



## Efficiency modeling of solidification/stabilization of multi-metal contaminated industrial soil using cement and additives

Grega E. Voglar<sup>a</sup>, Domen Leštan<sup>b,\*</sup>

<sup>a</sup> RDA – Regional Development Agency Celje, Kidričeva ulica 25, 3000 Celje, Slovenia

<sup>b</sup> Agronomy Department, Centre for Soil and Environmental Science, Biotechnical Faculty, University of Ljubljana, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

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### ABSTRACT

In a laboratory study, formulations of 15% (w/w) of ordinary Portland cement (OPC), calcium aluminate cement (CAC) and pozzolanic cement (PC) and additives: plasticizers cementol delta ekstra (PCDE) and cementol antikorođin (PCA), polypropylene fibers (PPF), polyoxyethylene-sorbitan monooleate (Tween 80) and aqueous acrylic polymer dispersion (Akrimal) were used for solidification/stabilization (S/S) of soils from an industrial brownfield contaminated with up to 157, 32,175, 44,074, 7614, 253 and 7085 mg kg<sup>-1</sup> of Cd, Pb, Zn, Cu, Ni and As, respectively. Soils formed solid monoliths with all cementitious formulations tested, with a maximum mechanical strength of 12 N mm<sup>-2</sup> achieved after S/S with CAC+PCA. To assess the S/S efficiency of the used formulations for multi-element contaminated soils, we propose an empirical model in which data on equilibrium leaching of toxic elements into deionized water and TCLP (toxicity characteristic leaching procedure) solution and the mass transfer of elements from soil monoliths were weighed against the relative potential hazard of the particular toxic element. Based on the model calculation, the most efficient S/S formulation was CAC + Akrimal, which reduced soil leachability of Cd, Pb, Zn, Cu, Ni and As into deionized water below the limit of quantification and into TCLP solution by up to 55, 185, 8750, 214, 4.7 and 1.2-times, respectively; and the mass transfer of elements from soil monoliths by up to 740, 746, 104,000, 4.7, 343 and 181-times, respectively.

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### 1. Introduction

Solidification and stabilization (S/S) has emerged as an efficient method for the treatment of sites contaminated with potentially toxic metals and metalloids (PTMs). S/S processes involve mixing binders, such as ordinary Portland cement, calcium aluminate, furnace slag, etc. into the soil, in order to transform soils into a solid material with low leachability of contaminants [1]. The main objective of S/S is therefore to develop a recipe (binder formulation) that produces a stable and sustainable end product, which will pose the minimum threat to the environment [2]. The high strength, low permeability and relatively high durability of products makes cement the most adaptable binder currently available for the immobilization of PTMs in soil [3]. It also has also the advantage that it is a consistent manufactured material with known hydration characteristics.

Cement treated soils and other waste products encapsulate PTMs by reducing the soil surface/leachant contact and by forming a stable pH environment in which many PTMs remain insoluble. In addition to physical encapsulation, various contaminated

soil-binder interactions occur to immobilize contaminants in the product chemically, further reducing the potential for pollutant transfer into the environment. The results of these interactions are cement-stabilized soil products that are non-hazardous, or significantly less hazardous than the original soil [3]. Despite incomplete information regarding the long-term durability of cement-stabilized soil monolith products, necessity, and the lack of other cost-effective and practical remediation methods, is driving these types of technologies to become widely used in many industrially oriented countries with an increasing number of abandoned industrial sites (brownfields). Cementitious S/S is today recognized as the “best demonstrated available technology” by the US Environmental Protection Agency for land disposal of toxic wastes.

There are numerous reports on cementitious S/S. Navarro et al. [4] examined the effectiveness of ordinary Portland cement, phosphoric acid and MgO in immobilizing Cu, Pb and Zn in contaminated soil. The effectiveness was evaluated using leaching experiments and geochemical modeling. Pb immobilization with H<sub>3</sub>PO<sub>4</sub> was related to the precipitation of chloropyromorphite, Zn was immobilized by ordinary Portland cement, while Cu was mobilized in all experiments. Gollmann et al. [5] studied S/S of Pb in cement matrices. Pb incorporated matrices have shown that a long cure time is more suitable for avoiding metal leaching. In a review paper, Chen et al. [6] discussed the interactions of toxic metals and

\* Corresponding author. Tel.: +386 1 423 1161; fax: +386 1 423 1088.

E-mail address: [domen.lestan@bf.uni-lj.si](mailto:domen.lestan@bf.uni-lj.si) (D. Leštan).

cement phases in the S/S process. Metals accelerate the hydration and decomposition of tricalcium silicate ( $C_3S$ ) and ordinary Portland cement, although they retard the precipitation of portlandite due to the reduction of pH resulting from hydrolysis of metal ions. The chemical mechanism relevant to the accelerating effect is  $H^+$  attacks on cement phases and the precipitation of calcium–metal double hydroxides, which consume calcium ions and then promote the decomposition of  $C_3S$ .

The town of Celje in central Slovenia has a long tradition of metallurgical and chemical industries, which started in 1874 with a zinc smelter. Industrial activities in the production of materials and chemicals gave rise to large quantities of tailings and hazardous wastes contaminated with PTMs, which, after the cessation of industrial production and the demolition of buildings, mixed with the parent soil and deposited on the site, spread over some 18 ha of what is now known as Cinkarna brownfield. The contamination pattern is fairly non-homogenous, with Cd, Pb, Zn, Cu, Ni and As being the major polluting PTMs.

In our previous work [7], the feasibility of cement-based S/S technology was evaluated on 40 site-representative soil samples from Cinkarna brownfield, using ordinary Portland cement (OPC). While S/S successfully immobilized Cd, Pb, Zn and Ni, it was less efficient for Cu and As. In fact, the addition of OPC in some samples significantly increased the leachability of these two elements. Cement-based S/S is under consideration as a remedial option for Cinkarna brownfield and improving the cementitious formulation, also in terms of immobilization of Cu and As, is essential. In this work, we assessed the S/S performance of three different cements in combination with five cement additives. Soils were selected from hot-spots contaminated with high concentrations of Cu and As in particular, indicated by an earlier site contamination survey [7]. The use of various cement chemical admixtures, such as retarders, accelerators and plasticizers, have a long tradition in civil engineering for obtaining certain special properties of cementitious products [8]. Similarly, Scanferla et al. [9] used ordinary Portland cement amended with water reducers and superplasticizers for the S/S of As, Cd, Hg, and Pb contaminated soil on the island of Murano (Venice, Italy). The S/S mixture was granulated in a rolling-plate system. Dense, low porous granular material demonstrated high mechanical strength, low porosity and leachability.

The efficiency of cementitious formulations for S/S is usually assessed by measuring the equilibrium leaching ( $El$ ) and mass transfer ( $Mt$ ) of PTM before and after S/S [10]. Formation of solid monoliths of S/S soil with sufficient mechanical strength is also an important factor [10]. However, in S/S of soil multi-contaminated with various PTMs, the physical and chemical mechanisms of encapsulation (or mobilization) are different for each PTM (as are, for example, the different effects of cement on the S/S of Cu and As described above). Furthermore, PTMs are not all equally toxic and hazardous. In order to select and optimize the cementitious formulation, a tool to assess the overall S/S efficiency for a given multi-metal contaminated soil is required. In this paper, we propose and apply an empirical S/S efficiency model to assess the performance of the tested cementitious formulations. To the best of our knowledge, this is the first study in which such a tool has been used.

## 2. Experimental

### 2.1. Contaminated site and soil sampling

Soils in Cinkarna brownfield are anthropogenic in origin and non-homogenous in contamination (Fig. 1). Sampling locations were determined based on a previous survey [7]. Contaminated soils were taken from the surface (0–30 cm) in a 1 m radius of the



Fig. 1. Orto-photo of the Cinkarna brownfield area with locations of sampling points, with X,Y Gauss-Krüger coordinates: Soil 1 (521,703, 121,076), Soil 2 (521,493, 121,071), Soil 3 (521,670, 121,025), Soil 4 (521,795, 121,079).

four pre-determined sampling points. Soils were uniformly mixed before further experimental work.

### 2.2. Cementitious formulations

Ordinary Portland cement (OPC) (CEM II/B-M 42.5 Salanit Anhovo, Anhovo, Slovenia), calcium aluminate cement (CAC) (CAC Calucem, Pula, Croatia) and pozzolanic cement (PC) (CEM V/A 32.5 Salanit Anhovo, Anhovo, Slovenia) were obtained from a local building materials store. We selected OPC as the most commonly used cement, CAC in view of its rapid hardening, high abrasion resistance and resistance to acid corrosion, and PC since it has a high content (up to 60%, EN 197-1) of pozzolana [11] and slug, and thus lower pH of cementation reactions [12].

