water. Three different voltage levels were applied, 12 V, 24 V and 60V during one month. Periodically during the experiment, concentration of the studied species, in both compartments, was monitored by taking aliquots of the solutions. The analytical technique for measuring the amount of Cs^+ was the spectrophotometry of atomic absorption, while Sr^{++} , Co^{++} and Fe^{+++} , concentrations were determined by means of a spectrophotometer IPC (Inductive Plasma Coupling).

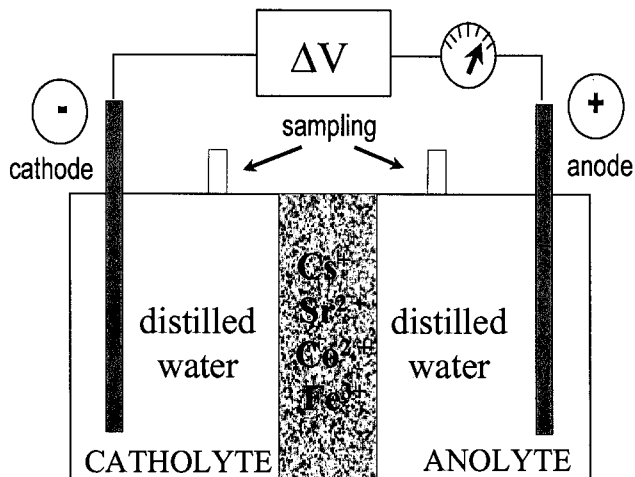


Fig 1: Experimental arrangement used for the extraction tests.

RESULTS AND DISCUSSION

Characterisation tests

Diffusion coefficients of Cs^+ , Sr^{++} , Co^{++} and Fe^{+++} obtained by migration and by natural diffusion tests, and calculated as described in [29] are given in table 3.

Table 3: Steady-state diffusion coefficients, D_s , obtained through steady state migration and diffusion tests.

	Diffusion coefficients, D_s , (m^2/s)	
	migration	diffusion
Cs^+	3.01E-12	1.18E-12
Sr^{++}	0.25E-14	1.32E-14
Co^{++}	3.70 E-17	4.73E-16
Fe^{+++}	2.57E-14	7.81E-16

Provided the scatter inherent of D_s determination even for the same test, it can be said from table 3, that for Cs^+ and Sr^{++} ions, there is enough good accordance between coefficients obtained from diffusion and migration tests. This was attributed to the fact that these ions move as single ionic species in the two kind of tests [29]. In the cases corresponding to Co^{++} and Fe^{+++} the accordance is not good. The explanation found as the most likely to occur was that, at the conditions of electrical potential and pH during the tests, the species that moved were different than those present during the natural diffusion tests [32].

Extraction tests

In figure 2 (a-d), it can be seen the evolution of the percentage extracted in for each one of the ions at the different drop of voltages applied. The same data are presented in a different way in figure 3 (a-c), where the percentage of the different species at the same potential applied has been plotted. In these figures, it can be seen that for the four ions, extraction takes place according a potential trend. That is to say, most of the amount is extracted in the first stages of the process.

