

Assessment of Heavy Metals Immobilization in Artificially Contaminated Soils Using some Local Amendments

Noha H. Abdel-Kader, R. R. Shahin* and H. A. Khater

Soils Department, Faculty of Agriculture, Cairo University,
Giza, Egypt.

THREE alluvial soil samples of different textures were artificially polluted with chloride solutions of Cd, Pb, Co and chromate solution for Cr. The aqua-regia extracted concentration ranges in the artificially polluted soils from 1134-1489 mg.kg⁻¹ for Pb, 854-938 for Cr, 166-346 for Co and 44 – 54 mg.kg⁻¹ for Cd. The aqua-regia extracted metals were the highest in the spiked clay soil due to its high adsorption capacity. Rock phosphate (RP), lime-stone (LS) and Portland- cement (Cem) were mixed with the spiked soils at 1% and 2% rates (w/w) and incubated at 30 °C for 2, 7, 14, 30, 60, 150 and 360 days. The extracted DTPA metals significantly decreased with different magnitudes with increasing the incubation period accompanied by increases in both pH and EC. The data showed that cement (Cem.) treatment dropped the DTPA-Pb from approximately 1000 to 400 mg.kg⁻¹ in all the studied soils (60% decrease) in the first 2 months while it gradually decreased from 400 to 200 mg.kg⁻¹, (20% decrease) in the next 10 months. Limestone (LS) and rock phosphate (RP) materials were relatively less effective in lowering DTPA-Pb after 12 months of incubation. The data showed also that cement (Cem) treatment was the most effective one in lowering DTPA-Cd by 60% as compared to the un-amended soils after 12 months of soil incubation. Extractable DTPA-Co and Cr showed consistent decreases with time down to nearly 50% of un-amended soils due to the effect of the added amendments after 12 months of incubation with superior reductions for the cement treatment in all the investigated soils. The statistical analysis confirmed that in all the studied metals and treatment, cement treatment (Cem) was significantly the most effective in lowering the DTPA extracted metals as indicated from LSD test. It was found that up to 73% and 57% of the applied Pb and Cd, respectively, were fixed by only 1% cement. However, the present study showed that from the practical and economic points of view, that 1% Cement was the best treatment to immobilize Pb and Cd in all the artificially polluted soils.

Keywords: Heavy metals, Immobilization efficiency, Rock phosphate, Portland cement, Lime-stone.

The contamination of soils with heavy metals is now worldwide concerned due to its hazard to ecosystem including soil, water, plant, animal and human life. The common international technologies of the remediation of the heavy metals contaminated sites

*Corresponding author: dredashahin@gmail.com

are physical, chemical and biological techniques. The immobilization technique is commonly recognized for the in-situ remediation of heavy metals contaminated soils (United State Environmental Protection Agency (EPA) 1999). Immobilization is the reduction of the solubility of heavy metals through chemical reactions (ion-exchange, adsorption, precipitation and complexation processes) making them less harmful or less mobile (Hashimoto *et al.*, 2009 and Wang *et al.*, 2009). The mostly applied amendments include clay material, cement, zeolites, phosphates, and organic composts (Finizgar *et al.*, 2006). Zhang and Pu (2011) used limestone (AL), rock phosphate (RP), palygorskite (PG) and calcium magnesium phosphate (CMP) to stabilize heavy metals in two urban soils (calcareous soil and acidic soil) polluted with cadmium, copper, zinc and lead for 12 months. The results showed that application of those amendments reduced exchangeable forms in the order of $Pb > Cd > Cu > Zn$. Phosphate and palygorskite treatments were more efficient than limestone and rock phosphate in stabilizing heavy metals. Padmavathiamma and Li (2010) found that lime application to H.M. polluted soil lowered plant available Pb and Mn, while rock phosphate decreased plant available Pb and increased plant Mn. Houben *et al.* (2012) found that the addition of lime $CaCO_3$ to heavy metals contaminated soils significantly reduced both the leaching and the availability of Cd, Zn and Pb metals. Chen *et al.* (2007) applied rock phosphate with a rate of $2500 \text{ mg P}_2\text{O}_5 \text{ kg}^{-1}$ soil and found that it could successfully reduce the bioavailability and increase the geochemical stability of Pb, Zn and Cd in soil. In addition, Chen *et al.* (2006) showed that rock phosphate of the smallest grain size (< 35 microns) was superior to all of other grain sizes more than 35 microns for reducing uptake in plant (*Brassica oleracea* L.) shoots for Cd (19.6-50.0%), Pb (21.9-51.4%) and Zn (22.4-34.6%), respectively, as compared with the soil without application of rock phosphate. Cao *et al.* (2009) stated that rock phosphate amendment significantly reduced Pb water solubility, phyto-availability and bio-accessibility by 72-100%, 15-86% and 28-92%, respectively due to the formation of insoluble Pb-phosphate minerals and reduced water soluble Cu and Zn by 31 – 80 % and 40 – 69 %, respectively. Al-Oud and Hilal (2003) found that the admixing 0.5% of cement could reduce the 0.5 N HNO_3 extracted Pb by values up to 65% in the polluted sandy soils in Saudi Arabia. Alpaslan and Yukselen (2002) conducted several leaching experiments for mixtures of different additives (lime, activated carbon, clay, zeolite, sand and cement) with artificially Pb contaminated (spiked) soil samples. They stated that lime and cement were significantly effective in Pb immobilization with 88% efficiency at 1:21 lime: soil ratio and 99% efficiency at 1:15 cement: soil ratio, respectively.