Cement additives applied can be classified into several groups. Cement plasticizers: cementol delta ekstra (PCDE) and cementol antikorodin (PCA), were both obtained from TKK Srpenica, Srpenica, Slovenia. Plasticizers reduce the surface tension of water and thereby increase the dispersion of cement in the cement paste. PCDE is a plasticizer with a water retention effect. Its function is to delay the initial hydration of cement. The hardening process is not substantially modified, so that an increase in mechanical strength is obtained in proportion to the reduction in mixing water. It increases the concrete's mechanical strength and improves durability. The dosage of PCDE was used according to EN 934-2 [13]. PCA is a powdered plasticizer, which greatly improves the resistance of concrete/mortar to various aggressive chemicals. Its function is to increase cohesiveness, greatly reduce bleeding, reduce the water-cement ratio, which gives the concrete the appearance of higher density and, simultaneously, expels air pores in the concrete. PCA gives high corrosion resistance throughout its entire mass, corrosion resistance is unaffected by surface damage, there is improved mechanical strength, increased resistance to water penetration and reduced capillary absorption. The dosage of PCA was used according to EN 934-2 [13]. Non-ionic detergent polyoxyethylene-sorbitan monooleate (Tween 80) was from Sigma–Aldrich, St. Louis, MO, USA. With the addition of non-ionic detergent, which presumably interacts with organic matter in soil, making it more hydrophilic, we attempted to involve organic matter in the cement hydration processes, because Cu is S/S problematic [7] and is known to associate strongly with soil organic matter. The dosage was defined arbitrarily. Fibrous material polypropylene fibers FIBRILS F120 (PPF) was from Motvoz, Grosuplje, Slovenia. PPF reduces the emergence of cracks in micropores in concrete, which start because

**Table 1**  
List of tested cementitious formulations for soil S/S.

Metric composition	Notation	Mix proportions (wt.%)			Additive (wt.% of cement)
		Soil	Cement	Water	
Ordinary Portland cement	OPC	68	10	22	–
Calcium aluminate cement	CAC	69	10	21	–
Puculanic cement	PC	68	10	22	–
Ordinary Portland cement + plasticizer cementol delta ekstra	OPC + PCDE	68	10	22	0.02
Calcium aluminate cement + plasticizer cementol delta ekstra	CAC + PCDE	68	10	22	0.02
Puculanic cement + plasticizer cementol delta ekstra	PC + PCDE	67	10	23	0.02
Ordinary Portland cement + plasticizer cementol antikorodin	OPC + PCA	68.5	10	21.5	0.51
Calcium aluminate cement + plasticizer cementol antikorodin	CAC + PCA	68.5	10	21.5	0.51
Puculanic cement + plasticizer cementol antikorodin	PC + PCA	68.5	10	21.5	0.51
Ordinary Portland cement + polyoxyethylene-sorbitan monooleate	OPC + Tween 80	68	10	22	0.05
Calcium aluminate cement + polyoxyethylene-sorbitan monooleate	CAC + Tween 80	68	10	22	0.05
Puculanic cement + polyoxyethylene-sorbitan monooleate	PC + Tween 80	68	10	22	0.05
Ordinary Portland cement + polypropylene fiber FIBRILs F120	OPC + PPF	68	10	22	0.04
Calcium aluminate cement + polypropylene fiber FIBRILs F120	CAC + PPF	69	10	21	0.04
Puculanic cement + polypropylene fiber FIBRILs F120	PC + PPF	68	10	22	0.04
Ordinary Portland cement + aqueous acrylic polymer dispersion Akrimal-E	OPC + Akrimal	65	10	25	1.37
Calcium aluminate cement + aqueous acrylic polymer dispersion Akrimal-E	CAC + Akrimal	67	10	23	1.39
Puculanic cement + aqueous acrylic polymer dispersion Akrimal-E	PC + Akrimal	67	10	23	1.39

of shrinkage during the process of drying. It is used in making industrial floors, pavements, plates, injected concretes, tunnels, fire-proof catching pools, roads, airports, silos, dams, support walls, hydroelectric station dams, support pillars, edges of bridges, pools for purifying plants, etc. The results of testing [14] have shown that the optimal properties are achieved by adding 0.91 kg of PPF/m<sup>3</sup> of concrete, as also used in our study. Aqueous acrylic polymer dispersion Akrimal-E (Akrimal) was obtained from Gras, Ljubljana, Slovenia. Akrimal is a cement repair mortar modified with aqueous acrylic polymer dispersion. Akrimal is a two-component additive. We added the ready-prepared aqueous acrylic polymer dispersion (component A) to the dry mixture of soil and cement (component B) in the prescribed proportion according to EN 1504 [15] and EN 1015 [16]. Akrimal is intended for building repair applications, patching of damaged parts of concrete and mortars, installations and repair of pavements, concrete elements, edgings and for filling joints.

### 2.3. Soil S/S

Soil samples (3 kg) were dried to a constant weight, sieved through a 0.5 cm sieve and mixed with 15% (w/w) of cement and a sufficient amount of deionized water (from 190 to 390 mL kg<sup>-1</sup>) to obtain material with appropriate plasticity. Cement additives were directly dissolved in deionized water before S/S, to the concentrations given in Table 1. Cemented soil was placed in 10 polyvinyl chloride (PVC) tube models ( $D=4.54$  cm,  $H=4.99$  cm) and into rectangle cube models EN 196-1 [17]. ( $W, H, L=4, 4, 16$  cm, respectively). After 24 h incubation, the obtained soil monoliths (cylinders from the tube models and rectangular cubes from the standardized models) were removed from the models and cured for 28 days at 15 °C and at 80% relative humidity, before mechanical strength (cubes) and PTM leachability and mass transfer (cylinders) were measured.

### 2.4. Mechanical strength

Rectangle cube monoliths were used to determine the mechanical strength of the cement-stabilized soil. Cubes were exposed to a pressure force using ToniNORM automatic pressure (Toni Technik, Berlin, Germany) until breaking point according to EN 196-1 [17]. Mechanical strength measurements were performed in triplicate and expressed in N mm<sup>-2</sup>.

### 2.5. Equilibrium leaching into deionized water

Equilibrium leaching (El) of PTMs into deionized water (DW) elutriates from the original (non-treated) soil and cement-S/S soil monoliths (cylinders) were assessed as defined by EN 12457-4 [18]. The soil samples and soil monoliths were ground and sieved through a 2.0 mm mesh. One hundred ml of deionized water was applied to each sample and agitated for 24 h at room temperature. Elutriates were filtered through a 0.45- $\mu$ m membrane filter. Concentrations of Cd, Pb, Zn, Cu, Ni and As were determined in triplicate using flame atomic absorption spectrometry (FAAS). The results are presented in mg of PTMs water – extractable from 1 kg of dry soil. The Slovenian statutory limit concentrations of Cd, Pb, Zn, Cu, Ni and As in soils extractable into deionised water according to procedure EN12457-4, are 0.03, 0.3, 18, 0.6, 0.6 and 0.3 mg kg<sup>-1</sup>, respectively, for soils used as land-filling or land-covering material [19].

### 2.6. Equilibrium leaching into TCLP solution

Equilibrium leaching (El) of PTMs from the original and S/S soil into the solution used in the toxicity characteristic leaching procedure (TCLP) was assessed as defined by the US Environmental Protection Agency [20]. The sample specimens were crushed and ground to reduce the particle size to less than 2.0 mm and agitated in 20 mL of 0.0992 M acetic acid and 0.0643 M NaOH extraction solution (1:20 ratio) with a pH of  $4.93 \pm 0.05$  for 18 h at 300 rpm. The leachate was filtered through a 0.45- $\mu$ m membrane filter to remove suspended solids and stored in the cold for determination of Cd, Pb, Zn, Cu, Ni and As present in the leachate, using FAAS. The extractions were conducted in triplicate. Limit concentrations of Cd, Pb, Cu, Ni and As in TCLP extracts are 1.0, 5.0, 25, 20 and 5.0 mg L<sup>-1</sup>, respectively, specified as hazardous by the US Environmental Protection Agency. There is no TCLP regulatory standard for Zn, because Zn is not classified as hazardous waste by the US Environmental Protection Agency [20].

