LEACHING RATIO FROM PELLET PACKAGE

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ABSTRACT

Radioactive concentrated liquid waste is dried and compressed into pellets. These pellets are solidified as a package, by pouring a solidifying agent into the spaces between them. This paper studies a leaching model for the pellet package and calculated results of the model are compared with long term experimental results, which were obtained using Na_2SO_4 pellets and cement-glass for a solidifying agent. The following conclusions are obtained:

- Diffusion coefficients and distribution factors can be evaluated by the volumetric average of cement-glass and pellet properties.
- Calculated results agreed with experimental ones obtained for a period of more than 600 days. The leaching ratio from a 200 ℓ pellet package could be estimated as 3×10^{-6} for the first year due to the low diffusion coefficient of the PIC barrier.

INTRODUCTION

A radioactive waste treatment system that can transform concentrated liquid waste generated from nuclear power plants into dry pellets has been developed to reduce waste volume (1). The concentrated liquid waste is dried into powder by a vertical thin film dryer. The powder is compressed into cylindrical (20ϕ X 10 mm) or almond-shaped (30 X 20 X 10 mm) pellets by a pelletizer. For final disposal in Japan, these pellets must be solidified as a package, by pouring an appropriate solidifying agent into the spaces between them. Cement-glass, which is a mixture of sodium silicate, silicon phosphate and cement, was developed to solidify the pellets in the container (2).

Evaluating leachability of the package is required for shallow land disposal. Previously, the leachability of cement of bitumen packages has been evaluated by solving the diffusion equation, because physical properties of the package can be regarded as the same throughout it (3). However, since the pellet package is clearly divided into the pellet and the solidifying agent regions, a new method is required to evaluate the leachability of heterogeneous packages.

In this paper, the diffusion equation for the pellet package is proposed, and its adequacy is studied by comparing calculated and experimental results.

LEACHING MODEL

Pellet Solidification System

Figure 1 shows a flow sheet of the pellet cement-glass solidification system. Pellets are poured into a 200 ℓ drum. After the measured amount of cement-glass powder and water is combined together in a mixer, the slurry is simply poured into the spaces between pellets to make a disposal package. Polymer impregnated concrete lining is made to increase the stability of the package.

Some part of the water in the cement paste is evaporated during the solidification reaction, and small pores remains in the concrete. These pores decrease the mechanical strength and allow water to permeate the concrete more easily. Therefore, steel fiber is added to increase mechanical strength. After cement paste is solidified, a polymer is injected into the pore to decrease the leaching ratio of radioactive species.

Basic Equations

Figure 2 shows a sectional view of a 200 ℓ pellet package and its leaching behavior. The pellet package is different

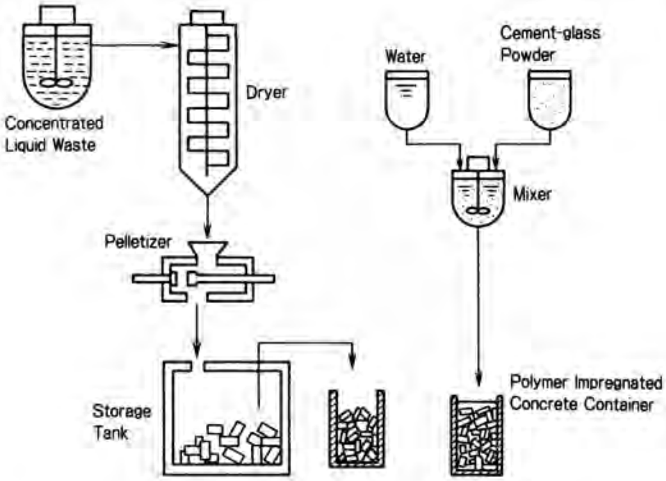


Fig. 1. Flow sheet of the radioactive waste treatment system.

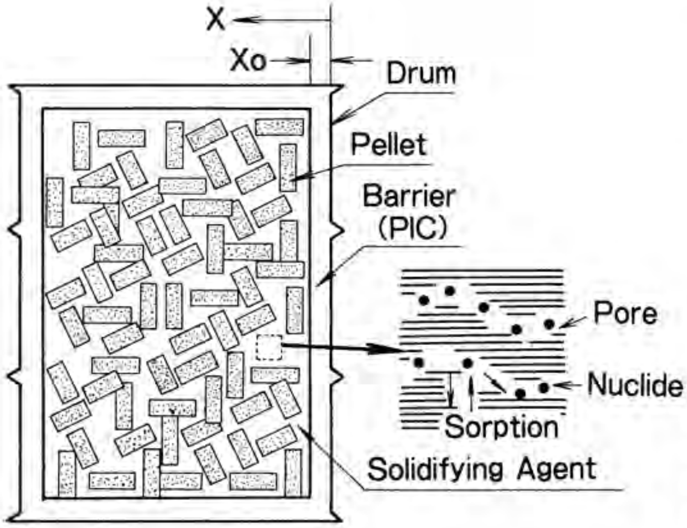


Fig. 2. Cross-sectional view of pellet package.

