U.P.B. Sci. Bull., Series B, Vol. 85, Iss. 4, 2023.   ISSN 1454-2331

LONG-TERM LEACHING ASSESSMENT OF ALKALI-ACTIVATED MATERIALS BASED ON COMPLIANCE LEACHING TESTS

Nicolaie MARIN[1], Cristina ORBECI[2]*, Liliana BOBIRICĂ[3], Magdalena BOŞOMOIU[4], Constantin BOBIRICĂ[5]

The objective of this study was to investigate the long-term leaching behavior of waste-based one-part alkali-activated materials by using data from Toxicity Characteristic Leaching Procedure (TCLP) compliance test. The results showed a clear difference between the short-term leachability of the contaminants (heavy metal ions) derived from TCLP tests, and their long-term leachability calculated from both TCLP results and diffusion controlled leching model. Thus, it was demonstrated that the long-term mobility of contaminants is much higher than that indicated by the TCLP compliance test. The comparison of the experimental data on the mobility of contaminants with those obtained from the reactive leaching model, which considers the participation of acetic acid from the leaching solution in reactions with solid contaminants, showed a good correlation between the two sets of data. This indicates a high long-term availability of contaminants from the tested materials to participate in reactions, which could subsequently lead to an increase in their leachability.

Keywords: one-part alkali-activated materials, compliance leaching tests, heavy metals, long-term leaching behavior

1. Introduction

Compliance leaching tests are often used to assess the environmental impact of various materials containing contaminants [1]. Although there are currently many standardized variants of compliance leaching tests [2], efforts are still being

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[1] PhD student, Faculty of Chemical Engineering and Biotechnologies, University POLITEHNICA of Bucharest, Romania, nicolaiemarin@yahoo.ro

[2] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, University POLITEHNICA of Bucharest, Romania, cristina.orbeci@upb.ro; *Corresponding author

[3] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, University POLITEHNICA of Bucharest, Romania, liliana.bobirica@upb.ro

[4] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, University POLITEHNICA of Bucharest, Romania, mbosomoiu@yahoo.com

[5] Department of Analytical Chemistry and Environmental Engineering, Faculty of Chemical Engineering and Biotechnologies, University POLITEHNICA of Bucharest, Romania, constantin.bobirica@upb.ro

made to develop appropriate test methods that provide the most complete information on the leaching behaviour of contaminants [3]. One of the most well-known compliances leaching tests is the Toxicity Characteristic Leaching Procedure – TCLP [4] designed to simulate the worst-case leaching conditions that could occur in domestic landfills. In fact, the acetic acid solution used as a leaching solution simulates the domestic landfill leachate [5]. The TCLP test was also applied to other types of materials than waste, materials designed to be stored in domestic landfills, especially alternative materials manufactured based on secondary raw materials [6,7]. However, numerous limitations of this leaching test have been reported, especially related to the leaching potential of some contaminants in materials under certain conditions in which they can end up [8].

Currently, there is an increased interest in the development of some environmental-friendly binders based on secondary raw materials, which could represent a viable alternative to classic binders such as Portland cement, with the clear aim to reduce the carbon footprint as much as possible [9]. One-part alkali-activated materials are part of this category, as they are generally manufactured from residues or industrial by-products [10]. The manufacture of these materials involves the activation of some aluminosilicate precursors such as fly ash, blast furnace slag, pyrite ash, etc., with solid alkaline activators which, in turn, can be also synthesized from waste such as discarded glass [11]. These materials, in addition to some mechanical characteristics that recommend them for the construction field, must present a reduced environmental impact in relation to the leaching of contaminants contained in the secondary raw materials used in their manufacture. The long-term mobility of contaminants in such materials can be assessed by leaching tests and appropriate leaching models [12]. Therefore, the objective of this work is to manufacture one-part alkali-activated materials based on fly ash and red mud, activated with solid activators synthesized from waste glass by alkaline fusion with sodium hydroxide, followed by testing their leaching behaviour by TCLP compliance leaching tests and leaching models.

