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ILT15 - A Computer Program for Evaluation of Accelerated Leach Test Data of LLW in the Hungarian NPP Paks

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Abstract

Computer Program ILT15 developed to accompany a new leach test for solidified radioactive waste forms in the Hungarian NPP Paks. The program is designed to be used as a tool for performing the calculations necessary to analyse leach test data, a modelling program to determine if diffusion is the operating leaching mechanism (and, if not, to indicate other possible mechanisms), and a means to make extrapolations using the diffusion models. The ILT15 program contains four mathematical models that can be used to represent the data, diffusion through a semi-infinite medium, diffusion through a finite cylinder, diffusion plus partitioning of the source term and solubility limited leaching. The program is written in C++ in the Borland C++ Builder programming environment. A detailed description of application of this modelling computer program is given.

Keywords

accelerated leach test, computer program, diffusion, fitting, cylinder

1 Introduction

For a number of years increasing attention has been given in Hungary to the management of the low and medium level radioactive wastes (LLW, MLW) being produced in Paks nuclear power plant.

Some of these wastes, for example, evaporator bottom concentrates, pond sludge and spent ion exchange media are produced in relatively large volumes. In addition to national programs on the development of immobilization processes, the European Community commissioned programs on the immobilization of LLW and MLW. These wastes are immobilized by incorporating them into cement. In order to optimize these immobilization processes, for example with respect to waste loading, it was necessary to characterize the products with respect to such properties as density, strength, dimensional stability, leach resistance and so on. In this article we report about an accelerated leach test and the developed computer program.

Computer Program ILT15 was developed to accompany a new leach test for solidified radioactive waste forms. The program is designed to be used as a tool for performing the calculations necessary to analyse leach test data, a modelling program to determine if diffusion is the operating leaching mechanism (and, if not, to indicate other possible mechanisms), and a means to make extrapolations using the diffusion models. The ILT15 program contains four mathematical models that can be used to represent the data.

The mathematical models describing leaching mechanisms are as below:

1. Diffusion through a semi-infinite medium (for low fractional releases),
2. Diffusion through a finite cylinder (for high fractional releases),
3. Diffusion plus partitioning of the source term,
4. Solubility limited leaching.

The program uses simple mathematical models described in the ASTM C1308-08 [1] standard and the fundamentals can be seen below in the next topic.

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2 The short description of models used for data processing

Recently, several test methods have been developed to measure diffusive releases including:

- ASTM C 1308, Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Fractional Leaching from Cylindrical Waste Forms (ASTM 2008).
- EPA Draft Method 1315, Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using as Semi-Dynamic Tank Leaching Test (EPA 2009b).
- ANSI/ANS-16.1-2003; R2008; R2017: Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure.

Unlike the ANS-16.1 and EPA 1315 methods, the ASTM 1308 method calculates a diffusion coefficient based on a cumulative release rather than an incremental release. It effectively calculates an average over the duration of the test and it was chosen for our investigation.

2.1 Leaching by diffusion

Mass transfer via diffusion is described by the Fick laws. In simplest case the diffusion is not depends on time and described by the Fick 1st law:

$$\Phi_m = -D\frac{\Delta C}{\Delta x} \qquad \Phi_m = \frac{\Delta m}{A \cdot \Delta t} \tag{1}$$

Φ_m	mass flow density (mass flux), mass of material diffused through a unit of area during unit of time	$kg/(m^2*s)$
D	diffusion coefficient	m^2/s
C	mass concentration	kg/m^3
x	diffusion path parallel with	m
m	mass in diffusion	kg
A	area (cross section) normal to diffusion	m^2
t	time	s

This process is ideal, supposing timeless inflow of diffusing material and constant concentrations in time at various distances.

