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ASSESSMENT OF THE SORPTION PROPERTIES OF MATERIALS PROPOSED FOR THE CONSTRUCTION OF INSULATION BARRIERS

Sorption properties of fine-grain mixtures of mineral waste proposed for construction of separation screens in landfill sites have been examined. The removal of heavy metals by the mixtures analysed was evaluated by the static batch method. It was found that they characterize by high ability to remove heavy metals at the level of over 99%, even with high contents of these elements. The sorption parameters have been determined based on the Langmuir and Freundlich isotherms. The alkaline character of some components of mixtures provides stabilization of pH, preventing removal of heavy metals to the environment in response to contact a barrier with acid solutions.

1. INTRODUCTION

Since storage in landfills appears to be the most popular method of waste disposal, the waste might represent a serious source of pollution for both soil and water. Therefore, it becomes necessary to separate the polluted areas by means of special purpose separation screens. Conventionally, construction of separation screens involves using synthetic materials (geomembranes) and natural materials which are present *in situ* in the rock mass. This typically means fine grain clay rock, with granulometric, mineral and chemical compositions that allow obtaining a low filtration coefficient, which is the basic and expected parameter of the screens used for separation. If natural clay rock is unavailable in the location of the storage area, the need arises for obtaining it from other deposits and then transporting it to specified places. Such activities usually cause degradation of the landscape and generation of additional waste of dead rock as well as changes in hydrographic conditions in the area of extraction. Therefore, it seems purposeful to look for the materials which would substitute clay rocks. Since the 90s of the

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last century the possibility of using ashes from the energy industry has been investigated [1]. These wastes were mostly used as an additive improving the parameters of mineral fillers, especially their alkalinity, which has been used for neutralization of acidic effluents. Interaction of polluted waters containing heavy metals with ashes allows their reduction in effluents.

The authors have demonstrated [2] the possibility of using waste mineral materials or by-products from the industry, particularly the components of anthropogenic origins, as their properties allow obtaining a barrier that combines physical separation with chemical activity with respect to various pollutants. In the present work, few types of waste materials (not only fly ash) used for construction of insulation barriers have been examined and described for the first time.

In order to provide a precise characterization of separation properties of mineral materials, it is necessary (due to various physical and chemical processes that occur in these materials) to analyse, apart from the filtration coefficient, some additional parameters, such as mineral composition, diffusion coefficient, sorption parameters and changes in the volume and moisture content [3] as well as filtration/adsorption processes [4]. As demonstrated by Claisse and Ganjian [5], one procedure which is essential for evaluation of usefulness of any material for building separation screens is evaluation their screening ability that in turn necessitates characterization of sorption properties. Heavy metal ions are one of the most toxic inorganic pollutants present in the soil. Some of them are toxic, even at very low concentrations [6, 7]. Therefore, the goal of the present study was to determine abilities of removal of selected heavy metals by a model screen based on the anthropogenic components.

2. EXPERIMENTAL

Substrate for the analysis. Previous studies of the authors [2] allowed focusing on the following types of materials used for preparation of the mixtures:

• Coal dust (M) sampled from filtration presses in the processing unit of a black coal mine.

• Ashes, i.e. combustion by-products generated by the energy sector during combustion of black coal in conventional and fluidized bed boilers, especially: fly ash from combustion of black coal in conventional boilers (PK), fly ash from combustion of black coal in fluidized bed boilers (PL), and bottom ash from combustion of black coal in fluidized bed boilers (PD).

• Barren rock clay from brown coal deposit in the Bełchatów mine (I).

Materials sampled were air-dried and then 3 mixtures were prepared, varying in the content of components. The main component of each mixture was coal dust (50 wt. %). The representative specimens were prepared by the quartering method. Their compositions and the filtration coefficients are given in Table 1.

Composition of mixtures

Mixture	Composition [wt. %]			Filtration coefficient [m/s]
	Coal dust	Ash	Clays	
MPKI	50	40[a]	10	$7.26 \cdot 10^{-10}$ (unpublished data)
MPLI	50	40[b]	10	$6.32 \cdot 10^{-10}$ [2]
MPD	50	50[c]	–	$3.0 \cdot 10^{-10}$ [2]

[a]Ash from combustion in conventional boilers.
[b]Ash from fluidized bed boilers.
[c]Bottom ash.

The mixtures were analyzed in terms of phase composition using X-ray analysis (X-ray diffractometer PANalytical X'PERT PRO-PW 3040/60). The quantitative analysis was performed by the Rietveld method.

Evaluation of cation exchange capacities of the mixtures. Cation exchange capacities (CEC) were determined based on the sorption capacity of methylene blue (MBC). The determination was made according to PN-B-04481:1988P [8]. Cation exchange capacities (CEC) as well as specific surface areas (S_t) were calculated from the equations [8, 9]:

$$CEC = 2.676 MBC \quad [cmol/kg] \tag{1}$$

$$S_t = k MBC \quad [m^2/g] \tag{2}$$

where MBC is the sorption capacity of methylene blue, g/100 g, k – the coefficient equal to 20.94 m^2/g.

Static sorption method (batch sorption). Research was done in two stages. The major goal of the first stage of the analysis was determination of optimal conditions (including achieving the equilibrium state) for the sorption process. The impact of the solid to solution ratio (doses of sorbents were: 50, 100 and 200 g/dm^3) and contact (mixing) time (0.5, 1, 2, 24 h) on the effectiveness of sorption have been examined. Optimization was carried out for the MPLI mixture. Zinc solutions were prepared by dissolving the appropriate weight of the respective salt ($ZnSO_4$, $ZnCl_2$) in deionized water. The initial concentration of zinc solution was 200 mg/dm^3.

Before sorption, due to alkalinizing effect of certain waste components (ash from energy industry) used for preparation of the mixture, the sorbent was washed (mixture MPLI) through mixing with deionized water for 24 h. Then it was dried and used for batch sorption tests.

