

LEACHING OF NUCLEAR POWER REACTOR WASTES FORMS

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ABSTRACT

The waste management research program foresees a number of tests that can provide data for characterization and quality assurance of the final radioactive wastes forms and its safe disposal from the human environment. In this way, leaching tests are developed and achieved in order to understand the mechanism of radionuclides loss from immobilized wastes and to predict its long-term performance under storage and disposal conditions.

This paper describes the leaching tests for immobilized power reactor wastes carried out at IPEN. These wastes forms consist mainly of spent resins and boric acid concentrates solidified in ordinary Portland cement. All tests were conducted according to the ISO and IAEA recommendations. Three years leaching results are reported. The cesium diffusivity coefficients determined out of these results are about $1 \times 10^{-8} \text{ cm}^2/\text{s}$ for boric acid waste form and $9 \times 10^{-10} \text{ cm}^2/\text{s}$ for ion exchange resin waste. Strontium diffusivity coefficients found are about $3 \times 10^{-11} \text{ cm}^2/\text{s}$ and $9 \times 10^{-11} \text{ cm}^2/\text{s}$ respectively.

INTRODUCTION

The leachability of radionuclides from solidified wastes forms is a significant data to evaluate the suitability of a given material as a safety mean to immobilize radioactive wastes, to risk analysis assessment when it concerns to radionuclides release into the environment and also to predict long-term performance of the waste form under disposal conditions.

Cement is widely used by the nuclear industry to conditioning intermediate and low level radioactive wastes, because it presents some advantages as low cost, radiation and thermal stability.

In the present work, within the on going program of wastes forms characterization, leaching from radioactive cement-based wastes forms containing specifically simulated reactor wastes were determined. Intermediate and low level reactor wastes consist mainly of evaporators concentrates and spent ion-exchange resins. For a PWR type reactor these concentrates have a high boric acid contents, which may vary between 90 to 260 g/kg of concentrates.

The procedures for leaching tests and data analysis were conducted according to the IAEA and ISO recommendations (1, 2). Since it is desirable to know the mechanisms of radionuclides release, in order to predict or extrapolate from short term data the behavior of the far future, experimental data were statistically analysed according to some equations found in the literature (3).

EXPERIMENTAL

Evaporator Concentrates Immobilization

As it is well known boric acid has a strong retarding action on the cement setting. This problem can be solved by using some accelerating additives such as sodium silicates or by neutralizing such action on the cement by transforming the boric acid into a neutral chemical form.

The direct neutralization of boric acid with sodium hydroxide leads to the tetraborate form, which precipitates at pH 9. It can be avoided by heating the solution to approximately 70° C, but the cement setting doesn't occur at short time. Hence the addition of a calcium salt or calcium hydroxide is convenient to form a calcium metaborate which has no retarding effect over the cement setting.

To prepare the leaching test samples, simulated evaporator concentrates were made, by neutralizing a boric acid solution (120 g/kg concentrate) with sodium hydroxide until pH 8. The solution was then heated to 70° C and added to a cement/additives/vermiculite blend. The additives consisted of setting accelerators as calcium chloride, sodium carbonate and barium hydroxide. Due to its adsorption capacity, a clay (vermiculite) was used to improve the cesium retention. The whole composition of the borate wastes forms is given in table I.

The cement used was the ordinary Portland cement, and the water/cement (W/C) ratio was 0.42. To all samples were added as radioactive tracers cesium-134 and strontium-90.

The experimental conditions for the leaching test were as follows:

- Samples are right cylinders with 5 cm diameter by 10 cm height, resulting in a volume to exposed surface of sample (V/S) equal to 1.
- Curing time was 28 days in a sealed atmosphere, i.e., 90-100% relative humidity.
- Leaching was conducted at room temperature, with renewal of leachant which was 1600 cm³ of distilled water and synthetic sea water whose composition is given in table II.

Ion - Exchange Resins Immobilization

Cemented samples containing simulated spent ion-exchange resins were prepared according to the compositions shown in the table III.

The experimental conditions were the same for evaporators waste, unless the leachant. In this case leaching was investigated only in distilled water.

Comparison with Actual Reactor Waste Cement Immobilized

In order to compare leaching behavior between actual and simulated wastes, it was made some samples containing actual reactor evaporators concentrates. It distinguishes two compositions of waste-forms: without vermiculite and with vermiculite. See table IV.

The activity measurements of the leachant were made by using NaI(Tl) well type gamma detector for cesium-134 and liquid scintillation detector for strontium-90.