### 2.7. PTMs mass transfer

The mass transfer (Mt) of PTMs from the original soils and cement-S/S soil monoliths (cylinders) was determined in triplicate, as described by Kosson et al. [10]. The original soil was filled into PVC vessels ( $D=4.54$  cm,  $H=4.99$  cm) and transferred into a glass jar with deionized water, ensuring that the soil surface at the open side of the tubes was exposed to deionized water. Nylon strings

were attached to the monoliths with S/S soil to allow the monoliths to be suspended and immersed in deionized water. The volume of deionized water was 323.8 and 321 mL for original and S/S soil, respectively. The volumes corresponded to the required ratio of 1:10 between the soil surface and water volume. The glass jars were sealed and incubated at 21 °C. After each leaching interval (2, 3, 3, 16, 24, 48, 96 and 192 h), the water in the jars was sampled, analysed for Cd, Pb, Zn, Cu, Ni and As using FAAS, replaced with fresh deionized water and the soil samples were weighed.

The mass transfer of PTMs from the original soils and soil monoliths was calculated according to the equations given below [21].

$$Mt_i = \frac{C_i \times V_i}{A} \quad (1)$$

In Eq. (1),  $Mt_i$  ( $\text{mg m}^{-2}$ ) is the mass of PTMs released during leaching period  $i$ ,  $C_i$  ( $\text{mg L}^{-1}$ ) is the PTM concentration in period  $i$ ,  $V_i$  (L) is the leachant volume in period  $i$  and  $A$  is the specimen surface area exposed to the leachant ( $\text{m}^2$ ).

$$EM_j = \sum_{i=1}^n \left( \left( \begin{array}{c} \text{Term 1} \\ 0.5 \times \frac{\Delta EIDW_{ji} \times m}{\sum_{j=1}^m \Delta EIDW_{ji}} \times \frac{\Delta EIDW_{ji}}{\sum_{i=1}^n \Delta EIDW_{ji}} \\ \text{Term 2} \\ + 0.5 \times \frac{\Delta EITCLP_{ji} \times m}{\sum_{j=1}^m \Delta EITCLP_{ji}} \times \frac{\Delta EITCLP_{ji}}{\sum_{i=1}^n \Delta EITCLP_{ji}} \\ \text{Term 3} \\ + \frac{\Delta Mt_{ji} \times m}{\sum_{j=1}^m \Delta Mt_{ji}} \times \frac{\Delta Mt_{ji}}{\sum_{i=1}^n \Delta Mt_{ji}} \\ \text{Term 4} \\ + \frac{\Delta Mt_{ji} \times m}{\sum_{j=1}^m \Delta Mt_{ji}} \times \frac{\Delta Mt_{ji}}{\sum_{i=1}^n \Delta Mt_{ji}} \\ \text{Term 5} \\ + \frac{\Delta Mt_{ji} \times m}{\sum_{j=1}^m \Delta Mt_{ji}} \times \frac{\Delta Mt_{ji}}{\sum_{i=1}^n \Delta Mt_{ji}} \\ \text{Term 6} \\ \times \left( 1 - \frac{LC_i}{\sum_{i=1}^n LC_i} \right) \\ \text{Term 7} \end{array} \right) \quad (3)$$

The apparent diffusion coefficient of PMTs was determined using the logarithm of cumulative  $Mt$  until the  $i$ -th period, plotted vs. the logarithm of time. In the case of a diffusion-control mechanism, this plot is expected to be a straight line with a slope of 0.5 and the diffusion coefficient can be calculated according to Eq. (2) [21].

$$D_a = \pi \left( \frac{Mt_i}{2 \times \rho \times U_{\max} \times (\sqrt{t_i} - \sqrt{t_{i-1}})} \right)^2 \quad (2)$$

In Eq. (2),  $D_a$  ( $\text{m}^2 \text{s}^{-1}$ ) is the apparent diffusion coefficient of PTMs, calculated for the  $Mt$  in a period  $i$ ,  $t_i$  (s) is the contact time until period  $i$ ,  $t_{i-1}$  (s) is the contact time until period  $i-1$ ,  $\rho$  ( $\text{kg m}^{-3}$ ) is the sample density and  $U_{\max}$  ( $\text{mg kg}^{-1}$ ) is the maximum leachable quantity of PTMs.

The apparent diffusion coefficient can be determined for each release in the period in which the slope is  $0.5 \pm 0.15$ . The overall apparent diffusivity for PTMs is then determined by taking the

$$EM_j = \sum_{i=1}^n \left( \left( \frac{0.5 \times (\Delta EIDW_{ji})^2 \times m}{\sum_{j=1}^m \Delta EIDW_{ji} \times \sum_{i=1}^n \Delta EIDW_{ji}} + \frac{0.5 \times (\Delta EITCLP_{ji})^2 \times m}{\sum_{j=1}^m \Delta EITCLP_{ji} \times \sum_{i=1}^n \Delta EITCLP_{ji}} + \frac{(\Delta Mt_{ji})^2 \times m}{\sum_{j=1}^m \Delta Mt_{ji} \times \sum_{i=1}^n \Delta Mt_{ji}} \right) \times \left( 1 - \frac{LC_i}{\sum_{i=1}^n LC_i} \right) \right) \quad (4)$$

average of the apparent diffusivities released in the period. Only apparent diffusion coefficients released in the period corresponding to a leaching period with slopes between 0.35 and 0.65 are included in the overall average apparent diffusivity [21,22].

## 2.8. Determination of PTMs

In order to assess the pseudo-total concentration of PTMs, air-dried soil samples (1 g) were ground, sieved through a 160  $\mu\text{m}$  mesh and digested for 2 h in 28 mL of aqua regia solution, consisting of HCl and HNO<sub>3</sub> in a 3:1 ratio (v/v). The digested samples were filtered through Whatman no. 4 filter paper and diluted with deionized water to a total 100 mL volume. The concentrations of Cd, Pb, Zn, Cu, Ni and As were determined using FAAS (Varian AA240FS). The concentrations of PTMs in the solutions were measured directly. A standard reference material used in inter-laboratory comparisons (WEPAL 2004.3.4, HBLFA Raumberg-Gumpenstein, Irnding, Austria) was used in the digestion and

analysis, as part of the QA/QC protocol. The limits of quantification (LOQ) were 0.02, 0.1, 0.01, 0.03, 0.1 and 0.09  $\mu\text{g mL}^{-1}$  for Cd, Pb, Zn, Cu, Ni and As, respectively. Reagent blank and analytical duplicates were used to ensure the accuracy and precision of the analysis.

## 2.9. Efficiency model of soil S/S

The proposed S/S efficiency model ( $EM$ ) enables selection and optimization of a cementitious formulation for a given multi-metal contaminated soil. In the  $EM$ , the significance of the data of the two equilibrium leaching ( $El$ ) measurements is equalled by the significance of the data of PTMs mass transfer ( $Mt$ ). Factor 0.5 is therefore attributed to  $El$  into deionised water ( $El DW$ ) and  $El$  into  $TCLP$  solution ( $El TCLP$ ) measurements, and factor 1 to  $Mt$  measurements Eq. (3). In the model  $\Delta El DW_{ji}$ ,  $\Delta El TCLP_{ji}$  and  $\Delta Mt_{ji}$  denote differences in  $El$  and  $Mt$  for each ( $i$ ) of the  $n$  PTMs before and after S/S of the soil with each  $j$  of the  $m$  tested S/S formulations:

Terms 1, 3 and 5 are S/S efficiency indexes. They indicate the efficiency of immobilization (encapsulation) of each PTM by specific S/S formulation, relative to the average immobilization efficiency of all tested formulations. Term 1 thus measures S/S efficiency by indexing  $El$  of PTM into  $DW$ , Term 2 is the index of  $El$  into  $TCLP$  solution and Term 3 is the index of  $Mt$ . S/S efficiency indexes are corrected with leachability (Terms 2 and 4) and mobility equivalence factors (Term 6). This is necessary since the magnitude of  $El$  and  $Mt$  are different for each of the PTMs in the soil. The leachability/mobility equivalence factors are calculated as the share of  $El$  and  $Mt$  of a particular PTM in the total  $El$  and  $Mt$  of all PTMs, for a given S/S formulation used. Finally, the model takes into account different toxicity and hazards of PTMs, and weights  $El$  and  $Mt$  data with the toxicity equivalence factor (Term 7). We defined the toxicity equivalence factor as the share of a particular PTM's hazard in the overall hazard of all PTMs in the soil. To calculate the toxicity equivalence factor, we used data on the allowable limit concentrations (LC) of PTMs stipulated by Slovenian legislation [23]. Eq. (3) can finally be re-arranged into Eq. (4):

where measured PTMs concentrations were below the LOQ, the LOQ data from the PTMs determination method (see section above) were used in the calculations. The highest calculated value obtained by  $EM$  calculation denotes the highest efficiency for a particular soil of the S/S formulation used.

