# Interaction of heavy metal ions with cement kiln dust

Margarita Giedrutë Klimantavièiûtë, Dalia Virbalytë, Vidas Pakðtas, Remigijus Juðkënas, Albinas Pigaga Institute of Chemistry, Vilnius, Lithuania The interaction of cement kiln dust (CKD) with water solutions of copper, nickel, lead, cadmium and cobalt salts (formation of compounds, maximal capacity and the ability of CKD to remove this HM to DCL) has been studied. The experiments have shown that CKD may be used for industrial wastewater decontamination, for neutralization of acidic wastewaters (the alkalinity 12-16 mg-eq/g) and for removal of HM ions such as Cu(II), Ni(II), Pb(II), Cd(II) and Co(II). CKD acts as an alkaline agent and sorbent. The main crystalline components of CKD are calcite - ${\rm CaCO}_{_3}$  (80% by mass), 10–15%  ${\rm SiO}_{_2}\!\!,$  and the remainder is the basic calcium silicate  $Ca_5(SiO_4)_2(OH)_2$ . The maximum capacity of CKD to remove Cu(II) is 0.29 g/g CKD (9.1 mg-eq/g), Ni(II) -0.14 g/g CKD (4.7 mg-eq/g), Pb(II) - 2.0 g/g CKD (19 mg-eq/g), Cd(II) – 0.42 g /g CKD (7.4 mg-eq /g) and Co(II) – 0.20 g /g CKD (6.8 mg-eq/g). The interaction of CKD with Cu(II) ions produces devillit  $Cu_4(CaSO_4)_2(OH)_6 \cdot 3H_2O$ , with Pb(II) – basic carbonate Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> and with Cd(II) ions - Cd(OH)Cl. The products of CKD interaction with Ni(II) and Co(II) ions are amorphous - apparently hydrated Ni(OH), and Co(OH),

Key words: heavy metal ions, cement kiln dustm, aqueous solutions, maximal capacity, removal

# **INTRODUCTION**

Nearly all industrial effluents are contaminated with heavy metals (HM). Mankind produces and consumes more and more goods, *i.e.* obtains and processes higher and higher amounts of chemical elements and their compounds. A large fraction of these compounds are xenobiotics, which do not naturally decompose and might be dangerous (toxic) to living organisms. One of the main principles of toxicology states that there are no toxic or non-toxic compounds; there are only dangerous or not dangerous concentrations of these compounds.

Very small amounts of HM, at ppm, ppb and even lower concentrations, are found in natural water resources, and living organisms are able to tolerate them in these concentrations. Some HM, *e.g.*, copper and cobalt, are even needed as microelements. However, high concentrations of HM are dangerous to living organisms. Most dangerous are cadmium, lead and mercury. It is believed that living organisms do not need them at all. One of the most important sources of pollution with HM is metal finishing industry. A certain portion of pollution with HM comes from farming, chemicals from laboratories and corrosion of various articles. However, a portion of HM is trapped by sewage sludge, complicating its usage (Paulauskas, 1999; Zakrzewski, 1991). The portion of HM that is not trapped by sewage sludge escapes into the environment and is the most dangerous one.

Considering that natural removal of heavy metals in ecosystems is relatively slow, it is necessary to prevent contamination with HM. The best way of HM removal is recycling, however, in most cases it is not economically viable. The other option is to lock HM into inoffensive compounds.

Copper is an irreplaceable microelement and serves as a cofactor for some oxidases, oxygenases and some other enzymes. Cattle need 6 to 12 mg and humans 2 mg of copper per day. However, if copper is present in excess concentrations, it catalyses formation of highly reactive oxygen species leading to lipid peroxydation, the lack of the reduced form of glutathion, enhancement of methemoglobin content (Èetkauskaitë, 1999). Generally, Cu accumulates in liver, in the lysosomes of hepatocytes.

