

Solubility model for the pore solution of leached concrete containing solidified waste

R. BARNA¹, P. MOSZKOWICZ¹, J. VERON¹ and M. TIRNOVEANU²

¹INSA Lyon, LCPAE, 20 av. A. Einstein, 69621 VILLEURBANNE, France

²Fac. Chim. Ind., 2 Piata Victoriei, 1900 TIMISOARA, Romania

ABSTRACT

The long term behaviour of leached blocks of solidified wastes must be modeled from the results of laboratory experiments in order to predict the conditions of a long and safe storage. The solidification with Portland cement of two wastes has been studied: air pollution control residues from municipal solid waste incineration (named REFIOM) and slag from lead secondary smelting (named SCORIE). Both wastes are essentially composed of mineral salts and contain a high level of heavy metals such as Pb. Long term laboratory leaching experiments (more than 1 year duration) allowed us to observe the release of the soluble species. The leaching experiments were performed by contacting the blocks with pure water. A very good fit of the experimental results with the simulated data has been obtained by using a 3 dimension diffusional model for the very soluble ions (Na). In contrast to this situation, the release of heavy metals (Pb) is controlled by the chemical interactions within the solid matrix and by the changes in the pore water composition. The simple diffusion model must be improved in order to include these phenomena.

INTRODUCTION

Stabilization/solidification using ordinary Portland cement is becoming an interesting way for a safe confinement of hazardous wastes before landfilling.

The leaching properties of the concretes is one of the most important properties which characterize the retention quality of the solidification process. A wide range of tests have been applied in order to evaluate the leaching properties of cement materials. Some of them are going to be regulatory [1], [2], [3], [4]. The purpose of the tests is to address the leaching potential and the leaching rate.

Modeling of leaching behaviour is necessary in order to have a reasonably good chance to evaluate the long term behaviour of cement stabilized wastes. Obtaining a complete model of leaching behaviour is not easy: cement matrix containing the waste is a very complex heterogeneous medium. The cement matrix itself reacts with the surrounding leaching solution: the "corrosion" of the cement paste occurs because the main component (portlandite) is soluble in the pore liquid. A consequence is a decalcification of the matrix. In the pore solution context, contaminants dissolve more or less and may be mobilized.

BULK DIFFUSION MODEL

Generally, the release phenomenas are described by a diffusional model [5]. The mobile species are initially present at the concentration c_0 in the block. They diffuse toward the external surfaces of the sample in contact with water. This phenomena is described by Fick's law using an effective diffusion coefficient D_e that reflects the microscopic physico-chemical phenomenas.

If leaching occurs on the six faces of a monolithic block, the three-dimensional equation is:

$$\frac{\partial c}{\partial t} = D_e \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right)$$

where:

- c [kg/m³] is the homogeneous concentration in the bulk medium,
- t is the time of leaching [s],
- x, y, z are the geometrical coordinates [m] and
- D_e is the effective diffusion coefficient [m²/s].

The initial condition is: $c = c_0$, when $t = 0$.

The limit condition is: $c = c_i$, at the solid-liquid interface. In the case where the removing of the leaching solution is sufficient, c_i is equal to zero.

The main assumptions of the model are:

- the contaminant is initially available uniformly in the bulk at the concentration c_0 ,
- the bulk remains homogeneous and D_e remains constant during all the leaching,
- no chemical reaction disturbs the physical mass transfer.

This model is a phenomenological description of the process, including at a macroscopic scale all what happens at the microscopic scale: dissolutions, chemical reactions, diffusion mass transfer and effect of the tortuosity of pore system.

The two parameters which characterize the intensity and the rate of contaminant release are c_0 and D_e .

The experimental identification of the two parameters allows to simulate the long term behaviour of a leached block. Two different tests are required for the identification of the two parameters: a short-term one, conducted on a crushed part of the solid block, with the aim to assess the available amount c_0 of the leachable contaminant; a leaching procedure conducted on the solid block aimed at measuring the effective diffusion coefficient D_e .

We proposed [6] a new approach based on the simultaneous identification of the two parameters, c_0 and D_e , from only one tank leaching test.

EXPERIMENTAL METHODS AND RESULTS

The solidification with Portland cement CPA 55 of the two wastes, REFION and SCORIE, was studied; the blocks were made with a waste/solid ratio=2.33.

The leaching tests were conducted on blocks of 4*4*8 cm³, one with pure concrete, one with concrete and REFION and one with concrete and SCORIE.

The blocks were contacted with pure water (25±2°C) at a liquid/solid ratio = 10. The renewal time of the contact solution was: 0.25, 1, 2, 4, 8, 16, 32, 64, 135, 285 and 379 days. In order to verify the reproducibility, the experiments were performed in parallel on two blocks. Samples of the leachates were analyzed to determine the content of ions (atomic absorption spectrometry, induced coupled plasma emission spectrometry).