In the second stage, batch sorption for all tested mixtures was examined for sorbent dose of 200 g/dm^3 and 24 h contact time . In this stage, the potential of tested mixtures for heavy metal removal (Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, $Cr^{2+}$and Pb^{2+}) from aqueous solutions were evaluated. Similar like in first stage of research, concentrations of heavy metals ions in the initial solution were prepared by dissolving the appropriate weight of the respective salt ($ZnSO_4$, $ZnCl_2$, $CdSO_4$, $CdCl_2$, $NiSO_4$, $NiCl_2$ $CoSO_4$, $CoCl_2$, $CrCl_2$, $Pb(NO_3)_2$) in deionized water. All of salts came from Chempur (Piekary Slaskie, Poland). Initial contents of heavy metals ions in solution used in the experiment in this stage are compared in Table 2.

Table 2

Concentrations of heavy metal ions in aqueous solutions

Initial concentration of heavy metal ion in solution (mg/dm^3)					
Zn^{2+}	Cd^{2+}	Ni^{2+}	Co^{2+}	Cr^{3+}	Pb^{2+}
10	5	5	0.1	10	10
50	10	10	0.5	50	50
100	50	50	1	100	100
200	150	150	5	200	200
500	200	200	10	500	500
1000	500	500	100	1000	1000

All batch experiments were carried out using 200 cm^3 glass-stoppered vessels containing 100 cm^3 of salts' solution of a known initial concentration of heavy metal ions and weight of the adsorbent. All experiments were performed at room temperature.

The vessels were agitated at a constant speed of 150 rpm for 0.5, 1, 2, 24 h (in the first stage) and 24 h (in the second stage) in a shaker (IKA POL HS 260 control) at 298 K. Initial pH of the solutions was 4.0 and no buffer control of pH was applied during the adsorption process. Then the solutions were filtered through a filter paper, and the eluates obtained were analysed with regard to the concentrations of tested metals. Concentrations of heavy metals were determined by means of the inductively coupled plasma atomic emission spectroscopy (ICP-OES). pH in all solutions was measured after sorption.

The equilibrium adsorption capacity (q_e) of heavy metals was calculated from the following equation [10]:

$$q_e = \frac{c_0 - c_{eq}}{m} \times V \quad [\text{mg/g}] \tag{3}$$

The percentage of heavy metals immobilized by the tested mixtures was calculated from [11]:

$$\text{Removal} = \frac{c_0 - c_{eq}}{c_0} \times 100 \quad [\%] \tag{4}$$

where c_0 is the initial concentration of the ions in the solution, c_{eq} – the equilibrium concentration of the ion in solution, V – the volume of the solution, m – the weight of the sorbent mixture.

The analysis of the experimental data was based on the Freundlich and Langmuir isotherms. The equation of the Langmuir isotherm model can be expressed as [11]:

$$\frac{c_{eq}}{q_e} = \frac{c_{eq}}{q_m} + \frac{1}{K_L q_m} \tag{5}$$

$$q_e = \frac{q_m K_L c_{eq}}{1 + K_L c_{eq}} \tag{6}$$

The Freundlich isotherm can be presented in the following form [11]:

$$\log q_e = \log K_F + \frac{1}{n} \log c_{eq} \tag{7}$$

$$q_e = K_F c_{eq}^{1/n} \tag{8}$$

where: q_m is the maximum adsorption capacity corresponding to the complete monolayer coverage, mg/g, K_L, K_F – the Langmuir constant and the Freundlich constant respectively, dm³/mg, n – experimental constant indicative of the adsorption intensity of the sorbent. Adsorption isotherm equation parameters were determined using the STATISTICA (nonlinear estimation test).

Sequential extraction. In order to determine the chemical forms of binding metals by individual phases of the heterogeneous material of the mixtures studied, the adsorbent samples were subjected to the modified sequential analysis according to Tessier et al. [12], who adopted this procedure due to the mineral character of the adsorbent. The extraction procedure has been described in Table 3.

Grain analysis. Evaluation of the effect of the solutions used on durability of screen material was carried out based on the analysis of changes in granulometric composition after reaction with model solutions. Analyses of the article size distribution of the materials tested (before and after sorption) were performed with a laser particle size analyzer LAU-10.

Procedure of sequential analysis used in the study

Stage	Solvents, conditions of extraction[a]	Forms of metals
I	10 cm^3 of 1 M MgCl$_2$, pH = 8.2, ambient temperature, contact time 1 h, continuous mixing	exchangeable
II	10 cm^3 of 1 M CH$_3$COONa acidified with CH$_3$COOH to pH = 7, ambient temperature, contact time 4–5 h, continuous mixing	bound with carbonates
III	20 cm^3 of 0.04 M NH$_2$OH·HCl in 25% CH$_3$COOH (vol. %), temperature 96±3 °C, contact time: 4–5 h, periodic mixing	bound with Fe and Mn oxides
IV	3 cm^3 of 0.02 M HNO$_3$ + 5 cm^3 of 30% H$_2$O$_2$, pH = 2, temperature 85±2 °C, contact time 2 h, periodic mixing 8 cm^3 of 30% H$_2$O$_2$, pH = 2, temperature 85±2 °C, contact time 2 h, periodic mixing, 5 cm^3 of 3.2 M CH$_3$COONH$_4$ in 20% HNO$_3$, ambient temperature, contact time 0.5 h, periodic mixing	bound with organic matter and sulphides
V	Mineralization 0.5 g of residue with 7 cm^3 HNO$_3$	other

[a]With respect to 1 g of dry matter of the mixture.

3. RESULTS AND DISCUSSION

3.1. PHASE MINERAL ANALYSIS

The phase compositions of the mixtures reflect the characteristics of their components Table 4). The dominant mineral phase in the mixtures was quartz. The MPD mixture

Phase composition of mixtures [wt. %]

Phase	MPKI	MPLI	MPD
Quartz	23	21	45
Mullite	11	–	–
Anhydrite	–	8	8
Smectite	20	21	–
Kaolinite	16	16	15
Illite	11	12	13
Chlorite	8	4	5
Amorphous matter/coal matter	11	12	8
Gypsum	–	2	–
Piryte	–	<1	1
Hematite	–	1	–
Calcite	–	1–2	–
Potassium feldspars	–	–	3
Dolomite	–	–	1
CaO	–	–	1

contained approximately twice the quartz in comparison to other mixtures. Minerals from the clay group consist primarily of kaolinite and illite, but due to the presence of clay in the MPKI and MPLI, also significant amounts of smectites were found. The analysis of the MPKI mixture revealed the presence of mullite which is a product of thermal decomposition of kaolinite. The identified share of amorphous matter was similar for all the mixtures. Each mixture contained mineral phases which can be classified as chlorites, but their percentage share is not higher than a few percent. Other found phases especially in the mixtures with ash from fluidised bed reactors are the result of using calcium sorbents in fluidised bed technologies.

