

**LEACHING TEST OF VITRIFIED FLY ASH  
AND CERAMIC SLAG FROM AN INCINERATOR OF MUNICIPAL  
SOLID WASTE (MSW) TREATED WITH  $\text{Ca}(\text{OH})_2$   
AT DIFFERENT CONCENTRATIONS AND WITH MARLSTONE**

**TEST DE LESSIVAGE DE CENDRES VITRIFIÉES  
ET DÉCHETS DE CÉRAMIQUES D'UN INCINÉRATEUR DE RÉSIDUS  
SOLIDES URBAINS, RSU TRAITÉS AVEC  $\text{Ca}(\text{OH})_2$   
À DIFFÉRENTES CONCENTRATIONS ET AVEC DE LA MARNE**

**TEST DI CESSIONE DI CENERI VETRIFICATE  
E SCORIE DI CERAMICHE DI UN INCENERITORE  
DI RIFIUTI SOLIDI URBANI (RSU) TRATTATE CON  $\text{Ca}(\text{OH})_2$   
A DIFFERENTI CONCENTRAZIONI E MARNE.**

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**Abstract**

A public property site, situated on an alluvial terrace of the Idice Stream (Emilia Romagna Region-Italy) was contaminated by a layer of waste, constituted by vitrified fly ashes and ceramic materials produced by an incinerator of municipal solid waste. The waste had high contents of heavy metals which exceeded the Italian legal concentration limits for Cd, Cu, Pb and Zn (D. Lgs. 152/06, all. 5, tab.1). The *in-situ* remediation of the area was possible. In this study, alternative materials than the Portland cement were tested for the environmental restoration and the further naturalization of the area. Leaching tests were carried out treating the ashes with different concentrations of hydrated lime ( $\text{Ca}(\text{OH})_2$ ) and also with lime at 20% concentration and smectic marlstone. At the end of the leaching test, most of the heavy metals in the waste were immobilized in the waste by the lime/marlstone treatment.

**Keywords:** *incinerator ashes; in-situ remediation; leaching test;  $\text{Ca}(\text{OH})_2$ ; smectitic marlstone; environmental restoration.*

**Résumé**

Un site de propriété publique, mis sur une terrasse alluviale du torrent Idice, (Émilie Romagne – Italie) s'est avéré contaminé constituée par une couche de scories constituée de matériel céramique et de cendres vitrifiées provenant d'une installation d'incinération d'ordures solides urbaines. Les scories avaient des concentrations élevées en métaux lourds qui dépassaient les limites admises par la  
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loi italienne D., Lgs. 152/06, all. 5, tab.1, pour Cd, Cu, Pb et Zn. La bonification in-situ le la zone étant possible, on a voulu tester l'usage de matériels inertes alternatifs au béton Portland et plus adaptés à l'amélioration du milieu et à sa renaturalisation. Des tests de lessivage ont été effectués sur les scories traitées soit avec des concentrations variées de chaux ( $\text{Ca(OH)}_2$ ) soit avec de la chaux additionnée de marnes smectitiques. C'est ce dernier traitement qui s'est montré le plus efficace pour l'immobilisation de la quasi-totalité des métaux lourds présents dans les scories.

**Mots-clés:** *déchets d'incinération; bonification en-situ; test de lessivage;  $\text{Ca(OH)}_2$ ; marnes smectitiques; re-naturalisation*

### **Riassunto**

Un sito di proprietà pubblica, posto su un terrazzo alluvionale del torrente Idice (Emilia Romagna-Italia) è risultato contaminato da uno strato di scorie costituite da materiale ceramico e ceneri vetrificate provenienti da un impianto di incenerimento di rifiuti solidi urbani. Le scorie presentavano concentrazioni in alcuni metalli pesanti (Cd, Cu, Pb, Zn) che superavano i limiti previsti dalla legge italiana (D. Lgs. 152/06, all. 5, tab.1). Essendo possibile la bonifica *in-situ* dell'area si è voluto testare l'uso di materiali di inertizzazione alternativi al cemento Portland, per un più idoneo recupero ambientale e per una successiva rinaturalizzazione dell'area. È stato applicato il metodo del test di cessione sulle scorie trattate con concentrazioni diverse di calce  $\text{Ca(OH)}_2$  e con calce addizionata a marne smectitiche. Quest'ultimo trattamento si è dimostrato il più efficace nell'immobilizzare la quasi totalità dei metalli pesanti presenti nelle scorie.