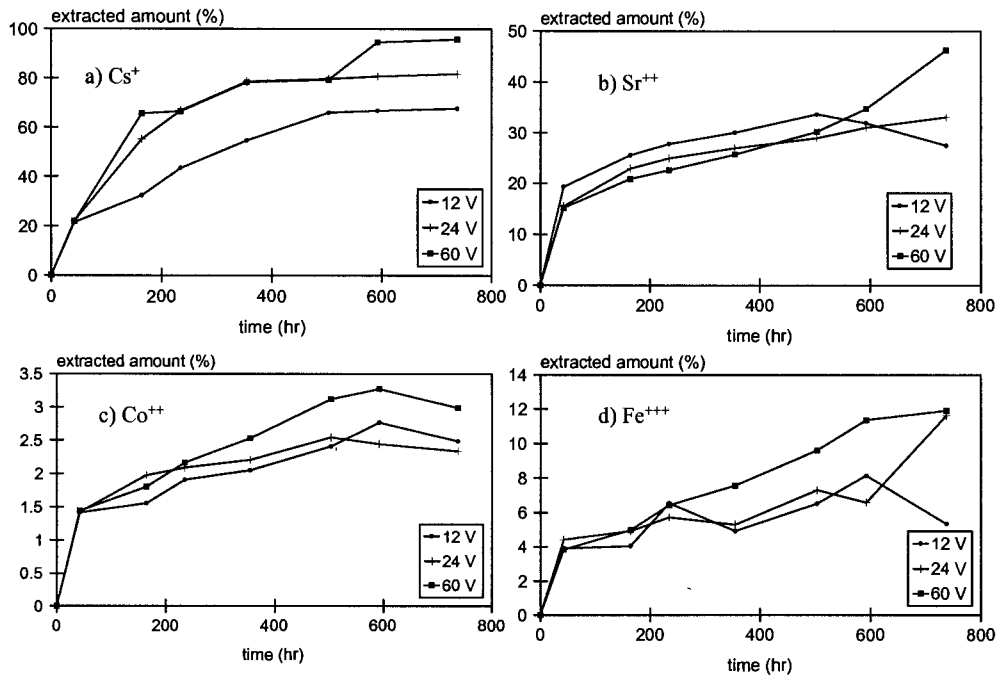


Fig 2 (a-d): Evolution of the percentages of Cs⁺, Sr⁺⁺, Co⁺⁺ and Fe⁺⁺⁺ extracted at the potentials applied.

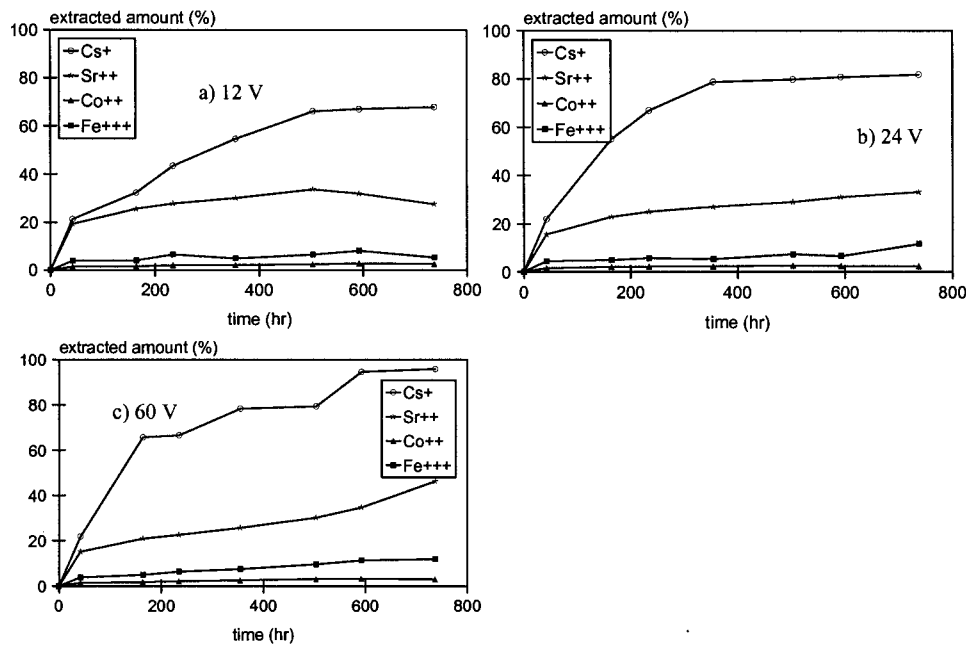


Fig 3 (a-c): Evolution of the percentages extracted at the 12, 24 and 60 V applied

From figures 2 and 3, it can be seen that Cs^+ ions can be extracted almost completely, and almost a 50% of the Sr^{++} has been eliminated. However, Co^{++} and Fe^{+++} are more difficult to extract, having decontaminated, when applying a voltage drop of 60V, the 3% and 12% respectively, after a month of experiment. This is due to the fact that these two ions precipitate inside the specimen (alkaline medium) in the form of hydroxides. This problem may be overcome by acidification of the matrix. Further experiments are being performed.

In figure 4, it has been represented the total percentage extracted after the tests, in function of the voltage applied. In it, it can be seen that for every species studied, the percentage extracted during a determined period, increases when increasing the voltage drop, according a potential trend.

