# LEACHING STUDIES ON ION EXCHANGE RESINS IMMOBILIZED IN BITUMEN MATRIX

C. E. Grosche Filho, J. P. Villalobos, U. Chandra


## ABSTRACT

To study radionuclide leaching from bitumen waste forms, many samples of bitumen mixed with ion-exchange resin labelled with $^{134}Cs$ were prepared. The resins used in the tests were nuclear grade mixed cationic/anionic bead resins. Different bitumen types were assayed: two distilled and two oxidized bitumens. Laboratory to scale samples, with surface/volume ratio (S/V) = 1, were molded to 5 cm diameter and 10 cm height. The composition of the mixtures were: 30, 40, 50 and 60 % by weight of dried resin with bitumen. The leachant was deionized water with a leachant volume to sample surface ratio of about 8 cm. Leached fractions were collected according to the recommendation of ISO method, with complete exchange of leachant after each sampling. The volume collected for analysis was one liter. Marinelli beckers were used for counting in a Ge(Li) detector. Up to now, results of 250 days have been accumulated. Samples prepared with distilled bitumen have shown a diffusion coefficient of the order of $10^{-14}$ $cm^2/sec$ and those prepared with oxidized bitumen yielded a diffusion coefficient of the order of $10^{-12}$ $cm^2/sec$. Mathematical models of transport phenomena applied to cylindrical geometry were employed to fit experimental data.


## INTRODUCTION

The comparation of various compositions of the radwaste bituminized products was studied by preparing different specimens of waste/bitumen while using two distilled and two oxidized bitumens.

The leaching experiments were conducted according the IAEA and ISO Standard recommendation.

Mathematical models of transport phenomena for cylindrical geometry were applied to fit the experimental data. This aims to explain leaching mechanism and to allow prediction of the long time behavior of the immobilized radionuclides. Three methods were used to investigate their ability to fit the experimental data: the first method was based on the time square- root versus leached fraction relationship; the second method tried was the log-log relationship; and the third method was based on diffusion law with concentration dependent dissolution rate.

## EXPERIMENTAL PROCEDURE

Nuclear grade granular ion-exchange resin, in $H^+$ and $OH^-$ form (IRN-150), loaded with Cs-134, was used for the study[4].

The resins were loaded by batch method, i. e. 4.5 kg of pure resins were equilibrated with 4.5 liters of distilled water containing 3.2 mCi of Cs-134. The labelling efficiency (> 99%) was determined by measuring the activity content in the solution after equilibrium. After loading, the resins were dried at 120° C for 16 hours.

**Table I**

Mathematical equations of transport mechanism

| Medium | Transport mechanism | Equation for release of the mobile species (cumulative fractional release) |
|---|---|---|
| semi - infinite homogeneous chemically inert | diffusion | $\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = 2\left(\frac{Dt}{\pi}\right)^{1/2}$ (EQ. 1) |
| semi - infinite uniform initial concentration | diffusion+ concentration- - dependent dissolution | $\left(\frac{\Sigma a_n}{A_o}\right)\left(\frac{V}{S}\right) = (KD)^{1/2}\left[(t+1/K)\ \mathrm{erf}\ (Kt)^{1/2} + (t/\pi K)^{1/2}\ e^{-Kt}\right]$ (EQ. 2) |

$\frac{V}{S}$ ≃ Volume surface ratio; t = time; D = effective diffusivity constant; K = dissolution rate constant; erf = error function

Specimens for leach tests were prepared by mixing bitumens with 30, 40, 50 and 60 wt% of dry resin. Bitumes used were: T 50/60 and V 85/100 distilled type and T 75/25 and VB 65 oxidized type. The range of surface/volume ratio of the specimens was of 0.86 - 1.2.

Leaching was carried out at room temperature in polyethylene bottles with 1.6 ℓ distilled water as the leachant. The sampling frequency adopted was as per recommendation of ISO[2]. The activities released in the leachant were determined by counting 1 liter of the leachant in Marinelli flasks using Ge-Li detector.

## RESULTS

The experimental results presented take into account leaching time of 1000 days[4]. Figures 1, 2, 3, and 4 show the cumulative leached fractions versus elapsed time for each bitumen type as a function of the waste composition.

For a better comparison, on the other hand, figures 5, 6, 7 and 8 show leaching from differents types of bitumen containing the same quantity of wastes load percents.

Mathematical models[3] based on transport phenomena applied for semi-infinite medium were used to fit the experimental data. Table I shows the matematical equations corresponding to these models.

Tables II and III show the values of diffusion constant D ($cm^2/seg$) and dissolution constant K ($seg^{-1}$) for a leaching interval of 250 days calculated by means of equations 1 and 2.

Equations 1 and 2 were used to predict the leaching fractions for a accumulative leaching time of 1000 days. The results so obtained are presented in the table IV.

## DISCUSSION

Analysis of experimental and predicted data could not establish any definite correlation between cumulative leach rate and the waste loads (ion-exchange resins) in the bitumen products for either type of bitumen employed. The D and K values obtained (tables II and III) are of the same magnitude and are independent of the waste load and bitumen type. In the case of distilled bitumen specimens, this behavior could be explained due to the fact that such wastes products present a greater trend of deformation, which changes the surface to volume ratio. On the other hand oxidized bitumem specimens did not suffer deformations but for the significant swelling of the resin due to water absorption.

