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EVALUATION OF ENGINEERED BARRIER MATERIALS FOR SURFACE DISPOSAL FACILITIES

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INTRODUCTION

As reported in the previously Research Coordination Meeting (RCM) held at Keswick/Sellafield, England, our country has no Low Level Waste (LLW) disposal site yet. However, some research are conducted to evaluate the behaviour of engineered barrier materials, are being developed for repackaging of some of the wastes originated from the Goiânia accident, to assure a safe interim storage until the construction of the Low-Level disposal facility.

The research aspects of the evaluation of engineered barrier materials for surface disposal facilities are being taken by two Institutes of the National Nuclear Energy Commission of Brazil (CNEN), namely, Instituto de Pesquisas Energéticas e Nucleares (IPEN) situated at São Paulo and Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) situated at Belo Horizonte. The activities for selecting and preparing the site for disposal of the wastes arising from the Goiânia accident are coordinated by the Nuclear Safety and Radioprotection Directorate of CNEN and the repackaging of the wastes is being done by CDTN.

The operation of the nuclear power plant ANGRA I, nuclear fuel cycle facilities, research centers, hospitals, industries, universities, etc., generates in Brazil an amount of wastes that is not high enough to justify yet the construction of a repository. The main concern in Brazil, at present, is the social impact caused by the wastes arising from the Goiânia accident. An effort has been put forward to establish, as soon as possible, a final site for those wastes.

The quality of safety assessments for a repository depends mainly on the data uncertainties used to model them. When the time scale involved is of several centuries no one can be sure of the all possible changes that can occur in the environment of the chosen site. The exposure pathways resulting from the release of radionuclides to the groundwater are of concern only after some hundred years following the closure of the repository. Anyway we believe that even if we could know, with high precision, our input values at some time t we will not be able to predict what will happen into a farther future, since we are dealing with no linear systems. This means that even a minimum uncertainty in the input parameters at the emplacement time can mean a quite tremendous discrepancy in the expected final results (future). As Sir Karl Popper says in his work "The logic of scientific discovery" we can never validate a hypothesis, only invalidate it!

In spite of this, we should continue to work in order to put some order in this puzzle and try to gain some confidence in the output results. To convince ourselves of the precision of our techniques and practices applied to final disposal.

Due to the economical problems that our country are facing, most of the research programmes related to the disposal of wastes were postponed. Nevertheless, the scope of the work associated with Research and Development Directorate of CNEN involves:

1. Study of diffusion of chloride ions through cementitious materials aiming to establish criteria for durability of such materials;

2. Study of concrete formulations for durability of concrete structures;

3. Study of corrosion of concrete by sulfate containing waters;

4. Study of bio-degradation of concrete by aerobic micro-organisms which grow in some special conditions and;

5. Strategy of packaging of waste from Goiânia for interim and final disposal.

DIFFUSION OF CHLORIDE IONS THROUGH CEMENTITIOUS MATERIALS

In general metallic structures of the reinforced concrete used in repositories are well protected against corrosion even if submitted to unfavorable conditions. However, there are situations when the reinforcement is exposed to aggressive agents that can cause damages to the structure. The diffusion of chloride ions in hardened concrete is widely recognized as being of importance in relation to the corrosion of reinforcing steel bars. The consequence of this process is an expansion caused by the oxide deposition on the steel. In this way, chloride diffusion investigation may provide some parameters related to the lifetime of a repository.

Some experiments(1) were carried out using small cells with cement pastes and mortars. The samples were made into 30 mm diameters PVC cylinders molds, sealed and cured for 28 days at room temperature. Then, they were cut with a small circular diamond saw and ground on both sides, before fitting into diffusion cells. The characteristics of the samples are shown in Table I.

The diffusion cells are composed of two 100 mL chambers which are separated by the samples. The chambers are filled with saturated calcium hydroxide solution with 1 M sodium chloride in chamber 1. The solution in chamber 2 is renewed regularly and the chloride concentration is determined by titration with $AgNO_3$. The diffusion coefficients obtained are shown in Table II.