The objective of the present work is to evaluate the efficiency of different local amendments to stabilize or immobilize heavy metals in different soil types artificially spiked with Pb, Cd, Cr and Co heavy metals.

Material and Methods

Three soil samples with different textures were taken from the most common polluted spots at Bahr el Bakar and Helwan districts. The collected samples were subjected to the physical and chemical analyses according to Sparks *et al.* (1996) and their characteristics are presented in Table 1.

TABLE 1. Some physical and chemical characteristics of the initial soil samples .

Soil texture	Particle size fraction (g/kg)			pH (1:2.5)	EC dS/m	OM (g/kg)	CaCO ₃ (g/kg)	CEC Cmol/kg
	Sand	Silt	Clay	1: 2.5 extract				
Sandy L.	748	144	108	7.79	1.14	1.5	11.6	9.4
Loamy	460	378	162	7.83	1.94	11.3	22.0	33.6
Clay	424	90	486	7.55	3.66	26.6	3.3	48.1
	Cd (mg/kg)		Pb (mg/kg)		Co (mg/kg)		Cr (mg/kg)	
	Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA
Sandy L.	1.02	0.08	20.3	0.3	3.20	0.53	16.30	7.37
Loamy	2.01	0.14	46.0	1.3	5.50	0.67	11.12	4.13
Clay	3.03	0.03	10.5	0.1	5.68	0.45	9.32	2.50

Solutions of different concentrations of cadmium (Cd), lead (Pb) and cobalt (Co) were prepared using metal chlorides and Cr as chromate, then sprayed onto the soil samples with continuous mixing to homogenize the distribution of the applied heavy metals. The spiked soils were allowed to be air-dried after each portion of sprayed metals solution. The total amounts of the metals were applied to exceed their maximum concentrations in soils as reported by EPA (2001). After spiking, the soil was supersaturated with de-ionized water and then mixed periodically for two weeks. The wetting and air dry cycle procedure was repeated five times to allow sufficient mixing of the applied metals and soil to imitate field conditions (Shanbleh and Kharabsheh, 1996 and Lin *et al.*, 1998). The aqua regia extraction was conducted and based on the procedure recommended by Cottenie *et al.* (1982) and standardized by the International Organization for Standardization (ISO 11466, 1995). In this procedure the soil sample intake was of 1 g, which were placed in 100 ml Pyrex digestion tubes, then 3 ml distilled water was added to obtain slurry. Thereafter, 7.5 ml of 37% HCl and 2.5 ml of 70% HNO₃ (3:1) mixture were added to the tube which was covered and left overnight. Then, the suspension was digested at 130°C for 2 hr, in a reflux condenser. The obtained suspension was then filtered through an ashless Whatman 41 filter, diluted to 25 ml with 0.5 mol l⁻¹HNO₃ and stored in polyethylene bottles at 4°C for analyses.

The available metal contents of soils were extracted with DTPA (diethylene-triamine-penta-acetic acid) according to Lindsay and Norwell (1978) as modified by ISO 14870 (2001). The DTPA-TEA solution was prepared by mixing of 0.005 mol l⁻¹ DTPA, 0.01 mol l⁻¹ CaCl₂, 0.1 mol l⁻¹ tri-ethanolamine (TEA) with pH adjusted to 7.3 with 1 mol l⁻¹ HCl solution. An amount of 5 g of soil sample (< 2 mm) was weighted into a 125 mL Erlenmeyer flask, then 20 ml of DTPA-TEA extracting solution was added and shaken for 2 hr at room temperature using a platform shaker. The soil suspension was centrifuged at 2000 rpm for 15 min and the clear supernatant was diluted to 50 mL with re-distilled water. Both aqua-

regia and DTPA-extractable contents were determined by a Perkin-Elmer model 1100B flame atomic absorption spectrometer (AAS).