2. Material and Methods

2.1 Materials

Cathode Ray Tubes (CRTs) waste glass (cullet), provided by a local collection and processing company of waste from electrical and electronic equipment (WEEE), as well as sodium hydroxide (98%, granular, analytical grade) were used to synthesize the solid activators by alkali fusion reaction. Before being used, the cullet was ground to the powder state in a ball mill. Fly ash, provided by a local thermal power plant, and red mud, provided by a local alumina refining industry, were used as precursors materials to prepare one-part alkali-activated materials. Before being used, the red mud was dried and ground to the powdery state. The oxide composition of raw materials is presented in Table 1.

Tabel 1

Oxide composition of the raw materials.

Oxide, % (wt.)	Waste glass	Fly ash	Red mud
SiO_2	57.12	47.4	11.15
Al_2O_3	5.70	24.8	21.3
CaO	1.50	3.30	5.63
Fe_2O_3	0.15	11.00	56.8
SO_3	7.60	2.2	1.10
K_2O	6.15	2.42	-
Na_2O	5.00	4.00	-
MgO	-	2.30	-
Cl	4.50	1.60	1.40
TiO_2	-	0.82	2.37
MnO_2	-	0.08	-
Cr_2O_3	-	0.03	0.25
NiO	0.02	-	-
CuO	0.04	0.02	-
ZnO	0.12	0.03	-
PbO	12.1	-	-

2.3 Solid activators synthesis

The waste glass powder and NaOH granules at three different mass ratios were mixed until a homogeneous mixture was obtained, and then kept for 2 hours in an electric kiln at 600°C for alkali fusion. Next, the synthetized solid alkaline activators were cooled and finely ground. The solid alkaline activators are coded and presented in Table 2.

Table 2

Activator assortments composition

Code	Synthesis temperature, °C	NaOH/glass (S/G) ratio, (wt.)
S/G 0.5	600	1:2
S/G 1		1:1
S/G 2		2:1

2.4 Preparation of one-part-alkali activated materials

The waste-based one-part alkali-activated materials were prepared by mechanical dry mixing the fly ash, red mud, and the solid activator until a homogeneous mixture was obtained. The solid activator/fly ash-red mud mass ratio was fixed at 0.2. Next, water was added to the formed mixtures at a water/solid mass ratio of 0.5, and then they were mechanically mixed until a homogeneous paste was obtained. The one-part alkali-activated materials are coded and presented in Table 3. The pastes were cast in polypropylene molds which are cylindrical in shape with the dimensions 5 cm (d) ×10 cm (l), and vibrated for 2 min. Next, the molds were sealed into plastic bags and cured at 80°C for 28 days (after the first 24 h of curing the samples are removed from molds, sealed into new plastic bags, and then allowed to harden for the next 27 days).

Table 3

Mixture proportions of waste-based one-part alkali-activated materials.

Assortments	**Fly ash, % (wt.)**	**Red mud, % (wt.)**	**Solid activator, % (wt.)**
S/G0.5/FA-RM/600	85	5	10
	80	10	
	75	15	
S/G1/FA-RM/600	85	5	
	80	10	
	75	15	
S/G2/FA-RM/**600**	85	5	
	80	10	
	75	15	

2.5 Leaching tests

The leaching behavior testing was carried out by means of the TCLP compliance leaching test [4]. In brief, it involves crushing the samples to a particle size of less than 9.5 mm and mixing them end-over-end with leaching solution (acetic acid solution at pH of 3) at a solid/liquid ratio of 1/21, for 18 hours. Next, the samples were filtered and prepared for measuring the concentration of heavy metal ions (all heavy metals that appear in the composition of the secondary raw materials used) by atomic absorption in the flame using a GBC 932 AA atomic absorption spectrometer with calibration standard solution for each heavy metal ion.

3. Results and discussion

3.1 Leaching model

There are several simple leaching models that are built by adopting a series of initial assumptions such as:

- the contaminants do not participate in reactions,
- the leaching bath is infinite,
- the solid from which the contaminants leach is infinite,
- the contaminants are homogeneously distributed in the solid phase before leaching.

