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Analysis of sorptive capabilities of post-flotation dolomites used in insulation barriers construction of dumping sites

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ABSTRACT

The paper presents a new concept of a barrier insulating the hazardous wastes from the environment. Ions of heavy metals migrating through are captured in the processes of chemical and/or physical sorption. It is proposed that such a barrier could be made of dolomite wastes from Zn–Pb ore flotation. The sorptive properties of the wastes were verified in conditions of a static sorption batch. Depending on the assumed initial concentration of metal and the conditions of the experiment, the maximum percentage of removing zinc was 80.4%, lead 99.1% and cadmium 92.2%. In order to confirm the lab observations also *in situ*, investigations were performed on the tank for flotation wastes. They consisted in taking samples of the waste from various depths, and determining the concentration of zinc ions. It was found that the layer of the depth of 5 m lowers the concentration about six times. The additional positive attribute of the waste is their fine granularity, which is significant for building the desired barrier. The granulometric analysis showed that 77% of waste grains have dimensions below 63 µm, thus increasing contact area solution—sorbent.

Keywords: Sorption; Flotation waste; Waste dumping; Insulating barriers; Heavy metals

1. Introduction

In many cases, due to technological and economic conditions, the basic method of utilization the waste containing heavy metals, due to the so-called extraction toxicity (EP toxicity), is their disposal in the environment. Heavy metal ions migrating from wastes can create the threat of water and soil contamination as a result of which the metals can get into a trophic chain. Commonly used protections against this threat are properly designed physical barriers sealing the subsoil and scarp of the dumping site in connection with drainage collecting leachates [1,2]. The practice of waste disposal clearly indicates the need to build mineral barriers on every site. In the absence of natural barriers in the form of complex argillaceous rocks of sufficient thickness, it must be replaced by the artificial geological barrier, so-called compacted clay liners—CCLS [3,4]. The most suitable material for their construction are clayey minerals characterized by a low rate of filtration and high sorption capacity,

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allowing to "capture" the largest possible amount of contamination, migrating with the leaching waters.

The use of natural minerals (minerals of clay as a clay or silt) to the construction of insulating barriers requires the acquisition of local deposits, which inevitably results in the generation of waste from mining and mineral treatment, the change of water and soil quality in the vicinity of excavations, the degradation of the landscape, and some additional costs including energy and suitability test material.

Therefore, it seems advisable to search for substitute materials, which could compete with natural resources, both in terms of technology and economy [5]. The most appropriate alternative to deposits of clay can be a fine industrial waste of minerals. The use of such materials reduces their amount deposited in landfills, and emerging in current industrial processes, allows for the use of waste deposited in advance, thereby reducing their impact on the environment. Research in this area confirmed the usefulness of the ash from the combustion of solid fuels [6–10], coal slurry from the enrichment process, and coals [11] and post-flotation wastes from the Zn–Pb ores enrichment [12,13] to the construction of insulating barriers.

The paper presents the possibility of using the sorptive capabilities of post-flotation wastes from Zn-Pb industry as one of the components used in the construction of insulating barriers, constructed on the basis of mineral waste materials or materials that are by-products of industrial activity. The concentrate usable in metallurgical industry is obtained by applying flotation to remove up to 95% of barren rock that accompanies the useful minerals; then the barren rock is deposited in settling tanks as waste. The main component of the post-flotation wastes which constitutes about 70% is dolomite [14]. A fraction of metals occurring in the ore cannot be extracted in applied processes and it remains in the waste. The main toxic components leached from the waste are SO_4^{2-} ions. The formation of acid by the oxidation of metal sulfides in the settling tanks can cause metal migration to aquifers [15]. However, this process is limited due to the mineralogical form of metals and alkaline reaction of the waste. The idea of using post-flotation dolomite wastes to build insulating barriers appeared after observations of soil and water environment around dumping sites.

Analysis of water taken from the tanks without drainage, run only rainwater that had previously been in contact with post-floatation wastes showed that the water infiltrating through the settling tanks does not contribute to the environment of a larger load of metal ions contained in the waste [16]. Lysimeter studies [17] have not identified the effects of mobility of heavy metals from the post-flotation wastes.