## 2.10. Statistical analysis

Fisher's least significant difference (LSD) multiple range test ( $p < 0.05$ ) (Statgraphics 4.0 for Windows) was used to determine differences in PTMs leachability and diffusion between the original soil samples and the cement-S/S soil monoliths.

## 3. Results and discussion

As mentioned in the Introduction, Cu and As were found in our previous study to be significantly less susceptible to S/S with OPC than other contaminating PTMs [7]. This could have occurred because the pH of the pore water in cement S/S soil often exceeded

**Table 2**

Pseudo-total concentrations of Cd, Zn, Pb, Cu, Ni and As in Soils 1–4 and their toxicity equivalence factors (TEF) derived from limit concentrations (LC) stipulated by legislation [23].

Metals and metaloides	Soils (mg kg <sup>-1</sup> )				LC (mg kg <sup>-1</sup> )	TEF <sub>LC</sub>
	1	2	3	4		
Cd	157	128	132	37	1	0.998
Pb	32,175	15,910	121	37	85	0.796
Zn	42,039	25,273	44,074	2074	200	0.519
Cu	514	7614	287	157	60	0.856
Ni	170	250	178	253	50	0.880
As	1902	7085	661	82	20	0.952

12 [24], when soluble Cu hydroxide complexes form [25,26]. Cu also binds strongly to soil organic matter, by forming coordinative bonds with carboxylic groups [27]. However, in alkaline conditions, organic matter depolymerises and becomes water-soluble [28], thus increasing the leachability of Cu. In relation to As, it forms insoluble compounds with Fe and Al (hydroxy) oxides in acidic–neutral conditions [29]. In alkaline S/S soil, however, Ca(OH)<sub>2</sub> forms as a result of cement hydration and much more soluble calcium arsenite (Ca–As–O) and calcium arsenates (CaAs<sub>3</sub>O<sub>4</sub>, Ca<sub>2</sub>As<sub>2</sub>O<sub>7</sub>, CaO–As<sub>2</sub>O<sub>5</sub>) are formed [30], which explains the enhanced As mobility. This behavior of As can also be explained using Pearson's hard and soft acids and bases concept (HSAB). As is a soft base and is therefore less likely to be involved in carbonation reactions of the cementation process (carbonate, CO<sub>3</sub><sup>2-</sup>, is a hard base according to HSAB). Cu (and also Cd) is a soft acid and according to HSAB reacts faster and forms stronger bonds with soft bases, while, on the other hand, other contaminating metals: Zn, Ni and Pb are borderline acids and have a higher affinity for a hard base carbonate [31]. Indeed, Zn was the element most strongly encapsulated by cementation [7].

Four soils with particularly high Cu and As concentrations were therefore selected, based on data of a soil contamination survey

reported earlier [7]. The locations of the sampling points and a map of Cinkarna brownfield are shown in Fig. 1. In all soil samples (except Pb and Cu in Soil 3 and Soil 4, and Ni in Soil 1 and Soil 3), concentrations of PTMs exceeded the critical concentrations of 12, 530, 720, 300, 210 and 55 mg kg<sup>-1</sup> of Cd, Pb, Zn, Cu, Ni and As, respectively, stipulated by Slovenian legislation [23], Table 2. Exceeding the critical concentration of contaminants signifies a hazardous soil, with no soil use allowed.

In the first phase of our experiment, we selected a single soil from the original four. The selection criterion was the efficiency of S/S with OPC, particularly the S/S efficiency for Cu and As. The selected soil was further used in the second phase of our study, in which we applied the S/S efficiency model to find the most effective cementitious formulation. In the final phase of our work, the selected cementitious formulation was tested on all four soils.

### 3.1. Initial soil selection

S/S efficiency was assessed by PTMs release mechanisms: *EI* (in DW and TCLP solution) and *Mt* tests [10,32], using 15% (w/w) OPC as a hydraulic binder. We used two different equilibrium leach-

**Table 3**

Concentrations of Cd, Pb, Zn, Cu, Ni and As leached into deionized water and TCLP solution (*EI DW*, *EI TCLP*) and PTMs cumulative mass transfer (*Mt*) during 384 h release period before and after S/S of Soils 1–4 with OPC. Results are presented as means of three replicates ± S.D. LOQ is the limit of quantification.

Soil	Cd	Pb	Zn	Cu	Ni	As
1						
<i>EI DW</i> (mg kg <sup>-1</sup> )	0.29 ± 0.00 <sup>a</sup>	1.87 ± 0.05	10.3 ± 0.1 <sup>a</sup>	LOQ <sup>a</sup>	LOQ	LOQ
<i>EI DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	1.18 ± 0.03	0.38 ± 0.03	0.67 ± 0.00	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> )	1.10 ± 0.00	27.7 ± 2.4 <sup>a</sup>	175 ± 9 <sup>a</sup>	LOQ	0.47 ± 0.06 <sup>a</sup>	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> ), S/S	0.60 ± 0.35	0.87 ± 1.50	0.47 ± 0.40	LOQ	LOQ	LOQ
<i>Mt</i> (mg m <sup>-2</sup> )	18.31 ± 0.78 <sup>a</sup>	194 ± 19 <sup>a</sup>	469 ± 49 <sup>a</sup>	1.54 ± 0.06 <sup>a</sup>	10.3 ± 2.3 <sup>a</sup>	5.42 ± 2.82 <sup>a</sup>
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	2.20 ± 0.06	21.8 ± 1.3	2.14 ± 0.31	7.7 ± 0.8	3.86 ± 0.29	0.10 ± 0.04
2						
<i>EI DW</i> (mg kg <sup>-1</sup> )	0.42 ± 0.00 <sup>a</sup>	1.37 ± 0.02	24.2 ± 0.1 <sup>a</sup>	LOQ <sup>a</sup>	LOQ	LOQ
<i>EI DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	0.24 ± 0.01	2.68 ± 0.02	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> )	1.06 ± 0.03 <sup>a</sup>	10.7 ± 1.2 <sup>a</sup>	200 ± 9 <sup>a</sup>	6.41 ± 0.49 <sup>a</sup>	0.15 ± 0.02 <sup>a</sup>	0.11 ± 0.01 <sup>a</sup>
<i>EI TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	2.67 ± 0.57	1.73 ± 0.45	0.11 ± 0.02	LOQ	0.17 ± 0.02
<i>Mt</i> (mg m <sup>-2</sup> )	21.52 ± 1.21 <sup>a</sup>	116 ± 1 <sup>a</sup>	999 ± 3 <sup>a</sup>	4.79 ± 0.59 <sup>a</sup>	10.3 ± 0.3 <sup>a</sup>	2.43 ± 1.66
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	2.18 ± 0.01	19.8 ± 0.6	2.34 ± 0.06	17.2 ± 1.0	2.56 ± 0.45	1.65 ± 0.11
3						
<i>EI DW</i> (mg kg <sup>-1</sup> )	0.93 ± 0.00 <sup>a</sup>	2.28 ± 0.01 <sup>a</sup>	35.8 ± 0.2 <sup>a</sup>	LOQ	LOQ	LOQ
<i>EI DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	1.27 ± 0.06	LOQ	0.48 ± 0.00	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> )	0.74 ± 0.02 <sup>a</sup>	15.7 ± 0.7 <sup>a</sup>	353 ± 16 <sup>a</sup>	LOQ	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	1.50 ± 2.60	1.67 ± 1.42	LOQ	LOQ	LOQ
<i>Mt</i> (mg m <sup>-2</sup> )	22.21 ± 1.03 <sup>a</sup>	144 ± 1 <sup>a</sup>	2080 ± 84 <sup>a</sup>	1.15 ± 0.25 <sup>a</sup>	10.1 ± 0.6 <sup>a</sup>	0.38 ± 0.35
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	2.09 ± 0.40	20.6 ± 3.9	2.11 ± 0.37	2.79 ± 0.26	2.26 ± 0.18	0.15 ± 0.12
4						
<i>EI DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	0.40 ± 0.02 <sup>a</sup>	LOQ	LOQ	LOQ
<i>EI DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	0.33 ± 0.03	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> )	0.09 ± 0.00 <sup>a</sup>	3.43 ± 0.25 <sup>a</sup>	14.3 ± 1.1 <sup>a</sup>	LOQ	LOQ	LOQ
<i>EI TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	LOQ	0.70 ± 0.17	LOQ	LOQ	LOQ
<i>Mt</i> (mg m <sup>-2</sup> )	7.62 ± 0.87 <sup>a</sup>	105 ± 2 <sup>a</sup>	33.2 ± 1.8 <sup>a</sup>	0.38 ± 0.10 <sup>a</sup>	7.54 ± 1.50 <sup>a</sup>	0.30 ± 0.10
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	1.31 ± 0.08	12.3 ± 2.0	1.17 ± 0.06	2.92 ± 0.24	1.45 ± 0.35	0.14 ± 0.11

<sup>a</sup> Denote statistically different concentration within category before and after soil stabilisation according to LSD test ( $p < 0.05$ ).