Analysis of variance and LSD were used to compare treatment means. All the statistical analyses were carried out using Costat software (2010).

The chemical and physical properties of the artificially contaminated soils are presented in Table 2.

TABLE 2. The chemical characteristics of the spiked soil samples and the different amendments used in the incubation experiment .

		pH	EC dS/m	Pb (mg/kg)		Cd (mg/kg)		Co (mg/kg)		Cr (mg/kg)	
		1: 2.5 extract		Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA	Aqua-Regia	DTPA
Spiked soils	Sandy loam	8.85	10.40	1134.2	988.42	54.09	34.65	229.32	18.62	937.99	189.10
	Loamy	8.58	5.00	1488.9	1027.18	52.71	31.65	346.10	23.97	878.21	153.78
	Clay	8.44	26.40	1421.1	1008.30	44.53	23.13	165.70	7.70	854.40	67.16
Amendment	P-Rock	8.2	1.8	2.1	0.004	4.80	0.11	1.26	ND*	3.5	0.03
	Limestone	10.2	0.6	3.0	0.017	0.16	0.02	0.08	ND	7.1	0.08
	Cement	11.9	8.8	9.3	0.230	0.10	0.01	4.78	0.01	18.1	0.12

ND*= Not detected .

Three local amendments were chosen, *i.e.*, rock Phosphate (RP), Limestone (LS) and Portland cement (Cem). Portions of 100 g from the artificially contaminated soils were mixed with 1 g and 2g of each amendment. A control treatment (C_0) for each soil with no amendment addition was also prepared. Each treatment was carried out in triplicates. Replications of the homogeneous soil mixtures were watered to saturation level and placed in sealed small polyethylene bags in order to maintain the moisture level. The sealed soil mixture bags were incubated for 2, 7, 14, 30, 60, 150 and 360 days at $31^\circ\text{C} \pm 2^\circ\text{C}$. The soil bags were thoroughly mixed during the incubation process. At each period, a replicate from each treatment was removed from the incubator and the DTPA-TEA extractable fractions of the studied metals in soils were determined after incubation. The difference in initial concentration and final concentration, knowing dry mass of soil, allowed for the calculation of the exact amount of heavy metals adsorbed per gram of soil. A standard solution was run with each batch to justify the data. The efficiency (E) of different tested amendments for immobilization heavy metals can be evaluated using the expression: $E(\%) = [(C_0 - C_{12})/C_0] \times 100$, Where E = immobilization efficiency % ; C_{12} = equilibrium extractable concentration (mg kg^{-1}) of single metal in the amended soil at the end of incubation experiment (12 months); C_0 = initial extractable concentration (mg kg^{-1}) of single metal in the amended soil at zero time.

Results and Discussion

The data of the spiked soil samples, showed tremendous increases in the Aqua-regia- extracted Pb, Cd, Co and Cr proportional to their applied amounts. Table 2 showed that the aqua-regia extracted metal concentrations were the highest in the clay soil due to its high adsorption capacity for all the tested heavy metals and the vice versa for the sandy soil. The highest concentration was recorded for Pb and the least for Cd in the different soils in the order: Pb > Cr > Co > Cd. This is due to the high geochemical affinity of Pb to react with soil constituents forming inner-sphere complexes and even precipitate in different forms. In contrast to Pb, Cd tend to be less and weakly adsorbed by different soils which facilitate its leaching (Irha *et al.*, 2009). Table 2 indicated that the concentrations of the labile heavy metal forms (*i.e.*, DTPA-extracted) were higher in the spiked sandy soil compared to clay one due to the lack of adsorbing/active surfaces in sandy soil. Li-Yi *et al.* (2007), Mbarki *et al.* (2008) and Selim (2012) concluded that the free heavy metal ion concentrations in sandy soils were higher than in clay one receiving the same pollutants. Fig. 1 showed the initially adsorbed fixed concentrations in the spiked soils for the investigated metals. These values were obtained by subtracting The DTPA from Aqua-regia extracted heavy metal concentrations. It was clearly noticed the clay soil initially adsorbed the highest concentrations of the investigated heavy metals while sandy one adsorbed the lowest values. Again, chromium (Cr) and lead (Pb) showed the highest concentrations initially adsorbed in all the investigated soils which may rendered to their high adsorption affinity and the formation of inner-sphere complexes with the active surfaces of soil constituents. This is in agreement with Gomes *et al.* (2001) whom observed that in a competitive situation Cr and Pb were the heavy-metal cations most strongly adsorbed by seven Brazilian soils, whereas Cd, Ni and Zn were the least adsorbed.