50% resin-bitumen products obtained with either type of bitumen showed better matrix integrity.

Experimental data of distilled bitumen specimens showed better fitting to mathematical models than oxidized bitumen specimens. In the case of oxidized bitumen specimens the estimated error in some cases were greater than the values of K and D.

**Table II**

Value of effective diffusivity ($cm^2/s$) calculated by transport equation 1

| Ion-resins | Bitumen type | | | |
|---|---|---|---|---|
| (%) | T 50/60 | T 75/25 | V 85/100 | VB 65 |
| 30 | 8.04E(-14) | – | – | 4.69E(-13) |
| | 3.75E(-13) | – | – | 6.72E(-13) |
| 40 | 7.07E(-13) | 4.12E(-13) | 2.85E(-13) | 1.11E(-12) |
| 50 | 3.63E(-13) | 2.27E(-13) | 3.18E(-13) | 3.29E(-13) |
| | 2.50E(-13) | 1.31E(-13) | 1.81E(-13) | 1.78E(-13) |
| 60 | 2.36E(-13) | 4.58E(-14) | 5.49E(-13) | 1.18E(-13) |

Table III

Value of effective diffusivity, D($cm^2/s$) and dissolution rate constant, K($s^{-1}$) calculated by transport equation 2

| Ion-resins | T 50/60 | | T 75/25 | | V 85/100 | | VB 65 | |
|---|---|---|---|---|---|---|---|---|
| (%) | D($cm^2/s$) | k($s^{-1}$) | D($cm^2/s$) | k($s^{-1}$) | D($cm^2/s$) | K($s^{-1}$) | D($cm^2/s$) | k($s^{-1}$) |
| 30 | 2.39E(-14) | 2.70E(-7) | – | – | – | – | * | * |
| | 1.17E(-14) | 3.48E(-6) | – | – | – | – | * | * |
| 40 | 8.14E(-14) | 8.76E(-7) | 2.64E(-13) | 6.73E(-8) | 1.79E(-13) | 1.46E(-7) | 9.20E(-13) | 1.23E(-8) |
| 50 | 6.56E(-15) | 6.11E(-6) | 2.09E(-13) | 7.28E(-11) | 2.98E(-13) | 8.45E(-9) | * | * |
| | 7.35E(-14) | 2.78E(-7) | 1.47E(-13) | 1.64E(-11) | 4.19E(-14) | 3.76E(-7) | 1.34E(-13) | 3.23E(-8) |
| 60 | 1.66E(-14) | 1.17E(-6) | 3.33E(-14) | 4.49E(-8) | 4.76E(-14) | 1.19E(-6) | * | * |

* Equation 2 was unable to fit the data

## Table IV

Comparison of the amounts leached from different bitumen after 1000 days to those predicted by equation 1 and equation 2

| Bitumen type | Ion-resins (%) | Experimental data (cm).E(-3) | Predicted by | |
|---|---|---|---|---|
| | | | EQ.1 (cm).E(-3) | EQ.2 (cm).E(-3) |
| T 50/60 | 30 | 6.0 | 5.8 | 7.1 |
| | | 9.8 | 6.4 | 17.5 |
| | 40 | 5.1 | 8.8 | 23.2 |
| | 50 | 3.6 | 6.3 | 17.3 |
| | | 4.2 | 5.3 | 12.6 |
| | 60 | 2.2 | 5.1 | 12.1 |
| T 75/25 | 40 | 4.0 | 6.7 | 12.5 |
| | 50 | 2.2 | 5.0 | 4.8 |
| | | 2.1 | 3.7 | 4.0 |
| | 6.0 | 5.8 | 2.2 | 3.7 |
| V 85/100 | 40 | 4.8 | 6.6 | 14.5 |
| | 50 | 2.7 | 5.9 | 7.0 |
| | | 2.2 | 4.4 | 11.0 |
| | 60 | 12.2 | 7.8 | 20.6 |
| VB 65 | 30 | 3.8 | 7.2 | – |
| | | 4.8 | 5.6 | – |
| | 40 | 4.9 | 11.0 | 4.3 |
| | 50 | 2.4 | 6.0 | – |
| | | 10.8 | 4.6 | 4.0 |
| | 60 | 6.4 | 3.6 | – |