**Parole chiave:** *scorie di incenerimento; bonifica in-situ; test di cessione;  $\text{Ca(OH)}_2$ ; marne smectitiche; rinaturalizzazione.*

### **Introduction**

To reduce environmental and human health risks, materials defined by the law as "hazardous waste", with high concentration of heavy metals or potential toxic elements (PTEs), have to be disposed into apposite sites (Ahel et al., 1998).

Instead, very often hazardous waste are illegally disposed. The illegal disposal of hazardous waste or contaminated materials is a serious and big problem, and it reflected in the fortuitous discovery of many polluted and compromise sites. According to Italian Law (D.Lgs 152/2006), the waste incineration of municipal solid waste (MSW) have to be subject to special disposal. The incineration of 1 ton of MSW, reduces the volume of the waste from 70 to 80% and produces 30 kg of fly ashes and 300 kg of bottom ashes. Bottom ashes are composed by silicates and oxides of metals. The principal problems related to the disposal of bottom ashes are risks of leaching of toxic substances, gas emissions (e.g H) (Bertolini et al., 2005), dispersion of chloride, sulphur and heavy metal powders into the atmosphere and the meaningful increase of the temperature of the material caused by chemical-physical reactions (Sabbas et al., 2003). In Italy, in according with the new CER

codes, bottom ashes, heavy ashes and slag are identified by means of two codes (190111 or 190112) depending on whether the material contains (or not) dangerous substances. Fly ashes are classified as dangerous waste identified by means of code 190105 (Sorlini et al., 2004). In order to landfill, the ashes must undergo treatment for the removal, the reduction and/or the total or partial immobilization of the contained hazardous materials. The principal *in-situ* chemical-physical remediation techniques available for contamination by inorganic pollutants are the encapsulation or the stabilization/solidification (Khan et al., 2004). Commonly, the Portland cement is used as material for the fixation treatment of materials polluted with inorganic substances (Gougar et al., 1996; Batchelor, 2006; Qiao et al., 2007; Gollmann, et al., 2010). The use of Portland cement limits the metals mobilization and encapsulates the waste into a monolithic solid of high physic stability. A very low permeability and the insoluble compounds formation reduces the leaching risk through precipitation phenomena. The aim of the present work was to experiment the immobilization of PTEs released and the confinement *in situ* of metals contaminated slag with hydrated lime at different concentration and with a mixture of hydrated lime and marlstone to create a good substrate for the successive naturalization of the contaminated area in the Municipality of Castenaso (Bologna, Italy).