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Ions of nickel enhance lipid peroxidation, reduce activity of glutathion peroxydase, lead to an increase of biologically active iron in tissues, induce DNA strand brakes, chromosome aberrations, formation of DNA adducts. The nickel-induced accumulation of iron may be directly responsible for the formation of reactive oxygen species and the subsequent enhancement of lipid peroxidation. This cation produces lung and nasal cancer (Paasvirta, 1991; Stinson et al., 1992; Stohs, Bagchi, 1995).

Pb inhibits activity of the enzymes that have sulfhydril groups (*e.g.*, Na, K-ATPases, dehydrogenases, etc.) in erythrocytes and haematopoietic tissues, and that results in the build-up of protoporphyrin, loss of intracellular potassium from erythrocytes and subsequently in anaemia. Lead replaces calcium in bones (Èetkauskaitë, 1999; Stohs, Bagchi, 1995). It is methylated and forms tetramethyl-lead in the living organisms, and builds up in various tissues (Paasvirta, 1991), especially in the liver and kidneys. Children are particularly susceptible even to a low-level lead intoxication, which creates a type of encephalopathy referred to as subclinical toxicity (Zakrzewski, 1991).

Cadmium causes intoxication of liver, kidneys, brain, lungs, heart and testicles. It is a carcinogen. However, the mechanisms of cadmium-induced intoxication are not well understood (Stohs, Bagchi, 1995; Zakrzewski, 1991).

Cobalt is a microelement involved in such essential processes as nitrogen fixation. The lack of cobalt can lead to abnormal angiogenesis and dangerous diseases in cattle, as it is a vital component of cobolamine (vitamin  $B_{12}$ ) (Анспок, 1990). On the other hand, despite of the fact that it is an essential microelement, at higher concentrations cobalt can have dangerous effects on living organisms. Cobalt compounds are classified as class II, which means they are not extremely toxic. However, one of the main potential effects of cobalt compounds is a decrease of natural ability of rehabilitation of water reservoirs. In plants, cobalt becomes toxic at a concentration of 0.1–0.3 mg/l. People exposed to cobalt compounds were reported to suffer from defective metabolism of proteins and carbohydrates, anaemia, Basedow disease, carcinogenic and mutagenic effects (Грушко, 1979).

The Lithuanian standard LAND 10–96 on discharge consent levels (DCL) specifies DCL for soluble compounds in wastewaters: Cu(II) – 1 mg/l, Ni(II) – 0.5 mg/l, Pb(II) – 0.5 mg/l, Cd(II) – 0.1 mg/l and does not specify DCL of cobalt compounds (Nuotekø..., 1997). However, the maximum allowed concentration of cobalt in wastewaters in the former USSR was 1 mg/l (Беспамятнов, Кротов, 1985). Bearing in mind that LAND 10–96 is under edition and broadening, we assumed that DCL for cobalt should be 1 mg/l.

It is very important to decontaminate wastewaters as efficiently and as cost-effectively as possible. There are several widely used methods: chemical precipitation, extraction, sorption, ion exchange and membrane separation. Synthetic ion exchange resins are especially good for removing heavy metals, but they are very expensive. Another option is to use natural ion exchange materials, which are much cheaper. For example, it is possible to remove heavy metals using clay, zeolite, ozocerite, opoka, glauconite, volcanic tuff, rock sapropel, peat. Some recycled materials may be used for this purpose as well. They are as follows: waste rubber, cement kiln dust, phosphogypsum, fly ash and biological materials, such as wooden sawdust, bark, peanut and fly larva shells, etc.