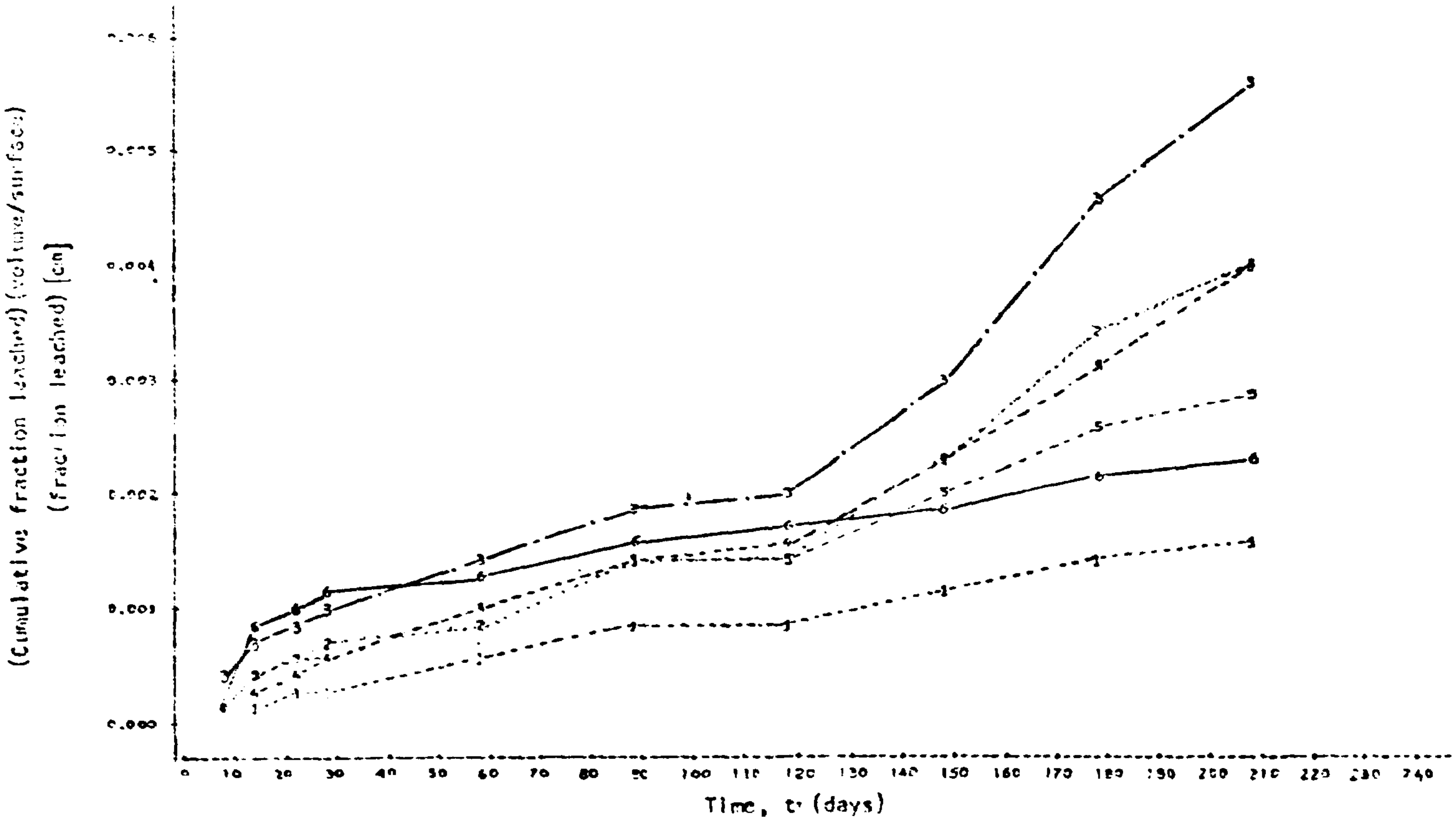


**Figure 1** — Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the distilled bitumen type T 50/60

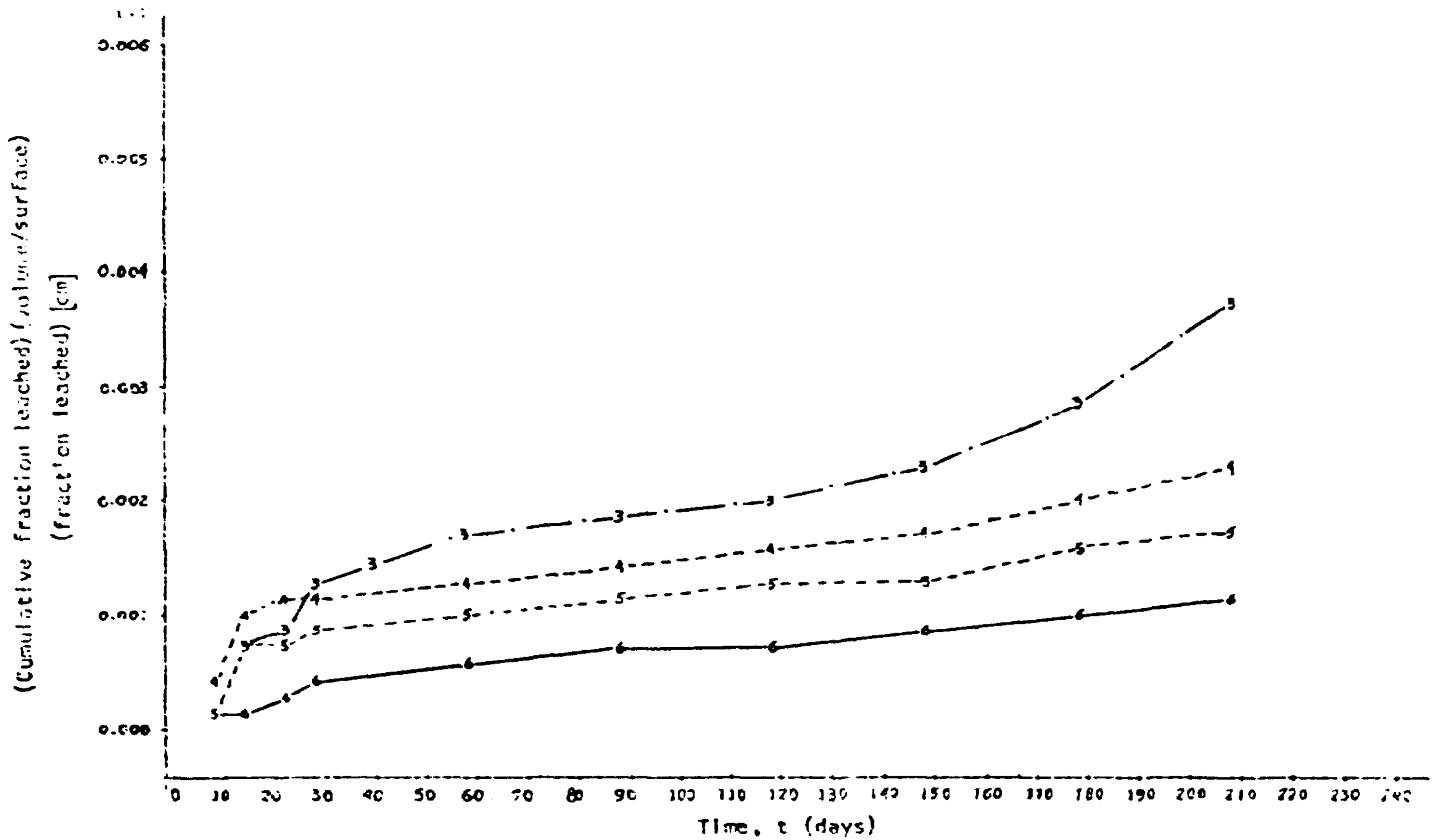