3.2. OPTIMISATION OF THE SORPTION PROCESS

Washout of MPLI had no effect on adsorption capacity of the mixture. Removal of zinc ions from aqueous solution of zinc chloride and zinc sulfate were 99.96% and 99.93%, respectively. Due to the lack of difference between the samples washed and not washed, the samples were not washed in further studies.
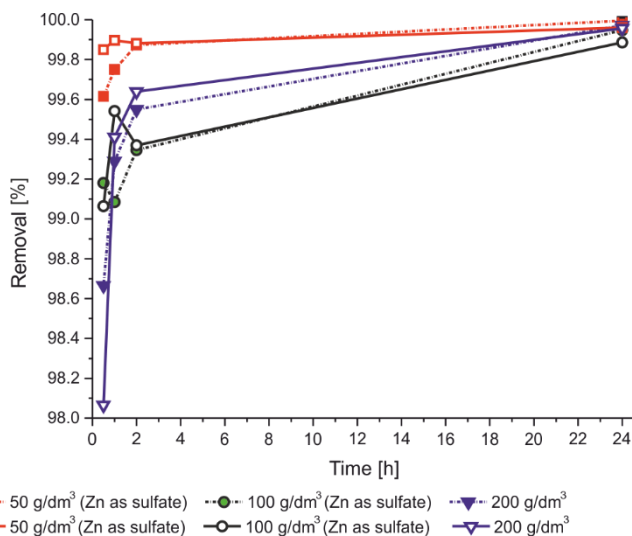

Fig. 1. Effect of contact time on the removal of zinc onto MPLI at various doses of sorbents (50, 100, and 200 g/dm^3), initial zinc concentration 200 mg/dm^3

The effects of contact time (0.5, 1, 2, 24 h) and dose of sorbents (50, 100, and 200 g/dm^3) are shown in Fig. 1. The highest removal of zinc ions for both tested salts was obtained for 200 g/dm^3 of sorbent and mixing time of 24 h, such conditions being used in the batch test in further experiments.

3.3. SORPTION CAPACITY

Figure 2 illustrates the specific surface areas, sorption capacity (MBC), cation exchange capacity (CEC, Eq. (1)) of the mixtures (MPKI, MPLI, MPD).
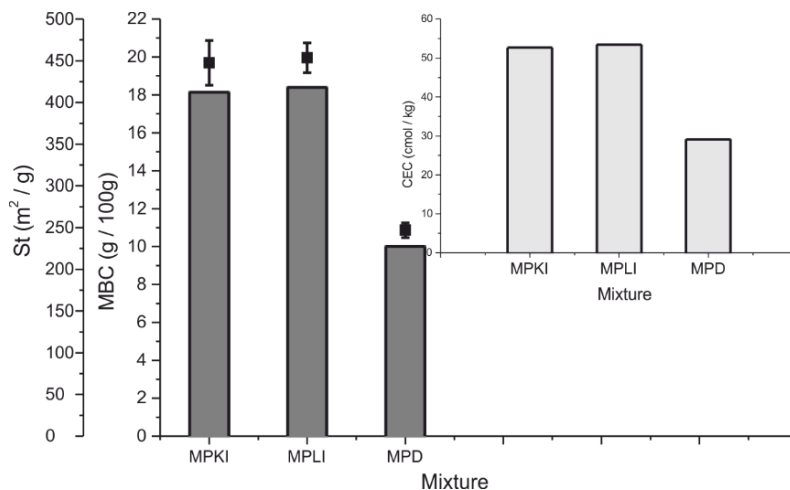

Fig. 2. Sorption capacity (MBC), cation exchange capacity (CEC)
and specific surface area (St) of mixtures used in the study

The specific surface areas ranged from 227 to 417 m^2/g, with the highest values observed for MPLI and the lowest for MPD. The sorption capacity ranged from 10.87 to 19.96 g/100 g d.b.[2], whereas CEC values were from 29.08 to 53.41 cmol(+)/kg. Since the materials studied are heterogeneous mixtures, their properties result from compilation of the properties of individual components. According to the literature data, the values of specific surface area and sorption capacity for natural mineral sorbents such as clay range from 10 to 800 m^2/g [13] and from 0.27 to 57 mg/g [14], respectively. With regard to fly ashes, the authors obtained the values of specific surface area of 0.25–0.45 m^2/g [15], whereas this value for coal dust is 73 m^2/g. Analysis of the results leads to the conclusion that the mixtures studied are the materials with well-developed specific surface area, which is connected with their fine-grain composition and presence of a number of porous and spherical grains with extended surface. Presence of loam in the mixture caused almost 50% increase in the specific surface area and the respective increase in sorption capacity. The results obtained in the study confirmed the expected sorption properties of the materials by demonstrating the similarity to natural sorbents such as clay.

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[2]d.b. – dry basis.

3.4. BATCH STATIC SORPTION

Based on Eq. (3), the authors calculated adsorption capacities of all metal ions in all mixtures studied (Table 5).

Table 5

Adsorption capacities [mg/g] of studied mixtures towards heavy metals (contact time 24 h)