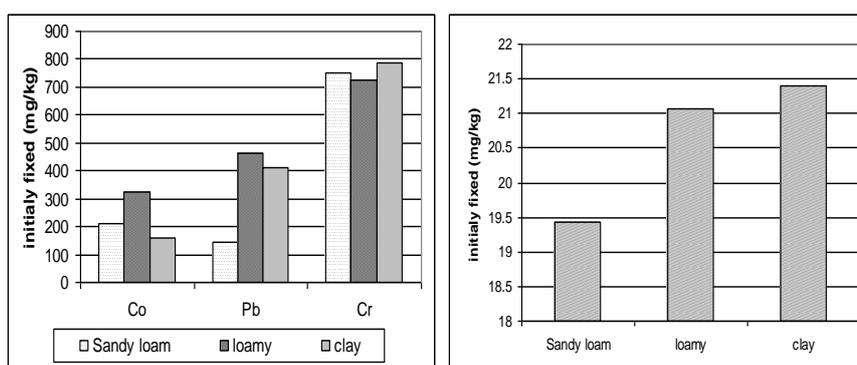


Fig. 1. Initially fixed heavy metal concentrations in the artificially contaminated soils.

The obtained data showed that the application of the different amendments had a significant effect on pH value of all the studied soils (Fig.2). Generally, in all treatments, the pH significantly increased within 2 days of incubation showing the highest jump between 60 and 150 days followed by steady increases upto 360

days. Soil pH value increased with increasing application rates of amendments. When the same rates of amendments were applied, the pH values increased in the sequence of Cem > LS > PR. With respect to pH changes in the investigated soils, significantly the highest pH values were recorded in the sandy soil as compared to the same treatments in the clay one. This could be rendered to the low buffering capacity of sandy soils and the lack of reserve acidity that can alleviate the alkalinity effect of the applied amendments. In addition, the initial pH values of the artificially polluted soil were more than 8.44 and 8.85, which may limit the buffering action to the bases produced from the hydrolysis of the highly alkaline components of Portland cement. Taylor (1997) stated that there are four chief minerals present in a Portland cement grain: tricalcium silicate (Ca_3SiO_5), dicalcium silicate (Ca_2SiO_4), tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_5$) and calcium aluminoferrite ($\text{Ca}_4\text{Al}_n\text{Fe}_{2-n}\text{O}_7$). The initial increase of pH is typical of cementitious systems because the cement produces high amount of $\text{Ca}(\text{OH})_2$ and high concentration of hydroxyl ions (Brown, 1987 and Taylor, 1997) as in the following reactions:

Tricalcium silicate



Dicalcium silicate



Tricalcium aluminate



The incubation of the amended soils also caused general increases in EC values with time in most of the investigated amendments (Fig.2). Limestons (LS) treatments showed the highest EC values followed by Cement (Cem.) as shown in loamy and clay soils and EC values increased by increasing the percent of application. It is clearly noticed that the majority of EC increases were recorded between 150 and 360 days of incubation period which could be rendered to the hydrolysis and solubility of Ca-compounds that may take longer time. The presence of siliceous-aluminous materials in cement composition creates some kind of high adsorption sites for metals found in soils. Moreover, the production of calcium hydroxide during cement hydrolysis, increase pH of the treated soils and subsequently decreasing the bioavailability of heavy metals in soils. Fig. 3 showed that cement (Cem.) treatment dropped the DTPA-Pb from approximately 1000 to 400 mg/kg in all the studied soils (60% decrease) in the first 2 months while it gradually decreased from 400 to 200 mg/kg (20% decrease) in the next 10 months. Limestone (LS) and rock phosphate (RP) materials were relatively less effective in lowering DTPA-Pb after 12 months of incubation. The data showed also that cement (Cem) treatment was the most effective one in lowering DTPA-Cd by 60% as compared to the un-amended soils after 12 months of soil incubation.

(Fig.2)

(Fig.3)

Extractable DTPA-Co and Cr. Fig.4 showed consistent decreases with time down to nearly 50% of un-amended soils due to the effect of the added amendments after 12 months of incubation with superior reductions for the cement treatment in all the investigated soils. The statistical analysis (Table 3) confirmed that in all the studied metals and treatment, cement treatment (Cem) was significantly the most effective in lowering the DTPA extracted metals as indicated from LSD test.