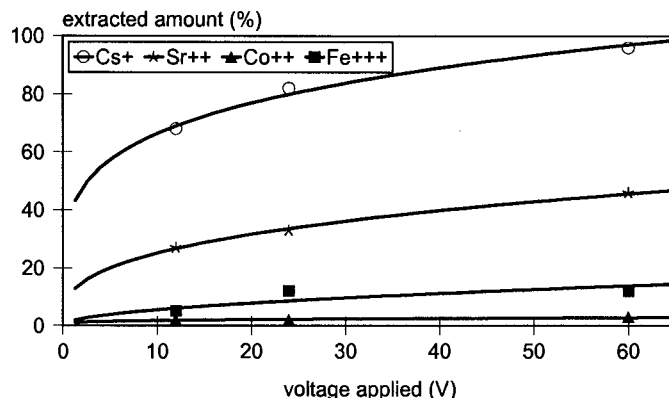


Fig 4: Extracted percentages, after a month of experiment, in function of the voltage applied

Another interesting point, that can be seen in figure 5 (a-d), is the fact that for Cs^+ and Sr^{++} , the amounts that were collected in the anodic compartment are negligible, (as it was expected, provided that they are species positively charged). However, in the case of Co^{++} , some of it appeared in the anolyte, while most of the extracted Fe^{+++} was collected in the positive side.

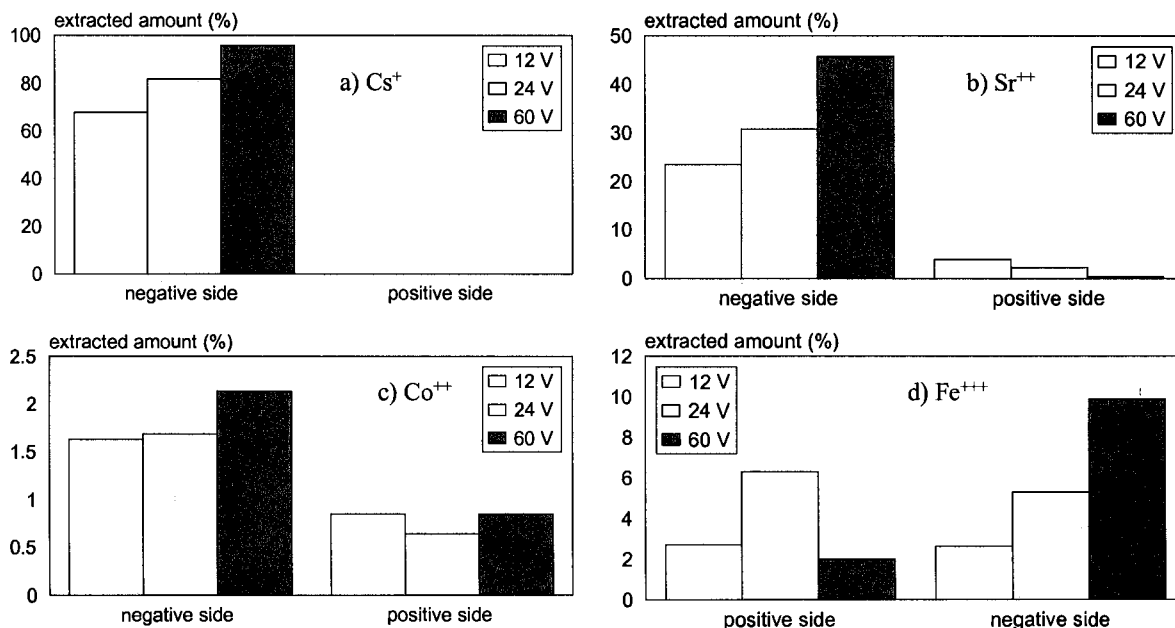


Fig 5 (a-d): Distribution of the percentages extracted, after the tests, between anolyte and catholyte

This behaviour has been attributed to the formation of the corresponding chloro-complexes $[\text{CoCl}_4]^{2-}$ and $[\text{FeCl}_4]^{2-}$ [32], whose negative charge is not attracted towards the cathode. In the case of cobalt, this is in agreement with the smaller diffusion coefficient found from migration tests in comparison with natural diffusion (see table 3), as long as the amount of cobalt that is really able to migrate to the negative compartment is smaller than the initial nominal concentration. In the case of Fe III, at the potentials operating during the test, the Fe^{+++} reduces to Fe^{++} [33], which is able to form the complex compound. This behaviour of the iron ions had been previously detected in characterisation tests described in [29], in which it was necessary to fill the cathodic chamber with the iron solution in order to notice the migration of these ions.