Mixture	c_0 [mg/ dm³]	Adsorption capacity (q_e)[a]									
		Zn²⁺		Cd²⁺		Ni²⁺		Co²⁺		Cr³⁺	Pb²⁺
		ZnCl₂	ZnSO₄	CdCl₂	CdSO₄	NiCl₂	NiSO₄	CoCl2	CoSO₄	CrCl₃	PbNO₃
MPKI	0.1	–	–	–	–	–	–	<	<	–	–
	0.5	–	–	–	–	–	–	<	<	–	–
	1.0	–	–	–	–	–	–	<	<	–	–
	5.0	–	–	0.0249	0.0249	<	<	<	<	–	–
	10.0	<	<	0.0498	0.0498	<	<	<	<	0.0476	<
	50.0	<	<	0.2497	0.2497	<	<	–	–	0.2486	<
	100.0	<	<	–	–	–	–	0.4999	0.4999	0.4946	<
	150.0	–	–	0.7488	0.7488	0.7433	<	–	–	–	–
	200.0	0.9996	0.9995	0.9983	0.9982	0.9895	<	–	–	0.9947	0.9997
	500.0	2.4988	2.4932	2.4950	2.4948	2.4992	2.4991	–	–	2.4946	2.4994
	1000.0	3.4188	2.9963	–	–	–	–	–	–	4.9996	4.9995
MPLI	0.1	–	–	–	–	–	–	<	<	–	–
	0.5	–	–	–	–	–	–	<	<	–	–
	1.0	–	–	–	–	–	–	<	<	–	–
	5.0	–	–	0.0250	0.0250	<	<	<	<	–	–
	10.0	<	<	0.0500	0.0500	<	<	<	<	<	<
	50.0	<	<	0.2499	0.2498	<	<	–	–	<	<
	100.0	<	<	–	–	–	–	0.4999	0.4999	0.4985	<
	150.0	–	–	0.7499	0.7498	0.7500	0.7500	–	–	–	–
	200.0	0.9996	0.9995	0.9998	0.9997	0.9999	0.9999	–	–	0.9958	<
	500.0	2.4960	2.4957	2.4999	2.5000	2.4997	2.4996	–	–	2.4951	2.4995
	1000.0	4.9990	4.9990	–	–	–	–	–	–	4.9819	4.9998
MPD	0.1	–	–	–	–	–	–	<	<	–	–
	0.5	–	–	–	–	–	–	<	<	–	–
	1.0	–	–	–	–	–	–	<	<	–	–
	5.0	–	–	0.0250	0.0250	<	<	<	<	–	–
	10.0	<	<	0.0500	0.0500	<	<	<	<	0.0497	<
	50.0	0.2497	0.2496	0.2499	0.2499	<	<	–	–	<	<
	100.0	0.4997	0.4994	–	–	–	–	0.4967	0.4968	0.4954	<
	150.0	–	–	0.7499	0.7499	0.7500	<	–	–	–	–
	200.0	0.9996	0.9995	0.9997	0.9996	0.9998	0.9999	–	–	0.9883	<
	500.0	2.4969	2.4967	2.4888	2.4902	2.4433	2.4509	–	–	2.4874	2.4996
	1000.0	4.9426	4.9553	–	–	–	–	–	–	4.9980	4.9991

[a]< below detection range: <0.005 for Zn, <0.001 for Ni, <0.001 for Co, <0.02 for Cr, <0.03 for Pb.

Figures 3–8 illustrate the effect of the type of ions of the metals studied and their initial content on the effectiveness of sorption process (Eq. (4)). For metals in which the equilibrium concentration was below the detection threshold (Table 5) we assumed that their removal is 100%. Since sorption of metals is closely related to pH of the environment [13, 14], in the figures, pH values determined for eluates after sorption are also presented.

Regardless of the initial concentrations of salts (except for $c_0 = 1000$ mg/dm^3) as well as of the type of the adsorbent mixture, the removal of zinc was higher than 99%. However, removal of zinc as sulfate was less effective than as zinc chloride. Regarding the concentration of 1000 mg/dm^3 for the mixture MPKI, a decrease in sorption ability to the level of 68.4% for Zn^{2+} in $ZnCl_2$ and 59.9% for Zn^{2+} in $ZnSO_4$ occurred (Fig. 3). A very high percentage of sorption (over 99%) was maintained in the mixture MPLI, while in the mixture MPD, it decreased by 1% for Zn^{2+} in $ZnCl_2$. Furthermore, the decrease in sorption ability of MPKI mixture was accompanied by a substantial decrease in pH to ca. 6. Slightly lower decrease occurred in the mixture MPD and the mixture MPLI exhibited stabilization of pH, regardless of the initial concentration (pH ranged from 10.1 to 12.48).
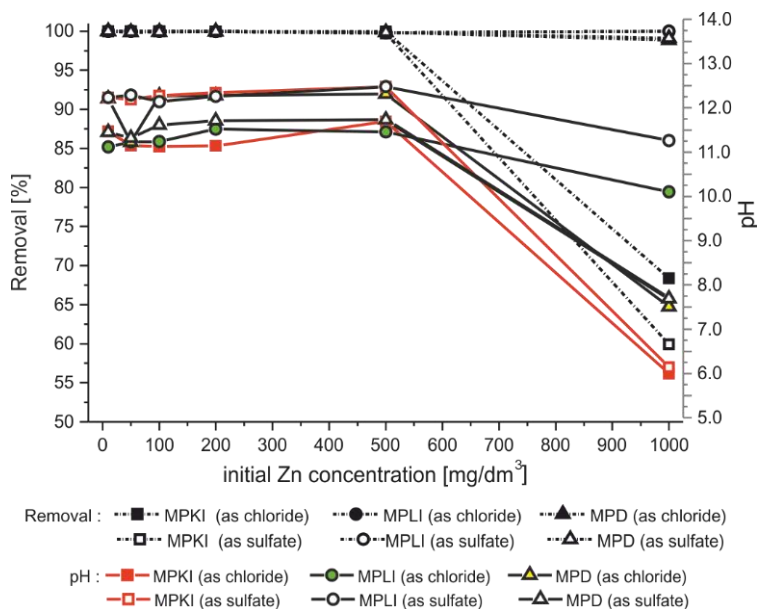

Fig. 3. Effect of initial concentration on removal of zinc
(as chlorides and sulfates) and pH of the solution; adsorbent dose 200 g/dm^3,
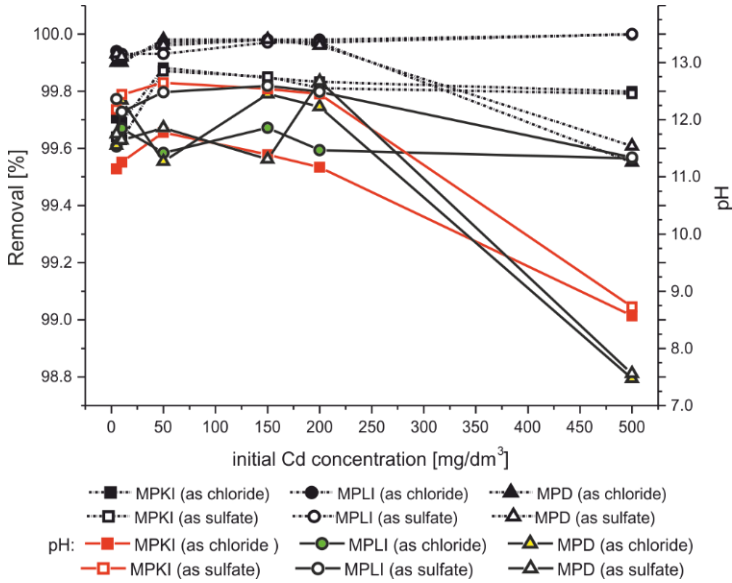agitation rate 150 rpm, contact time 24 h, temperature 298 K, initial pH 4)