**Figure 2** – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the oxidized bitumen type T 75/25

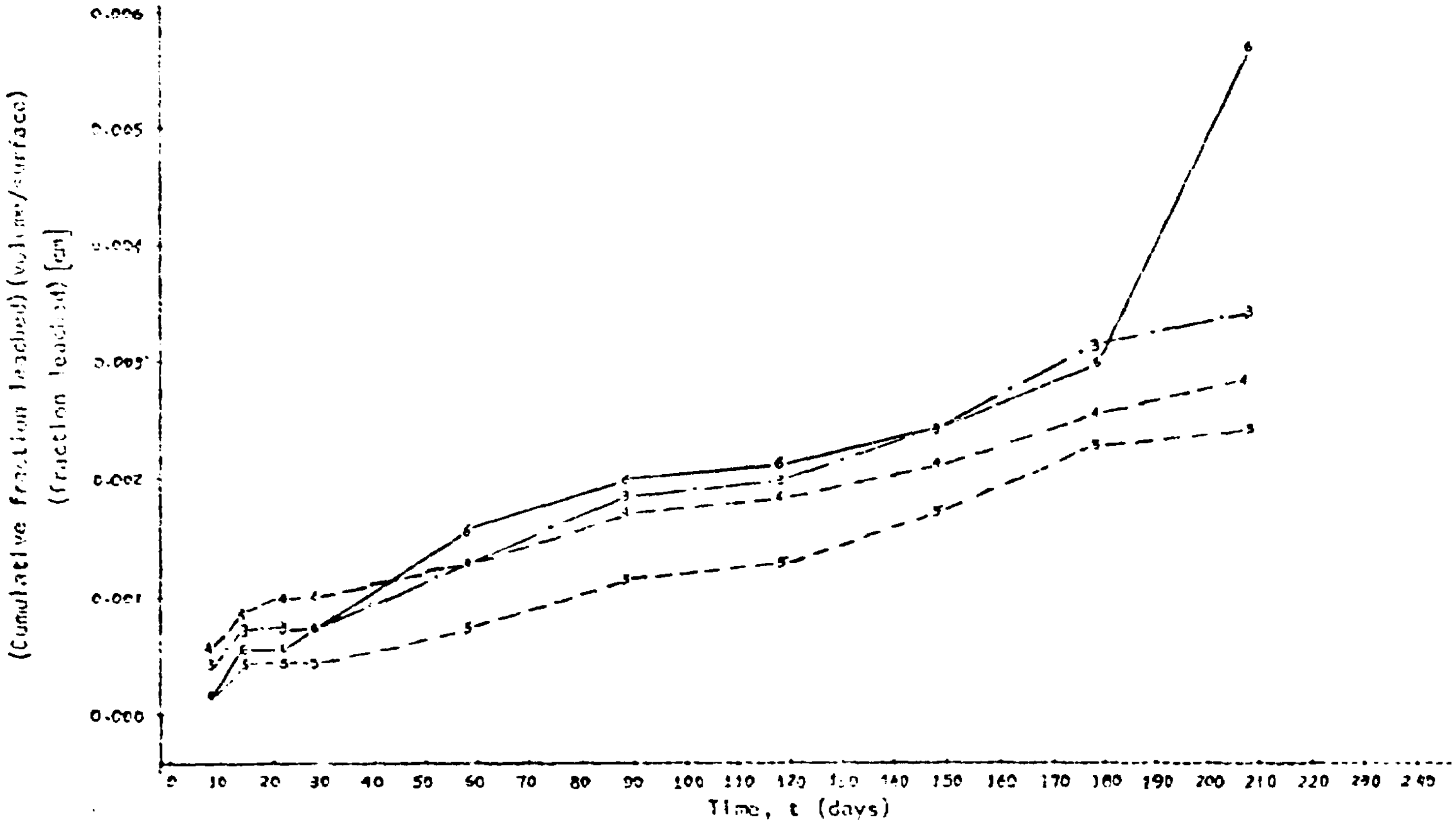


**Figure 3** – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the