In case of changing concentrations in space and time the Fick 2nd law describes the phenomena:

$$\frac{\Delta C}{\Delta t} = D\frac{\Delta\left(\frac{\Delta C}{\Delta x}\right)}{\Delta x} \tag{2}$$

where:

$\frac{\Delta\left(\frac{\Delta C}{\Delta x}\right)}{\Delta x}$ linear concentration gradient change in space

In general form:

$$\Phi_m = -D\frac{dC}{dx} \quad \text{Fick 1}^{\text{st}} \text{ law} \tag{3}$$

$$\frac{\partial C}{\partial t} = -D\nabla^2 C \quad \text{Fick 2}^{\text{nd}} \text{ law} \tag{4}$$

2.2 Basics of the test and requirements for the test components

The base of the leach test is a semi dynamic method, when a cylindrical specimen is immersed in a leach solution (water or aqueous solution), then usually in time the specimen is exchanged with a new one end the leached concentration or mass is determined. This compared to the original total concentration or mass results the Incremental Fraction Leached (IFL). Summing the IFL values till a given leach time we get the Cumulative Fraction Leached (CFL) values. More frequent exchange of specimens during the test results more exact modelling with the Fick 2nd law, but the leached amount of material will be lower and the determination uncertainty will be larger. Because of the above restrictions the leaching time intervals are optimized. For that reason the leach test should be completed under standard conditions, including the specimen and leach solution characteristics as well as the leach vessel material and auxiliary conditions (specimen fixation, mixing, filtering etc.).

2.2.1 Requirements for the leaching liquor

- the leach solution will not react with the material of the specimen and will not modify it
- the leach solution should not contain such a component, which modifies the leaching mechanism

2.2.2 Requirements for the leaching vessel

- the wall of the vessel could not react with the solution and leached components
- the exchange of the solution should be easy and the solution in the vessel should not evaporate

2.2.3 Requirements for the auxiliary components

- their materials should not react with the solvent and with the leached materials
- the filtered leached materials could be analysed
- the filter will remove particles with diameter > 45 µm
- the hanging the specimen should not influence the leaching and should not cover more than 1 % of the surface

2.2.4 Requirements for the specimen

- the specimen is a cylindrical body with a diameter/height ratio 1/1 and their value is 2.5 cm
- the specimen composition should be identical with the waste composition
- the distribution of the radioactive isotope(s) or heavy metal material should be uniform in specimen
- the structure of the specimen material should be the identical at the surface and in the bulk
- every specimen's geometry, mass and embedded radioactive or heavy metal content should be accurately determined

2.2.5 Other requirements

- the temperature during leaching should be constant with a maximum fluctuation less then: 1°C
- surface to volume ratio for specimen should be constant during leach test(s) and the ratio should be:

$$S_V = \frac{S_S}{V_L} = 0.1\left(\text{cm}^{-1}\right) \tag{5}$$

where:

S_V	specific surface	1/cm
S_S	specimen surface	cm^2
V_L	volume of leaching liquid	cm^3

Regularly at determined term in the leaching liquid should be changed the amount of the leached material or activity should be determined. These intervals should be from the start of leaching 2h, 7h, 24h, 48h, till the end of the 11$^{\text{th}}$ day.

By using the determined leached amounts of material (s) or activities one can calculate the Incremental/Cumulative Fraction Leached *IFL*/*CFL*):

$$IFL = \frac{a_{i,j}}{A_{i,0}}$$
$$CFL = \frac{\sum_{j=1}^{n} a_{i,j}}{A_{i,0}} = \sum_{j=1}^{n} IFL_j \tag{6}$$

where:

i	index of the radioactive isotope or heavy metal	
j	index of the leach time interval	
a	leached in the actual-time interval activity (concentration) for the actual- isotope or heavy metal	Bq
$A_{i,0}$	activity or concentration of the actual-radioactive isotope or heavy metal in the specimen before the start of leaching	Bq

Using the *IFL*/*CFL* values the D_e effective diffusion coefficient could be determined. Accuracy of fitting of the leach data could be characterized by the following equation:

$$E_{R^2} = \frac{\sum_{j=1}^{n}\left(CFL_{j,model} - CFL_{j,measured}\right)^2}{CFL_{n,measured}} \tag{7}$$

where:

	fitting error between the measured and calculated *CFL* values at a given fitting model	%
%n	number of leaching time intervals	
$CFL_{j,model}$	calculated by fitting model *CFL* value at the j-th interval	
$\mathbf{CFL}_{j,measured}$	measured leached *CFL* value at the j-th interval	
$CFL_{n,m}$	measured leached *CFL* value at the n-interval (sum)	