Fig. 4. Effect of initial concentration on removal of cadmium
and pH of the solution; adsorbent dose – 200 g/dm^3, agitation rate 150 rpm,
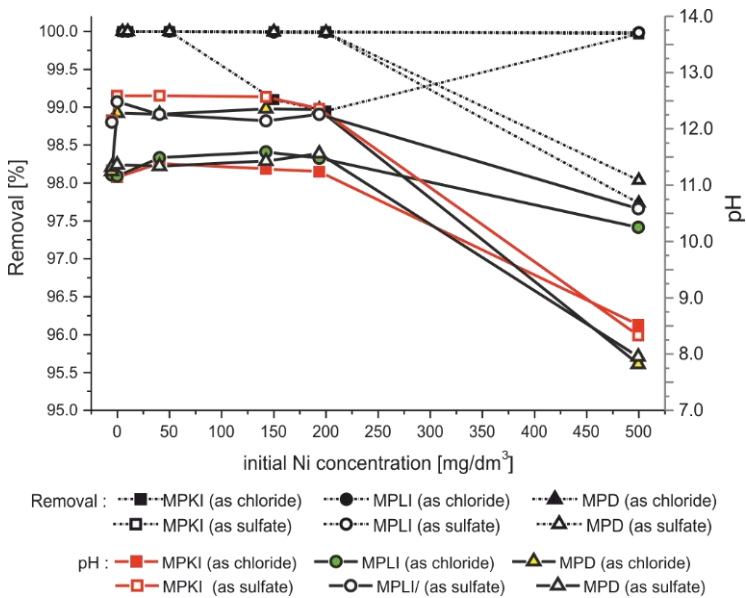contact time 24 h, temperature 298 K, initial pH 4

Fig. 5. Effect of initial concentration on removal of nickel
and pH of the solution; adsorbent dose 200 g/dm^3, agitation rate 150 rpm,
contact time 24 h, temperature 298 K, initial pH 4

The mixtures studied, regardless of the initial concentration, exhibited cadmium ions removal rate at the level of 99% (Fig. 4). Only the mixture MPKI was characterized by a reduced (by ca. 0.3%) sorption ability. The most stable conditions of sorption of cadmium were observed in the mixture MPLI. With initial concentration of 500 mg/dm^3 in the cases of MPKI and MPD, a reduction in pH value within the range of 7.5–8.7 was observed.

As shown in Figure 5, all the mixtures removed nickel ions in 100%, when the initial concentration amounted up to 50 mg/dm^3. In the case of nickel sulfate, this metal was removed totally up to initial concentration of 200 mg/dm^3 and 150 mg/dm^3 respectively for mixture MPKI and MPD. The mixtures MPKI and MPD demonstrated higher capability of removal of nickel ions in the form of sulfates. No effect of the type of salt ions on sorption ability was observed for the mixture MPLI. Maximum decrease of this ability in all the types of mixtures was found for the initial concentration of 500 mg/dm^3. Changes in pH values are analogous as for the previously discussed metals.
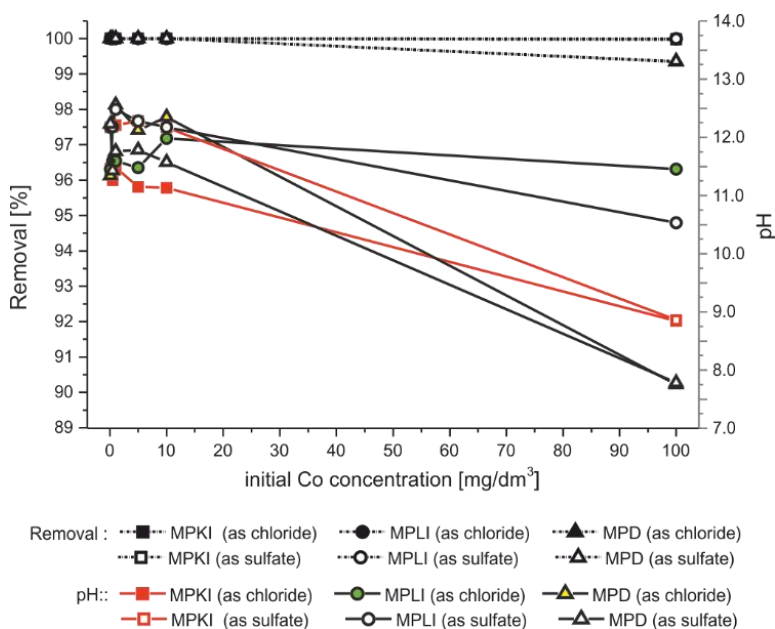
Fig. 6. Effect of initial concentration on removal of cobalt and pH of the solution; adsorbent dose 200 g/dm^3, agitation rate 150 rpm, contact time 24 h, temperature 298 K, initial pH 4
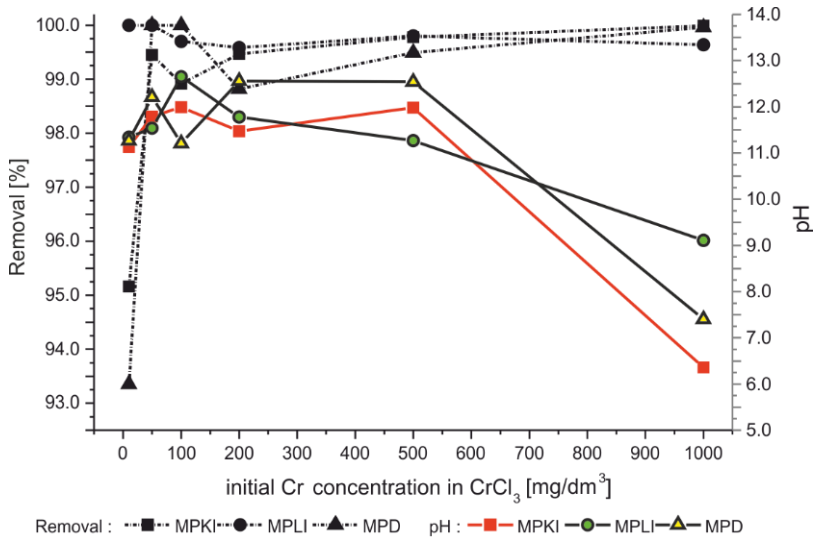
Fig. 7. Effect of initial concentration on removal of chrome
and pH of the solution; adsorbent dose 200 g/dm^3, agitation rate 150 rpm,
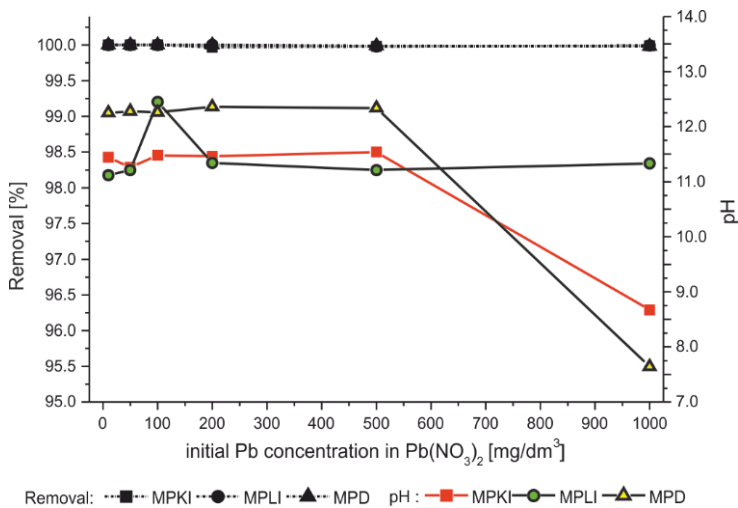contact time 24 h, temperature 298 K, initial pH 4