As can be seen the diffusion increases with the increasing of the A/C ratio and the decreasing of the thickness. This occurs because as the A/C ratio of the samples increases higher is the porosity of the samples. From this small scale test its seems to be possible to infer, with some confidence, that we can extrapolate to higher thickness. This we plan to test in near future in spite of the long time spent for this experiment. As can be observed from Table II the diffusion coefficients are rather similar for different thickness of samples for the same A/C ratio and are consistent with other results reported in the literature. Those values were obtained by adjusting the experimental values to the expression :

$$\frac{C}{Co} = \mathrm{erfc}\left(\frac{x}{2\sqrt{D\,t}}\right)$$

where erfc is the complementary error function, x is the concrete slab thickness, C is the concentration os Cl ions in time t, Co is the concentration of ions of Cl in the initial time and D is the diffusion coefficient given in cm^2/s.

STUDY OF CONCRETE FORMULATIONS WITH ADDITIVES TO IMPROVE RETENTION OF RADIONUCLIDES

Special attention is drawn to establish a convenient formulation for immobilization of wastes and decreasing the possible liberation of radionuclides to the environment.

Usually the cesium present in LLW and ILW is rather soluble, not interacting chemically nor physically with the cement matrix. The present study[2] uses bentonite clays existing in Brazil as an additive to reduce the leaching of cesium of the cement matrix.

Four types of bentonite were tested. Two of them are sodic (G and B) and the other two calcic (F and N). Their exchange capacities are shown in Table III.

They were assayed in weigh proportions of 7, 10, 12 and 15% of the final product.

Several other tests complemented the assays, such as: compressive strength, set time, viscosity, temperature development in the final product, leaching, cesium sorption, etc.

The diffusion coefficients obtained for cesium of the cemented wastes after the leaching tests are shown in Table IV.

The compressive strength of the test samples (CP32, 10% of Bentonite, 10% of incorporated salts simulating a typical intermediate level radioactive waste) are shown in Table V.

After one year test, the results show that the bentonite greatly reduce the cesium release.

STUDY OF CORROSION OF CONCRETE BY WATERS CONTAINING SULFATE

The concrete is a porous material and its characteristics of retention of water or its properties of mass transport may be useful for durability studies. As time goes on several chemical, physical or combined processes add to degraded the concrete.

In tropical climates the movement of aggressive ions and the development of bacteria species is greater. In this way the degradation is faster. The choice of cement, its formulation according the environment, etc are very important to reduce the effects of climate.

Corrosion by sulfates may result in swelling caused by the precipitation of calcium sulfate ($Ca_2SO_4.nH_2O$) or ettringite ($2CaO.Al_2O_3.3CaSO_4.3H_2O$) in the pore structure of the cement, depending on the temperature. This may cause swelling and disintegration of the structure and the development of microfissures.

The damage caused by sulfates in concrete, in hot climates, has already been observed in India and Africa[6,7]. To reduce those effects special formulations using additives to reduce the production of expansive products are required.

To verify the resistance of cements to such aggressive components a program including evaluation of the soils pH, soil water composition, SO_4^{-2} content as well laboratory sulfate attack of concrete samples is been conducted[4].

The Koch & Steinegger method, with some modifications was used to observe sulfate aggressivity on cementitious samples. Use was made of prisms with 3/8"x 3/8" x 2 3/8" sample size and the aggressivity of sulfate solutions was evaluated by means of the ratio:

$$R_t = \frac{\text{Mechanical strength after aggressive solution immersion}}{\text{Mechanical strength after water immersion}}$$

where t is the time of immersion and the mechanical strength is measured by flexural strength testing.

The experiments were conducted with samples having a solution volume to surface ratio equal to 10 (V/S=10). That is the same criterion used by ISO standard applied to radionuclide leaching from waste forms.

The mean value of R_t to evaluate the damage caused by sulfate as suggested by Koch & Steinegger is 0.7. Values above this value indicate that the structure isn't affected by action of sulfates.

The mechanical strength of samples immersed in solution containing several concentrations varying from 0.005 to 0.5 M of sulfates do not present drastic variations for immersion times varying in 2, 4 and 8 weeks. The aim of this study is to correlate the decrease of the sulfate in the solution with the chemical resistance index. The maximum variation obtained till now was less than 4%. Preliminary results indicate that the chemical resistance increases after four weeks of immersion and then decreases. Those data are presented in Table VI.

ACTION OF MICROORGANISMS

Under certain conditions, concrete structures are known to be susceptible to attack promoted by microorganisms. Those microorganisms can influence the release of radionuclides from a repository into the biosphere by several processes. Those processes can be: gas production, uptake of radionuclides by mobile species, change of the properties of the engineered barriers as well as of the natural backfill and change of the geochemistry of the repository (inside and around the construction). In all the cases of biologically induced attack on concrete, the bacteria involved have been of the aerobic type that produce acid in their life cycle. For example the oxidation of H_2S to H_2SO_4 in sewage outlets. It is the acid so produced that attacks the concrete by dissolving $Ca(OH)_2$ and C-S-H gel from the cement. Since such bacteria require oxygen they are unlikely to cause any problems once the repository is sealed and anaerobic conditions prevail.