CKD is a by-product of cement industry. During the process of cement manufacturing, gas which comes out of the rotatory furnace carries out a lot of CKD. That CKD is filtered out by electrical filters and stored. CKD is used for decontamination of sewage sludge in the N-Viro process, where CDK serves as an HM-trapping and antimicrobial agent (Paulauskas, 1999). There are also suggestions to use CDK for brick, glass wool, asphalt or concrete production. The joint stock company "Akmenës cementas" produces 20-30 thousand tons of CKD per year, which costs 30-50 Lt per ton, and is used mainly as a fertilizer (for liming and as a potassium-containing fertilizer). The chemical composition of CKD produced by "Akmenës cementas" is as follows: Al<sub>2</sub>O<sub>3</sub> 3-8%, Fe<sub>2</sub>O<sub>3</sub> 2-5%, SiO<sub>2</sub> 11-15%, CaO 38-48%, CaO<sub>free</sub> 3-7%, MgO 2-4%, Na + K,O 2-8%, SO, 3-8% (according to the Lithuanian standard TS 5290342-04-92). The dust particles are extremely small (less than 0.01 mm), their remainder on the sieve No. 008 is less than 8% (according to GOST 310.2). Scanning electron microscope studies have shown that the dust is composed of spherical particles with a core of calcium carbonate and clay and an alkali coating (Wilson, Anable, ...).

In this study we have investigated the interaction of CKD with copper, nickel, lead, cadmium and cobalt salt water solutions: compound formation, maximal capacity and the ability of CKD to remove these HM to DCL.

#### **EXPERIMENTAL**

Metal removal experiments were conducted by pouring 100 ml of solution onto 2 or 10 g CKD and mixing for 0.5 min four times a day, while some were conducted under continuous stirring by a magnetic stirrer.

The maximal capacity of CKD to remove HM was determined at a concentration of 0.02 mol/l. A portion of 100 ml of the solution was poured onto

2 g of CKD stirred for 6 h and then allowed to settle for 18 h. Then the solution was poured off, its pH was measured and the residual HM concentration was determined. After that CKD was reused until the residual concentration of HM after interaction remained nearly the same.

Residual concentrations of HM in the solutions were determined by atomic absorption spectroscopy using an AAS-603 Perkin-Elmer spectrophotometer with acetylene-air flame. The source of light was a lamp with a hollow cathode. Standard solutions were prepared from monoelement stock solutions containing 1000 mg/l of HM. The intensity of Cu 324.8, Ni 232.0, Pb 283.3, Cd 228.8 and Co 241.4 nm spectral lines was measured.

Every measurement was done three times, and then the arithmetical mean and standard deviations were calculated.

The pH was measured using a pH-673 pH-meter-millivoltmeter at a 0.1 deviation.

The X-ray diffraction (XRD) patterns were recorded using a DRON-2 X-ray diffractometer and Cu K<sub> $\alpha$ </sub> radiation selected by a secondary graphite monochromator. A continuous scan mode was used in the range of 5°  $\leq$  2  $\Theta \leq$  60° with a scan rate of 1° 2  $\Theta$  min<sup>-1</sup>.

The crystal phases, formed after HM saturation were identified using ASTM Powder Diffraction Files (Powder..., 1977). Their amount was approximately estimated by the height of the most intensive peak.

All the experiments were performed using CKD obtained from the joint stock company "Akmenës cementas" according to TS 5290342-04-92 and GOST 310.2 regulations. CKD was dried at 105 °C for 24 h before use.

The solutions were prepared using "pure for analysis" and "chemically pure" grade chemicals. All the experiments were performed at room temperature  $18 \pm 2$  °C.

#### **RESULTS AND DISCUSSION**

#### **Investigation of CKD**

First we studied the interaction of CKD suspension in distilled water (20 g/l CKD) with 0.4 N  $H_2SO_4$  solution under equilibrium and non-equilibrium conditions.

These results indicated that interaction between hydrogen ions and CKD was slow (a matter of few hours). The main reason perhaps was a slow diffusion through the shell of the reaction products (gypsum, basic salts, etc.) to the core of the particle. At the equilibrium state, the alkaline basic equivalent of CKD was 12–16 mg-eq/g.

XRD analysis has shown that the main component (80% by mass) of CKD is calcite  $CaCO_3$ . There is also 10–15%  $SiO_2$ , and the remainder is the basic calcium silicate  $Ca_5(SiO_4)_2(OH)_2$ . However, it should be noted that XRD does not read out any amorphous material.