A fitting model is suitable to describe the measured leaching *CFL* data if $E_{R^2} < 0.5$ %

3 Leaching models used in the program

3.1 Diffusion leaching model

Model uses two calculation methods:

- diffusion in semi-infinite specimen
- diffusion in finite cylindrical specimen

Calculation starts with the diffusion in semi-infinite specimen using some early leaching data pairs (*CFL* < 0.2) determining the diffusion coefficient, and continues the calculations with diffusion in finite cylindrical specimen. Diffusion in semi-infinite specimen method uses the following equation:

$$CFL = \frac{\sum_{j=1}^{n} a_j}{A_0} = 2\frac{S}{V}\left[\frac{D_e t}{\pi}\right]^{1/2} \tag{8}$$

where:

a_j	activity leached in the actual time interval	Bq
A_0	sum of activity present in specimen at t=0	Bq
n	number of time intervals	
S	surface area of the specimen	cm^2
V	volume of the specimen	cm^3
D_e	effective diffusion coefficient	m^2/s
t	time of leaching	s

If the $CFL > 0.2$ calculation continues using the diffusion in finite cylindrical specimen method, where the cumulative fraction leached (CFL) is calculated using a double series expression,

$$S_p aCFL = \frac{\sum_{j=1}^{n} a_j}{A_0} = \left(1 - \frac{32}{\pi^2} S_p(t) S_c(t)\right) \tag{9}$$

with the series nd S_c defined in the standard.

Calculations for CFL values in the program are based using equations developed by Pescatore [2, 3].

3.2 Diffusion plus Partition leaching model

In the partition model a fraction of the contaminant is considered to be immobile and not leachable. This model uses the model for diffusion from a finite cylinder (or a semi-infinite cylinder) if the CFL leached is less than 0.0124, but alters the result by reducing the original source term so that the cumulative fraction leached is determined according to the following equation:

$$CFL = \frac{\sum_{j=1}^{n} a_j}{PA_0} = 2\frac{S}{V}\left[\frac{D_e t}{\pi}\right]^{1/2} \tag{10}$$

where P is the source term partitioning factor between 0 and 1.

3.2.1 Solubility-Limited leaching model

This model accounts for the leaching system in which diffusion is affected by the limited solubility of a radioactive isotope or heavy metal. The model is based on the concept that the leached incremental fractions will be the same at the end of each 1-day sampling interval in case of solubility-limited leaching. This is a nondiffusion controlled leaching.

4 Using the program in the NPP

4.1 Running the program

When the program begins to run after the installation the following main menu will appear on the screen waiting for the input data from the keyboard or from a "csv" data file.

We entered the measured leach data from experimental results (e.g., leach time and counts per minute–cpm or – concentration). Additionally we input the height and diameter of the solid cylindrical specimen, volume and surface and material of lecher, and the number of summa count of radioactivity or concentration. Alternatively we input the leaching data from an earlier saved „csv" data file.

As an example we input the Cs-137 leach test data using the leach test data measured from a c400 cement cylinder with the embedded evaporator bottom residue of the tank 02TW10B002 of the NPP (Fig. 1).

After completing data input (and/or editing) we selected the fitting model form the „Calculation" menu. (Fig. 2)

First we chose the „Diffusion Leaching Model" and clicking on „Calculation" button the following windows appeared (Fig. 3).

The resulted window contains the measured and calculated (fitted) CFL values for each leach time as well as the determined diffusion coefficient in cm^2/sec and in cm^2/day unit and the relative error of fitting in percent. A fit is usable if the relative error is less than 0.5 %.