RESULTS AND DISCUSSIONS

Up to now leaching time has reached 3 years for simulated wastes and about one year for the actual waste. As recommended by IAEA, leach results are reported as a cumulative fractional release ($\sum a_n/A_0$), corrected for the volume to surface ratio as a function of the total elapsed leaching time ($\sum t_n$) up to each sampling time. Leached fractions of cesium and strontium to distilled water and sea water from evaporators concentrates wastes are plotted in figure 1. Figure 2 and 3 show the results obtained for spent resins wastes forms and actual reactor wastes. The comparison of both, simulated evaporators concentrates and actual wastes is shown in the figure 4.

Since diffusion seems to be the main process of the radionuclides loss from immobilized

cement-based wastes forms, it can be characterizing the leach behavior according to the mass transport equation solution for a semi-infinite medium (3) as follow:

$$\frac{\sum a_n}{A_0} \cdot \frac{V}{S} = 2 \left(\frac{D \cdot t}{\pi} \right)^{\frac{1}{2}} \quad (1)$$

Where V is the volume and S surface of the specimen. D is the diffusivity coefficient or leach coefficient, which characterizes leach behaviour of mobile species. Linear least square regression was used to fit experimental data to the equation in order to determine D.

Table I

Composition of the cemented evaporator concentrates

Compounds	% Weight
Cement	61.25
Vermiculite	3.0
Waste	30.15
Additives (*)	5.5

(*) 2% calcium chloride, 1.5% barium hydroxide and 2% sodium carbonate

Table II

Synthetic sea water composition

Compounds	Concentration (g/l)
NaCl	27.213
MgCl ₂	3.807
MgSO ₄	1.658
CaSO ₄	1.260
K ₂ SO ₄	0.863
CaCO ₃	0.123
HgBr ₂	0.076

pH = 8.1

Another approach to determine D was attempted using the diffusion equation with concentration dependent dissolution rate, as described by Godbee (3). In this equation was introduced an analysis by error function (erf) expressed as:

$$\frac{\sum a_n}{A_0} \cdot \frac{V}{S} = (K.D)^{1/2} \left[\left(t + \frac{1}{2R} \right) \operatorname{erf} (K.t)^{1/2} + \left(\frac{t}{K.\pi} \right)^{1/2} e^{-K.t} \right] \quad (2)$$

Where K is dissolution rate constant.

The diffusivity coefficients obtained from first model are listed in table V. It can be observed that strontium has release rate smaller than cesium by a magnitude factor of 2, even for the specimens that contain vermiculite as additive, it was demonstrated that vermiculite has a deleterious effect on the

Table III

Spent resins wastes forms composition

Compounds	% Weight
Cement	63.3
Waste (*)	32.3
Additives (**)	4.4

(*) Wastes with 20% strong cationic resin-IRA 120

(**) 1.1% barium hydroxide, 1.65% calcium chloride and 1.65% sodium carbonate

Table IV

Composition of actual reactor concentrates immobilized into cement.

Compounds	Without clay % Weight	With clay % Weight
Cement	58.8	53.8
Calcium hydroxide	6.0	6.0
Waste (*)	35.2	36.2
Vermiculite	—	6.0
W/C ratio	0.62	0.54

(*) Wastes arising from Germany reactor Stade gMBH.

strontium leaching. The higher the vermiculite load the higher is the strontium release (4), also the mechanical strength decreases with increasing of the vermiculite load.

The analysis of this waste has resulted:

pH = 7.6

d = 1.130 kg/m³

Solid content: 165 kg/m³ (mainly boric acid)

Isotopic analysis:

Isotope	Isotopic %
Co-60	32.26
Sr-90	14.79
Y-90	14.79
Sb-125	2.65
Te-125	0.53
Cs-134	1.90
Cs-137	16.54
Ba-137m	16.54
U-235	4.3 E-04

Table V

Comparison of the effective diffusivity constant calculated by transport equations (model 1) in distilled water and seawater leachant medium. D(cm²/s)

Isotope	Simulated waste form		
	Borate		Resins
	Distilled water	Seawater	Distilled water
Cs-134	9.61×10^{-9}	2.05×10^{-8}	8.28×10^{-9}
Sr-90	3.75×10^{-11}	7.92×10^{-12}	8.24×10^{-11}

In table VI are presented cesium diffusivity constants calculated by means of equation 1, for simulated and actual borate wastes.