**Table 4**  
Concentrations of Cd, Pb, Zn, Cu, Ni and As leached into deionized water and TCLP solution (*El DW*, *El TCLP*) and PTMs cumulative mass transfer (*Mt*) during 384 h release period before and after S/S of Soil 2 with various cementitious formulations. Results are presented as means of three replicates  $\pm$  S.D. LOQ is the limit of quantification. S/S efficiencies were calculated using an empirical S/S efficiency model.

Soil 2	Cd	Pb	Zn	Cu	Ni	As	S/S efficiency
Before S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	0.42 $\pm$ 0.00	1.37 $\pm$ 0.02	24.2 $\pm$ 0.1	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> )	1.06 $\pm$ 0.03	10.7 $\pm$ 1.2	200 $\pm$ 9	6.41 $\pm$ 0.49	0.15 $\pm$ 0.02	0.11 $\pm$ 0.01	
<i>Mt</i> (mg m <sup>-2</sup> )	21.52 $\pm$ 1.21	116 $\pm$ 1	999 $\pm$ 3	4.79 $\pm$ 0.59	10.3 $\pm$ 0.3	2.43 $\pm$ 1.66	
OPC, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	0.24 $\pm$ 0.01 <sup>a</sup>	2.68 $\pm$ 0.02 <sup>a</sup>	LOQ	LOQ	1.672
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	2.67 $\pm$ 0.57 <sup>a</sup>	1.73 $\pm$ 0.45 <sup>a</sup>	0.11 $\pm$ 0.02 <sup>a</sup>	LOQ	0.17 $\pm$ 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	2.18 $\pm$ 0.01 <sup>a</sup>	19.8 $\pm$ 0.6 <sup>a</sup>	2.34 $\pm$ 0.06 <sup>a</sup>	17.2 $\pm$ 1.0 <sup>a</sup>	2.56 $\pm$ 0.45 <sup>a</sup>	1.65 $\pm$ 0.11	
CAC, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	1.40 $\pm$ 0.21	0.13 $\pm$ 0.06 <sup>a</sup>	LOQ	LOQ	LOQ	1.760
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.41 $\pm$ 0.02 <sup>a</sup>	0.12 $\pm$ 0.02 <sup>a</sup>	0.03 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	0.18 $\pm$ 0.02 <sup>a</sup>	5.11 $\pm$ 0.73 <sup>a</sup>	0.53 $\pm$ 0.03 <sup>a</sup>	1.11 $\pm$ 0.19 <sup>a</sup>	0.00 $\pm$ 0.00 <sup>a</sup>	0.24 $\pm$ 0.05	
PC, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	1.93 $\pm$ 0.08 <sup>a</sup>	0.20 $\pm$ 0.04 <sup>a</sup>	2.39 $\pm$ 0.24 <sup>a</sup>	LOQ	1.99 $\pm$ 0.16 <sup>a</sup>	1.702
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.42 $\pm$ 0.05 <sup>a</sup>	0.58 $\pm$ 0.12 <sup>a</sup>	0.09 $\pm$ 0.00 <sup>a</sup>	LOQ	0.28 $\pm$ 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.38 $\pm$ 0.36 <sup>a</sup>	7.36 $\pm$ 0.76 <sup>a</sup>	2.69 $\pm$ 0.70 <sup>a</sup>	9.03 $\pm$ 6.81	0.00 $\pm$ 0.00 <sup>a</sup>	3.14 $\pm$ 0.31	
OPC + PCDE, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	2.21 $\pm$ 0.04 <sup>a</sup>	0.18 $\pm$ 0.02 <sup>a</sup>	2.19 $\pm$ 0.21 <sup>a</sup>	LOQ	LOQ	1.739
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.36 $\pm$ 0.03 <sup>a</sup>	0.24 $\pm$ 0.01 <sup>a</sup>	0.06 $\pm$ 0.01 <sup>a</sup>	LOQ	0.44 $\pm$ 0.00	
<i>Mt</i> (mg m <sup>-2</sup> )	0.84 $\pm$ 0.09 <sup>a</sup>	6.44 $\pm$ 0.41 <sup>a</sup>	2.17 $\pm$ 0.22 <sup>a</sup>	11.0 $\pm$ 1.9 <sup>a</sup>	1.27 $\pm$ 0.06 <sup>a</sup>	2.51 $\pm$ 0.19	
CAC + PCDE, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	1.766
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.32 $\pm$ 0.17 <sup>a</sup>	0.05 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	0.91 $\pm$ 0.04 <sup>a</sup>	8.75 $\pm$ 0.52 <sup>a</sup>	0.50 $\pm$ 0.06 <sup>a</sup>	1.16 $\pm$ 0.22 <sup>a</sup>	1.46 $\pm$ 0.29 <sup>a</sup>	0.30 $\pm$ 0.03	
PC + PCDE, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	1.60 $\pm$ 0.10	0.16 $\pm$ 0.01 <sup>a</sup>	0.99 $\pm$ 0.26 <sup>a</sup>	LOQ	2.46 $\pm$ 0.50 <sup>a</sup>	1.646
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.30 $\pm$ 0.01 <sup>a</sup>	0.51 $\pm$ 0.04 <sup>a</sup>	0.06 $\pm$ 0.02 <sup>a</sup>	LOQ	0.28 $\pm$ 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.08 $\pm$ 0.02 <sup>a</sup>	4.07 $\pm$ 0.69 <sup>a</sup>	1.35 $\pm$ 0.05 <sup>a</sup>	7.72 $\pm$ 0.57 <sup>a</sup>	0.76 $\pm$ 0.40 <sup>a</sup>	1.33 $\pm$ 0.06	
OPC + PCA, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	1.34 $\pm$ 0.30	0.15 $\pm$ 0.04 <sup>a</sup>	1.71 $\pm$ 0.07 <sup>a</sup>	LOQ	1.04 $\pm$ 0.09	1.748
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.26 $\pm$ 0.02 <sup>a</sup>	0.06 $\pm$ 0.02 <sup>a</sup>	0.09 $\pm$ 0.01 <sup>a</sup>	LOQ	0.58 $\pm$ 0.70 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.24 $\pm$ 0.06 <sup>a</sup>	4.72 $\pm$ 1.02 <sup>a</sup>	1.28 $\pm$ 0.04 <sup>a</sup>	2.83 $\pm$ 0.06 <sup>a</sup>	1.52 $\pm$ 0.18 <sup>a</sup>	1.32 $\pm$ 0.12	
CAC + PCA, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	1.766
<i>El TCLP</i> (mg L <sup>-1</sup> )	0.03 $\pm$ 0.01 <sup>a</sup>	0.35 $\pm$ 0.08 <sup>a</sup>	0.06 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	LOQ <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.59 $\pm$ 0.22 <sup>a</sup>	10.1 $\pm$ 2.4 <sup>a</sup>	0.71 $\pm$ 0.27 <sup>a</sup>	1.51 $\pm$ 0.50 <sup>a</sup>	0.52 $\pm$ 0.57 <sup>a</sup>	0.23 $\pm$ 0.07	
PC + PCA, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	1.34 $\pm$ 0.06	0.12 $\pm$ 0.03 <sup>a</sup>	2.99 $\pm$ 0.14 <sup>a</sup>	LOQ	2.23 $\pm$ 0.29	1.584
<i>El TCLP</i> (mg L <sup>-1</sup> )	0.03 $\pm$ 0.00 <sup>a</sup>	0.37 $\pm$ 0.06 <sup>a</sup>	1.09 $\pm$ 0.10 <sup>a</sup>	0.12 $\pm$ 0.02 <sup>a</sup>	LOQ	0.34 $\pm$ 0.04 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.07 $\pm$ 0.02 <sup>a</sup>	4.71 $\pm$ 0.54 <sup>a</sup>	1.31 $\pm$ 0.06 <sup>a</sup>	8.43 $\pm$ 0.85 <sup>a</sup>	0.95 $\pm$ 0.65 <sup>a</sup>	1.40 $\pm$ 0.15	
OPC + Tween 80, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	3.41 $\pm$ 0.17 <sup>a</sup>	LOQ	1.04 $\pm$ 0.15	1.665
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.29 $\pm$ 0.02 <sup>a</sup>	0.05 $\pm$ 0.01 <sup>a</sup>	0.11 $\pm$ 0.01 <sup>a</sup>	LOQ	0.59 $\pm$ 0.00 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.09 $\pm$ 0.03 <sup>a</sup>	4.43 $\pm$ 0.26 <sup>a</sup>	1.09 $\pm$ 0.34 <sup>a</sup>	11.4 $\pm$ 4.3	1.21 $\pm$ 0.13 <sup>a</sup>	1.25 $\pm$ 0.20	
CAC + Tween 80, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	1.771
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.26 $\pm$ 0.03 <sup>a</sup>	0.09 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	0.13 $\pm$ 0.04 <sup>a</sup>	3.40 $\pm$ 1.47 <sup>a</sup>	0.42 $\pm$ 0.04 <sup>a</sup>	0.94 $\pm$ 0.18 <sup>a</sup>	1.11 $\pm$ 0.40 <sup>a</sup>	0.08 $\pm$ 0.09	
PC + Tween 80, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	2.79 $\pm$ 0.17 <sup>a</sup>	LOQ	2.14 $\pm$ 0.26 <sup>a</sup>	1.629
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.33 $\pm$ 0.01 <sup>a</sup>	1.08 $\pm$ 0.60 <sup>a</sup>	0.08 $\pm$ 0.02 <sup>a</sup>	LOQ	0.32 $\pm$ 0.03 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.23 $\pm$ 0.00 <sup>a</sup>	3.35 $\pm$ 0.48 <sup>a</sup>	0.75 $\pm$ 0.07 <sup>a</sup>	4.10 $\pm$ 0.19	1.33 $\pm$ 0.12 <sup>a</sup>	1.18 $\pm$ 0.14	
OPC + PPF, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	1.26 $\pm$ 0.09 <sup>a</sup>	LOQ	1.11 $\pm$ 0.37	1.744
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.37 $\pm$ 0.09 <sup>a</sup>	0.04 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	0.69 $\pm$ 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.00 $\pm$ 0.00 <sup>a</sup>	7.54 $\pm$ 3.06 <sup>a</sup>	0.84 $\pm$ 0.43 <sup>a</sup>	17.9 $\pm$ 1.4 <sup>a</sup>	0.00 $\pm$ 0.00 <sup>a</sup>	0.78 $\pm$ 0.30	
CAC + PPF, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	1.769
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.29 $\pm$ 0.01 <sup>a</sup>	0.07 $\pm$ 0.01 <sup>a</sup>	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	0.18 $\pm$ 0.03 <sup>a</sup>	3.71 $\pm$ 0.80 <sup>a</sup>	0.52 $\pm$ 0.23 <sup>a</sup>	4.74 $\pm$ 0.58 <sup>a</sup>	1.26 $\pm$ 0.84 <sup>a</sup>	0.63 $\pm$ 0.40	
PC + PPF, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	1.57 $\pm$ 0.14 <sup>a</sup>	LOQ	1.28 $\pm$ 0.79	1.748
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.31 $\pm$ 0.05 <sup>a</sup>	0.79 $\pm$ 0.33 <sup>a</sup>	LOQ	LOQ	0.32 $\pm$ 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.09 $\pm$ 0.08 <sup>a</sup>	2.11 $\pm$ 1.06 <sup>a</sup>	0.61 $\pm$ 0.14 <sup>a</sup>	16.0 $\pm$ 1.4 <sup>a</sup>	0.00 $\pm$ 0.00 <sup>a</sup>	0.96 $\pm$ 0.03	