from ordinary cement or bitumen packages in the following points: (1) Physical properties, such as diffusion coefficient or distribution factor, differ in pellet and solidifying agent regions; (2) A polymer impregnated concrete (PIC) lining is manufactured as a barrier.

When the package is buried in a shallow land disposal site, it may be immersed in ground water. Polymer impregnated concrete, pellets and cement glass are porous. When pores are filled with ground water, the radionuclides are released by diffusion through them. Based on Fick's diffusion law, a one-dimensional diffusion rate is expressed as Eq. 1.

$$\frac{\partial C}{\partial t} = \frac{D}{\alpha}\frac{\partial^2 C}{\partial x^2} \qquad \text{(Eq. 1)}$$

where C = the concentration of radionuclide, $C = C_s \cdot \rho + C_p \cdot \varepsilon$(Bq/m $^{3)}$

t = the time(s)

D = the diffusion coefficient excluding sorption (m^2/s)

a = the sorption factor (-)

x = the length from the package surface (m).

Diffusing radionuclides in the pores are sorbed on the surfaces of the porous medium, and this sorption reaction is instantaneous and reversible. Then a linear law of equation (2) can be applied. The relation of the distribution factor K_d in equation 2 can be applied. The relation of the distribution factor K_d in equation 2 and the sorption factor a in equation 1 is expressed by Eq. 3.

$$K_d = \frac{C_s}{C_p} \qquad \text{(Eq. 2)}$$

$$a = \varepsilon + K_d\rho \qquad \text{(Eq. 3)}$$

where C_s = the concentration of sorbed radionuclide (Bq/kg)

C_p = the concentration of radionuclide in pore water (Bq/m^3)

ε = the porosity (-)

K_d = the distribution factor (m^3/kg)

ρ = the bulk density (kg/m^3).

Since the leaching ratio from the pellet package is very small due to the PIC barrier, only radionuclides near the barrier are leached. Then the one-dimensional diffusions equation can evaluate the leaching ratio with sufficient accuracy. Physical properties of the PIC can be applied for equation 1 in the barrier region ($x \leqq x_0$, x_0 is the thickness of the PIC barrier).

Then the volumetric averages of the pellet and the solidifying agent properties can be applied for equation 1 in the pellet solidified region ($x > x_0$). The volumetric averages for diffusion coefficients D and sorption factors a are expressed by equations 4 and 5.

$$D = D_s r + D_p(1-r) \qquad \text{(Eq. 4)}$$

$$a = a_s r + a_p(1-r) \qquad \text{(Eq. 5)}$$

where r = the volumetric ratio of solidified agent (-)

D_s = the diffusion coefficient of the solidified agent (m^2/s)

D_p = the diffusion coefficient of the pellet (m^2/s)

a_s = the sorption factor of the solidified agent (-)

a_p = the sorption factor of the pellet (-).

The pellet package is more complex than an ordinary cement package, because it is divided into two regions. Then equation 1 is solved numerically by the Crank-Nicolson method. The number of meshes in the x direction for each region is 1,000 and the time interval is 8,000s.

EXPERIMENTAL

Parameter Measurement for Calculation

For the experiments, pellets made of sodium sulfate were used as this is the main component of concentrated liquid waste generated from BWR plants. Cement-glass was selected as a solidifying agent. Since cement-glass shows a high distribution factor for cation radionuclides, cation radionuclides move very slowly in the pellet package. As discussed later, Na_2SO_4 pellets dissolve and, the dissolved ions moved much faster than the radionuclides. It could be assumed that the solidified pellet region was replaced by Na_2SO_4 saturated solution when radionuclides diffused through the pellets. Then properties of the pellet were evaluated by those of Na_2SO_4 saturated solution.

Properties of cement-glass and the PIC were measured as follows. The bulk density was calculated by sample size and weight. Porosity was measured by a mercury porosimeter.