Statistical analysis by the second model demonstrated a good fitness for the experimental data of strontium, as it can be seen from table VI, but it cannot be concluded the same for cesium, whose experimental data don't fit adequately to the model. The simple diffusion process cannot explain satisfactorily the leach mechanisms from these forms. This seems to occur after some elapsed time when the water has already penetrated the cements pores. At the first few days the behavior may be due to an initial surface wash-off, on the other hand, at long leaching times, the dissolution rate of the matrix takes

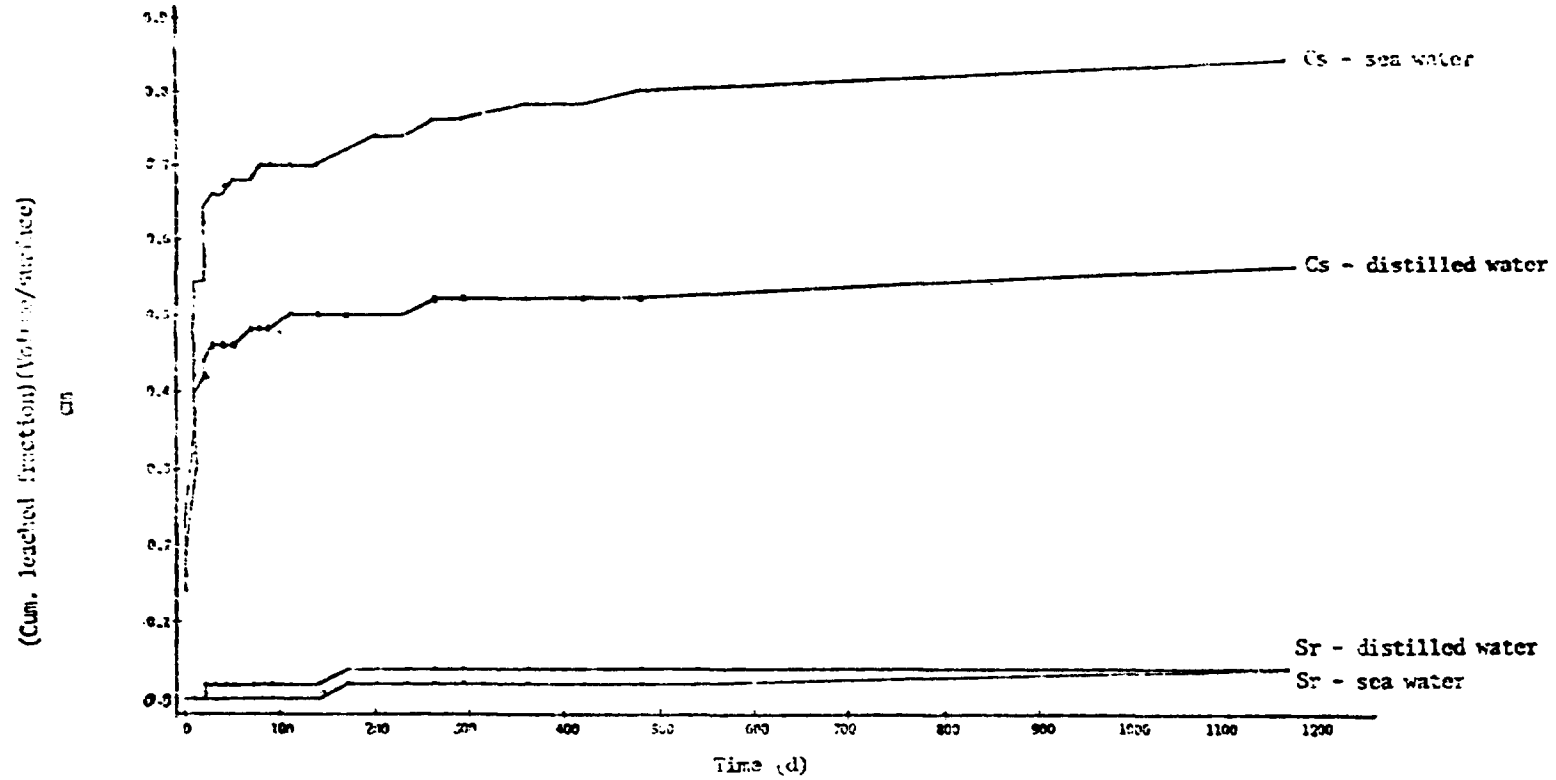


Figure 1 - Cesium and strontium leaching from cemented borate waste-forms, in distilled water and synthetic sea water, at room temperature