In addition, LSD test showed that cement treatment was significantly decreased all the DTPA extractable metals, and the increased of the applied cement from 1 to 2% didn't show any significant differences, which indicated that only 1% of cement was enough to get the lowest DTPA extracted metals in all the investigated soils.

Table 4 showed the heavy metals concentrations that immobilized by the effect of the different local amendments, it was obtained by subtracting concentration at the end of the incubation experiment, *i.e.*, 12 months (C_{12}) from the relevant concentration in the polluted soil at zero time (C_0), so amendment immobilized metal = (C_0)- (C_{12}). The obtained data showed that the immobilized concentrations by the different amendments could be in the order: Pb >> Cr > Cd > Co in all the studied treatments. Again, it could be concluded that cement (Cem) had the most effective immobilization in all the investigated heavy metals polluted soils. Cobalt (Co) showed the lowest response to the added amendments as its immobilized concentration was 2.72 to 9.89 mg.kg⁻¹, as compared to that of immobilized Pb-concentrations (515 to 807 mg.kg⁻¹).

Figure 5 showed that the immobilization efficiency ($E(\%) = [(C_0 - C_{12})/C_0] \times 100$) of lead (Pb) was the highest (68– 78%) among the other heavy metals in all the investigated soils especially those treated with cement. The immobilization efficiency for Cd was 41 - 58 %, for Cr it was 42 -46 % and for Co it ranged between 39 – 58 % of the initial DTPA concentrations were fixed by only 1% cement. However, the present study showed that from the practical and economic points of view, that 1% Cement was the best treatment to immobilize Pb and Cd from all the artificially polluted soils.

According to Ganjidoust *et al.* (2009), it is found that the hydrating cement product enhances the heavy metals precipitation on the surfaces of their particles as shown in Fig. 6. Lead (Pb) and Cd were found in stabilized forms of $\text{Ca}_2\text{Pb}_2\text{O}_5(\text{OH})_2$, and $\text{CaCd}(\text{OH})_4$, respectively.

In addition, Komisarek and Wiatrowska (2009) stated that cementitious material has the potential ability to immobilize heavy metals by adsorption, precipitation surface complexation and isomorphous substitution.

Fig. 4.

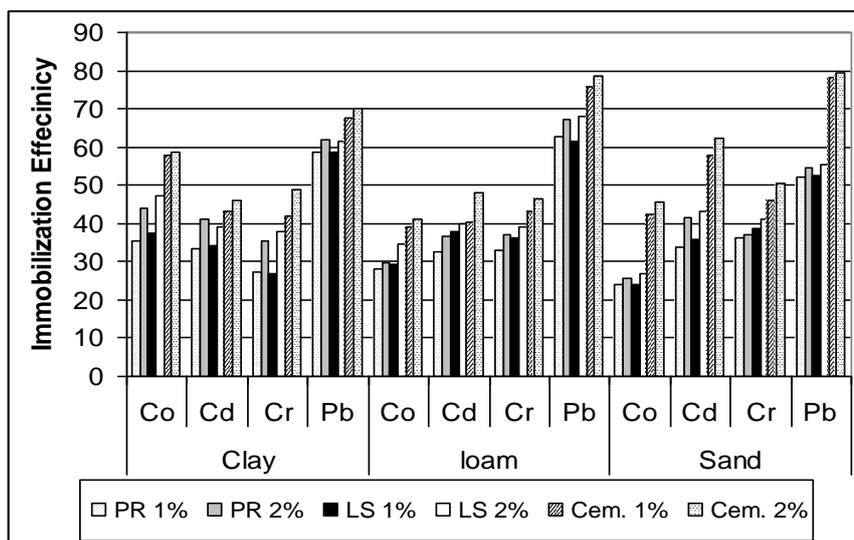
TABLE 3. LSD analysis of the mean concentrations of different metals in the different treatments and soils at the end of the incubation experiment .