Distribution factors of ^{134}Cs, ^{85}Sr and ^{60}Co were measured by a batch technique which has been widely used (4). ^{134}Cs and ^{85}Sr were used to simulate ^{137}Cs and ^{90}Sr. ^{137}Cs, ^{90}Sr and ^{60}Co represent the majority of radionuclides in radioactive waste generated from nuclear power plants. Solidified cement-glass and PIC were crushed to powder of 0.25 to 0.5 mm particles. Powder (1g) was immersed in Na_2SO_4 saturated solution (50 cm^3) for 21 days at 25°C. The activities of ^{134}Cs, ^{85}Sr and ^{60}Co were 20 kBq. After equilibrium was obtained, the radioactivity of the solution and the powder were measured by Ge detector. In this experiment, Na_2SO_4 saturated solution (22 wt% at 25°C) was used, because pore water was saturated with Na^+ and SO42- ions which were generated by dissolving the Na_2SO_4 pellet.

Figure 3 shows the experimental apparatus for measuring the cement-glass diffusion coefficient. A cement-glass disk (50ϕ X 5 mm) was attached to the bottom of the inner cylinder and both cylinders were filled with Na_2SO_4 saturated solution. Cs chemical tracer was added to the inner cylinder until the Cs concentration was 5,000 ppm. The Cs concentration change in the outer cylinder was measured and the diffusion coefficient was calculated by a steady state Eq. (6).

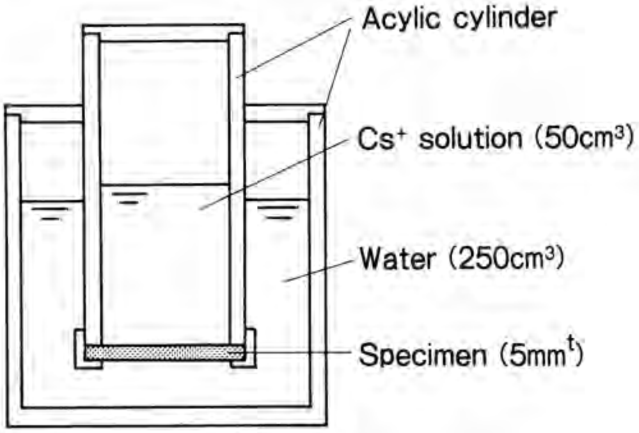


Fig. 3. Schematic diagram of diffusion cell for through-diffusion experiment.

$$D = \frac{h}{S \times C_i} \times \frac{dQ}{dt} \qquad \text{(Eq. 6)}$$

where h = the thickness of the disk (m)

C_i = the Cs concentration of the inner cylinder (Bq/m^3)

S = the surface area of the disk (m^2).

Q = leaching amount (Bq)

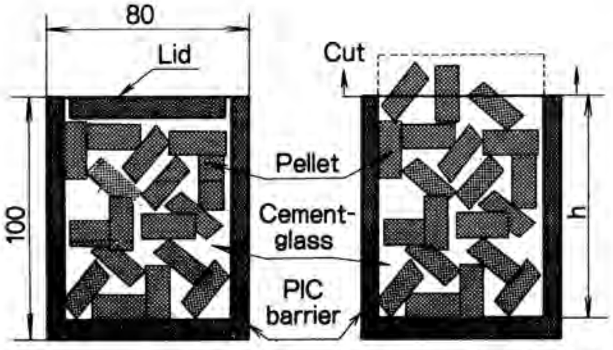
Since the Cs concentration profile in the disk did not change in the steady state, no sorption of radionuclide was occurred. Then the sorption effect on the diffusion rate could be neglected. When measuring the PIC diffusion coefficient, the PIC container itself was used instead of the disk.

Measurement of Leaching Ratio from Pellet Package

Figure 4 shows two types of leaching samples. Figure 4 (a) sample was used to measure the leaching ratio from the pellet package. About thirty pellets were put in a PIC container and cement-glass was poured into the spaces between them. A lid was tightly placed on the cement-glass paste so that no voids formed.

The activities of ^{134}Cs, ^{85}Sr and ^{60}Co were 0.8, 1.6 and 4 MBq. The diffusion coefficient of PIC was so small that its properties determined the overall leaching ratio from the package for a short time experiment. It was difficult to study the effect of pellets on the leaching ratio by the Fig. 4 (a) sample.