In the first six figures are plotted the experimental cumulated leaching data of sodium and calcium.

In figures 7-12 are plotted the experimental flux data and the simulation results for sodium and calcium. The simulations were performed after the identification of the two parameters of the model, c_0 and D_e , by using an optimal search method [6].

The logarithm data representation (logarithm of release flux $[kg/m^2s]$ against the logarithm of time $[s]$) offers the possibility to identify the diffusional release mechanism.

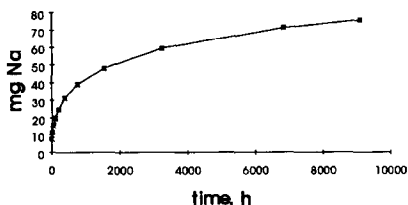


Fig. 1: Cumulative leaching of Na from pure concrete

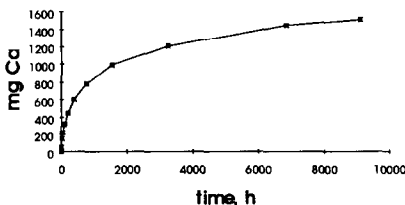


Fig. 2: Cumulative leaching of Ca from pure concrete

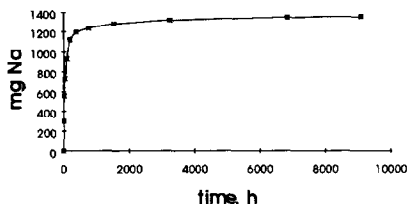


Fig. 3: Cumulative leaching of Na from REFION

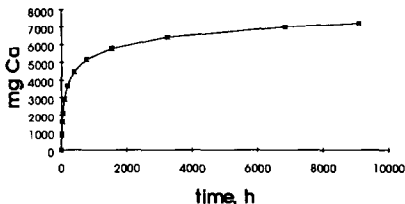


Fig. 4: Cumulative leaching of Ca from REFION

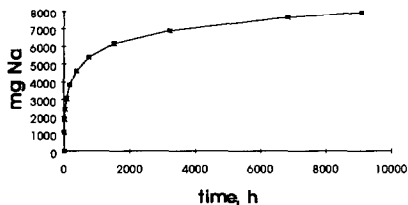


Fig. 5: Cumulative leaching of Na from SCORIE

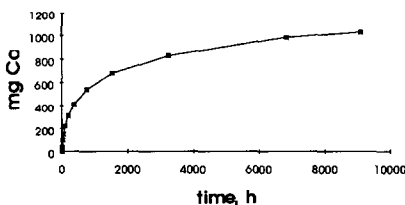


Fig. 6: Cumulative leaching of Ca from SCORIE

Before the depletion of the core occurs, the release flux J must be proportional to $t^{-0.5}$ (the slope of the graph = - 0.5). The experimental data (Figs. 7-12) for Na and Ca fit rather well the diffusional approach, showing the very good reproducibility of the experimental results, the depletion after 1 to 3 days and a "residual" flux appearing after 60-80 days of leaching; this flux is greater than the theoretical diffusional flux