Soil type	Treatment symbol	Concentration (mg/kg soil)							
		Pb		Cd		Co		Cr	
Sandy loam	Control	990.6	a	34.67	a	23.960	a	153.1	a
	PR 1%	795.9	b	30.97	b	21.159	b	140.1	b
	PR 2%	787.2	b	30.91	b	20.939	b	139.0	b
	LS 1%	763.8	b	30.59	b	20.730	b	130.6	c
	LS 2%	738.4	b	30.35	b	20.677	b	125.2	c
	Cem 1%	563.8	c	28.19	b c	20.121	b	117.4	d
	Cem 2%	538.0	c	26.81	c	19.870	b	115.8	d
	LSD 0.05	99.1		2.29		0.913		7.4	
	Loamy	Control	1026.6	a	31.587	a	18.64	a	188.9
PR 1%		821.2	b	28.899	b	17.71	ab	175.9	b
PR 2%		812.2	b	28.640	b	17.05	b	174.0	b
LS 1%		715.9	b c	28.154	b c	16.89	b	173.7	b
LS 2%		677.7	c	27.650	b c	16.69	b	165.9	b
Cem 1%		570.0	d	26.401	c d	15.61	c	146.9	c
Cem 2%		543.7	d	25.171	c d	14.85	c	142.5	c
LSD 0.05		104.5		1.532		0.98		9.8	
Clay		Control	1012.6	a	23.064	a	7.689	a	67.16
	PR 1%	770.1	b	20.221	b	7.039	b	63.83	b
	PR 2%	760.6	b	19.901	b	6.949	b	62.42	b
	LS 1%	736.2	b	19.760	b	6.847	b	59.31	c
	LS 2%	722.1	b	19.654	b	6.737	b	57.39	c d
	Cem 1%	687.8	b	18.961	b c	6.016	c	55.98	c d
	Cem 2%	572.2	c	18.406	c	5.890	c	54.61	d
	LSD 0.05	88.7		0.943		0.354		2.85	

*Means within a column followed by the same letter are not significantly different according to Fisher's Protected LSD test at $p \leq 0.05$.

TABLE 4. Immobilized concentrations of heavy metals in different polluted soils amended with local materials (C₀- C₁₂) mg kg⁻¹.

Soil	Metal	PR 1%	PR 2%	LS 1%	LS 2%	Cem. 1%	Cem. 2%	Initial-DTPA
Sandy loam	Co	4.45	4.8	4.5	5.02	7.86	8.52	18.62
	Cd	11.68	14.44	12.46	14.89	20.1	21.57	34.65
	Cr	68.35	69.98	72.78	77.67	86.67	95.13	189.1
	Pb	515.1	538.77	519.31	547.1	774.44	784.07	988.42
loamy	Co	6.73	7.15	6.98	8.3	9.34	9.89	23.97
	Cd	10.33	11.61	12.02	12.65	12.81	15.25	31.65
	Cr	50.73	56.87	55.46	60.16	66.42	71.68	153.78
	Pb	643.08	688.17	632.72	698.65	778.97	806.77	1027.2
Clay	Co	2.72	3.39	2.89	3.65	4.46	4.53	7.7
	Cd	7.75	9.51	7.96	9.04	10.03	10.66	23.13
	Cr	18.25	23.81	18.13	25.33	28.26	32.78	67.16
	Pb	592.08	622.59	589.33	618.2	682.21	706.98	1008.3

**Fig. 5.** The efficiency of the heavy metals immobilization for different types and rates of local amendments.

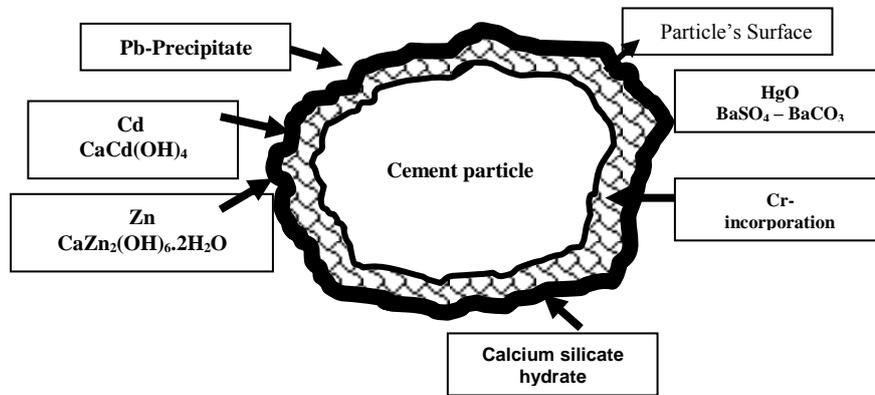


Fig. 6. Immobilization of heavy metals by hydrated particle of Portland cement as suggested by Ganjidoust *et al.* (2009).