The experimental data for such models come from dynamic leaching tests, in which the solid under test is in the form of a monolith. Based on these assumptions, the material balance equation can be solved, thus establishing the concentration profile of the contaminants inside the solid, as shown in equation (1), in which M_t/M_0 is the fraction of contaminant leached at time t, D_e is effective diffusivity of the contaminant, L is the distance from the edge of the monolith to its center, and t is the time from which the leaching started [13].

$$\frac{M_t}{M_0} = \left(\frac{4D_e}{\pi L^2}\right)^{0.5} t^{0.5} \tag{1}$$

However, in many cases the contaminants participate in reactions inside the solid during leaching. It is also the case of heavy metal ions which, depending on the solid characteristics, it can participate in specific reactions. Therefore, equation (1) could be rewritten (2) in terms of observable diffusivity (D_{obs}) instead of effective diffusivity (D_e). When the mobile contaminant fraction (F_m) is small in the solid at the beginning of the leaching process, it results that for precipitation/dissolution reactions D_{obs} is expressed by means of equation (3), while for sorption reactions it is expressed by means of equation (4).

$$\frac{M_t}{M_0} = \left(\frac{4D_{obs}}{\pi L^2}\right)^{0.5} t^{0.5} \tag{2}$$

$$D_{obs} = \frac{\pi F_m D_e}{2} \tag{3}$$

$$D_{obs} = F_m D_e \tag{4}$$

These models can also be adapted for batch conditions of TCLP leaching test. Thus, if L in equation (2) is approximated with volume/area ratio of the particles (V_p/A_p), then the equation (2) can be written in terms of contaminant concentration both after leaching and before leaching, as shown in equation (5), where C_0 is the initial contaminant concentration into solid (g/kg), and M_p/V_l is the solid/liquid ratio corresponding to the TCLP leaching test.

$$C_{TCLP} = C_0 \frac{M_p}{V_l} \frac{A_p}{V_p} \left(\frac{4D_{obs}}{\pi}\right)^{0.5} t^{0.5} \quad (5)$$

The main issue is the fact that in the TCLP leaching test, acetic acid is used as a leaching solution at a pH of 3 or 5 depending on the characteristics of the material subjected to the leaching test. This could lead to an increase in the leaching rate of contaminants as the acetic acid enters the solid end reacts with contaminants. Under these conditions, the observable diffusivity will depend on the concentration of acetic acid used for leaching, as shown in equation (6), where C_0 is the immobile contaminant concentration at start of leaching, $D_{e,Ac}$ is the effective diffusivity of the acetic acid, C_{Ac} is the concentration of the acetic acid, and n is the ratio of acetic acid reacting to contaminant dissolving.

$$D_{obs} = \frac{\pi D_{e,Ac} C_{Ac}}{2nC_0} \quad (6)$$

In these conditions, the leaching of contaminants is described both according to the characteristics of the solid subject to leaching, and the characteristics of the leaching solution. However, estimating the effective diffusivity of the species participating in the leaching process (acetic acid and contaminants) into the solid represents an important issue. Since this cannot be calculated from the results of the leaching tests (it would require the adoption of the hypothesis that the contaminants do not react inside the solid during the leaching process, which in the present case is not valid), the best method of determination remains the one based on electrical conductivity measurements of both the solid and its porewater [14]. The ratio between the conductivity of the solid and the conductivity of the porewater represents MacMullin's number, and this in turn is equal to the ratio between the molecular diffusivity and the effective diffusivity of the species of interest in the leaching process, as shown in equation (7).

$$N_M = \frac{D_m}{D_e} \quad (7)$$

3.2 TCLP test results

The results of the TCLP tests performed on the one-part alkali-activated materials are presented in Fig. 1. As it can be seen, these materials have a very reduced leachability in relation to the contaminants present in the raw materials used in their manufacture (Table 1).