Fig. 8. Effect of initial concentration on removal of lead
and pH of the solution; adsorbent dose 200 g/dm^3, agitation rate 150 rpm,
contact time 24 h, temperature 298 K, initial pH 4

With initial concentration of up to 10 mg/dm^3 for all the mixtures, regardless of the type of salt ions, sorption percentage for cobalt was maximum (concentration below the analyser detection threshold) (Fig. 6). At the concentration of 100 mg/dm^3, it decreased

to 99.9% for the mixtures MPKI and MPLI and to 99.3% for the mixture MPD. This relationship is connected with pH value with the biggest decrease observed also for the mixture MPD. The mixture MPLI had also biggest ability to neutralize changes in pH occurring in the sorption process.

Chromium ion removal for the mixtures MPKI and MPD was the lowest for the lowest initial concentrations studied (10 mg/dm^3, Fig. 7). These mixtures showed different pattern: the sorption percentage increases for the highest initial concentrations. Changes in pH were similar to those for other metals. Similar results have been observed by other authors [16]. For instance, Kelleher et al. [17] reported at low initial concentrations film diffusion effects contributing to limiting the overall rate of adsorption while at higher initial Cr^{3+} concentrations pore diffusion became more important. These authors also shown that adsorption process was best described by the Langmuir model.

The mixture MPLI showed the highest stabilization of pH. In all the cases, the percentage of lead removal was over 99.9%, whereas the decrease in its value with the increase in initial concentration is insignificant (Fig. 8). The mixtures MPKI and MPD exhibited total removal of lead from the solution of the initial concentration of 200 mg/dm^3.

Fly ash as an additive in the mixtures was found to be effective for the removal of heavy metals from aqueous solution, for example wastewater. The difference in the removal of metals may be due to mineralogical compositions of mixtures as well as kinds of heavy metal used in the tests [18], their ionic sizes, stability of bonds between heavy metals and adsorbent [7].

The main mechanism of the removal of heavy metals in aqueous solution consists of the following processes: a) surface precipitation – co-precipitation of insoluble hydroxides of heavy metals insoluble hydroxides form successive layers on the sorbent surface, b) bulk solution precipitation; c) ion exchange, d) adsorption. The factor which decides which mechanisms dominate is pH of the solution [19]. The mechanism of precipitation of metal hydroxides describe equations:

$$M(OH)_2\,(s) \leftrightarrow M^{2+} + 2OH^- \qquad (9)$$

$$M^{2+} + OH^- \leftrightarrow M(OH)^+ \qquad (10)$$

$$M^{2+} + 2OH^- \leftrightarrow M(OH)_2 \qquad (11)$$

$$M^{2+} + 3OH^- \leftrightarrow M(OH)_3^- \qquad (12)$$

$$M^{2+} + 4OH^- \leftrightarrow M(OH)_4^{2-} \qquad (13)$$

The initial metal concentration in solution significantly affects the removal of tested metals [20]. Similarly as in this study, in most cases the increase of initial metal concentration resulted in an increase of the adsorption capacity (Table 5) and a decrease of the removal efficiency (Figs. 3–8). According to Arief et al. [21] the effect described depends on a combination of the following factors: the ability of surface functional groups to bonding metal ions (especially at high concentrations) and the availability of specific surface functional groups.

Another important factor influencing adsorption efficiency as well as mobility of heavy metals in matrix is pH [6, 7]. The alkaline nature of fly ash makes it a good neutralising agent (Figs. 3–8). For almost all mixtures (with the exception of a mixture of MPKI and Zn and Pb) regardless of the initial concentration of metal, final pH was higher than 7 and sorption of metal cations increased upon increasing pH. The heavy metal ion adsorption data were correlated with the isotherm models of Langmuir (Eqs. (5) and (6)) and Freundlich (Eqs. (7) and (8)). Table 6 presents the constants for the analysed models for the data which obtained high correlation coefficient. For other cases, the results of the analysis revealed that they cannot be described with the models tested or they lack sufficient amount of data for the analysis (the cases where removal percentage was at the level of 100% and no metals studied were found in eluates).