Table 4 (Continued)

Soil 2	Cd	Pb	Zn	Cu	Ni	As	S/S efficiency
OPC + Akrimal, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	2.90 ± 0.36 <sup>a</sup>	LOQ	LOQ	1.637
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.23 ± 0.01 <sup>a</sup>	0.02 ± 0.00 <sup>a</sup>	0.06 ± 0.01 <sup>a</sup>	LOQ	0.67 ± 0.05 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.15 ± 0.11 <sup>a</sup>	5.26 ± 3.86 <sup>a</sup>	0.49 ± 0.25 <sup>a</sup>	24.7 ± 2.0 <sup>a</sup>	0.12 ± 0.21 <sup>a</sup>	0.93 ± 0.34	
CAC + Akrimal, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	1.774
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.16 ± 0.03 <sup>a</sup>	0.04 ± 0.01 <sup>a</sup>	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	0.13 ± 0.12 <sup>a</sup>	2.16 ± 1.90 <sup>a</sup>	0.26 ± 0.08 <sup>a</sup>	1.02 ± 0.42 <sup>a</sup>	0.03 ± 0.05 <sup>a</sup>	0.07 ± 0.00	
PC + Akrimal, S/S							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	LOQ	2.83 ± 0.26	LOQ	1.29 ± 0.13 <sup>a</sup>	1.684
<i>El TCLP</i> (mg L <sup>-1</sup> )	LOQ	0.20 ± 0.02 <sup>a</sup>	0.64 ± 0.02 <sup>a</sup>	LOQ	LOQ	0.35 ± 0.02 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> )	0.23 ± 0.08 <sup>a</sup>	5.21 ± 0.94 <sup>a</sup>	0.83 ± 0.24 <sup>a</sup>	17.2 ± 0.58 <sup>a</sup>	0.01 ± 0.02 <sup>a</sup>	1.58 ± 0.18	

<sup>a</sup> Denote statistically different concentration within category before and after soil stabilisation according to LSD test ( $p < 0.05$ ).

ing tests (*El DW* (EN12457-4) and *TCLP*) since there is no single generally accepted leaching test for S/S.

S/S with OPC effectively reduced the *El* of most PTMs below the LOQ (Table 3). Nevertheless, the *El DW* of Pb from Soils 1 and 3 exceeded the concentration limits specified by Slovenian legislation for the disposal of materials for land-filling and covering [19], even after S/S. Interestingly, the highest Pb leachability occurred in Soil 3, which contained only 121 mg kg<sup>-1</sup> of Pb. Similar results were reported by Dermatas et al. [33] and referred to different Pb immobilization mechanisms that may hold sway. The *El DW* of Cu increased after S/S in all four soils, in Soil 1 and, especially, in Soil 2 even over the stipulated limit specified by Slovenian legislation [19].

Although several studies have addressed the limitations of *TCLP* in S/S technologies [2,10,34], it is still one of the most sought-after leaching tests for cement-based materials [35,36]. Since the *TCLP extraction solution* is slightly acidic (pH 5), increased leachability of PTMs in *El TCLP* compared to *El DW* was expected [29]. Leaching of PTMs showed a significant decrease after S/S, except for As in (again) Soil 2, in which the leachability increased (Table 3). Soil 2 was also the soil with the highest As concentration (7085 mg kg<sup>-1</sup>; Table 2). The concentrations of PTMs were otherwise below the limits specified as hazardous by the US Environmental Protection Agency [20] or even below LOQ.

In general, measurements of *Mt* of PTMs from monoliths of cement S/S soil offer a more realistic assessment of stabilization efficiency than the measurement of *El* from grounded soils. The *Mt* of Cd, Pb, Zn, Cu, Ni and As over 8 leaching intervals (calculated as cumulative mass transfer; i.e., total mass release per surface area over the sum of leaching intervals) are reported in Table 3. The addition of OPC evidently reduces the *Mt* of Cd (5.8–11-times, compared to the original soil), Pb (5.9–8.9-times), Zn (28–986-times) and Ni (2.7–5.2-times) and As (1.5–54-times), while the *Mt* of Cu increased (3.6–7.7-times), presumably due to mechanisms explained in Section 1.