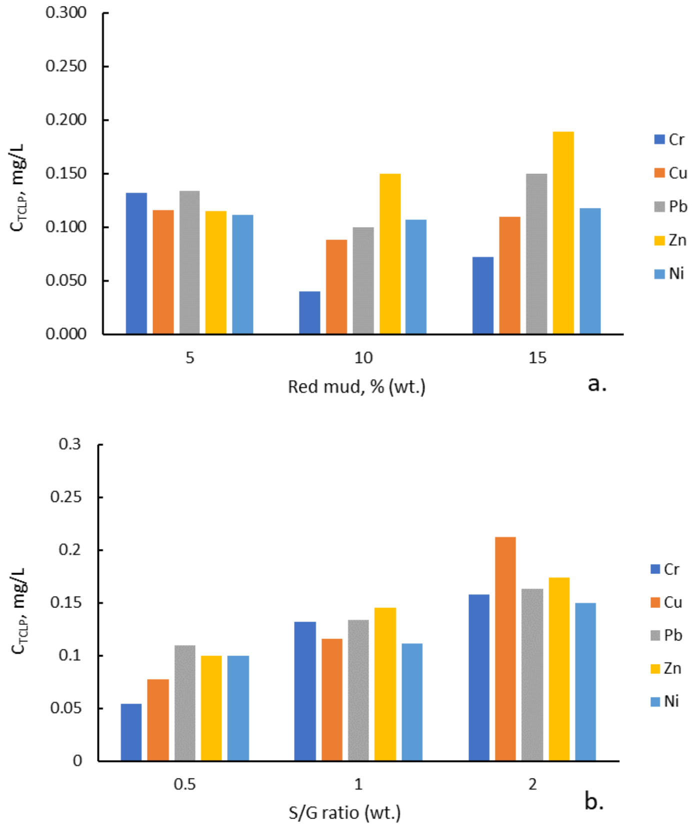

Fig. 1. TCLP tests results: a. concentration in the leachate depending on the mass percentage (wt.) of red mud added to the synthesis mixture; b. concentration in the leachate depending on the mass ratio (wt.) of sodium hydroxide/CRT glass (S/G) used in the synthesis of solid activators.

The highest concentration of Cr measured in the leaching solutions (0.158 mg/L) is approximately 30 times lower than the limit concentration established by the test (5 mg/L). The same result was recorded for Pb (0.163 mg/L in the leaching solution versus 5 mg/L, the limit concentration established by the test. These results clearly indicate that the materials obtained are not hazardous in relation to the heavy metals contained.

3.3 Long-term leaching behavior assessment

Fig.2 shows the mobility of contaminants in one-part alkali-activated materials, expressed as the negative logarithm of the observable diffusivity (-logD_{obs} or pD_{obs}), depending on the conditions for the synthesis of the solid activators and the preparation of the one-part alkali-activated materials. The results indicate that only nickel has high mobility, except for S/G 0.5 assortment. At the medium/high mobility limit is the case of copper and zinc for the assortments with

15% red mud, and copper and lead for the S/G 2 assortments (Fig. 2a and b). It should be mentioned that the higher the value of the logarithm of the observable diffusivity, the lower the mobility of the contaminant in the solid.