Table 6

Isotherm parameters and correlation coefficients
calculated based on experimental data

Mixture	Salt	Freundlich isotherm			Langmuir isotherm		
		K_F [dm^3/mg]	$1/n$	R^2	K_L [dm^3/mg]	q_m [mg/g]	R^2
MPKI	ZnCl$_2$	2.06	0.09	0.9342	6.86	3.50	0.9876
	ZnSO$_4$	1.84	0.09	0.9420	4.63	2.96	0.9995
MPLI	ZnCl$_2$	–	–	–	19.11	3.66	0.7140
	ZnSO$_4$	–	–	–	18.42	3.58	0.6981
MPD	ZnCl$_2$	2.18	0.34	0.9765	1.64	5.17	0.9952
	ZnSO$_4$	2.14	0.39	0.9731	1.28	5.40	0.9935
MPKI	CdCl$_2$	2.49	0.84	0.9990	0.38	9.00	0.9993
	CdSO$_4$	2.40	0.86	0.9984	0.34	9.57	0.9986
MPD	CdCl$_2$	1.89	0.36	0.9644	10.72	2.60	0.9923
	CdSO$_4$	1.96	0.38	0.9702	9.18	2.63	0.9914
MPLI	NiCl$_2$	–	–	–	155.41	2.77	0.99659
	NiSO$_4$	–	–	–	347.54	2.55	0.95758
MPD	NiCl$_2$	1.68	0.15	0.9996	21.92	2.42	0.94265
	NiSO$_4$	1.94	0.10	0.9997	453.26	2.45	0.9993
MPLI	CrCl$_3$	1.81	0.80	0.9729	0.16	13.65	0.9751
MPKI	Pb(NO$_3$)$_2$	–	–	–	2.64	14.95	0.7373
MPD		–	–	–	2.76	14.78	0.9996

Higher values of the correlation coefficient (R^2) corresponded to better adjustment of the theoretical model to the experimental isotherm [22]. Data summarized in Table 6 shown that both models can describe the experimental data. However, analysis of the data contained in the Table 6 reveals that the mixture MPLI does not exhibit good match to the Freundlich model for zinc and nickel ions. Similar effect was observed for mixtures MPKI and MPD in the case of removal of lead ions. For other analysed metals, this mixture is characterized by better match to the Langmuir model. In conclusion, one can assume that in all the mixtures for which the match to either of the isotherms analysed could be calculated, the coefficients of this match were at a very high level.

3.5. SPECIATION ANALYSIS

Due to a different character of the phenomena which might occur during the process of removal of metals on the mixtures studied, the authors carried out the speciation analysis of the mixture MPLI for zinc ion sorption at its initial concentration of 100 mg/dm^3. The procedure of speciation was carried out for the sorbent both before and after sorption. MPLI was chosen due to its high capability of removal of all the analysed ions, Zn due to its high mobility in the environment. The results are presented in Fig. 9.
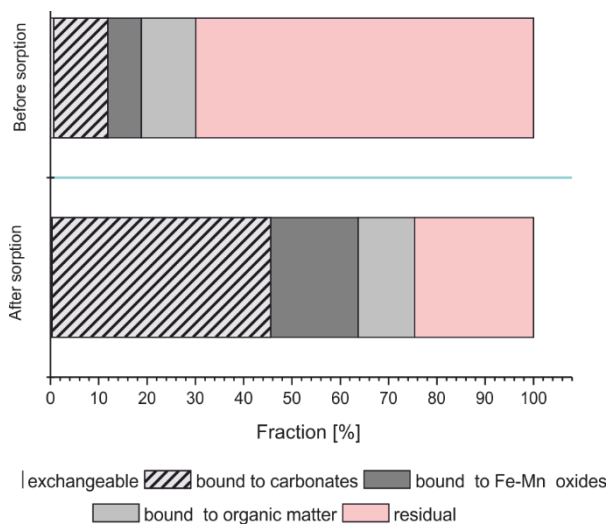

Fig. 9. Speciation of Zn in mixture (MPLI) after and before sorption;
adsorbent dose 200 g/dm^3, agitation rate150 rpm, contact time 24 h, temperature 298 K,
initial pH 4, initial metal concentration in ZnCl$_2$ 100 mg/dm^3

According to Jun Yao et al. [23], among the five fractions, the exchangeable fraction and the fractions bound with carbonates and Fe–Mn oxides are unstable and susceptible to release, whereas the fractions connected with the organic matter and sulfides are regarded relatively stable and with low bioavailability [24]. The results obtained in the

study confirmed the expected distribution of zinc in individual fractions which resulted from alkaline character of the components of the mixture and the content of clay minerals included in both clay and coal sludge. Zinc in MPLI mixture before sorption is present mainly in the residual/silicate fraction (69.9%) that includes the forms contained in the crystalline network of primary and secondary minerals included in composition of individual components of the mixture. Fractions II and IV contain comparable amounts of metals at the level of 11.2%, whereas the easiest leachable exchangeable fraction contains barely 0.7% of zinc. Reaction of the mixture with the solution containing 100 mg/dm^3 zinc ions caused a change in the distribution of metal content in individual fractions. The results of sorption carried out by the batch method for the analysed mixture showed total removal of zinc ions from the solution (equilibrium concentration below the analyser detection threshold). Material after sorption is characterized by the increase in the amount of zinc mainly in the carbonate fraction and connected with Fe and Mn oxides, whereas a noticeable loss of zinc was connected with the crystalline fraction. The zinc amount present in the fraction connected with the organic matter and sulfates remained at a comparable percentage. Despite finding that bounding metal mainly by the unstable fractions (II and III), the alkaline character of the mixture proposed for construction of the separation screen should effectively prevent from the desorption of metal as a result of reduction in pH of the environment.