# Interaction with copper (II)

Results of copper (II) removal from quite a concentrated ( $c \operatorname{Cu}^{2+} = 3.95 \text{ g/l}$ )  $\operatorname{CuSO}_4$  solution by stirring for 30 s four times a day are given in Table 1. As we can see from these data, if CKD is present at 100 g/l, the copper ion concentration after 24 h of interaction is reduced down to 0.9 mg/l, which is lower than DCL (1.0 mg/l). The rate of copper removal under continuous stirring increases about 3-fold and DCL is reached after ~8 h. When the concentrations of Cu(II) ions are not high ( $\leq$ 0.5 g/l) and are similar to those in electroplating rinsing waters, DCL is reached after 0.5 h of mixing with 20 g/l of CKD. Such rate of copper removal is acceptable for industrial decontamination of rinsing waters of copper electroplating.

We have determined that the maximal capacity of CKD to remove  $Cu^{2+}$  is 0.29 g/g CKD (9.1 mg-eq /g).

We would suggest to use spent CKD as a microfertilizer additive, because copper is an irreplaceable microelement.

The main components of copper-saturated CKD are devillit  $Cu_4(CaSO_4)_2(OH)_6 \cdot 3H_2O$  and gypsum  $CaSO_4 \cdot 2H_2O$ , approximately 40% each, as was determined by means of XRD.

## Interaction with nickel (II)

Results of nickel (II) removal from a relatively concentrated (c Ni = 3.1 g/l) NiCl<sub>2</sub> solution by stirring for 30 s four times a day are presented in Table 1. If CKD was present at 100 g/l, nickel concentration after 24 h of interaction was reduced down to 0.2 mg/l, which is lower than DCL (0.5 mg/l). When Ni (II) ions were present at a relatively low concentration (0.5 g/l), DCL was reached after 2 h of mixing with 20 g/l CKD (Table 2).

The maximal capacity of CKD to remove  $Ni^{2+}$  was 0.14 g/g CKD (4.7 mg-eq /g).

As the diffractograms of nickel-saturated CKD did not have any additional peaks, this apparently indicates that nickel may be present in the form of amorphous  $Ni(OH)_{a}$ .

#### Interaction with lead (II)

Data on lead removal from  $Pb(NO_3)_2$  solutions are shown in Tables 1 and 2. If CKD was present at 20 g/l, lead ion concentrations were reduced below DCL (0.5 mg/l) after 12 days of interaction by stirring for 30 s four times a day when the initial  $c Pb^{2+} \leq$ 0.06 g/l. Similar results were obtained after 7 h under continuous stirring (Table 2).

It is known that CKD acts as both an alkaline reagent and a sorbent (El-Awady, Hamdy, 1996; El-

CD, g/l	Duration, h	c Cu, mg/l	pН		72	$72   9 \pm 1$
20	0	3950	4.2		144	
	24	$1100~\pm~100$	5.4		288	
	96	$20 \pm 2$	6.5	CD, g/l		
100	0	3950	5.45	20		
	24	$0.9 \pm 0.1$	9.0 7.0	20	20 0 24	
CD /	<u>96</u>	$0.2 \pm 0.03$	7.3		48	
CD, g/l	Duration, h		pH		168	
20	0 24	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	7.5 7.5	100		
	24 96	$870 \pm 40$ 220 ± 20	7.5 6.8	100	24	
100	96 0	$\begin{array}{r} 220 \pm 20 \\ 3100 \end{array}$	6.8 10.8		48	
100	24	$0.2 \pm 0.03$	10.8		168	
	48	$0.2 \pm 0.03$ $0.2 \pm 0.03$	10.6	20		
					24	
CD, g/l		<i>c</i> Pb <sup>2+</sup> , mg/l	рН		48	48 1.9 ± 06
20	0	9000	4.6		168	$168    0.9 \pm 0.3$
	24	$6500~\pm~200$	9.4	20	20 0	20 0 60
	72	$3130~\pm~60$	10.0		24	24 1.2 ± 0.4
	144	$2590~\pm~60$	10.1		48	$48 \qquad 0.09 \pm 0.03$
	288	$28 \pm 5$	10.3	CD, g/l	CD, g/l Duration, h	CD, g/l Duration, h c Co <sup>2+</sup> , mg/l
100	0	9000	4.6	20	U	
	24	$3410 \pm 60$	11.9	20	20 0	
	72	$2880 \pm 60$	11.7		48	
	144	$1420 \pm 20$	11.7		384	
00	288	$11 \pm 2$	11.7	20		
20	0	750	4.9	20	24	
	24 72	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	11.6		48	
	72 144	$170 \pm 20$ 80 ± 10	11.5 11.5		384	
	144 288	$80 \pm 10$ 9 ± 2	11.5	20		
100	200 0	$9 \pm 2$ 750	4.9		24	
100	24	$120 \pm 10$	4.9 11.5		48	
	24 72	$120 \pm 10$ 90 ± 20	11.5		384	
	144	$30 \pm 20$ $26 \pm 4$	11.5	100	100 0	100 0 6700
	288	$20 \pm 4$ $3.3 \pm 0.4$	11.5		24	
20	0	$5.5 \pm 0.4$	5.0		48	$48    0.6 \pm 0.1$
	0	00	5.0		384	$384 \qquad 0.08 \pm 0.03$