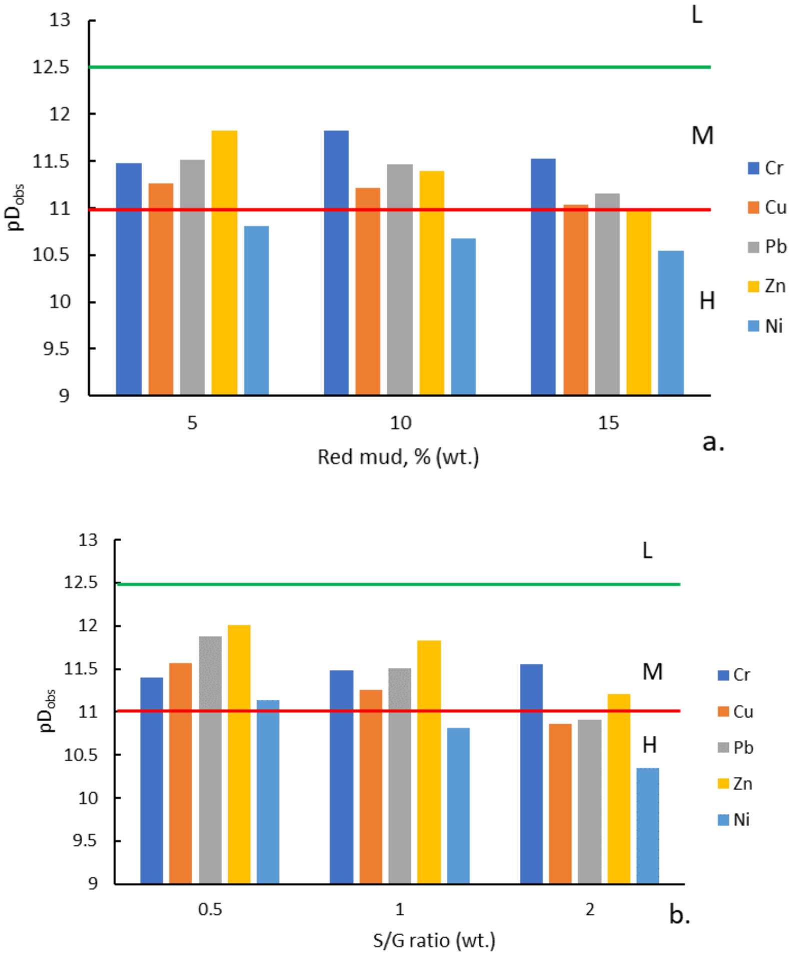

Fig. 2. Contaminant mobility assessment a. mobility depending on the mass percentage (wt.) of red mud added to the synthesis mixture; b. mobility depending on the mass ratio (wt.) of sodium hydroxide/CRT glass (S/G) used in the synthesis of solid activators; H-high mobility, M-medium mobility, L-low mobility.

It is expected that the addition of an increasing amount of strongly alkaline red mud will increase the total alkalinity of one-part alkali-activated materials. As consequence, the solubility of contaminants is expected to increase as a result of increasing the porewater pH of the solid (pH > 11), forming oxyanions such as $Pb(OH)^{-3}$, $Pb(OH)_4^{-2}$, $Cu(OH)^{-3}$, $Zn(OH)^{-3}$, etc [15]. Similarly, when the S/G ratio increases in the synthesis of solid activators. Upon contact of the solid with the acidic leaching solution, the pH of the porewater starts to decrease, and the contaminants will probably precipitate again in the form of their hydroxides. As the acid diffuses inside the solid, the contaminants will dissolve again, forming a precipitation/redissolution front inside the solid particle that migrates from the outside to the inside of it [16]. This could be the explanation of the increase in the mobility of the contaminants, except for chromium, with the increase in the proportion of red mud in the materials, respectively with the increase in the mass ratio of sodium hydroxide to glass in the synthesis of solid activators (Fig. 2).

Regarding the chromium assessment, it is possible to find it mainly in the hexavalent form (CrO_2^{-4}), and thus be less influenced by the variation of pH of the porewater. However, it could participate in sorption processes competing for the active sites with the acetate ions from the leaching solution [17]. As it can be seen in Fig. 2, chromium mobility does not have a clear tendency to increase or decrease depending on the alkalinity of the system. To verify these explanations, the results regarding the mobility of the contaminants obtained from the leaching tests were compared with those obtained with the reactive leaching model that considers the participation of acetic acid from the leaching solution in reactions (precipitation/dissolution or sorption) with contaminants in the solid during the leaching process. Thus, this comparison is presented in Fig. 3, specifying that the MacMullen number necessary to calculate the effective diffusivity of the acetic acid for particles of less than 10 mm was obtained from literature data by interpolation (Fig. 3).