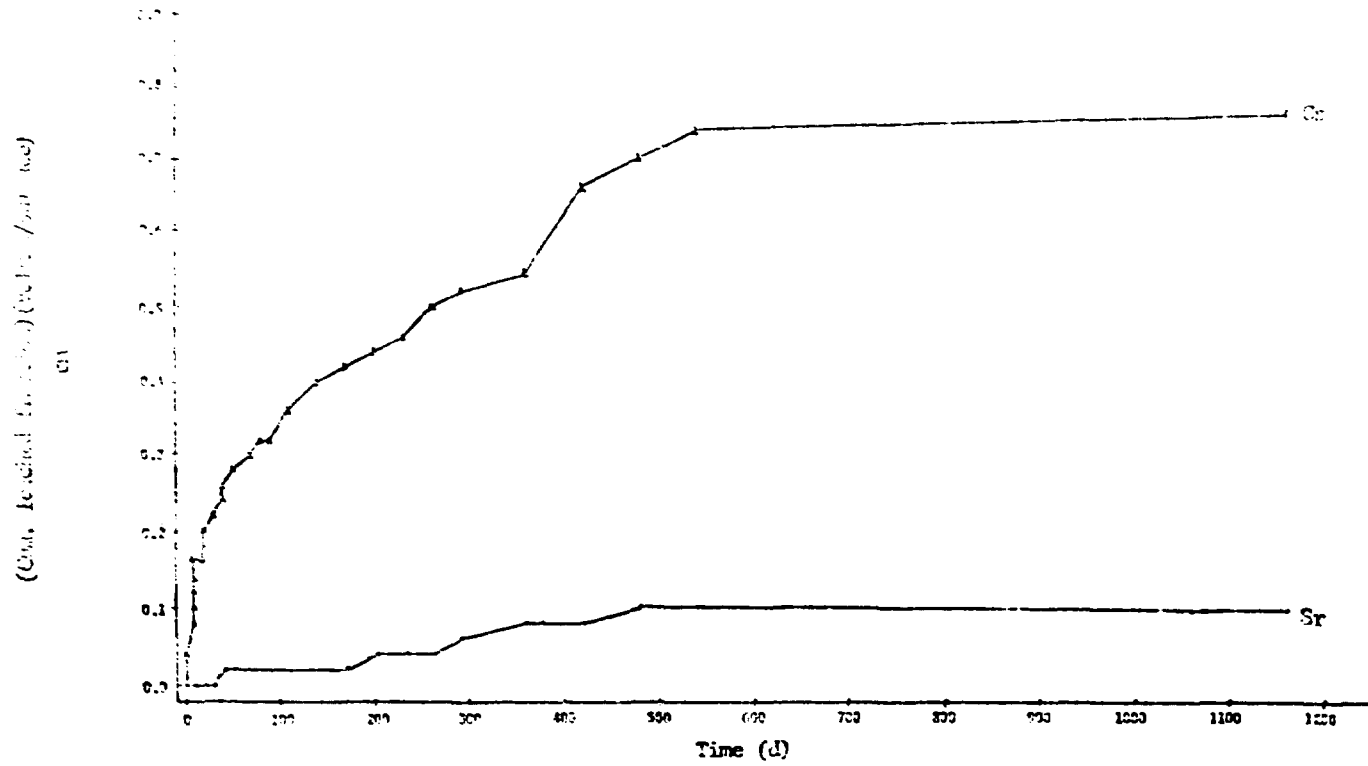


Figure 2 — Cesium and strontium leaching from cemented spent-resins waste-form, in distilled water at room temperature