Table 1. Dependence of residual  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Pb^{2+}$   $Cd^{2+}$  and  $Co^{2+}$  concentration on solution – cement kiln dust interaction duration. Solutions were stirred for 30 s four times a day

 ${\rm Table \ 2. \ Dependence \ of \ residual \ Ni^{2+}, \ Pb^{2+} \ and \ Cd^{2+} \ concentrations \ on \ solution \ - \ cement \ kiln \ dust interaction \ duration.}$ 

Solutions	were	stirred	continuously

Duration, h	c Ni <sup>2+</sup> , mg/l		c Pb <sup>2+</sup> , mg/l			$c \operatorname{Cd}^{2+}, \operatorname{mg/l}$		
0	3000	500	6350	750	60	6000	120	60
0.5	$2100~\pm~200$	$82 \pm 8$						
1.0	$1900~\pm~200$	$6.1~\pm~0.5$	$240~\pm~30$	$47~\pm~4$	$9 \pm 2$	$3300~\pm~200$	$4.2~\pm~0.3$	$2.0~\pm~0.3$
2.0	$1600~\pm~100$	$0.36~\pm~0.08$	$170 \pm 10$	$32 \pm 4$	$6.1 \pm 0.7$	$2800~\pm~200$	$1.8~\pm~0.3$	$1.3~\pm~0.3$
3.0			$52 \pm 5$	$9 \pm 1$	$4.7~\pm~0.6$			
4.0	$1400~\pm~100$	$0.16~\pm~0.05$	$11 \pm 2$	$7 \pm 1$	$2.4~\pm~0.3$	$2100~\pm~100$	$0.9~\pm~0.2$	$0.6~\pm~0.1$
6.0	$1100~\pm~100$	$0.06~\pm~0.03$				$1700~\pm~100$	$0.4~\pm~0.2$	$0.08~\pm~0.03$
7.0			$5.3 \pm 0.5$	$5.2~\pm~0.5$	$0.4 \pm 0.1$			
8.0	$920~\pm~60$	$0.06 \ \pm 0.03$						

Awady, Sami, 1997). In order to estimate the importance of both components for Pb<sup>2+</sup> removal, CKD was rinsed with distilled water. 100 ml of distilled water was poured onto 2 g of CKD and continuously mixed for 6 h with a magnetic stirrer. On the next day the solution was poured out and the pH of the solution was measured. The rinsing was continued until pH of the rinsed solutions remained unchanged (7.5). We have determined that the maximal capacity of washed CKD to remove Pb2+ is 1.3 g /g CKD (12 mg-eq /g) and of non-washed CKD 2.0 g/g CKD (19 mg-eq/g). In another set of experiments we investigated the kinetics of Pb<sup>2+</sup> removal under continuous stirring with rinsed and nonrinsed CKD. The data indicated that the main factor of Pb<sup>2+</sup> removal was hydrolysis during the first hour of interaction, and sorption was the main factor in some subsequent hours.