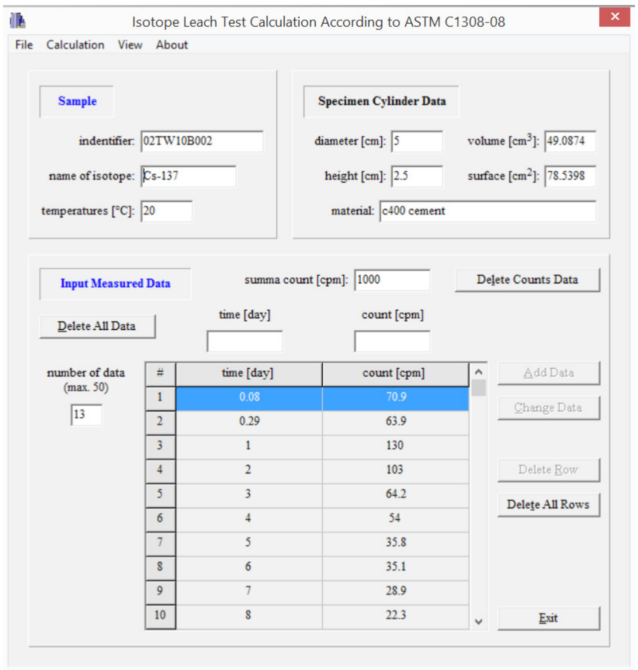

Fig. 1 Input leach test data of cemented evaporator bottom residue of tank 02TW10B002

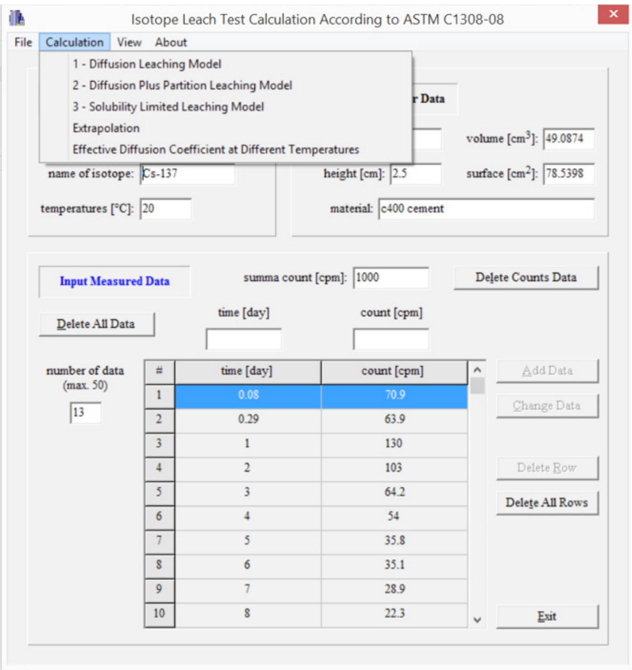

Fig. 2 Choosing the diffusion leaching model for fit

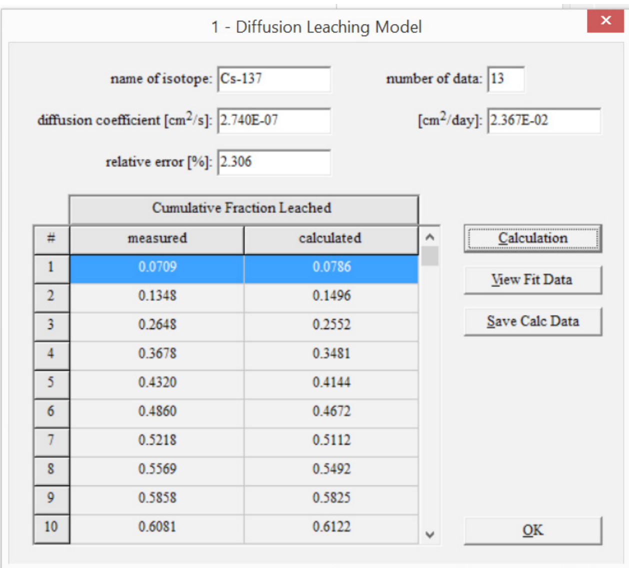

Fig. 3 Calculation results choosing the „Diffusion Leaching Model"

By clicking on the „View Fit Data" button the following diagram appeared (Fig. 4)

After saving the data and diagram we used the other two fitting models too to find the most accurate fitting model.