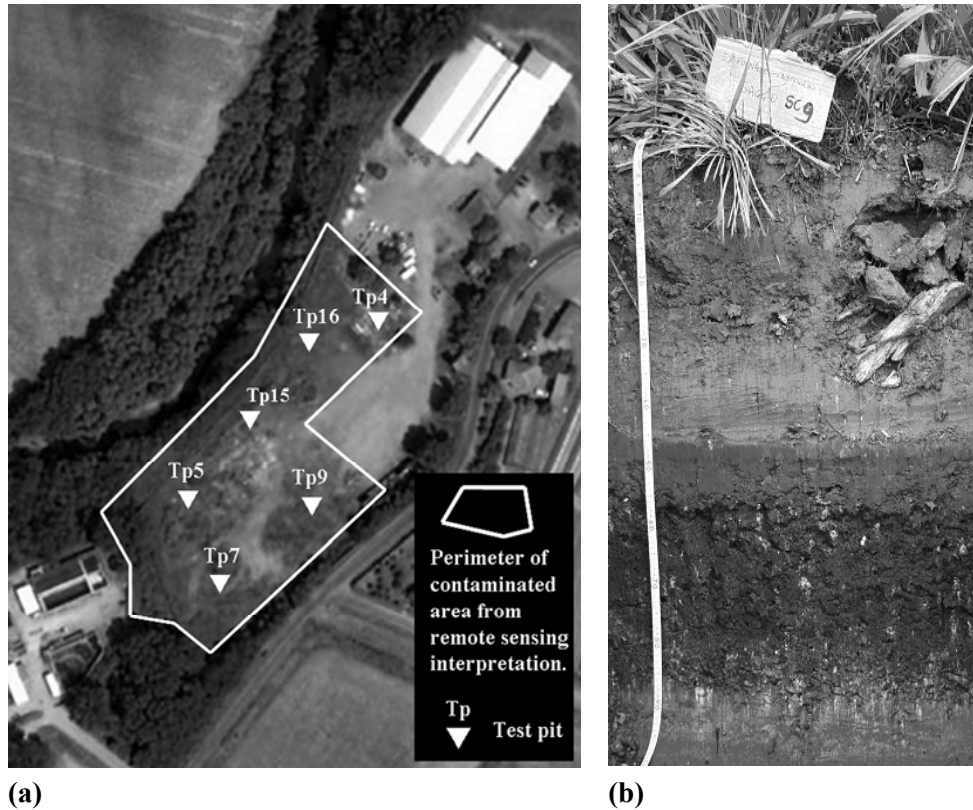
### **Materials and methods**

The contaminated area was a old kiln, where, at the end of the productive activity, vitrified fly ashes of MSW, ceramic and inert materials composed by glass pieces and bricks were concealed.

This area is located in the Municipality of Castenaso (Province of Bologna-Italy) over an alluvial terrace near the bed of the Idice stream. The geological survey shows that the layer of slag (S) has a thickness included from 70 to 150 cm and lies over sedimentary layers with silt-clay texture and low permeability. From the interpretation of satellite images the area has an extension of 24.000 mq (Fig.1a). Samples of S were collected for the PTEs concentrations analysis from six test pits (Fig. 1b). The PTEs concentrations in S samples are determined as following: 0.25 mg of S material (<2 mm of diameter) was mineralized with Aqua Regia (HNO<sub>3</sub>:HCl 3:1 suprapure, Merck) in a micro-wave oven (Milestone 1200) in a teflon vessel. After digestion and cooling the mineralized solution was transferred at 20 ml volumetric flask. The solution was analyzed using a Spectro Inductively Coupled Plasma Optical Emission Spectrometer (Circular Optical System CIR.O.S.<sup>CCD</sup>). The treatments with hydrated lime and hydrated lime/marlstone were carried out opening six pits with a known volume (300 cm ø x 70cm depth) in the slag layer. Using a concrete mixer, the S was mixed up with different volume of hydrated lime: +5% (S/CA5%), +10% (S/CA10%) and +20% (S/CA20%), respectively. In the fourth treatment S were mixed with +20% CaOH<sub>2</sub>+1%

smectitic marlstone (S/CA20%/M). These different mixture were replaced in the pits and maintained *in-situ*, in natural condition of air and humidity, for 10 days.

**Figure 1** – Definition over a “Quick Bird” satellitar image, of the survey area characterized by materials with a different spectral signature (a). Pedological survey and determination of the thickness of the slag layer (b).



The Italian Law provide that contaminated materials treated for the remediation, should be subjected to the leaching test carried out by applying the method UNI EN 12457-2, as described in the enclosure 3 of the D.M. 5.2.1998.

