LEACHING STUDIES IN MANAGEMENT OF INDUSTRIAL WASTE IN CEMENT MATRIX

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Abstract
Results of a series of experimental tests performed to determine the influence of matrix characteristics on the leaching mechanism of copper aluminum oxychloride immobilized into cement matrices are presented. The objective of this research was to investigate the leaching mechanism of copper as a constituent of copper aluminum oxychloride **(CAOX)**. Transport phenomena involved in the leaching of a waste material from a composite matrix into surrounding water were investigated using three methods based on theoretical equations. These were: Method I, diffusion equation derived for a plane source model, Method II, rate equation for diffusion coupled with a first-order reaction. The leaching data were also analyzed by an empirical method employing a polynomial equation, Method III. These three methods are compared with respect to their applicability to the leaching data.
Key words: Immobilization, leaching, waste, cement, bentonite, diffusion

Introduction

Immobilization keeps gaining stature as a key technology for remedying hazardous waste. The technique consists of entrapping the waste within a solid matrix having high structural integrity, minimizing the risk of escape by leaching. Wastes from a wide range of industrial sources have been solidified. Among these industries are chemical, metal, textile, wood processing and petroleum refining. The waste may consist of liquids, sludge, slurries, or contaminated soil and sediments.
Solidification techniques are usually categorized by the type of solidifying agents used. Chemical fixation of toxic and hazardous waste using cement has been practiced for many years. Portland cement is the most popular solidification agent for inorganic wastes. Its high pH tends to keep metals in their most insoluble forms (i.e., as hydroxides and carbonates), thus minimizing subsequent leaching. Portland cement is less useful with organics, since some of them interfere with the overall setting and curing process.(1,2,3)

*Copper aluminum oxychloride **(CAOX)** description*

"CAOX" is a waste material produced in methanol and acetic acid industry as a product of solvent "**COSORB**" (cuprous aluminum tetrachloride). The most common compound which will react with the "**COSORB**" solvent is water. Water reacts irreversibly with the "**COSORB**" solvent to precipitate cuprous chloride, liberate hydrogen chloride, and produce copper aluminum oxychloride. This reaction takes place in 2 steps as follows:

$$2CuAlCl_4 \bullet C_7H_8 + H_2O \rightarrow HCl + CuCl + CuAlCl_4 \bullet Al(OH)Cl_2 \bullet C_7H_8$$

$$CuAlCl_4 \bullet Al(OH)Cl_2 \bullet C_7H_8 \rightarrow HCl + CuAlCl_4 \bullet AlOCl \bullet C_7H_8$$

The first reaction takes place immediately after introduction of water into the absorber. Part of the HCl formed will exit the absorber in the overhead gas. A small part of the HCl will be absorbed into the solvent and be coproduced with the carbon monoxide.

The second reaction takes place more slowly and requires heat to drive the reaction to completion. The HCl produced from the second reaction will be coproduced with the carbon monoxide exiting the stripper overhead. The aluminum oxychloride produced by the water reaction will complex with the **COSORB** solvent. This new complex still retains its ability to complex carbon monoxide; however, the solubility of the aluminum oxychloride complex is less than that of the original complex. Plugging of the unit will start at higher temperature as the water contamination continues and the concentration of the aluminum oxychloride complex increases in the COSORB solvent. The absorption ability of the **COSORB** solvent is proportional to the concentration of the copper in the solvent. This paper describes initial results obtained from series of experimental tests carried out on three different formulas of cementing matrices for immobilized copper aluminum oxychloride. Copper (C_u) was chosen as the contaminant element.

Materials and mortar composition

Grout samples have been made of:
- Portland cement PC-45 MPa,
- Water ,
- Additives: Super Fluidal (plasticizer),
-Bentonite clay (63% SiO_2 ; 18% Al_2O_3 ; 4% Fe_2O_3 ; 2,6% MgO and 3,3% CaO)
- "**CAOX**".

Composition of grout-waste forms are shown in Table 1.

Table 1. Grout-waste compositions in g/100 cm^3

	Formula
"CAOX" (g)	50.0 (A_o=1.5x10^4 Cu)
Cement (g)	114.0
H_2O (ml)	42.0
Additive (ml)	1
Bentonite (g)	2

Experimental procedure

After sufficient mixing of the constituents shown in Table 1, the paste is poured into a cylindrical vessel (diameter and height 5 cm). The curing time of specimens was 28 d. The leaching test was carried out according to the method recommended by literature (4). The specimen taken from a cylindrical vessel immediately before the test was immersed in the leaching vessel containing 200 ml of tap water at 21°C. Duration of leaching renewal period (d), was 30 days. At intervals the leachant was removed and the concentration of copper measured using a PERKIN-ELMER Atomic Absorption Spectrophotometer.

Theoretical methods

Transport phenomena involved in the leaching of waste material from a composite matrix were investigated using three methods based on theoretical equations.
Three methods are compared with respect to their applicability to experimental leaching data (1,2,3,5,6,7,8)

Method I: Diffusion equation based on a plane source model

In this model the fraction f leached at time, t(d) is given in literature data (4,5,6)

$$f = \frac{\Sigma a_n}{A_0} \quad \frac{2S\sqrt{Dt_n}}{V\sqrt{\pi}} \tag{1}$$

where

Σa_n= cumulative fraction leached of contaminant for each leaching period (mg Cu),
A_o= initial amount of contaminant in sample (mg Cu),
V= volume of sample (cm^3),
S= exposed surface area of sample (cm^2),
t_n= duration of leachant renewal period (d).