distilled bitumen type V 85/100

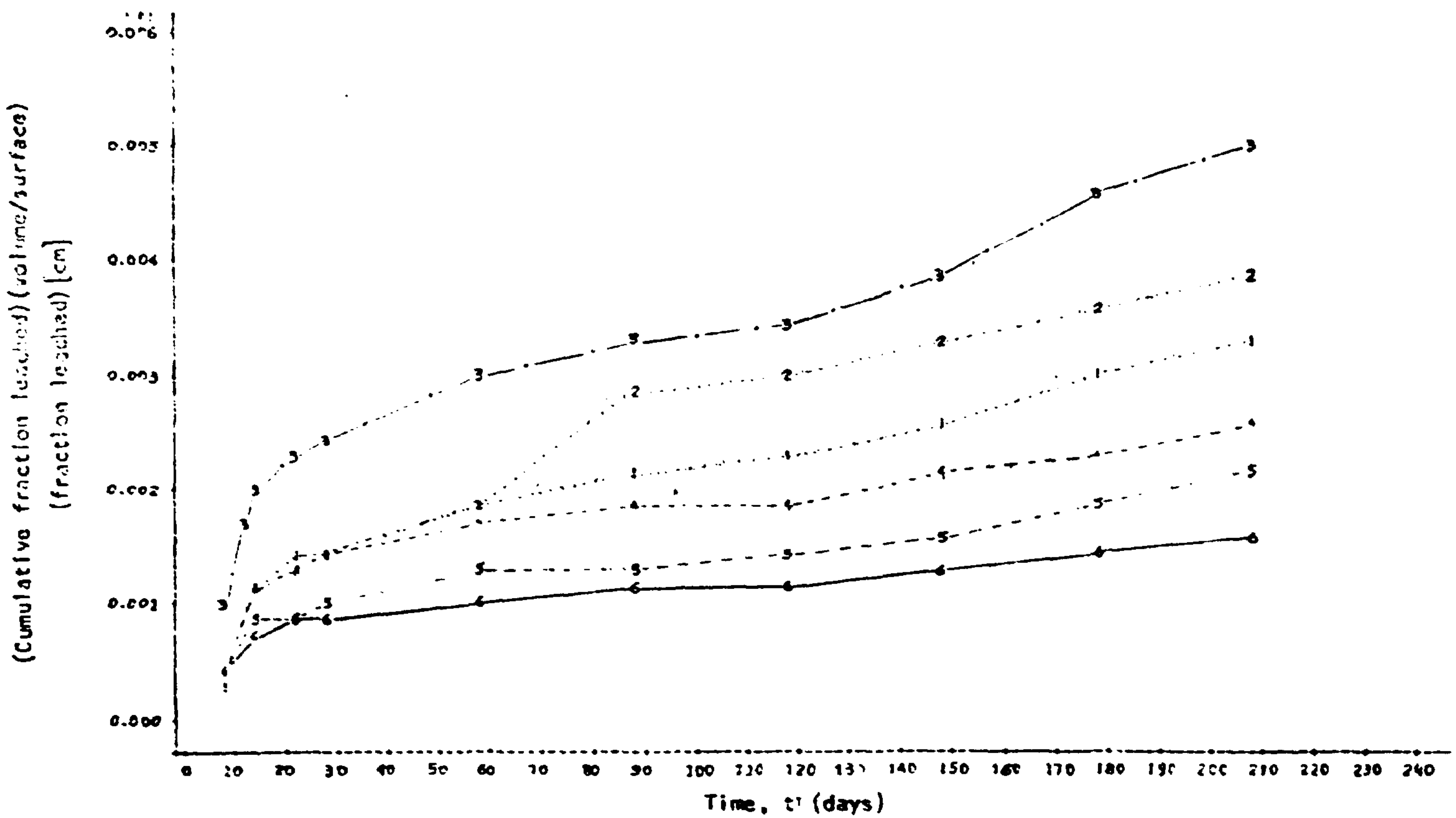


Figure 4 – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the oxidized bitumen type VB 65