The leaching test was carried out with the S and with the S by adding of different mixtures of  $\text{Ca}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$  with marlstone, after 10 days of incubation. 100g of S or S-mixtures were placed in polyethylene containers and immerse in 500 ml of deionizer  $\text{H}_2\text{O}$ .

At times of 2, 8, 24, 48, 72, 102, 168 and 384 hours, the analysis of pH (using a Crison pH-meter) and the electrical conductivity (EC at constant temperature  $20\pm 5^\circ\text{C}$ ), were performed. At each time, 20 ml of supernatant were sampled and restored with distilled water. The 20 ml of solution were filtered with Wathman 42 and then acidified to pH 2 with  $\text{HNO}_3$  suprapure 1M ( $\text{HNO}_3$  65%, Merck).

The samples were stored at  $+4^\circ\text{C}$ . The PTEs content in the leaching water was determined using a Spectro Inductively Coupled Plasma Optical Emission

Spectrometer (Circular Optical System CIR.O.S.<sup>CCD</sup>). As the Law provide, the leaching water samples obtained from 8 leaching phases, were analyzed in one analytical sequence. The value obtained by the summation sign of the contents of elements in the 8 leaching phases was compared with the threshold values indicated in the DM 5/2/1998. As regard the results of the leaching test As, Cd and V were under the *detection limit* (DL= 4.1, 0.5, 1.5 µg/L for As, Cd and V, respectively).

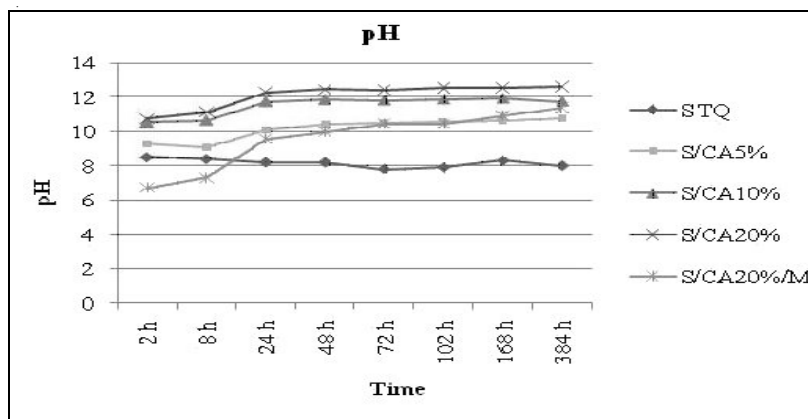
### Results and Discussion

The PTEs concentrations of S, determined in Aqua Regia, showed that As, Cd, Co, Cr, Cu, Ni, Pb and Zn exceeded the Italian Law limit established in the D.Lgs 152/2006 for urban parks and residential use (Tab. 1)

**Table 1** – PTEs concentration (mg/kg) in the slag material as sampled (S). The Italian Law limit (D. Lgs 152/2006 – All. 5 – tab. 1) referred to urban parks and residential use (A) and commercial and industrial use (B), are reported.

Trace elements	Mean	SD	Max	Min	Italian Law Limit	
					A	B
As	23	7	35	18	20	50
Cd	28	14	62	15	2	15
Co	29	5.9	34	26	20	250
Cr	249	10.7	300	203	150	800
Cu	1822	7.9	2172	1562	120	600
Mo	15	0,4	18	10	NM	NM
Ni	191	6.8	246	146	120	500
Pb	3821	196.3	7444	2528	100	1000
V	81	8.2	146	50	90	250
Zn	5726	113.1	7280	4828	150	1500

SD = standard deviation – NM = not mentioned



**Figure 2**  
pH trend's during the leaching test

The Italian Law defines the stability and the risk of PTEs leaching from the slag with a water leaching test. The pH of the leaching water of S is in all the times slightly alkaline (min 7.8- max 8.5) (Fig. 2).