References

- AL-Oud, S.S. and Helal, M.I.D. (2003) Immobilization of Pb in polluted soils using natural and synthetic chemical additives. National groundwater association (NGWA) *Conference on Remediation*. Nov. 13-14, New Orleans, Louisiana, USA.
- Alpaslan, B. and Yukselen, M.A. (2002) Remediation of Lead Contaminated Soils by Stabilization/Solidification. *Water, Air and Soil Pollution* **133**(1-4): 253-263.
- Brown, P. W. (1987) Early hydration of tetracalcium aluminoferrite in gypsum and lime gypsum solutions. *J. Am. Ceram. Soc.* **70**: 493-496.
- Cao, X., Wahbi, A., Ma, L., Li, B. and Yang, Y. (2009) Immobilization of Zn, Cu and Pb in contaminated soils using phosphate rock and phosphoric acid. *J. Hazard Mater.* **164** (2-3): 555-64.
- Chen, S., Xu, M., Ma, Y. and Yang, J. (2007) Evaluation of different phosphate amendments on availability of metals in contaminated soil. *Ecotoxicol. Environ. Saf.* **67**(2): 278-85
- Chen, S.B., Zhu, Y.G. and Ma, Y.B. (2006) The effect of grain size of rock phosphate amendment on metal immobilization in contaminated soils. *J. Hazard Mater.* **134** (1-3):74-9
- Costat 2.1 (2005) CoHort Software, 798 Lighthouse Ave PMB 320, Monterey, CA, 93940.
- Cottenie, A., Verloo, M., Kiekens, L., Velgh, G. and Camerlynch, R. (1982) "Chemical Analysis of Plants and Soils", Lab. Anal. Agrochem., State Univ., Ghent, Belgium, 63.

- EPA (Environmental Protection Agency) (2001)** Integrated Risk Information System (IRIS). National center for Environmental Assessment, Office of Research and Development, Washington, DC.
- Finžgar, N., Kos, B. and Leštan, D. (2006)** Bioavailability and mobility of Pb after soil treatment with different remediation methods. *Plant, Soil and Environment* **52**(1): 25-34.
- Ganjidoust, H., Hassani, A. and Ashkiki, A. R. (2009)** Cement-based solidification /stabilization of heavy metal contaminated soils with the objective of achieving high compressive Strength for the Final Matrix. *Transaction Civil Engineering* **16**(2): 107-115.
- Gomes, P.C., Fontes, M.P.F., Silva, A.G., Mendonca, E.D. and Netto, A. R. (2001)** Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. *Soil Science Society of America Journal* **65**: 1115-1121.
- Hashimoto, Y., Matsufuru, H., Takaoka, M., Tanida, H. and Sato, T. (2009)** Impacts of chemical amendment and plant growth on lead speciation and enzyme activities in a shooting range soil: an X-ray absorption fine structure investigation. *J. Environmental Quality* **38**(4):1420–1428.
- Houben, D., Pircar, J. and Sonnet, P. (2012)** Heavy metal immobilization by cost-effective amendments in a contaminated soil: Effects on metal leaching and phyto-availability. *J. Geochemical Exploration*. **123**: 87 – 94.
- Irhaa, N., Steinnesb, E., Kirsoa, U. and Petersellc, V. (2009)** Mobility of Cd, Pb, Cu, and Cr in some Estonian soil types. *Estonian J. Earth Sci.* **58**(3): 209:214.
- ISO 11466. (1995)** Soil quality, Extraction of Trace Elements Soluble in Aqua Regia. ISO, International Organization for Standardization.
- ISO 14870 (2001)** Soil quality -- Extraction of trace elements by buffered DTPA solution. ISO, International Organization for Standardization.
- Komisarek, J. and Wiatrowska, K. (2009)** Effectiveness of Oxide-Amendments in the Stabilization Process of Cu, Pb and Zn in Artificially Contaminated Soil. *Polish J. of Environ. Stud.* **18**(6):1029-1038.
- Lin, C.F., Lo, S.S., Lin, H.Y. and Lee, Y. (1998)** Stabilization of cadmium contaminated soil using synthesized zeolite. *Journal of Hazardous Material*. **60**(10): 217–226.
- Lindsay, W. L. and Norwell, W. A. (1978)** Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **42**: 421-428.
- Li-Yi, Hong, Y. Wang, D. and Zhu1, Y. (2007)** Determination of free heavy metal ion concentrations in soils around a cadmium rich zinc deposit. *Geochemical Journal* **41**: 235 -240.