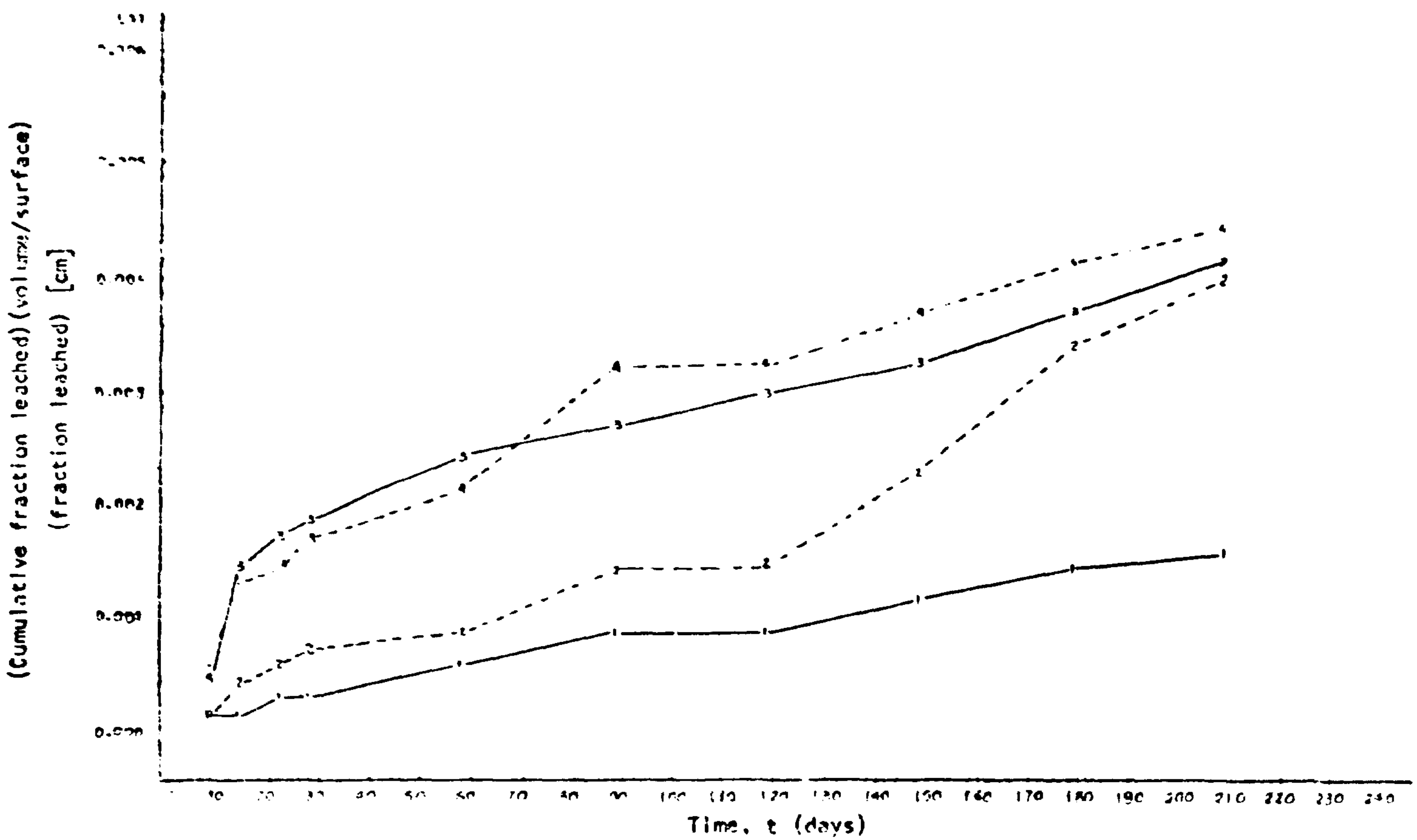


**Figure 5** — Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the different type of bitumen studied containing 30% by weight of the ion exchange resin.