The CE is lower than  $300\mu\text{S cm}^{-1}$  (Fig. 3). Cr, Cu, Ni e Pb are determined in leaching water and their concentrations exceeded the threshold limit of the DM 5/2/1998, besides a big release of Mo and Zn are shown (Tab. 2).

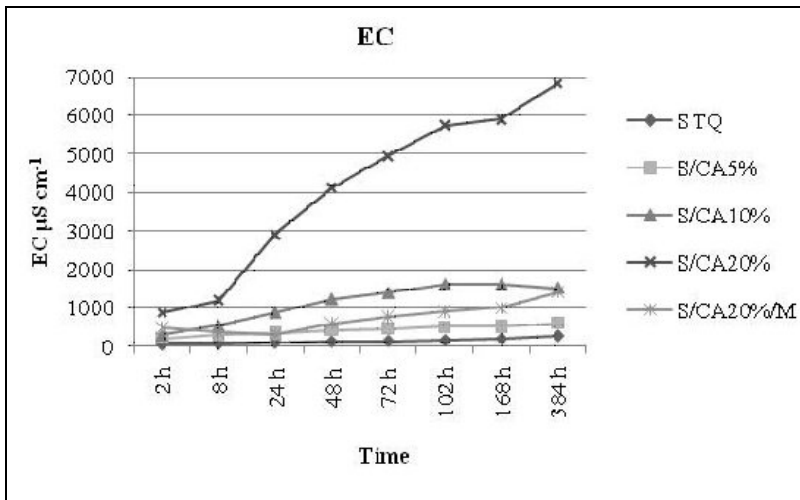
**Table 2** - Concentration of trace elements ( $\mu\text{g/L}$ ) in leaching test on S, S treatment with hydrated lime S/CA 5%, 10%, 20% respectively and S treatment with hydrated lime and smectitic marlstone (S/CA20%/M) after 10 days of incubation in situ. Leaching test according to Italian Law (DM 4/2/1998 – All. 3) - <sup>a</sup> the Italian Law limits of leaching test are reported.

Trace element	Treatments	Mean values during the leaching phases									DM <sup>a</sup>
		hours									
		2	8	24	48	72	102	168	384	$\Sigma$	
<b>Cr</b>	S	28	28	34	39	41	43	47	53	<b>312</b>	50
	S/CA5%	92	102	148	189	201	222	225	240	<b>1417</b>	
	S/CA10%	39	33	40	53	62	73	94	149	<b>543</b>	
	S/CA20%	13	12	16	18	22	23	24	34,2	<b>162</b>	
	S/CA20%/M	4	6	8	17	16	17	19	24	<b>111</b>	
<b>Cu</b>	S	200	100	100	50	50	50	50	50	<b>650</b>	500
	S/CA5%	232	249	358	483	662	595	654	802	<b>4034</b>	
	S/CA10%	298	292	366	470	537	658	852	1358	<b>4829</b>	
	S/CA20%	133	110	179	242	265	312	373	607	<b>2219</b>	
	S/CA20%/M	7	28	48	88	110	120	155	247	<b>801</b>	
<b>Mo</b>	S	24	32	47	60	63	75	96	134	<b>527</b>	NM
	S/CA5%	280	365	572	797	854	944	1014	1110	<b>5935</b>	
	S/CA10%	135	145	207	286	331	406	511	710	<b>2730</b>	
	S/CA20%	37	32	57	89	104	118	133	160	<b>730</b>	
	S/CA20%/M	2	7	19	31	41	42	52	89	<b>283</b>	
<b>Ni</b>	S	30	7	7	7	7	7	7	28	<b>97</b>	10
	S/CA5%	17	18	27	15	17	<DL	<DL	16	<b>109</b>	
	S/CA10%	14	<DL	<DL	13	<DL	13	18	17	<b>75</b>	
	S/CA20%	<DL	<DL	<DL	<DL	9	<DL	<DL	<DL	<b>9</b>	
	S/CA20%/M	2	2	1	1	1	2	<DL	1	<b>10</b>	
<b>Pb</b>	S	490	105	150	110	85	20	20	20	<b>1000</b>	50
	S/CA5%	<DL	<DL	<DL	<DL	321	<DL	<DL	<DL	<b>321</b>	
	S/CA10%	<DL	<DL	<DL	<DL	28	7	<DL	<DL	<b>35</b>	
	S/CA20%	<DL	<DL	<DL	<DL	4	<DL	<DL	<DL	<b>4</b>	
	S/CA20%/M	<DL	<DL	<DL	<DL	<DL	12	<DL	<DL	<b>12</b>	
<b>Zn</b>	S	1050	350	350	250	200	250	150	150	<b>2750</b>	3000
	S/CA5%	161	72	<DL	<DL	744	<DL	<DL	<DL	<b>977</b>	
	S/CA10%	114	76	<DL	<DL	85	<DL	<DL	<DL	<b>275</b>	
	S/CA20%	<DL	83	<DL	54	63	102	107	161	<b>571</b>	
	S/CA20%/M	94	5	11	8	14	<DL	<DL	<DL	<b>132</b>	