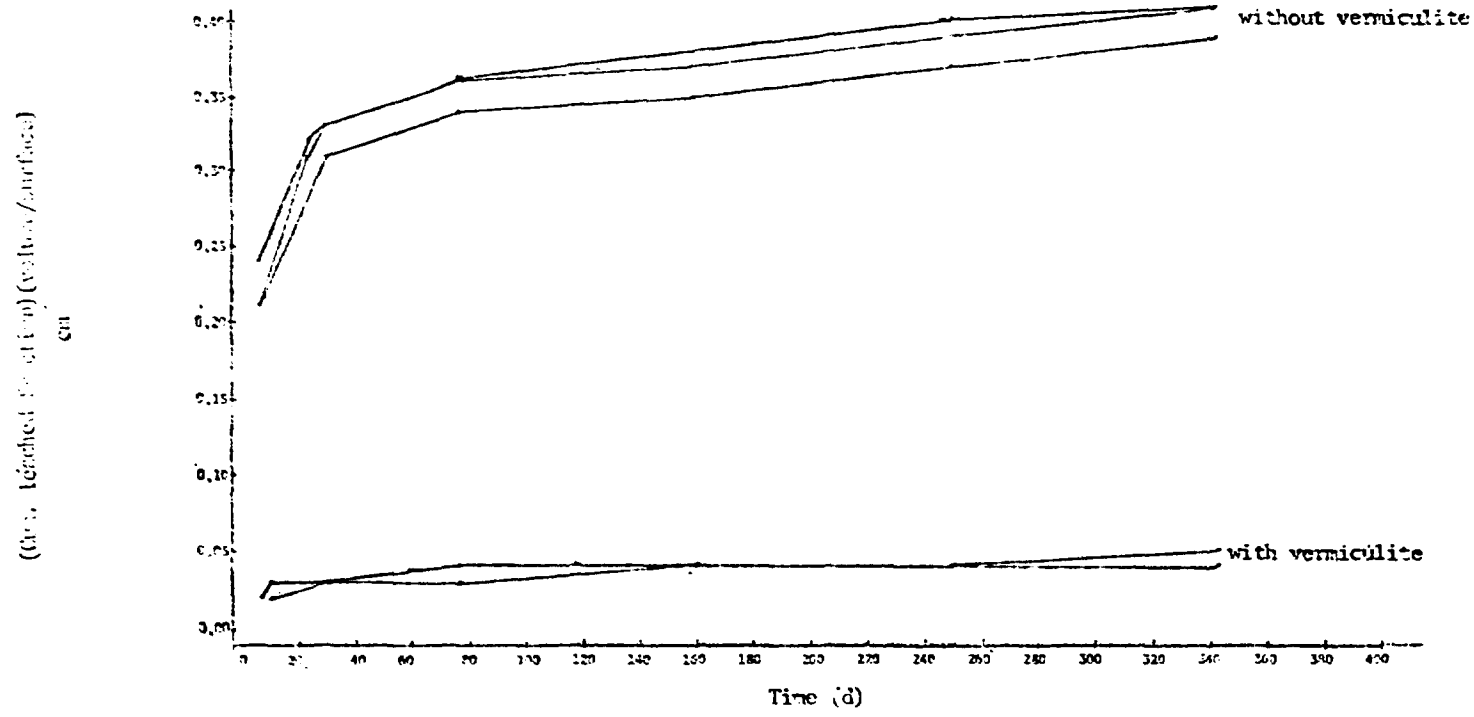


Figure 3 - Cumulated leached fraction of cesium from actual cemented waste

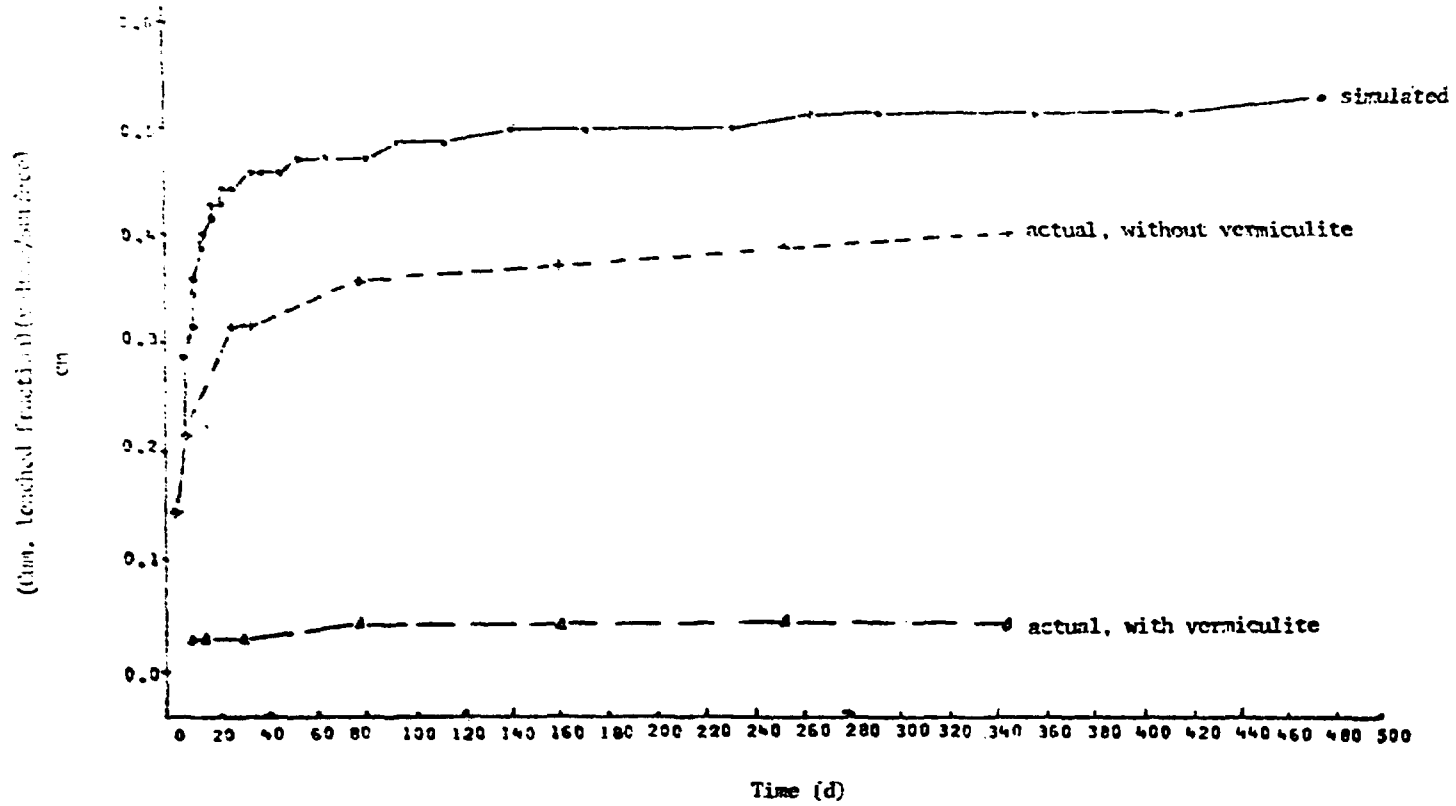


Figure 4 - Comparison between cesium leached fraction from actual and simulated cemented wastes

place as a predominant factor. So, to model the kinetics of the leach mechanisms for wastes forms containing additives, it must be taken into account another factors that contribute to the leach rate. Reactions as ion-exchange or retention by clay or ion-exchange resins between cement-additives, cement-wastes, waste-additives are some of those reactions that may occur, other than the interactions between whole waste form of the surrounding aqueous medium. Thus it becomes necessary to determine quantitatively each of these contributions and the degree of the modifying factors that should be introduced to compose a kinetic model for a quantitative approach for the leaching behavior.

More accurate laboratory investigations on the impact of some of these interactions on the leach rate is the purpose for a future work, in order to obtain adequate data that could be helpful to the comprehension of leaching mechanisms.

Table VI

Effective cesium diffusivity constant calculated by transport equations (model 1)