Then a sample was prepared in which pellets could directly contact with the leachant to allow study of leaching



(a) Sample for simulation of whole package (b) Sample for simulation of pellet solidified region

Fig. 4. Leaching sample for pellet package.

behavior in the pellet solidified region. As shown in Fig. 4 (b), pellets were put in a PIC container until parts of them were above the ridge of the container. After the cement-glass was solidified, the pellet solidified region was cut horizontally at the ridge. Chemical and radio isotope tracers were used for Fig. 4 (b) samples.

Cement-glass was cured at 25°C for 21 days. Samples were immersed into 1,500 cm^3 deionized water in polyethelene beakers and stored at 25°C. All the leachant was replaced at every sampling time. Chemical tracer and SO_4^{2-} concentrations of the leachant were measured by inductively coupled plasma (ICP) emission spectroscopy, and radio isotope concentration was measured by Ge detector. SO_4^{2-} concentration was measured to study the leaching ratio of Na_2SO_4 pellets.

RESULTS AND DISCUSSION

Leaching Behavior of Pellet Solidified Region

Table I lists the parameters determined for the calculation. Cement-glass shows high distribution factors for cation ions because it contains many Na^+ ions. PIC shows a very small diffusion coefficient because its pores were plugged by the injected polymer.

Figure 5 plots Co and Na_2SO_4 leaching ratios from Fig. 4 (b) samples. It takes three days to dissolve the surface Na_2SO_4 pellets, which directly contacted with the leachant. This low dissolving rate is controlled by diffusion, because the leachant was motionless. After the surface pellets are dissolved, the leaching rate of pellets in the cement-glass is also controlled by diffusion in the solidified region. The experiments show the Na_2SO_4 leaching behaviors until and after the third day are almost the same. Then the Na_2SO_4 leaching ratio appeared to increase in proportion to square root of time. The leaching ratio of Co was almost the same as that of Na_2SO_4 until the surface pellets had been dissolved. After that, Co leaching rate is much smaller than Na_2SO_4, because most of the diffusing Co ion is sorbed by cement-glass.

TABLE I
List of Determined Parameters

Parameter		Cement-Glass	PIC	Na_2SO_4 Pellet
Diffusion coefficient: D (m^2/s)		3×10^{-11}	2×10^{-17}	1.3×10^{-9}
Distribution factor: K_d (m^3/kg)	Cs	0.087	<0.0001	<0.0001
	Sr	4.3	0.019	<0.0001
	Co	0.59	0.93	<0.0001
Bulk Density: ρ (g/cm^3)		1.48	2.46	2.2
Porosity: ε (-)		0.26	0.05	1.0

Equation 1 is approximated by Eq. 7 for Fig. 4 (b) samples, because leaching through the PIC barrier can be neglected.

$$q = \frac{1}{C_0 \times h} \int_0^t \frac{D}{\alpha} \times \left(\frac{\partial C}{\partial x}\right)_{x=0} dt \qquad \text{(Eq. 7)}$$

$$= \frac{2}{h} \times \left(\frac{D \times t}{\pi \times \alpha}\right)^{0.5}$$

where q = leaching ratio (-)

C_0 = the initial concentration of radionuclide

h = the height of the pellet solidified region (m).

The solid line in Fig. 5 is calculated by Eq. 7. But the experimental results deviate greatly from it, because Co in the surface pellets is leached without being sorbed by cement-glass. Then Eq. 7 is modified to Eq. 8.

$$q = \frac{2}{h} \times \left(\frac{D}{\pi \times \alpha}\right)^{0.5} \times \left(t^{0.5} - t_0^{0.5}\right) + q_0 \qquad \text{(Eq. 8)}$$

Three days is the period until the surface pellets have dissolved or t_0. The ratio of surface pellets weight to total is q_0 and is 0.05. Calculated results of equation 8 are shown in