The bacteria which present more aggressivity to the concrete are those belonging to genus *Thiobacillus*. This aggressivity is due the capacity of them oxide inorganic compounds of sulfur producing sulfuric acid as final product. The data obtained till now show that some components of concrete used in Brazil are susceptible to such kind of bacteria. Some studies are also been developed to search the possibility of oxidation of calcium sulphite present in blast furnace slag.

PACKAGING OF WASTE FROM GOIÂNIA FOR INTERIM AND FINAL DISPOSAL

The radioactive wastes generated in Goiânia as a result of the radiological accident was collected and conditioned in different types of packaging and stored at the temporary storage site near Abadia de Goias.

The accident occurred in September 1987, at Goiânia, capital of the State of Goias, in Brazil. The headstock of a teletherapy equipment containing a sealed source , of Cesium 137, was stolen and opened spreading most of its contents in the environment. Table VII presents the main characteristics of that source.

During the phase of intervention and decontamination the wastes were collected in packages available at the moment due to the emergency situation and now they are being better encapsuled, The physical inventory[8] of the wastes resulting of the accident are shown in Table VIII and in Table IX is shown the distribution of wastes according their category distribution.

For purpose of deposition the wastes were classified in 5 categories (groups) as shown in Table X. This was done considering the technical instruction CNEN-IT-01/91 that recommends a value of 0.3 mSv/a as limit of dose for the public individual due the presence of the repository[3,5,9,10].

The total activity of each package was evaluated as well its density in order to estimate the specific activity. In Tables XI, XII and XIII are shown data of each kind of recipient used to store the wastes[8].

The proposal for the final repository will be a large container in concrete on the surface of the soil keeping a maximum distance from the water table. It would be desirable that it support the maximum possible earthquake in the region and the material be placed inside according to their origins. As a security methodology the void spaces between the packages will be filled with compressed bentonite clay in order to keep the structural conditions and reduce the migration of cesium to outside of the repository. The final aspect of the repository should be a big monolith of concrete. As in other types of repositories it will be covered with earth, small root vegetation and having proper drainage systems to keep under control any eventual leakage.

TABLE I - Conditions for diffusion experiments

Water/cement ratio (W/C)	Sand/cement ratio (s/C)	Thickness (mm)
0.4	0	3
0.4	2	3
0.4	2	5
0.5	2	3
0.5	2	5
0.6	2	3
0.6	2	5

TABLE II - Results of diffusion experiments in paste and mortar slabs

Sample	Thickness (mm)	s/C	W/C	Type	Diffusion Coeff. (cm^2/s)
1	3	0	0.4	paste	1.52×10^{-9}
2	3	2	0.4	mortar	2.76×10^{-9}
3	3	2	0.5	mortar	3.12×10^{-9}
4	3	2	0.6	mortar	3.19×10^{-9}
5	5	2	0.4	mortar	2.52×10^{-9}
6	5	2	0.5	mortar	3.22×10^{-9}
7	5	2	0.6	mortar	5.67×10^{-9}

TABLE III - **Characteristics of clays used for immobilization of wastes in cement**

Type	meq/100g	granulometry (mesh)
G	80	200
B	110	200
F	80	200
N	110	200

TABLE IV - **Diffusion coefficients obtained with the clays added to cement**

Bentonite Type	Mixture	Percentage of bentonite (%)	Diffusion Coeff. (m^2/s)
G	G7	7	4.6×10^{-13}
	G10	10	2.4×10^{-13}
	G12	12	1.5×10^{-13}
	G15	16	7.2×10^{-14}
F	F7	7	2.5×10^{-13}
	F10	10	2.2×10^{-13}
N	N7	7	3.0×10^{-13}
	N10	10	2.4×10^{-13}
	N12	12	1.9×10^{-13}
B	B7	7	3.6×10^{-13}
	B10	10	3.3×10^{-14}
	B12	12	4.9×10^{-14}
	B15	15	3.1×10^{-14}

TABLE V - **Compressive strength of cemented wastes (CP32, bentonite 10% and salts incorporated)**