for actual and simulated borate waste.

Simulated	Actual	
(cm ² /s)	With vermiculite (cm ² /s)	Without vermiculite (cm ² /s)
9.61×10^{-9}	1.56×10^{-10}	2.54×10^{-10}

Table VII

Effective diffusivity constant, D(cm²/s) and dissolution rate constant, K(s⁻¹)
calculated by transport equations (model 2) for strontium-90

Leachant	Simulated waste form			
	Borate		Resins	
	D (cm ² /s)	K (s ⁻¹)	D (cm ² /s)	K (s ⁻¹)
Distilled water	3.91×10^{-11}	7.02×10^{-9}	6.53×10^{-11}	1.24×10^{-8}
Seawater	6.74×10^{-12}	5.93×10^{-9}		

REFERENCES

1. HESPE, E. D. Leach testing of immobilized radioactive waste solids, a proposal for a standard method. *At. Energy Rev.*, **9** (1):195-207, 1971.

2. INTERNATIONAL STANDARDS ORGANIZATION. *Long-term leach testing of radioactive waste solidification products*. Oct., 19, 1982. (ISO/TC 85/SC 5/WG 38, Draft ISO/DIS 6961)
3. GODBEE, H. W. & JOY, D. S. *Assessment of the loss of radioactive isotopes from waste solids to the environment. Part I: Background and theory*. Oak Ridge, Tn., Oak Ridge National Lab., 1974. (ORNL-4333)
4. LEE, D. J. & BROWN, D. J. *Factors affecting the leachability of cesium and strontium from cemented simulant evaporators wastes*. Winfrith, UKAEA Atomic Energy Establishment, Aug. 1981. (AEEW-R1461)