3.6. ANALYSIS OF SORBENT GRAIN COMPOSITION

The results of grain size analysis of the mixtures used in the study before and after sorption are presented in Figs. 10–12.
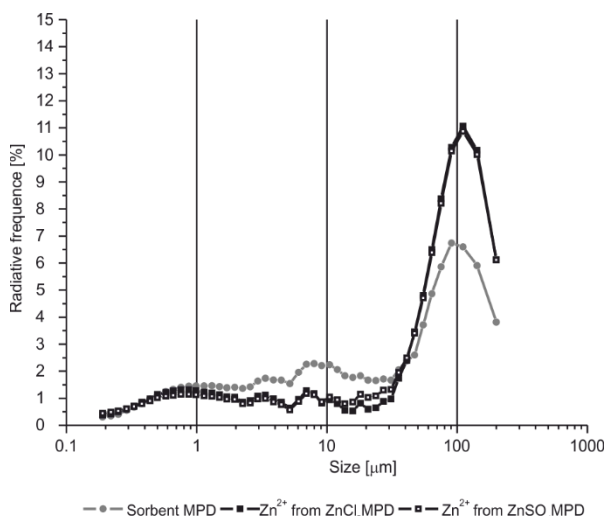

Fig. 10. Distribution of grain size in MPD sample before sorption
and after sorption of zinc ions with initial concentration c_0 of 200 mg/dm^3
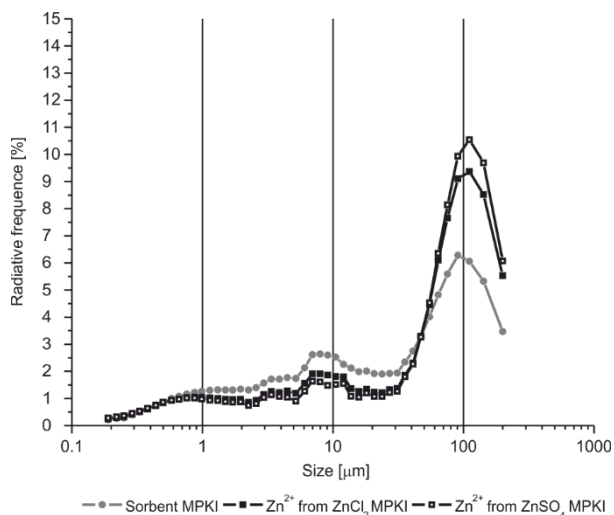
Fig. 11. Distribution of grain size in MPKI sample before sorption
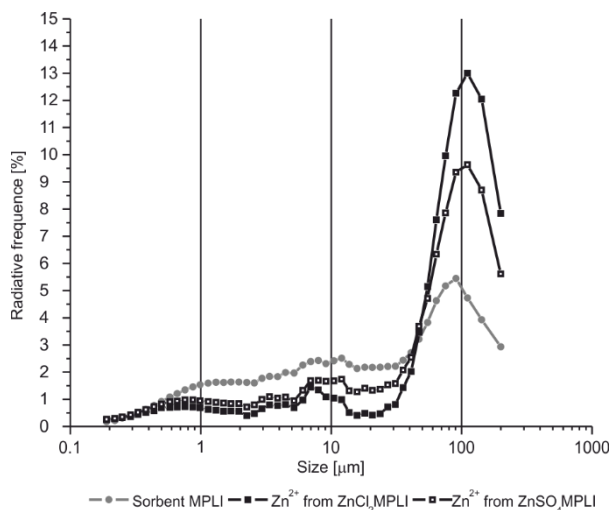and after sorption of zinc ions with initial concentration c_0 of 200 mg/dm^3

Fig. 12. Distribution of grain size in MPLI sample before sorption
and after sorption of zinc ions with initial concentration c_0 of 200 mg/dm^3

The analysis was carried out in order to verify the hypothesis that the phenomena occurring during removal of metals from the solution in contact with sorbent might consist, among other things, in precipitation of new mineral phases as a result of chemical reactions. The new mineral phases which appeared in grain distribution might have manifested themselves in development of fine grain size fractions. Hence the material used for analysis of sorbent before and after sorption was sieved until the fraction of

<200 μm was obtained. With regard to grains with size of 0.1–1 μm, no changes in their content in the material after sorption were observed for mixtures MPD and MPKI. A decrease in the content of 1 μm grains was observed only for the mixture MPLI after sorption. An interesting pattern can be observed in the curves of grain distribution for the mixtures studied: a higher content of 100 μm grains was found after sorption. For the MPD mixture, the type of the sorbed zinc ions did not affect this phenomenon. Considering other mixtures, the effect of the type of ions was found, with the greatest increase in the content of 100 μm grains observed in the mixture MPLI for chloride ions and sulfate ions in MPKI. Therefore, the proposed hypothesis was not verified, although based on the analysis of the phenomena occurring in fly ashes used as additives to cement [25], it can be assumed that the reactions in the materials are of pozzolanic reaction character. As a result of reaction with water, calcium oxide present in the ashes is transformed into calcium hydroxide, which then dissociates. The greater amounts of Ca^{2+} released with considerable presence of silicon ions $H_3SiO_4^-$ and aluminium ions $H_4AlO_4^-$ in the solutions create hydrates which cover the crystalline phase of the material and increase the grain size.

4. CONCLUSIONS

• The mixture of coal dust, fly ash from fluidized bed boilers and clays (MPLI) points to the highest sorption capacity of heavy metals compared to mixture of ash from combustion in conventional boilers, coal dust and clays (MPKI) as well as mixture of coal dust and bottom ash (MPD).

• The highest stability of pH during sorption, regardless of the initial concentration of metal ions and the type of salts, was observed for the mixture MPLI. pH decreased only for the maximum initial concentration (1000 mg/dm^3 for Zn^{2+}, Cr^{3+} and Pb^{2+}, 500 mg/dm^3 for Cd^{2+} and Ni^{2+}, 100 mg/dm^3 for Co^{2+}). This effect is desirable in the light of the opportunities of using this material for construction of separation screens since it is able to prevent the process of discharging ions of heavy metals to the environment as a result of acidification.

• All the mixtures studied are characterized by high ability to remove of heavy metals at the level of over 99%, even with high contents of metal ions and the differences are practically negligible. The only exception is the mixture MPKI, where the percentage of sorption of zinc ions at initial concentration higher than 500 mg/dm^3 decreases to the level of 60–70%.

• Speciation analysis demonstrated that the most of zinc is bound in unstable phases: carbonate phase and Fe and Mn oxides. However, the ability of the mixture MPLI to stabilize pH confirmed in the batch test guarantees the stability of the metal in these phases.

• The phenomenon of the increase of mineral aggregates during sorption processes is desirable since the bigger grains improve separation properties of the material through narrowing the intergranular space and therefore allowing migration of the solutions through the material that creates the separation screen in the landfill sites.

ACKNOWLEDGEMENTS

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