As a result, it is necessary to point out that each species behaves in a different way when submitted to the electrical field, and not always in the same way than in "natural conditions". Therefore, although the extraction of ionic species seems feasible by applying electrical fields (this method of decontamination has been patented by ENRESA (Spanish Company for the Management of Radioactive Wastes) in association with the IETcc), it remains the optimisation of operational variables which could make profitable the generalization of the technology.

CONCLUSIONS

From present study, it can be concluded that migration is a reliable and fast method to calculate diffusion coefficients of ions which move as single ionic species, such as Cs and Sr. The shortening of the testing time is particularly interesting when working with radioactive species. However, for ions such as Co and Fe, whose amount or type of species that move are different during migration and natural diffusion conditions, the accordance between coefficients is not so good.

Concerning the decontamination, it has also to be taken into account that each radioactive species behaves in a different way when submitted to the electrical field. Therefore, it is necessary to study the behaviour of the contaminant ions present in the structure to be treated, in order to determine whether the species involved during the process, are the same than those in natural conditions, and overcome all of the problems eventually detected. As a result, the application of electrical fields to contaminated structures may be used to extract radioactive ions from concrete.

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REFERENCES

1. MacPhee, D.E.; Glasser, F.P.: "Immobilization science of cement systems". MRS Bulletin; pp 66-71, March, 1993.
2. Morcos, N.; Dayal, R; Weiss, A.J.: NUREG/CR-2617, April, 1982.
3. Glasser, F.P.; McCullough, C. (Eds.): "Characterisation of radioactive waste forms, Progress Report EUR 11354 EN, 1986.
4. Smith, D.L.G.; Green, T.H. (Eds.): "Characterisation of radioactive waste forms, Vol 1&2, Progress Report, CEC Luxembourg, 1988.
5. Fuhrmann, M; Pietrzak, R.; Heiser III, J.; Franz, E.M.; Colombo, P.: "The effects of temperature on the leaching behaviour of cement waste forms- The cement/sodium sulfate system." Materials Research Society Symposium Proceedings., pp 75-80; Volume 176, Boston, Massachusetts, USA, November 27-30, 1989.
6. Seveque, J.L., de Cayeux, M.D.; Elert, M.; Nougier, H.: "Mathematical modelling of radioactive waste leaching". Cement and Concrete Research, Vol 22, pp 477-488, 1992.
7. Goñi, S.; Hernández, M.S.; Guerrero, A; Lorenzo, M.P.: " Materiales base cemento y sus características confinadoras de residuos líquidos sumulados de media y baja radiactividad. II. Lixiviación del ión cesio". Actas del III congreso internacional de química de la ANQUE. Puerto de la Cruz, Tenerife, España, diciembre, 1994.
8. Atkinson, A., Nickerson, A. K.: "The diffusion of ions through water-saturated cement". Journal of Materials Science, 19, pp 3068-307, (1984).
9. Takashi Nishi, Osamu Kuriyama, Masami Matsuda, Koichi Chino, Makoto Kikuchi: "Porosity and ion diffusivity of latex modified cement" Materials Research Society Symposium Proceedings. Volume 176, pp 109-114, Boston, Massachusetts, USA, November 27-30, 1989.