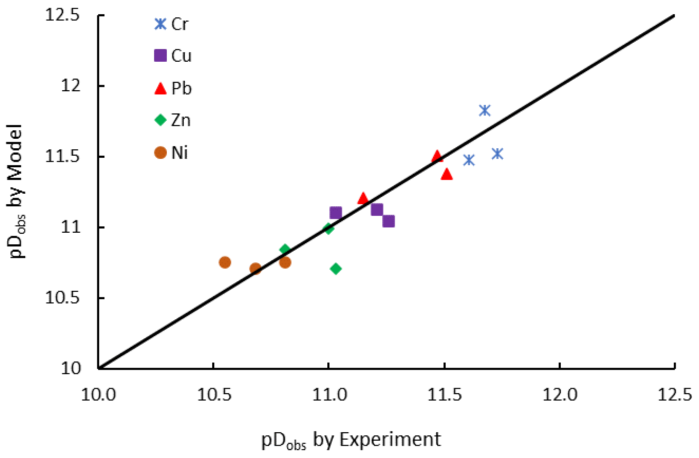

Fig. 3. Comparison between mobility predicted by reactive model and calculated from TCLP test results.

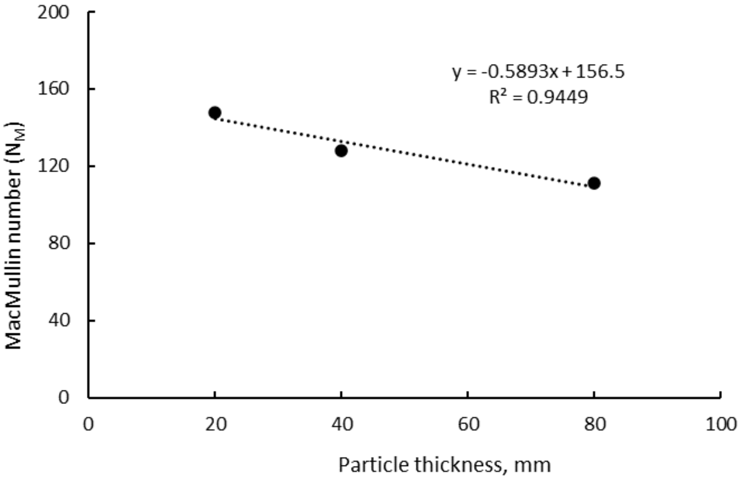

Fig. 4. Estimation of the MacMullin number by interpolation from literature data

As it can be seen from Fig. 3, there is a good correlation between the two data sets for all contaminants considered in this work. However, there is a tendency for some metals regarding their mobility to be under-predicted, which could indicate that some metal species, under certain conditions, precipitate in a somehow more stable form than their hydroxides or can be up taken by the solid phases of the system.

4. Conclusions

The objective of this work was to evaluate the leaching behavior of the contaminants contained in the waste-based one-part alkali-activated materials based on the data obtained from compliance leaching tests such as Toxicity Characteristic Leaching Procedure (TCLP). The results obtained indicated an average mobility of the contaminants, sometimes even high depending on the characteristics of the material, for the contaminants investigated, although the direct results of the compliance test indicate a reduced leachability of the contaminants in the tested materials. Increasing the alkalinity of the system through the addition of raw materials with a strong alkaline character generally leads to an increase in the mobility of contaminants in the tested materials. The participation of the acetic acid from the leaching solution to reactions with contaminants during the leaching process was highlighted by comparing the data calculated from the experimental results with the data obtained with the reactive model. In this respect, a good correlation between the two data sets was obtained. It can be concluded that more attention must be paid in the future to the development of long-term leaching compliance tests for different materials and wastes, in order to correctly evaluate the leaching behavior.

Acknowledgment

This work has been funded by the European Social Fund from the Sectoral Operational Programme Human Capital 2014-2020, through the Financial Agreement with the title "Training of PhD students and postdoctoral researchers in order to acquire applied research skills - SMART", Contract no. 13530/16.06.2022 - SMIS code: 153734.

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