The graphical fitting results of the "Diffusion Plus Partition Leaching Model" and the "Solubility Limited Leaching Model" are shown in Figs. 5-6.

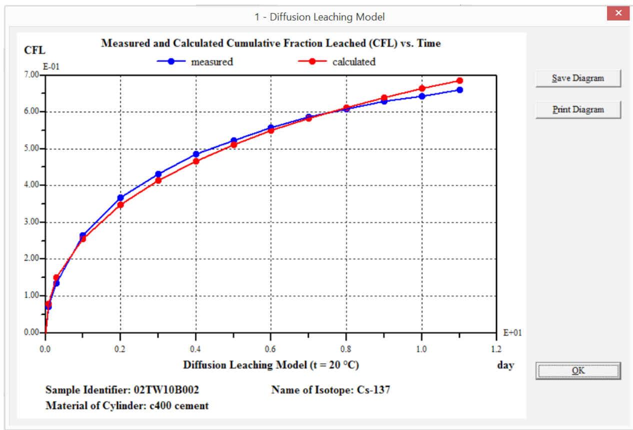

Fig. 4 Graphical result of fit Diffusion Leaching Model

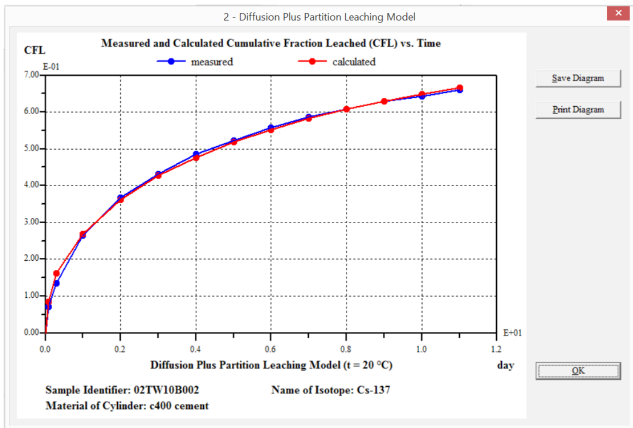

Fig. 5 Graphical result of fit Diffusion Plus Partition Leaching Model

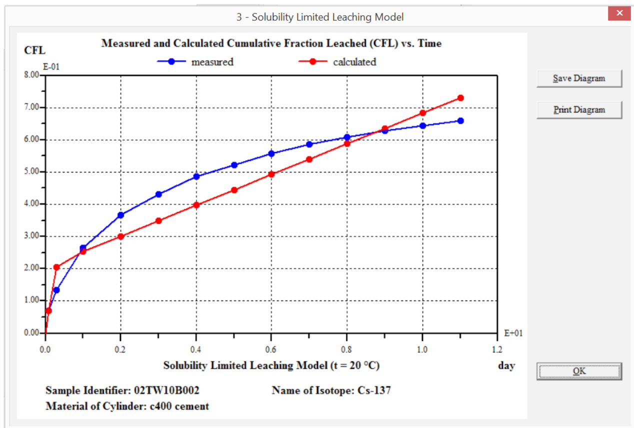

Fig. 6 Graphical result of fit Solubility Limited Leaching Model

5 Results

According to the results of the three model fitting, the most accurate model for the description of leaching Cs-137 from c400 cement matrix in case of embedded evaporator bottom residue (tank 02TW10B002) is the Diffusion Plus Partition Leaching Model. Table 1 contains the relative errors in percent and the determined diffusion coefficients.

Table 1 Model fitting results for Cs-137 leaching from c400 cement

Leaching model	relative error (%)	D(cm^2/s)
Diffusion	0.531	1.25×10^{-7}
Diffusion plus partition	0.121	2.56×10^{-7}
Solubility limited	-	2.28×10^{-7}

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