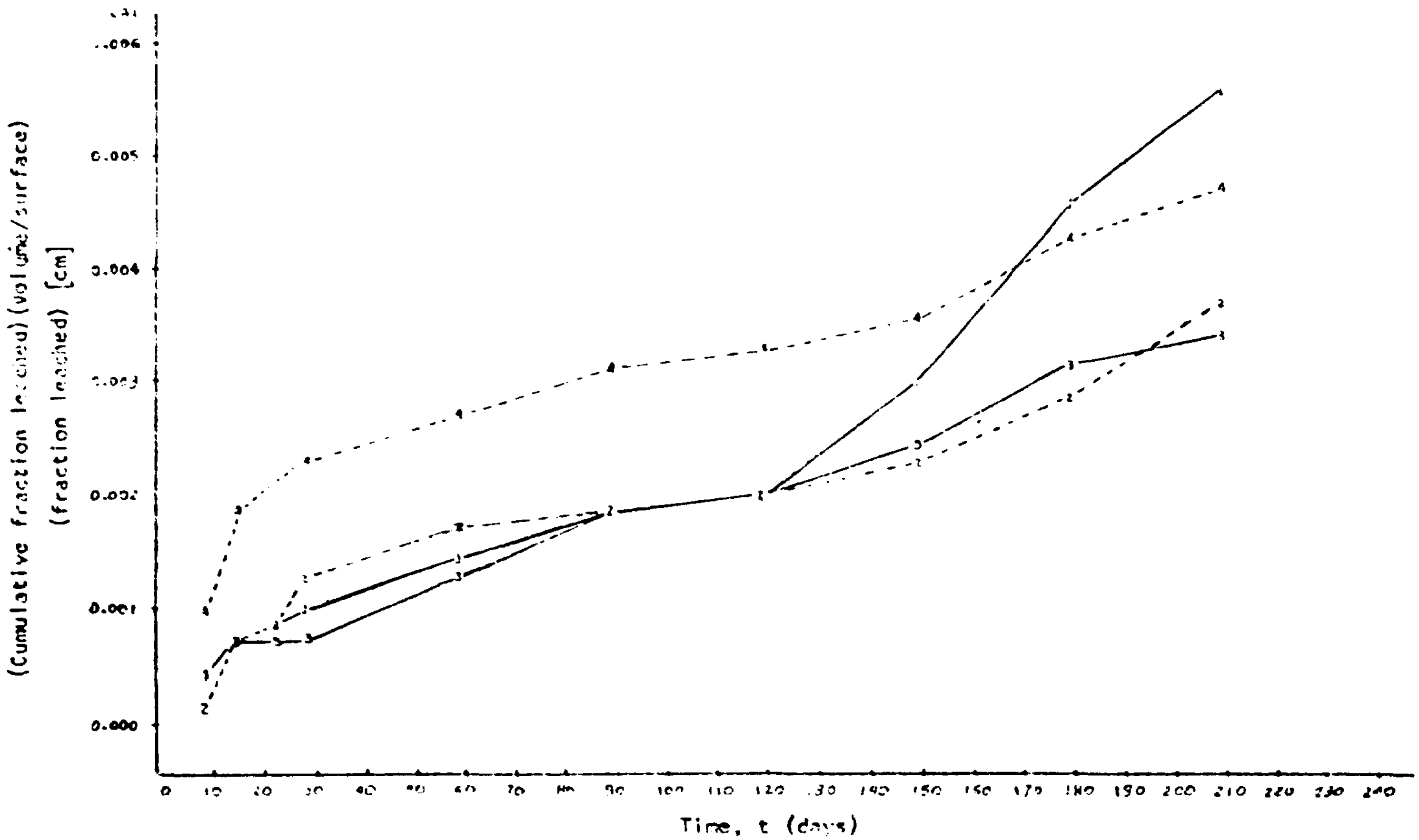


**Figure 6** – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the different type of bitumen studied containing 40% by weight of the ion exchange resin.