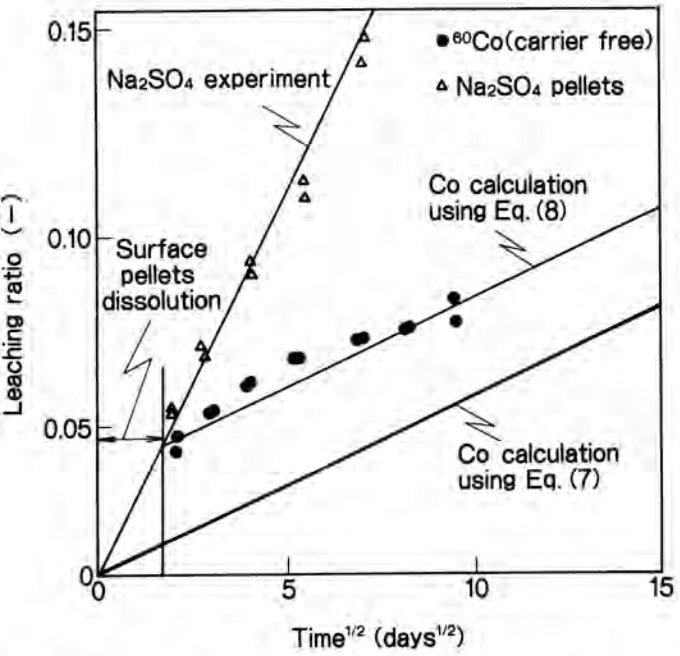


Fig. 5. Na_2SO_4 and Co leaching ratios from solidified pellet region.

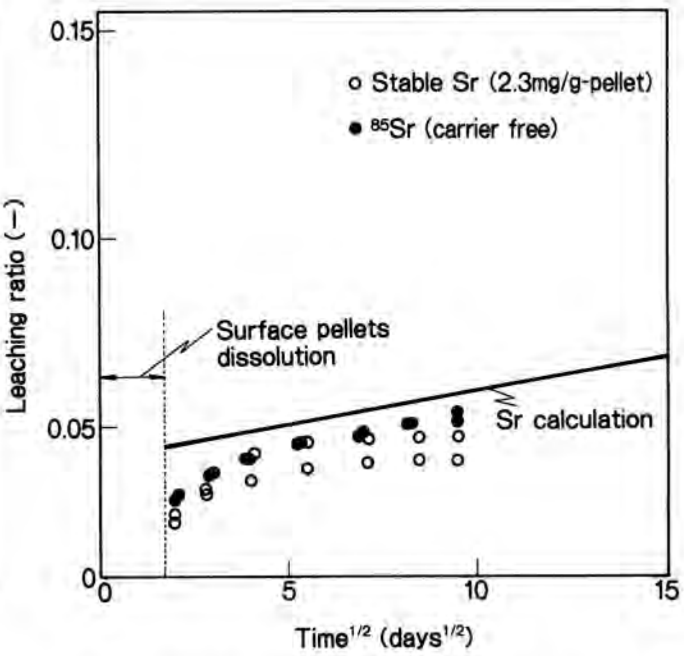


Fig. 7. Sr leaching ratio from solidified pellet region.

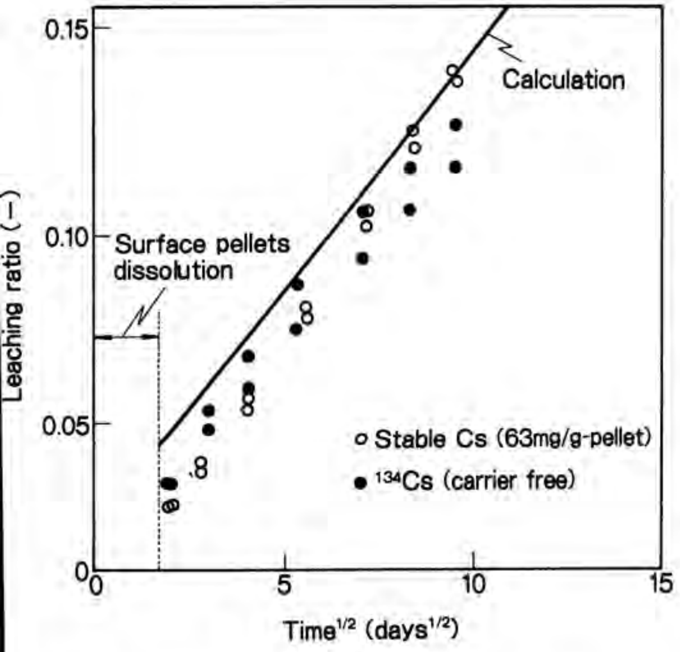


Fig. 6. Cs leaching ratio from solidified pellet region.

Fig. 5 by a dotted line, and agreement with experimental results is good.

Leaching ratios of Cs and Sr are shown in Figs. 6 and 7. Experimental results using chemical tracers are scattered among those using radio isotopes. No difference is found between chemical tracer and radio isotope for the leaching study. Solid lines in both figures are calculated results of equation 8. The difference between calculated results depends on the distribution factor of each nuclide. Although the distribution factor of Cs is much higher than that of SO42-, the leaching ratio of Cs is close to that of Na_2SO_4. This is because the maximum SO42- concentration in pore water is repressed by the Na_2SO_4 saturated solubility. Since good agreement is obtained between calculated and experimental results, the diffusion behavior in the solidified pellet region can be evaluated by the volumetric average of the saturated Na_2SO_4 solution and cement-glass.