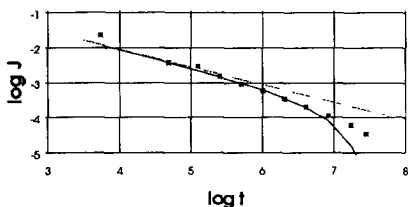


Fig. 7: Leaching of Na from pure concrete

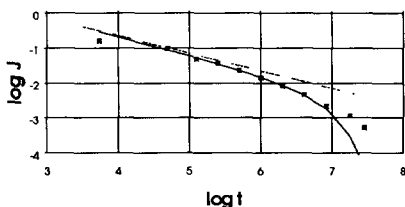


Fig. 8: Leaching of Ca from pure concrete

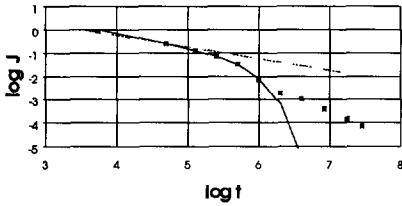


Fig. 9: Leaching of Na from REFIONM

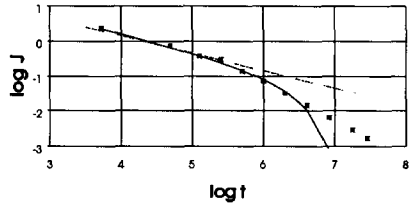


Fig. 10: Leaching of Ca from REFIONM

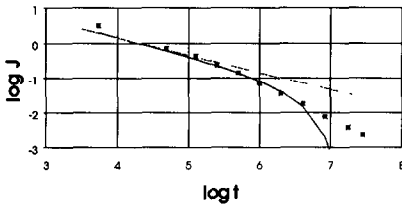


Fig. 11: Leaching of Na from SCORIE

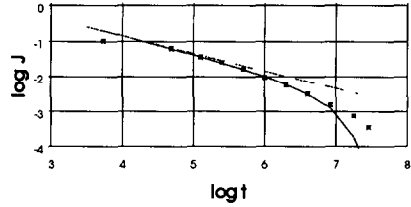


Fig. 12: Leaching of Ca from SCORIE

DISCUSSION

Calcium and sodium

The concentration of Na is about 1g/kg in the cement, about 100 g/kg in the SCORIE and about 20 g/kg in the REFIONM.

The calculated optimal values c_0 are in good agreement with the total content (Table 1).

Table 1. Optimal values (using the 64 days leaching data) of the diffusional model parameters

Material	Na		Ca	
	c_0 [kg/m ³]	D_e [m ² /s]	c_0 [kg/m ³]	D_e [m ² /s]
concrete	0.44	$1.3 \cdot 10^{-11}$	10	$1.3 \cdot 10^{-11}$
REFIONM	10	$20 \cdot 10^{-11}$	44	$4 \cdot 10^{-11}$
SCORIE	45	$3.5 \cdot 10^{-11}$	7	$1.4 \cdot 10^{-11}$

The differences for the D_e values are in agreement with the physical properties of the blocks (particularly the porosity).

The c_0 values for Ca show a difference due to its origine: brought by the waste or by the cement. c_0 decreases for SCORIE in comparison to concrete (dilution effect) but increases for REFIONM. That means that not all the Ca-content of concrete is leacheable; an explanation could be related to the different components of the hydratated cement: portlandite and CSH [7]. The portlandite, more soluble, can have an essential contribution to the "immediate" leacheable Ca fraction.

The lower values of D_e for Ca (in comparison with Na) are due to the limitation of the solubilisation of Ca in water within the pores.

Lead

The Pb content of the two wastes is different: about 100 g/kg SCORIE (major chemical component: PbS) and some g/kg REFIOU (major chemical component: PbO).

The cumulated leaching results of the two solidified wastes (fig. 13 and 14) and their leaching flux data (fig. 15 and 16) indicate that a simple diffusion mechanism of Pb leaching cannot be derived.

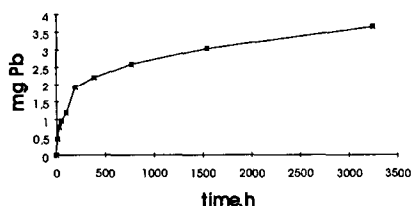


Fig. 13: Cumulative leaching of Pb from REFIOU

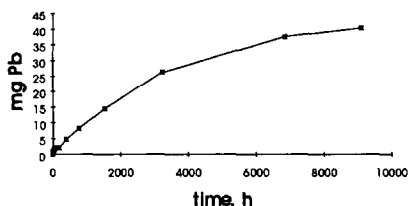


Fig. 14: Cumulative leaching of Pb from SCORIE

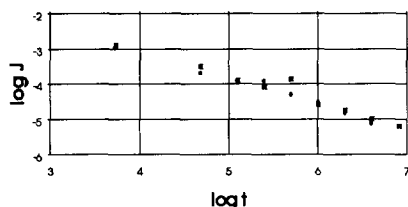


Fig. 15: Leaching of Pb from REFIOU

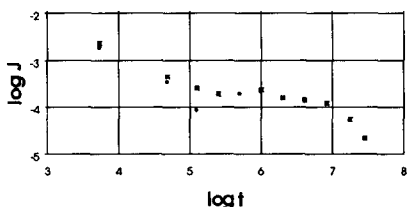


Fig. 16: Leaching of Pb from SCORIE

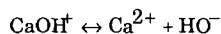
For REFIOU, the Pb release flux J is proportional to $t^{-0.75}$ (for 379 days), with a good reproducibility.

For SCORIE, the reproducibility and the regularity of the phenomena are less obvious. The flux decreases in a first step and seems constant from 2 to 64 days. Decrease starts again after this period.

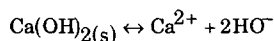
The flux values are of the same order, in spite of the different initial concentration of Pb in the two wastes. It seems that the Pb release model must take account the chemical phenomenas of solubilisation. The pH (≈ 12.4) of pore solution is the limiting factor of the solubilisation of Pb [8].

A mass-transfer model coupled with solubilisation, controlled by the chemical conditions of the pore solution (by example, the pH evolution is function of Ca release) must be improved, including chemical equilibria and diffusional mass transfer.