DL = detection limit. DL of Ni: 0,5  $\mu\text{g/L}$  – DL of Pb: 0,8  $\mu\text{g/L}$  – DL of Zn: 3  $\mu\text{g/L}$

The treatments with different concentration of hydrated lime and with hydrated lime/marlstone showed difference for pH and EC values and PTEs release. The treatment S/CA20% showed a strong increase of pH until alkaline values ranged from 10.8 to 12.6; the treatments S/CA5% and S/CA10% remained at intermediate

values, whereas the treatment S/CA20%/M started from neutral values and increased until 11.4, without reaching strong alkaline values  
 The EC trends showed a clear division between the treatments in two different groups (Fig.3).



**Figure 3**

*EC trend's during the leaching test*

In the S/CA20% treatment, the EC increased during the 384 hours until 7000  $\mu\text{S cm}^{-1}$ , whereas the EC values of treatments with 5 and 10% of hydrated lime and the treatment with marlstone remained below 2000  $\mu\text{S cm}^{-1}$ .

The PTE's concentration summation highlighted that the treatments with different concentration of hydrated lime showed different efficacy in PTEs release and the treatment efficiency growing scale may be summarized as follow: S/CA5% << S/CA10% < S < S/CA20% < S/CA20%/M.

The S/CA5% and S/CA10% treatments have increased the release of PTEs from the slag (S) (Fig.4). Cu and Mo concentrations were higher in the leaching water in both treatment than S (4034  $\mu\text{g/L}$  and 5935  $\mu\text{g/L}$  for S/CA5% and 4828  $\mu\text{g/L}$  and 2730  $\mu\text{g/L}$  for S/CA10%, respectively), and also the Cr release (1417  $\mu\text{g/L}$  for S/CA5% and 543  $\mu\text{g/L}$  for S/CA 10%, respectively).

The most effective treatment with hydrated lime is S/CA20%. In fact, the S/CA20% treatment increased the release of Cu and Mo respect to the S but reduced Cr and Zn concentrations in leaching water and immobilized Ni and Pb. The high alkalinity conditions could highlight a transitory efficiency of S/CA20% treatment.