10. Atkinson, A.; Claisse, P.A.; Harris, A.W.; Nickerson, A.K.: "Mass transfer in water saturated concretes." *Materials Research Society Symposium Proceedings.*, pp 741-749; Volume 176, Boston, Massachusetts, USA, November 27-30, 1989.
11. Roy, D.M.; Kumar, A.; Rhodes, J.P.: "Diffusion of chloride and Cesium ions in Portland cement pastes and mortars containing blast furnace slag and fly ash"; SP 91-70 .
12. Revertegat, E; Richet, C; Gégout, P.: " Effect of pH on the durability of cement pastes". *Cement and Concrete Research*, Vol 22, pp 259-272, 1992.
13. De la Huebra, A.G.; Murillo, R.; Fabrellas, B.; Almodovar, A.; Romero, N.: "Caracterización físico-química de residuos de baja y media radiactividad". *Segundas Jornadas de I+D en la gestión de residuos radiactivos de ENRESA, España . Vol I, Junio, 1995.*
14. Ohnuki, T; Robertson, D.E.: "Migration of anionic species of radioactive cobalt through soil." *Materials Research Society Symposium Proceedings.*, pp 615-622; Volume 176, Boston, Massachusetts, USA, November 27-30, 1989.
15. Zamorani, E.: "Deeds and misdeeds of cement composites in waste management". *Cement and Concrete Research*, Vol 22, pp 359-367, 1992.
16. Andrade, C.: "Calculation of chloride diffusion coefficients in concrete from ionic migration measurements". *Cement and Concrete Research*, Vol 23, Nº 3, pp 724-742, (1993).
17. MacDonald, K.A.; Northwood, D.O, "Experimental measurements of chloride ion diffusion rates using a two-compartment diffusion cell: Effects of material and test variables". *Cement and Concrete Research*, **25**, (7) (1995) 1407-1416.
18. Gilleece, P.R.V.; Basheer, A.E.; Long, A.E.: "The effect of concentration on the accelerated chloride ion migration tests for modified concretes". *Proceedings of the International RILEM Workshop, St- Rémy-les-Chevreuse, France (1995)* pp 161.
19. Tang, L., Nilsson, L.O., "Rapid determination of the chloride diffusivity in concrete by applying an electrical field". *ACI Materials Journal*, Technical Paper, (1992) 49-53.
20. Andrade, C., Sanjuán, M.A., Recuero, A., Río, O., "Calculation of chloride diffusivity in concrete from migration experiments, in non steady-state conditions". *Cement and Concrete Research*, **24**, (7) (1994) 1214-1228.
21. Dhir, R.K.; Jones, M.R.; Ahmed, H.E.H.; Senevirate, A.M.G.: "Rapid estimation of chloride diffusion coefficient in concrete". *Magazine of Concrete Research*, 42, Nº 152, pp 177-185, (1990)
22. El-Belbol, S.M.T.; Buenfeld, N.R.: "Accelerated chloride ion diffusion tests in pore structure and permeability of cementitious materials". Edited by L.R. Roberts and J.P. Skanly, *Materials Research Symposium Proceedings*, Vol 137, pp 203-208, (1989).
23. El-Belbol, S.M.T.: "Acceleration of chloride ion diffusion in concrete". PhD Thesis, Department of Civil Engineering, Imperial College, London, (November 1990).
24. Zhang, T.; GjØrv, O.E.: "An electrochemical method for accelerated testing of chloride diffusivity in concrete". *Cement and Concrete Research*, Vol 24, Nº 8, pp 1534-1548, (1994).
25. Sha'at, A, Basheer, P.A.M; Long, A.E; Montgomery, F.R.: "Reliability of the accelerated chloride migration test as a measure of chloride diffusivity in concrete". *Proceedings of the International Conference on Corrosion and Protection of Steel in Concrete.* 24-28 July. Sheffield. (1994).
26. Xu, A.; Chandra, S.: *Cement and Concrete Research*, Vol 24, Nº 2, pp 375-379, (1994).
27. Andrade, C.; Sanjuán, M.A.: "Experimental procedure for the calculation of chloride diffusion coefficients in concrete from migration tests". *Advances in Cement Research*, 6, Nº 23, pp 127-134, (1994).
28. Prince, W; Ollivier, J.P.: "A new approach to the accelerated test of chloride migration in concrete". *Proceedings of the International Symp. On high performance and reactive powder concretes, Sherbrooke, Canadá*, pp 315-321, (1998).
29. Castellote, M., Andrade, C., Alonso, C.: "Characterisation of transport of caesium, strontium, cobalt and iron ions through concrete by steady-state migration and natural diffusion tests". *Advances in Cement Research*, 1999, 11, Nº 4, Oct. 161-168.
30. Lankard, D. R., "Neutralization of chloride in concrete". *Battelle Columbus Laboratories, FHWA Report Nº FHWA-RD-76-6*, September 1975.
31. Morrison, G.L., "Chloride removal and monomer impregnation of bridge deck concrete by electro-osmosis". *Kansas Dep. Of Transport.*, FHWA Report Nº FHWA-KS-82-2, August 1982.
32. Greenwood, G.; Earnshaw, A.: "Chemistry of the elements". Pergamon Press, Oxford, (1984).
33. Pourbaix, M.: "Atlas d'Equilibres Electrochimiques à 25°C". Ed. Gauthiers-Villars, Paris, (1963).