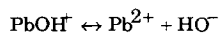
-chemical equilibria:



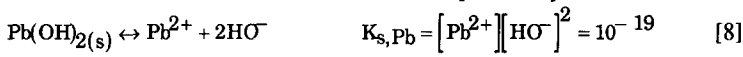
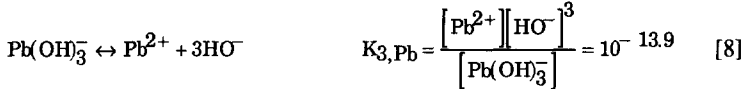
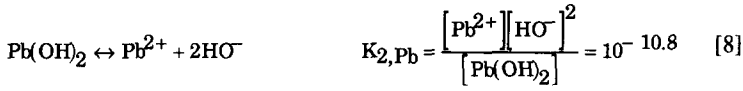
$$K_{1,\text{Ca}} = \frac{[\text{Ca}^{2+}][\text{HO}^{-}]}{[\text{CaOH}^{\dagger}]} = 10^{-1.15} \quad [9]$$



$$K_{\text{s},\text{Ca}} = [\text{Ca}^{2+}][\text{HO}^{-}]^2 = 10^{-5.2} \quad [9]$$



$$K_{1,\text{Pb}} = \frac{[\text{Pb}^{2+}][\text{HO}^{-}]}{[\text{PbOH}^{\dagger}]} = 10^{-5.8} \quad [8]$$



-mass transport, for each of the solution components:

$$\frac{\partial c}{\partial t} = D_e \frac{\partial^2 c}{\partial x^2} - \frac{\partial S}{\partial t} \quad (\text{one dimensional})$$

where:

c is the macroscopical concentration, kg in solution/m³ block considered homogeneous,

S is the local solid waste concentration, kg solid waste/m³ homogeneous block.

If $S = 0$, the solid waste is consumed and the solid-liquid equilibria disappears.

An appropriate discretisation model can consider the pore solution of the waste form as a completely mixed reactor in contact with the porous matrix. So, the matrix can be divided into n slices of equal thickness Δx , each slice can be considered a completely mixed chemical reactor. An analogy can be made with a serie of completely mixed chemical reactors. Each reactor contains, at $t=0$, a homogeneous mixture of the saturated pore solution and the solid phases of the matrix. The mass transport between the reactors is diffusive. It generates physical-chemical reactions, based on the equilibrium chemistry of the pore solution and on the mass balance in each reactor.

CONCLUSIONS

The diffusional mechanism is confirmed for the leaching behaviour of Na from concrete solidified wastes.

Decalcification of cemented wastes occurs with an apparent diffusional mechanism.

The parameters of the model (c_0 and D_e) can be identified using the only leaching results.

In the case of heavy metals, particularly for Pb, the solubility in the pore water must be considered in order to predict the long term behaviour of the solidified wastes.

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REFERENCES

- [1] American Nuclear Standard ANSI/ANS-16.1-1986, Measurement of the leachability of solidified low-level radioactive waste by short test procedure. American Nuclear Society, Lagrange Park, 1986.
- [2] Proposed evaluation protocol for cement-based solidified wastes, Wastewater Technology Centre (WTC) Environment Canada, Ontario, Canada 1990.

- [3] Essai de lessivage d'un déchet solide initialement massif ou généré par un procédé de solidification. Association Française de Normalisation (AFNOR), 1993, d'après le projet de l'INSA de Lyon et de l'IRH (WASCON 91), France.
- [4] NVN 5432 Draft. Determination of the maximum leachable quantity and the emission of potentially hazardous components from construction materials and stabilized waste products of mainly inorganic character. Recently issued as NEN 7345.
- [5] G. J. de Groot, H. A. van der Sloot, Determination of leaching characteristics of waste materials in relation to environmental product certification. Proc. Sec. Int. Symp. Stabilization/solidification of Hazardous, Radioactive and Mixte Wastes. Williamsburg, Virginia, 1990.
- [6] J. Méhu, R. Barna, P. Moszkowicz, Evaluation des déchets solidifiés. Quel crédit accorder aux différentes procédures de lixiviation?, *Environnement & Technique*, 125, pp. 58-62, 1993.
- [7] E. Zamorani, G. Serrini, H. Blanchard, Calcium release from cement samples, *Cement and Concrete Research*, vol. 16, pp. 394-398, 1986
- [8] P. L. Côté. Thesis: Contaminant leaching from cement-based waste forms under acidic conditions. MacMaster University, Hamilton, Canada, 1986.
- [9] Werner Stumm, James J. Morgan, *Aquatic Chemistry*, Wiley Interscience, New York, pp. 242, 2nd ed., 1981.