The *Mt* of contaminants can be controlled by diffusion or desorption from the soil surfaces and wash-off. Diffusion-controlled release occurs when the contaminant flow is predominantly at the external boundary of the monolithic materials. According to de Groot and van der Sloot [21], the controlling mechanism can be identified by determining the slope of the logarithm of cumulative *Mt* until the *i*-th period plotted vs. the logarithm of time. For PTMs dissolving from the surface and for the short initial release of surface-deposited PTMs (surface wash-off), the slopes are expected to be >0.65 and <0.35, respectively. In the case of a diffusion-control mechanism, this plot is expected to be a straight line, with a slope of approximately 0.5. Analysis of *Mt* (plots are not shown) revealed that the release of Pb and Zn from the original (non-S/S) soils was diffusion controlled (except for Zn in Soil 4). The calculated average apparent diffusion coefficient ( $D_a$ ), expressed as  $-\log D_a$

(m<sup>2</sup> s<sup>-1</sup>), ranged from 7.714 ± 7.366 (Soil 4) to 8.288 ± 9.563 (Soil 3) for Pb and from 8.275 ± 8.548 (Soil 1) to 8.693 ± 9.653 (Soil 3) for Zn (results are presented as means of three replicates ± S.D.). According to Nathwani and Phillips [37], the mobility of contaminants can be evaluated by an index that varies from very mobile 9 (for  $-\log D_a = 9 \text{ m}^2 \text{ s}^{-1}$ ) to immobile 19 (for  $-\log D_a = 19 \text{ m}^2 \text{ s}^{-1}$ ). Pb and Zn were therefore highly mobile in the original soils. For Cd, Cu, Ni and As in the original soils and for all PTMs in S/S soils, *Mt* mechanism analysis revealed the plot slope (log cumulative *Mt<sub>i</sub>* vs. log *t*) to be <0.35 and surface wash-off to be the predominant mechanism of PTMs release. Soil solidification with OPC therefore facilitates the chemical inclusion of mobile Pb and Zn in a calcium silicate matrix, while other PTMs were further physically incorporated into solidified soil monoliths, i.e., by sealing the pores with Ca(OH)<sub>2</sub> formed during the carbonation reaction of the cementation process [30].

Overall, Soil 2 stands out among tested soils in terms of the difficulty to inducing Cu and As stabilization by OPC addition and it was therefore selected for further S/S testing with different cementitious formulations.

### 3.2. Optimization of S/S formulation and S/S efficiency modeling

The cementitious formulations tested and conditions for S/S are shown in Table 1.

In the building and civil engineering industry, OPC is the most frequently used cement; CAC is used for demanding constructions that require high initial and final mechanical strengths. PC has a lower pH reaction, which could result in lower extractability of metaloides such as As [29]. According to Spence and Shi [8], additives can significantly impact on the hydration characteristics of cements. In our study, we used plasticizers (PCDE and PCA), polypropylene fibers (PPF), acrylic polymer (Akrimal) and the non-ionic detergent Tween 80.

As shown in Table 4, the *El DW* of Cd and Ni were below the LOQ for all tested formulations after soil S/S. The concentration of Zn was also significantly reduced or below the LOQ. Some formulations increased the leachability of Pb, Cu and As. Although the addition of non-ionic detergent was intended to stabilize Cu, the results in fact showed the highest *El DW* of Cu for the formulation with OPC + Tween 80 (Table 4).

The *El TCLP* of Cd and Ni after S/S was also below the LOQ for all formulations, and the leachability of Pb, Zn and Cu was significantly reduced (Table 4). The *El TCLP* of As was, however, higher after soil S/S for most cementitious formulations. Various studies have shown that alkaline materials, e.g., lime, fly ashes or hydroxyapatite, increase As mobility [38,39].

All cementitious formulations significantly reduce the *Mt* of Cd (24–307-times, compared to the original soil), Pb (12–55-times), Zn (371–3842-times) and Ni (6.8–1030-times), Table 4. There was no *Mt* of Cd from OPC + PPF stabilized and Ni from CAC, PC, OPC + PPF

and PC + PPF stabilized soil, meaning that the two elements were entirely physically encapsulated. Again, the *Mt* of Cu after soil S/S was higher for most formulations. In general, the *Mt* of As was lower after soil S/S, except for PC and OPC + PCDE mixes. We assume that the increase in As and Cu *Mt* can partly be explained by the surface wash-off mechanism of elements attached to the outer surface of the S/S soil monoliths.

Data on the *El DW*, *El TCLP* and *Mt* for all tested cementitious formulations were fed into the S/S efficiency model, *EM* Eq. (3). The rationale behind the proposed empirical *EM* is simple. The model calculates the overall S/S efficiency by summarizing the contributions of the relative stabilization efficiencies of each contaminating PTM. To account for differences in PTM's toxicity, their relative stabilization efficiencies are weighted with a toxic equivalence factor (share of PTM in the total PTMs hazard,  $TEF_{LC}$  in Table 2). To define the toxic equivalence factors, we used data of allowable PTMs limit concentrations from national legislation [23]. We propose the use of national and international legislative concentration limits (allowable, warning, critical), since they reflect both aspects of hazard; toxicity and bio-accessibility of contaminants although these are, of course, to a certain degree arbitrary. Purely toxicological data are indeed exact, but do not include the bio-accessibility aspect from different environments. The mechanical strength of soil monoliths is also often used as one of the S/S efficiency indicators. It was not included in the proposed *EM*, since it can often be improved by using different fibers as armature, which, however, does not reflect physical and chemical mechanisms of PTMs encapsulation.

The *EM* data for all tested cementitious formulations are shown in Table 4; a higher value denotes a higher S/S efficiency. The formulation with CAC + Akrimal is the most effective and was used further for S/S of soil from all four sampling locations. It is also evident from the *EM* data that CAC was more efficient in soil S/S than the other two cements. In fact, the choice of cement was more important than the choice (or even use) of additives. For example,

the S/S efficiency of CAC + Akrimal was only 0.8% higher than the S/S efficiency of CAC alone, while CAC was 5.3% and 3.4% better than OPC and PC without additives (Table 4).

Our empirical model is the first to address the S/S efficiency of multi-metal contaminated soils based on PTMs potential hazard. There have, however, been several attempts to model the long-term leaching of contaminants from S/S materials. In a study by Tiruta-Barna et al. [40], the combination of a pore water test, the acid neutralization capacity test and dynamic monolith leach test (type of tank test, mass transfer test) has been identified as a suitable combination to derive the required parameters for prediction of leaching behavior. Nevertheless, there is still some debate about how well long-term leaching behavior in specified scenarios can be predicted based only on laboratory leaching tests. The same constraints and uncertainties are also relevant for the use of our model. In recent studies, a number of authors [2,41–43] have performed geochemical modeling to reproduce the characteristic pH dependent release patterns for PTMs. However, according to van der Sloot et al. [2], using a too limited set of elements in geochemical modeling can have definite limitations in reaching a proper chemical description of release from a material.

### 3.3. S/S with selected formulation

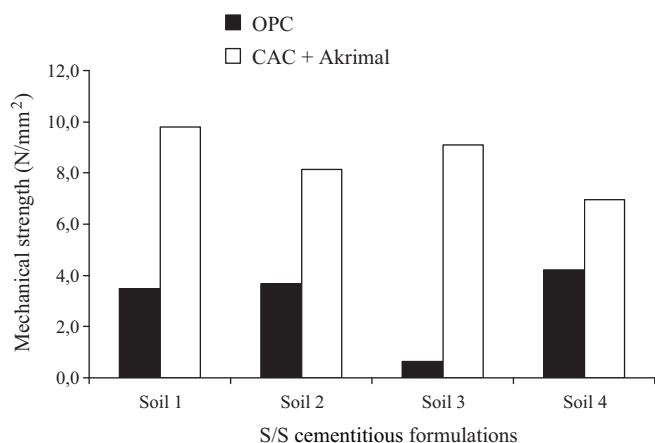
The selected S/S formulation (CAC + Akrimal) was effective in controlling the release of all PTMs. The results of *El DW* showed that after S/S, the concentrations of all measured PTMs in the water extract were below the LOQ in mixes of all four soils (Table 5). The results in Table 5 also show that after S/S, the *El TCLP* of Pb and Zn significantly decreased, while concentrations of Cd, Cu, Ni and As in *TCLP* solutions were again below the LOQ for all soils. The selected formulation significantly reduced the *Mt* of PTMs from all soils except the *Mt* of Cu from Soil 4 (Table 5). Analysis of *Mt* (plots are not shown) revealed that the mechanism of release of all PTMs

**Table 5**  
Concentrations of Cd, Pb, Zn, Cu, Ni and As leached into deionized water and *TCLP* solution (*El DW*, *El TCLP*) and PTMs cumulative mass transfer (*Mt*) during 384 h release period before and after S/S of Soils 1–4 with CAC + Akrimal. Results are presented as means of three replicates  $\pm$  S.D. LOQ is the limit of quantification. An increase of the S/S soil efficiency of CAC + Akrimal (the most effective formulation) against OPC, calculated using an S/S efficiency model, is also shown.