Leaching Behavior of Pellet Package

Figure 8 shows Cs leaching ratio from Fig. 4 (a) samples. The leaching ratios from Fig. 4 (a) samples are smaller by a factor of 1,000 than those from Fig. 4 (b) samples due to the low diffusion coefficient of the PIC barrier. The leaching ratio appear to be nearly in proportion to the relative surface area as shown in equation 9.

$$q \propto \frac{S}{V} \qquad \text{(Eq. 9)}$$

where S = the surface area of the sample (m^2)

V = the volume of the sample (m^3)

The S/V of Fig. 4 (a) sample was 14 times bigger than that of a 200ℓ drum package. And the Cs leaching ratio from the 200ℓ pellet package may be less than 3 X 10^{-6} during the first year.

A numerical solution of Eq. 1, which considers both barrier and pellet solidified regions is shown by the solid line in Fig. 8. Experimental results are well predicted for more than 600 days by solving Eq. 1.

CONCLUSION

A leaching model for pellet packages was proposed. Calculated results were compared with long term experimental results, which used Na_2SO_4 pellets and cement-glass for a solidifying agent. The following conclusions were obtained:

1. Diffusion coefficients and distribution factors of the pellet solidified region could be evaluated by the volumetric average of cement-glass and pellet properties.
2. results calculated using the volumetric average agreed with experimental results obtained for data of more than 600 days. The leaching ratio from a 200ℓ pellet package could be estimated as 3 X 10^{-6} for the first year due to the low diffusion coefficient of the PIC barrier.
3. Even if some pellets were in direct contact with the leachant, the leaching ratio was evaluated by the diffusion behavior after the surface pellets were dissolved.

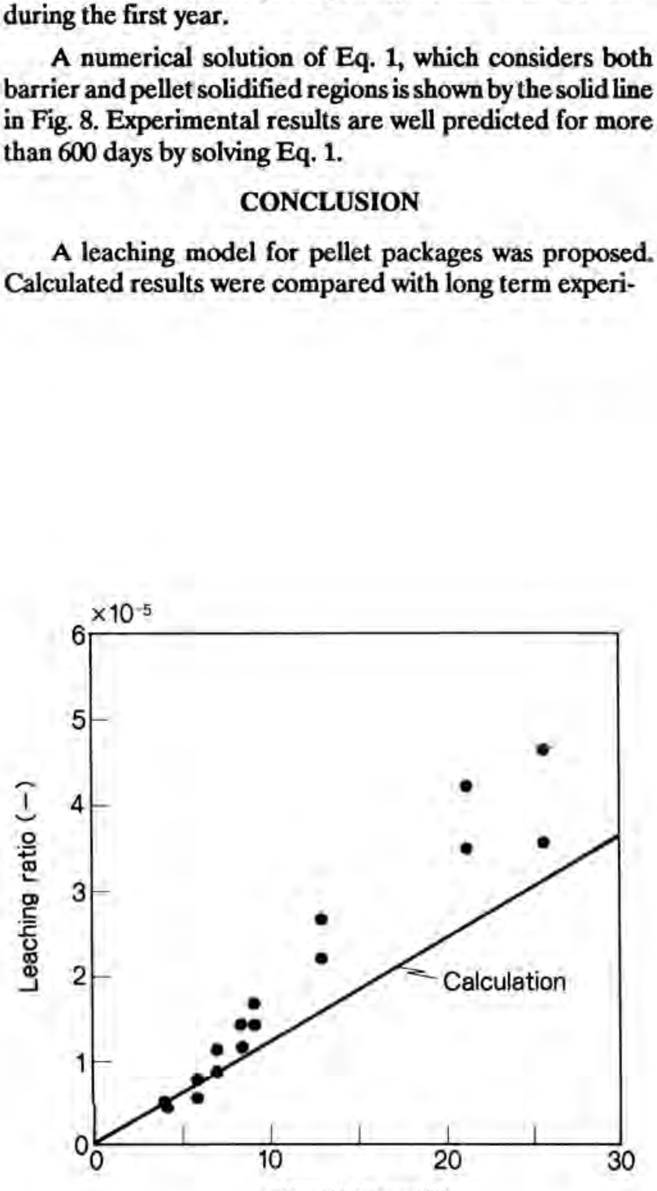


Fig. 8. Leaching experiment with PIC barrier.

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