W/C	Compression Strength (MPa)
0.31	25.3
0.35	25.6
0.41	270.
0.45	18.3
0.51	20.3
0.55	14.9
0.61	15.8
0.65	11.1
0.69	12.2

TABLE VI - Chemical aggressivity coefficient R_d

Water/Cement ratio	Concentration (mol/L)	Time of immersion (weeks)		
		2	4	8
0.4	5×10^{-3}	0.85	0.76	0.53
	1×10^{-2}	0.93	0.72	0.62
	5×10^{-2}	0.89	0.65	0.54
	1×10^{-1}	0.87	0.82	0.64
	5×10^{-1}	1.14	1.12	0.40
0.5	5×10^{-3}	1.11	1.06	0.96
	1×10^{-2}	1.00	1.09	0.92
	5×10^{-2}	1.21	1.26	1.09
	1×10^{-1}	1.18	1.33	1.18
	5×10^{-1}	1.22	1.23	0.82
0.6	5×10^{-3}	1.02	1.13	1.13
	1×10^{-2}	1.10	1.06	1.07
	5×10^{-2}	1.07	1.10	1.20
	1×10^{-1}	1.36	1.39	1.20
	5×10^{-1}	1.19	1.39	0.87

TABLE VII - Main characteristics of the source of ^{137}Cs

Source Activity	50.9 TBq
Dose rate at one meter distance	4.56 Gy/h
Volume	31.05 cm^3
Mass	93 g
Specific Activity	0.55 TBq/g

TABLE VIII - Physical inventory of the wastes

- 4201 drums of 200 L - 1350 metallic boxes - 8 concrete containers -10 maritime containers - 1 special concrete container for the headstock of the source

TABLE IX

Group 1	Wastes with concentrations equal or bellow to 8.7 x 10^4 Bq/kg
Group 2	Wastes with time for decay to the condition of group 1 equal to or less than 90 years
Group 3	Wastes with time for decay to the condition of group 1 higher than 90 years or less than 150 years
Group 4	Wastes with time to decay to the condition of group 1 higher than 150 years and less than 300 years
Group 5	Wastes with time to decay to the condition of group 1 higher than 300 years

TABLE X - Metallic boxes (1.2 x 1.2 x 1.2 m)

Group	Time (a)	Quant.	Volume (m^3)	Activity	
				(Ci)	(TBq)
1	t=0	404	686.8	1.00	3.7 x 10^{-2}
2	$0<t\leq 90$	356	605.2	10.61	3.9 x 10^{-1}
3	$90<t\leq 150$	287	487.9	35.84	1.3
4	$150<t\leq 300$	275	467.5	342.90	1.3 x 10^{1}
5	$t>300$	25	42.5	796.15	3.0 x 10^{1}
Total		1347	2289.9	1186.50	4.5 x 10^{1}

TABLE XI - Metallic boxes (1.2 x 1.2 x 1.2 m)

Group	Time (a)	Quant.	Volume (m^3)	Activity (Ci)	Activity (TBq)
1	t=0	407	691.9	1.00	3.7×10^{-2}
2	$0<t\leq 90$	356	605.2	10.61	3.9×10^{-1}
3	$90<t\leq 150$	287	487.9	35.84	1.3
4	$150<t\leq 300$	276	469.2	343.00	1.3×10^{1}
5	$t>300$	24	40.8	598.50	2.2×10^{1}
Total		1350	2295.0	≈989	3.7×10^{1}

TABLE XII - Drums (200 L)

Group	Time (a)	Quant.	Volume (m^3)	Activity (Ci)	Activity (TBq)
1	t=0	2688	537.6	0.63	2.7×10^{-2}
2	$0<t\leq 90$	980	196.0	2.32	8.6×10^{-2}
3	$90<t\leq 150$	314	62.8	3.85	1.4×10^{-1}
4	$150<t\leq 300$	217	43.4	18.14	6.7×10^{-1}
5	$t>300$	2	0.4	1.72	6.4×10^{-2}
Total		4201	840.2	23.66	9.9×10^{-1}

TABLE XIII - Other packages

Type	Quant.	Volume (m^3)	Activity		Group
			(Ci)	(TBq)	
Concrete package (VBA)	8	11.4	19.77	0.731	5
Maritime containers	10	320.0	0.3	0.011	1
"Headstock"	1	2	121.0	4.477	5
Total	19	323.6	141.07	5.219	

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