In a Russian patent (Патент..., 1997) it was shown that Pb<sup>2+</sup> removal ability of opoka may be improved by heating it up to 700 °C. We have determined that the heating of CKD minutely improves the CKD ability to remove Pb<sup>2+</sup>. We have also tested whether pre-treatment of CKD with water affects Pb2+ removal. 10 ml of distilled water was poured onto 2 g of CKD and continuously mixed for 6 h. On the next day Pb(NO<sub>3</sub>)<sub>2</sub> solution was added and continuously mixed. The usage of pretreated CKD speeds up the process significantly: in the experiment with 20 g/l of CKD and  $Pb(NO_3)_{2}$ solution with  $c \operatorname{Pb}^{2+} = 0.75 \text{ g/l}$  it was necessary to continuously mix for ~5 h until the reaction reached the equilibrium state, however, the usage of pre-treated CKD brings the time down to ~2 h.

The main components of lead-saturated CKD are basic carbonate –  $Pb_3(CO_3)_2(OH)_2$  (50%), calcite –  $CaCO_3$  (~25%), quartz –  $\alpha$ -SiO<sub>2</sub> (~5%) and ~20% of a phase that we could not identify, as determined by means of XRD.

#### Interaction with cadmium (II)

Data on cadmium removal from  $CdCl_2$  solutions are presented in Tables 1 and 2. They are similar to the data obtained for the other HM studied. DCL for cadmium ions is the lowest for the HM studied. It was achieved after 2 days of interaction by stirring for 30 s four times a day or after 6 h under continuous stirring when the initial  $c Cd^{2+} \leq 0.06$  g/l.

The maximal capacity of CKD to remove  $Cd^{2+}$  is 0.42 g/g CKD (7.4 mg-eq /g).

The main cadmium component of cadmium-saturated CKD is Cd(OH)Cl, as determined by means of XRD.

#### Interaction with cobalt (II)

Data on cobalt  $\text{Co}^{2+}$  removal from  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions are given in Table 1. If  $c \text{ Co}^{2+} \leq 0.75$  g/l and CKD was present at 20 g/l, the cobalt ion concentration after 24 h was reduced down to 0.1 mg/ l, which is ten-fold lower than DCL. Longer interaction times (up to 16 days) did not result in any pH or concentration change, indicating that 24 hours are enough to reach the equilibrium state. We investigated cobalt removal from cobalt nitrate, chloride and sulphate solutions when  $c \operatorname{Co}^{2+} = 1$  g/l. Under a constant mixing and at CDK concentration 20 g/l, half an hour was enough to reduce cobalt concentration down to 0.1 g/L. Further interaction affected neither residual  $c \operatorname{Co}^{2+}$  nor pH.

Later we investigated whether different anions affect the maximum capacity of CKD to remove cobalt at a concentration  $c \operatorname{Co}^{2+} = 0.02 \text{ mol/l}$ . We have determined that CKD is able to remove 0.18, 0.20 and 0.20 g of cobalt ions per gram of CKD in the experiments with cobalt nitrate, sulphate and chloride, respectively.

Cobalt-saturated CKD was subjected to XRD analysis. Diffractograms obtained from cobalt-saturated CKD were compared to diffractograms of CKD rinsed with water. As the diffractograms of cobalt-saturated CKD did not have any additional peaks, this apparently indicates that cobalt was present in the form of amorphous  $Co(OH)_{g}$ .