The results may also be expressed by the cumulative fraction of contaminant. Leach test results are plotted as cumulative fraction of contaminant leached from the samples as a function of the square root of total leaching time:

$$\frac{\sum a_n}{A_o} \; versus \; \sqrt{\sum t_n} \tag{2}$$

When this is true, a plot of $\Sigma a_n/A_o$ versus $\sqrt{\Sigma t_n}$ is a straight line and the diffusion coefficient D_e is expressed by:

$$D_e = \frac{\pi}{4} m^2 \frac{V^2}{S^2} (cm^2 s^{-1}) \tag{3}$$

where

D_e = diffusion coefficient (cm^2 s^{-1}),
m = $(\Sigma a_n/A_o)$ $(1/\sqrt{\Sigma t})$, slope of straight line ($d^{-1/2}$).

Method II: Rate equation for coupled diffusion and simultaneous first- order reaction

In this model, the rate equation is

$$\frac{\partial C}{\partial t} = D(\partial^2 C/\partial X^2) + g(C) \tag{4}$$

Here,a the special case was considered where g(C) is directly proportional to the concentration C, i.e. a first-order reaction. The initial and boundary conditions are,

$$t=0, \infty > x > 0 , C=C_o \tag{5}$$
$$t=0, x < 0 , C = 0 \tag{6}$$
$$t > 0 , x = 0 , C = 0 \tag{7}$$

From this, the fraction leached from a specimen having a surface area S(cm^2) and volume $V(cm^3)$ is

$$f = (S/V) \sqrt{D/k} \, [\, (kt + 1/2) \bullet \mathrm{erf} \sqrt{kt} + \sqrt{kt/\pi} \, \exp(-kt) \,] \quad (8)$$

Where k is the rate constant (proportional constant) of the first-order reaction.

$$erf(u) = err.function = (2/\sqrt{\pi}) \int_o^u \exp(-z^2) \, dz \quad (9)$$

Method III: Polynomial equation

The orthogonal polynomial is one of the most useful empirical equations. Its general form is

$$y(x) = \sum_{i=1}^{n} A_i \, \phi_i (x) \quad (10)$$

where:

A_i - is the parameter to be determined, and

φ_i - is a function of x. Here, φ_i (x) - is taken as $t^{i/2}$, and the leaching fraction is given by

$$f = \sum_{i=1}^{n} A_i \, t^{i/2} \quad (11)$$

To simplify the mathematical treatment, a fifth degree polynomial of the form.

$$f = A_o + A_1 t^{1/2} + A_2 t + A_3 t^{3/2} + A_4 t^2 \quad (12)$$

was fitted to the leaching data.

For this type of model, extrapolation to longer term leaching is not advisable since the arbitrary constants do not necessarily have any physical significance.

Results

Experimental data shows the fraction of copper leached from cement composites as a function of the square root of leaching period. Linear relation between f and $t^{1/2}$ is not observed throughout the tested period. From the application of Method I to the leaching data we obtained:

$$f_I = 6{,}3 \bullet 10^{-5} \sqrt{t} + 4{,}80 \bullet 10^{-12} \quad (13)$$

The diffusion coefficients predicted by Method I are

$$D_I = 3{,}60 \bullet 10^{-9} \, (cm^2/d)$$

Method II was applied to the leaching data to obtain the unknown parameters D and k. From this we obtained:

$$D_{II} = 3{,}70 \bullet 10^{-9} \, (cm^2/d)$$
$$k_{II} = 3{,}40 \bullet 10^{-2} \, (d^{-1}) \quad (14)$$

Using the method of least squares, Method III yielded:

$$f_{III} = -4{,}2 \bullet 10^{-6} + 2{,}30 \bullet 10^{-4} t^{1/2} - 5{,}0 \bullet 10^{-6} t - 6{,}30 \bullet 10^{\;7} \; t^{3/2} + 4{,}80 \bullet 10^{-8} t^2 \quad (15)$$

Fig.1.and Fig.2. present plots of f against **t** for leaching data of copper from cement matrix, for Methods I and Method III.

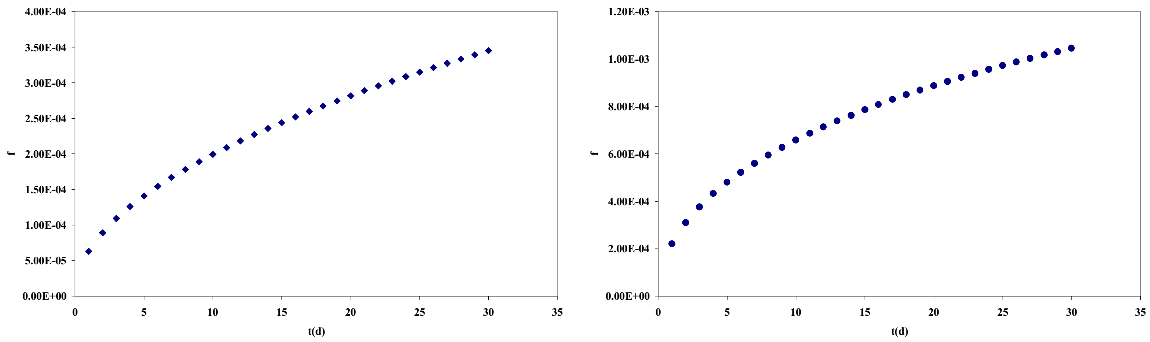

Fig.1(Method I and Method III).
Plot of f against **t** for leaching of copper from cement matrix

Conclusion

Method I cannot describe the whole leaching process; but it is very convenient to simulate leaching over a long period because of its simplicity. Despite the very complex numerical treatment required, the fit obtained using Method II is no better than that obtained using of Method I. Method III gives the best approximation over the whole test period. The results presented in this paper, give values that are similar to those reported in the literature. (6)

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