- Mbarki, S., Labidi, N., Mahmoudi, H., Jedidi, N. and Abdelly, C. (2008)** Contracting effects of municipal compost on alfalfa growth in clay and sandy soils: N, P, K content and heavy metal toxicity. *Bioresource Technology* **99**(15):6745-50.
- Padmavathiamma, P.K. and Li, L.Y. (2010)** Phytoavailability and fractionation of lead and manganese in a contaminated soil after application of three amendments. *Bioresource Technology* **101**(14): 5667–5676.
- Selim, H. M. (2012)** Competitive Sorption and Transport of Trace Elements in Soils and Geological Media. CRC/Taylor and Francis, Boca Raton, FL (425 p). doi: 10.3176/earth.2009.3.05.
- Shanbleh, A. and Kharabsheh, A. (1996)** Stabilization of Cd, Ni and Pb in soil using natural zeolite. *Journal of Hazardous Material* **45** (11): 207–217.
- Sparks, D.L. (1996)** "Methods of Soil Analysis. Part 3, Chemical Methods". Soil Science Society of America, Book Series, No. 5, Madison .
- Taylor, H.F.W. (1997)** "Cement Chemistry", 2nd ed., Academic Press, London.
- United States Environmental Protection Agency (EPA). (1999)** Solidification/ Stabilization Resource Guide. Office of Solid Waste and Emergency Response (5102G), EPA/542-B-99-002.
- Wang, Q.L., Luo, L., BMa, Y., Wei, D. P. and Hua, L. (2009)** In situ immobilization remediation of heavy metals-contaminated soils: a review. *Chinese J. Applied Ecology* **20**(5):1214–1222.
- Zhang, M. and Pu, J. (2011)** Mineral materials as feasible amendments to stabilize heavy metals in polluted urban soils. *J. Environmental Sciences* **23**(4): 607–615.

(Received 28/7/2013;
accepted 28/8/2013)

تقييم تثبيت الفلزات الثقيلة فى الاراضى الملوثة صناعيا باستخدام بعض المحسنات المحلية

نهى حمدى عبد القادر ، رضا رجب شاهين و حسن احمد خاطر
قسم الاراضى – كلية الزراعة – جامعة القاهرة – الجيزة – مصر.

اختيرت ثلاث عينات رسوبية مختلفة القوام وتم تلويثها صناعيا بمحاليل من كلوريد الكاديوم والرصاص والكوبلت ومحلول كرومات البوتاسيوم . الاراضى الملوثة صناعيا تراحت تركيزات العناصر المستخلصة بالماء الملكى من 1134 الى 1489 مجم/كجم للرصاص ، من 854 الى 938 مجم /كجم للكروم، من 166 الى 346 مجم /كجم للكوبلت ، من 44 الى 54 مجم / كجم للكاديوم . وكان تركيز العناصر المستخلصة بالماء الملكى اعلى فى التربة الطينية وذلك يرجع لسعتها الادمصاصية العالية. تم خلط صخر الفوسفات ، الحجر الجيرى ، الاسمنت مع الترب الملوثة بمعدلى 1% و 2% (وزن/وزن) ثم التحضين على درجة 30 درجة مئوية لفترات 2 ، 7 ، 14 ، 30 ، 60 ، 150 و 360 يوم .تركيز العناصر المستخلصة بـ DTPA انخفضت انخفاض معنوى مع زياده فتره التحضين مصحوبا بزياده فى كلا من pH و EC . النتائج اظهرت ان معاملة الاسمنت خفضت تركيز الرصاص المستخلص بـ DTPA من 1000 الى 400 مجم / كجم فى الترب محل الدراسة (انخفاض 60 %) خلال الشهرين الاولين ، فى حين انخفضت تدريجيا من 400 الى 200 مجم / كجم (انخفاض 20%) فى العشر اشهر التالية. الحجر الجيرى و صخر الفوسفات مواد كانت اقل فاعلية نسبيا فى خفض تركيز الرصاص المستخلص بـ DTPA بعد 12 شهر من التحضين . كما اظهرت النتائج ايضا ان معاملة الاسمنت كانت اكثر كفاءه فى خفض تركيز الكاديوم المستخلص بـ DTPA (60%) مقارنة بالتربة الغير معاملة بعد 12 شهر من التحضين وكانت تركيزات كلا من الكوبالت والكروم المستخلصة بـ DTPA اوضحت انخفاض ما يقرب 50% مقارنة بالترب الغير معاملة نتيجة لتاثير اضافة المحسنات والتحضين لمده 12 شهرا مع تفوق معاملة الاسمنت فى خفض التركيزات فى الترب محل الدراسة . اكد التحليل الاحصائى من خلال اختبار اقل فرق معنوى ان معاملة الاسمنت كانت اكثر كفاءه معنوية فى خفض تركيزات العناصر المستخلصة بـ DTPA خلال فتره التحضين . تبين ان اكثر من 73 % و 57 % من تركيزات الرصاص والكاديوم على التوالى تم تثبيتها بواسطة الاسمنت 1 % . اظهرت هذه الدراسة ان من الناحية الاقتصادية والعملية كانت معاملة الاسمنت 1% افضل معاملة لتثبيت الرصاص والكاديوم فى الاراضى الملوثة صناعيا .