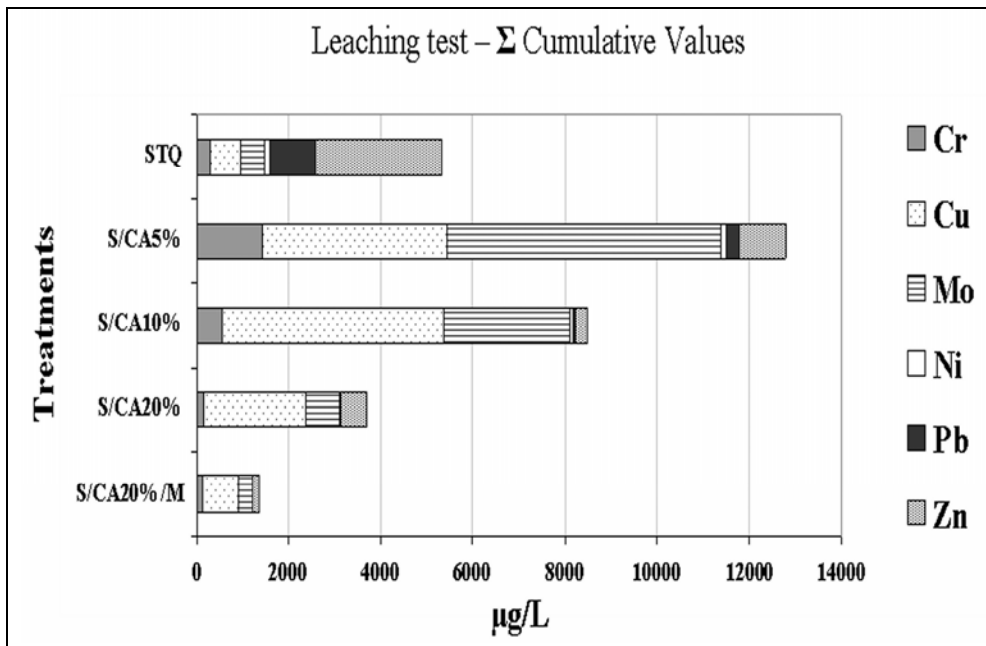
The high concentration of hydroxyls in the system can allow the selective precipitation of some hydroxides (Halim et al., 2003) in the leaching water and the system can appear to be particularly unstable because the high pH values may be a possible risk for amphoteric elements, like lead, with mobility controlled by pH

(Cocke, 1990; Sabbas et al., 2003), that increased when the pH reach values very low or very high (Jing et al., 2004).

The treatment with addition of marlstone with high smectitic contents has achieved good results with the reduction of the PTE's in leaching water respect to the S.

The action of the marlstone is twofold. The dissociation of the  $\text{CaCO}_3$  in the presence of  $\text{OH}^-$  reduce the pH value ( $\text{pH} < 11.5$ ) and the  $\text{CO}_2$  produced carried out to the probable precipitation of some metals, such Pb, in form of carbonates ( $\text{PbCO}_3$  cerussite) and bicarbonates ( $\text{Pb}_3(\text{CO}_3)_3(\text{OH})_2$  hydrocerussite). Moreover, there is the high cationic exchange capacity of the smectitic clay minerals to bind cations with low ionic potential and low hydration energy, such as Cd and Pb.

**Figure 4** - Cumulative release of EPT during the leaching test carried out on the STQ and the slag with different inertization treatments.



### Conclusions

The leaching test carried out on the slag mixed with 20% of  $\text{Ca}(\text{OH})_2$  and small quantities of smectitic marlstone (1%) highlights a significant decrease of the PTEs concentration.

Therefore, the use of marlstone may be an effective contribution for the mitigation of the prohibitive environmental conditions caused by the use of only hydrated lime such as very high pH and EC values and for the evolution of a subsoil suitable for the rooting of plant species.



The application of the UNI EN 12457-2 method, which is aimed at assessing the leaching of PTEs from special waste and slag and from the same materials subjected to inertization, has proved effective for the significance and reproducibility of the analytical results, for the slag-water contact that simulates the behavior of the contaminated materials under natural conditions and at least, to compare the effectiveness of different treatments on the release of PTE as regards from the slag as sampled.

It highlights the necessity to protract the test longer than 384 hours because, as pointed out by other authors (Stegemann et al., 2009) the properties of treated materials may change during the phase of stabilization and hardening.

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