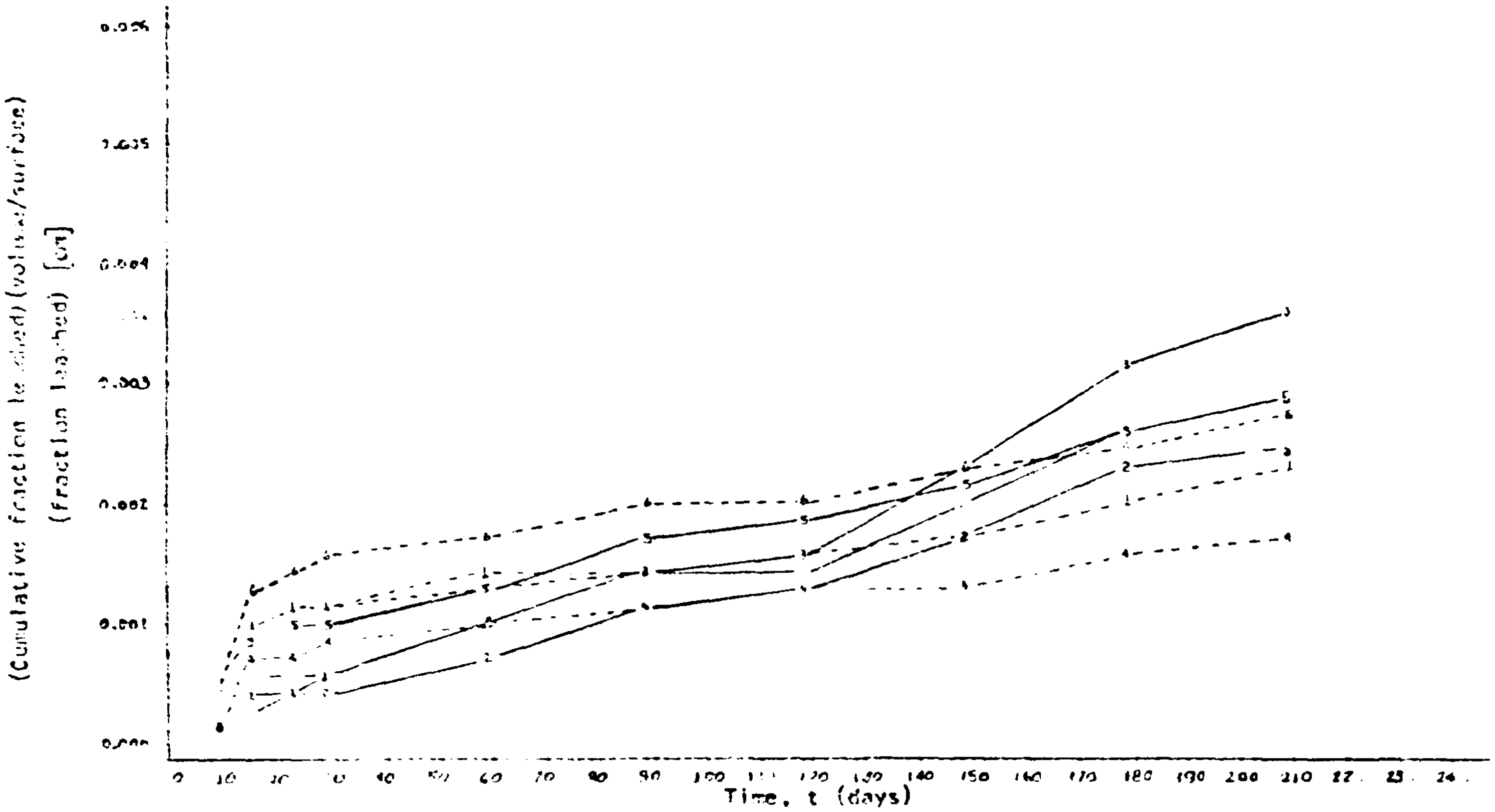


**Figure 7** – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the different type of bitumen studied containing 50% by weight of the ion exchange resin.

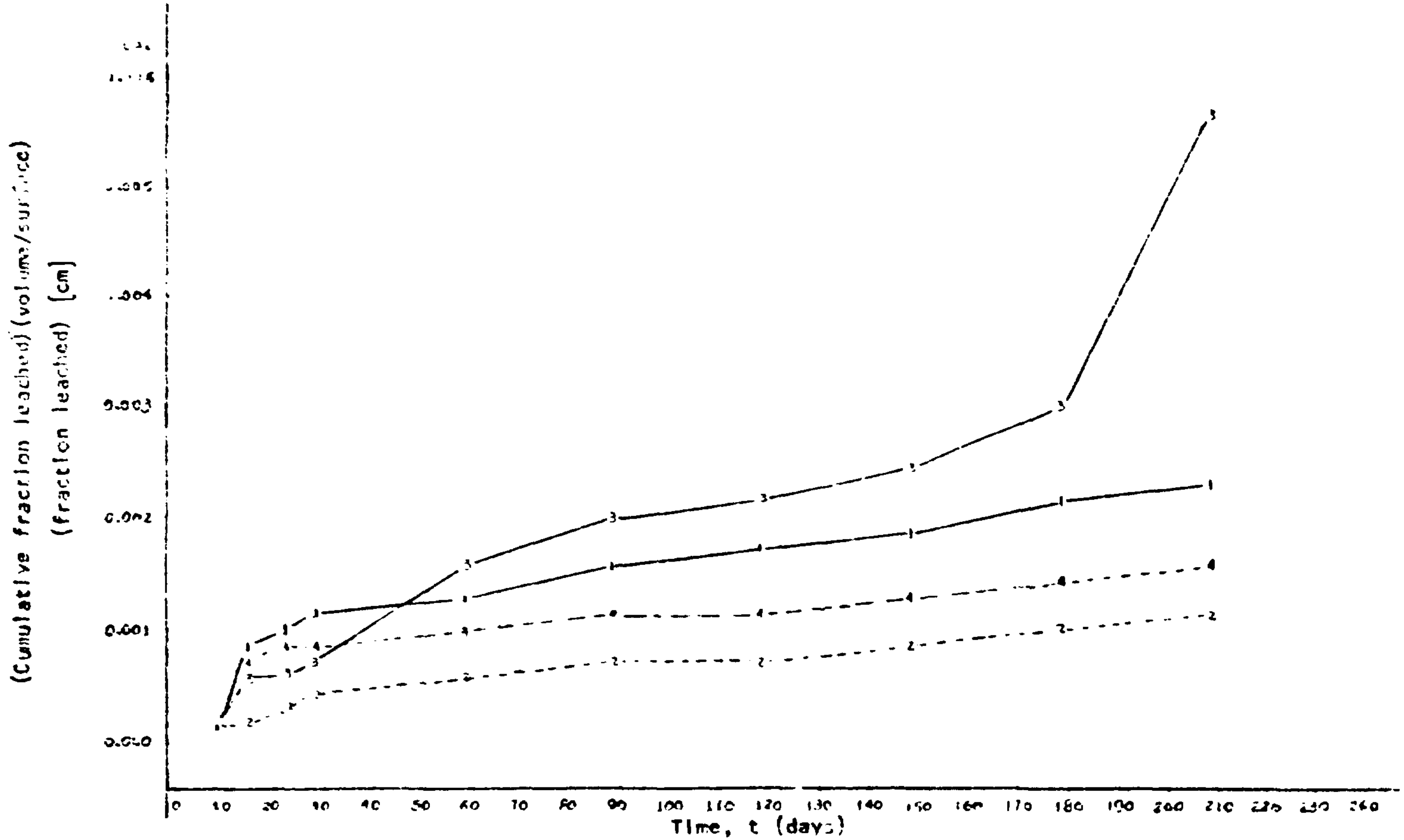


**Figure 8** – Cumulative fraction leached multiplied by the volume-surface ratio plotted against time for the different type of bitumen studied containing 60% by weight of the ion exchange resin.

## 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., 10, 1981. (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., (ORNL - TM - 4333)

4. GROSCHE Fº, C. E. *Estudo da betuminização de rejeitos radioativos de atividades baixa e média gerados em reatores tipo PWR.* (Dissertação de mestrado, IPEN-CNEN/SP - em preparação)