I. Shashkova et al. studied the removal of heavy metal ions (Pb2+, Cr3+, Fe3+) from aqueous solutions by alkaline-earth metal phosphates (Shashkova et al., 1999; Шульга, Шашкова, 1999). The efficiency of phosphates in the removal of Pb(II), Cr(III) and Fe(III) ions has been shown to decrease in the following sequence:  $Mg_3(PO_4)_2 >$ tic stability series. The maximum capacity decreases for Pb(II) from 22.8 mg-eq/g of  $Mg_3(PO_4)_2$  to 0.6-9.6 mg-eq/g of  $Ca_{10}(PO_4)_6(OH)_2$ . Similar data were obtained for the other HM, namely  $Cr^{3+}$  and  $Fe^{3+}$ . The data obtained in our studies show that the efficiency of Pb(II) removal by CKD is similar to the most effective alkaline-earth metal phosphates. As CKD is a cheap by-product of cement industry, it is promising for decontamination of electroplating rinsing waters or similar non-concentrated HM solutions. We suggest to use spent CKD saturated with copper and cobalt as a microfertilizer additive. CKD containing other HM may be used for brick, asphalt or concrete production locking HM into inoffensive compounds.

#### CONCLUSIONS

The results of this study have shown that CKD (a cheap by-product of cement industry) is efficient in the processes of HM removal from aqueous solutions. The efficiency of CKD in removal of HM is similar to that of alkaline-earth phosphates. The interaction between HM (or hydrogen) ions and CKD

is slow (a matter of several hours). The main reason perhaps is a slow diffusion through the shell of the reaction products (basic salts or hydroxides of HM, gypsum, etc.) to the core of the particle. However, when the concentrations of Cu(II), Ni(II) or Co(II) ions are not high ( $\leq 0.5$  g/l) and are similar to those in electroplating rinsing waters, DCL is reached after 0.5 h of mixing with 20 g/l of CKD. We suggest to use spent CKD saturated with copper and cobalt compounds as a microfertilizer additive. CKD containing other HM may be used for brick, asphalt or concrete production locking HM into inoffensive compounds.

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## SUNKIØJØ METALØ JONØ SÀVEIKA SU CEMENTO DULKËMIS

Santrauka

Cemento dulkës (CD) yra cemento gamybos atlieka. Tai labai smulkios (< 0,01 mm), ðarminës kilmës (12–16 mg-ekv/g) dalelës. Ámonëje "Akmenës cementas" gaminamø CD cheminë sudëtis:  $Al_2O_3$  (3–8%),  $Fe_2O_3$  (2–5%),  $SiO_2$  (11–15%), CaO (38–48%), CaO<sub>1</sub> (3–7%), MgO (2–4%), (Na + K)<sub>2</sub>O (2–8%), SO<sub>3</sub> (3–8%). Jas galima naudoti rûgðtiems tirpalams neutralizuoti ir sunkiesiems metalams ið jø paðalinti. CD veikia kaip ðarminis agentas ir kaip sorbentas.

Tyrimas parodë, kad CD verta naudoti galvanikos plovimo vandenims ir kitiems skiestiems sunkiøjø metalø tirpalams nukenksminti kaip pigià ir efektyvià vietinæ þaliavà.

Cemento dulkiø geba nusodinti Cu(II) yra 0,29 g/g CKD (9,1 mg-ekv/g), Ni (II) – 0,14 g/g CD (4,7 mg-ekv/g), Pb (II) – 2,0 g/g CD (19 mg-ekv/g), Cd(II) – 0,42 g/g CD (7,4 mg-ekv/g) ir Co(II) – 0,20 g/g CD (6,8 mg-ekv/g). S<sup>1</sup>veikaujant CD su Cu(II) jonais susidaro devilitas – Cu<sub>4</sub>(CaSO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub> ·  $3H_2O$ , su Pb(II) – bazinis karbonatas Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub>, su Cd(II) jonais – Cd(OH)Cl. Sàveikaujant CD su Ni(II) ir Co(II) jonais susidaro amorfiniai junginiai, tikëtiniausia – Ni(OH)<sub>2</sub>, ir Co(OH)<sub>2</sub>.

Manoma, kad CD, prisotintà Cu(II) ir Co(II) junginiais, bûtø tikslingiausia sunaudoti gaminant tràðas su mikropriedais. Kitas panaudotas CD reikëtø jungti á laikinai nepavojingus junginius gaminant plytas, betono blokus, asfaltbetoná

Raktaþodþiai: sunkieji metalai, cemento dulkës, vandens tirpalai, geba nusodinti, nukenksminimas