Soil	Cd	Pb	Zn	Cu	Ni	As	S/S efficiency increase (%)
1							
<i>El DW</i> (mg kg <sup>-1</sup> )	0.29 $\pm$ 0.00 <sup>a</sup>	1.87 $\pm$ 0.05 <sup>a</sup>	10.3 $\pm$ 0.1 <sup>a</sup>	LOQ	LOQ	LOQ	6
<i>El DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> )	1.10 $\pm$ 0.00 <sup>a</sup>	27.7 $\pm$ 2.4 <sup>a</sup>	175 $\pm$ 9 <sup>a</sup>	LOQ	0.47 $\pm$ 0.06 <sup>a</sup>	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	0.15 $\pm$ 0.02	0.02 $\pm$ 0.01	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	18.31 $\pm$ 0.78 <sup>a</sup>	194 $\pm$ 19 <sup>a</sup>	469 $\pm$ 49 <sup>a</sup>	1.54 $\pm$ 0.06	10.3 $\pm$ 2.3 <sup>a</sup>	5.42 $\pm$ 2.82 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	0.04 $\pm$ 0.02	0.26 $\pm$ 0.24	0.12 $\pm$ 0.10	1.53 $\pm$ 0.22	0.15 $\pm$ 0.06	0.03 $\pm$ 0.05	
2							
<i>El DW</i> (mg kg <sup>-1</sup> )	0.42 $\pm$ 0.00 <sup>a</sup>	1.37 $\pm$ 0.02 <sup>a</sup>	24.2 $\pm$ 0.1 <sup>a</sup>	LOQ	LOQ	LOQ	10
<i>El DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> )	1.06 $\pm$ 0.03	10.7 $\pm$ 1.2 <sup>a</sup>	200 $\pm$ 9 <sup>a</sup>	6.41 $\pm$ 0.49	0.15 $\pm$ 0.02	0.11 $\pm$ 0.01	
<i>El TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	0.16 $\pm$ 0.03	0.04 $\pm$ 0.01	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	21.52 $\pm$ 1.21 <sup>a</sup>	116 $\pm$ 1 <sup>a</sup>	999 $\pm$ 3 <sup>a</sup>	4.79 $\pm$ 0.59 <sup>a</sup>	10.3 $\pm$ 0.3 <sup>a</sup>	2.43 $\pm$ 1.66	
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	0.13 $\pm$ 0.12	2.16 $\pm$ 1.90	0.26 $\pm$ 0.08	1.02 $\pm$ 0.42	0.03 $\pm$ 0.05	0.07 $\pm$ 0.00	
3							
<i>El DW</i> (mg kg <sup>-1</sup> )	0.93 $\pm$ 0.00 <sup>a</sup>	2.28 $\pm$ 0.01 <sup>a</sup>	35.8 $\pm$ 0.2 <sup>a</sup>	LOQ	LOQ	LOQ	2
<i>El DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> )	0.74 $\pm$ 0.02 <sup>a</sup>	15.7 $\pm$ 0.7 <sup>a</sup>	353 $\pm$ 16 <sup>a</sup>	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	0.10 $\pm$ 0.08	0.27 $\pm$ 0.35	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	22.21 $\pm$ 1.03 <sup>a</sup>	144 $\pm$ 1 <sup>a</sup>	2080 $\pm$ 84 <sup>a</sup>	1.15 $\pm$ 0.25 <sup>a</sup>	10.1 $\pm$ 0.6 <sup>a</sup>	0.38 $\pm$ 0.35	
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	0.03 $\pm$ 0.03	0.36 $\pm$ 0.32	0.02 $\pm$ 0.01	0.27 $\pm$ 0.13	0.10 $\pm$ 0.00	0.03 $\pm$ 0.05	
4							
<i>El DW</i> (mg kg <sup>-1</sup> )	LOQ	LOQ	0.40 $\pm$ 0.02 <sup>a</sup>	LOQ	LOQ	LOQ	14
<i>El DW</i> (mg kg <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> )	0.09 $\pm$ 0.00 <sup>a</sup>	3.43 $\pm$ 0.25 <sup>a</sup>	14.3 $\pm$ 1.1	LOQ	LOQ	LOQ	
<i>El TCLP</i> (mg L <sup>-1</sup> ), S/S	LOQ	LOQ	LOQ	LOQ	LOQ	LOQ	
<i>Mt</i> (mg m <sup>-2</sup> )	7.62 $\pm$ 0.87 <sup>a</sup>	105 $\pm$ 2 <sup>a</sup>	33.2 $\pm$ 1.8 <sup>a</sup>	0.38 $\pm$ 0.10 <sup>a</sup>	7.54 $\pm$ 1.50 <sup>a</sup>	0.30 $\pm$ 0.10 <sup>a</sup>	
<i>Mt</i> (mg m <sup>-2</sup> ), S/S	0.06 $\pm$ 0.10	0.40 $\pm$ 0.60	0.03 $\pm$ 0.03	0.76 $\pm$ 0.13	0.11 $\pm$ 0.01	0.03 $\pm$ 0.05	

<sup>a</sup> Denote statistically different concentration within category before and after soil stabilisation according to LSD test ( $p < 0.05$ ).





**Fig. 2.** Indicative mechanical strength of soil (1–4) monoliths, S/S with 15% (w/w) OPC (closed squares) and CAC + Akrial (open squares) and cured for 28 days. Data are averages of two measurements.

after S/S was surface wash-off from monoliths. Table 5 also presents the percentage increases of efficiency of soil S/S of CAC + Akrial against OPC, calculated using EM. The selected formulation was up to 14% more efficient.

The formation of soil monoliths and their mechanical strength relates to the progress of hydration reactions in the cement-S/S soil and, together with leaching resistance for contaminants, is an important parameter of S/S efficiency. According to Malviya and Chaudhary [3], the minimum required mechanical strength for a stabilized material should be evaluated on the basis of the design loads: for example, S/S material with a strength of  $0.35 \text{ N mm}^{-2}$  is considered by the U.S. EPA to have a satisfactory mechanical strength for materials placed on it in a landfill. In the UK, the required 28-day strength is  $0.7 \text{ N mm}^{-2}$  but as low as  $0.35 \text{ N mm}^{-2}$  is also considered acceptable, depending on the test specimen [44].

In our case, the addition of all formulations produced soil monoliths. The formulation of CAC + PCA attained the highest mechanical strength ( $>12 \text{ N mm}^{-2}$ , Soil 2) and OPC + Akrial yielded the lowest strength value ( $1.9 \text{ N mm}^{-2}$ , Soil 2). Again, the use of CAC based formulations resulted in superior strength development (up to three times) compared to OPC and PC. Given the range of adequate mechanical strength explained above, all formulations gave monoliths of suitable strength. As shown in Fig. 2, the highest mechanical strength using the selected formulation (CAC + Akrial) was obtained with Soil 1 ( $9.8 \text{ N mm}^{-2}$ ) and the lowest with Soil 4 ( $6.95 \text{ N mm}^{-2}$ ).

#### 4. Conclusions

The following conclusions can be drawn from our study:

- The novel empirical model for multi-contaminated soil employing measurements of equilibrium leaching and mass transfer of contaminating metals can be used in combination with the contaminants toxicity equivalence factor, derived from legislation, to calculate the S/S efficiency of cementitious formulation.
- Calcium aluminante cement reduced leachability and the diffusion of metallic contaminants more efficiently than ordinary Portland and pozzolanic cements and produced S/S soil monoliths of much higher mechanical strength.
- Additives: plasticizers, fibers, acrylic polymer and non-ionic detergent did not significantly contribute to the S/S efficiency of cementitious formulations.
- Cu and As were consistently less susceptible to cementitious S/S since formation of soluble Cu hydroxides and calcium arsenite

and arsenates in alkaline pore water of cemented soil. Zn and Pb were the elements most strongly encapsulated into calcium silicate matrix due to their affinity for carbonate during cementation reactions. Surface wash-off was the predominant mechanism of metallic contaminants release from S/S soils.

- The most efficient S/S formulation was Calcium aluminante cement and the addition of acrylic polymer Akrial, which reduced soil leachability of Cd, Pb, Zn, Cu, Ni and As into deionized water below the limit of quantification and into TCLP solution by up to 55, 185, 8750, 214, 4.7 and 1.2-times, respectively; and the mass transfer of elements from soil monoliths by up to 740, 746, 104,000, 4.7, 343 and 181-times, respectively. Applying this cementitious formulation would enable the use of S/S treated soils from Cinkarna brownfield as a land-filling and land-covering material according to Slovenian legislation.

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