To confirm the possibility of using dolomite wastes to build the barrier blocking, the migration of heavy metal ions, some investigations of their sorptive capabilities in the conditions of static sorption batch were carried out.

2. Materials and methodology

In the investigations, the post-flotation samples taken from settling tanks in Bytom region were used because of terminating ore exploitation there and relatively short time of storing the wastes due to which the wastes were rather homogeneous. Samples were taken using drill pipe in the range depth of 0.45–6.00 m. After preliminary preparations by drying to the air-dry state, the acquired material was analyzed chemically. The determinations of SiO_2, S as SO_4^{2-}, and CO_2 were performed using a gravimetric method, while CaO, MgO, Al_2O_3, and Fe were determined by a complexometric method. The content of Zn and Pb were determined by atomic absorption with spectrophotometer.

The phase composition of the waste was determined by using X-ray diffractometer Philips PW 3710 and a thermal analysis using a derivatograph Labsys^{TM} of Setaram.

Since the degree of sorption depends on grain size distribution, which is connected with the active surface on which the processes of sorption occur [18], also granulometric analyses were carried out using a laser analyzer LAU-10.

The verification of sorptive capabilities of post-flotation wastes was carried out in the conditions of a static sorption batch and using standard solutions in the form of nitrates of Zn, Pb, and Cd in various concentrations. Three series of investigation were done, varying the way of sorbent preparation and ions of heavy metals used during the sorption, i.e.

(1) series 1—the sorbent in air-dry state, the solution with ions of Zn, Pb, and Cd;
(2) series 2—the sorbent in air-dry state previously soaked by deionized water where the proportion of sorbent to water was 1:10 and time of shaking 2 h, the solution with ions of Zn, Pb, and Cd as in series 1; and
(3) series 3—the sorbent as in series 1, the solution with Zn ions, only. This series served to determine the competitiveness during sorption of metal ions from the solutions.

Table 1
Average chemical composition of post-flotation waste

Component	Contents (mass%)
Zn	2.56
Pb	0.73
Fe	7.33
SiO_2	2.90
Al_2O_3	0.62
S/SO_4^{2-}	2.39
CaO	27.71
MgO	15.39
CO_2	38.78

Table 2
Chemical composition of post-flotation waste

Mineral	Contents, %
Dolomite $CaMg[CO_3]_2$	60
Bassanite $CaSO_4 \cdot 0{,}5\ H_2O$	15
Smithsonite $ZnCO_3$	12
Pyrite (and/or sphalerite) FeS_2	8
Calcite $CaCO_3$	Some
Quarz SiO_2	Some
Goslarite-epsomite $ZnSO_4 \cdot 7\ H_2O$—$MgSO_4 \cdot 7\ H_2O$	Negligible amount

In each series, 10 g of sorbent and 100 mL of solution were used for each sample. The flasks with samples were shaken throughout the period of 2 h and put away for another 22 h. Then the solutions were filtered through a filter paper, and the obtained eluats were analyzed with regard to the concentrations of Zn, Pb, and Cd ions using atomic absorption with spectrophotometer (model ASA TECHTRON, VARIAN).

In order to confirm laboratory observations *in situ*, investigations directly on the post-flotation waste settling tank were also performed. They consisted in acquiring samples from different depths and determining the concentration of Zn ions in them. The zinc ions were used because of their significant mobility in soil and water environment [19–22]. The investigations served to determine how the concentration of Zn changes as water infiltrates down.

3. Results and discussion

Average chemical composition of post-flotation waste is presented in Table 1.

Dolomite is the main mineral in the samples and is often substituted with Fe^{2+} for Mg^{2+} in the structure, which puts it in a series of close ferruginous dolomite. Basic mineral composition of the waste is presented in Table 2.

The ambiguous determination of the content of certain minerals results from their quantity in the sample near the limit of quantification methods. Also, proper estimating the incidence of sphalerite or distinguishing it from the pyrite is difficult due to the high reflection proximity position of both mineral phases since some of the results evaluated as “some”. XRD pattern (Fig. 1) was also analyzed for the possible presence of galenite PbS, anglesite $PbSO_4$, cerussite $PbCO_3$, and various simple and complex sulfates of

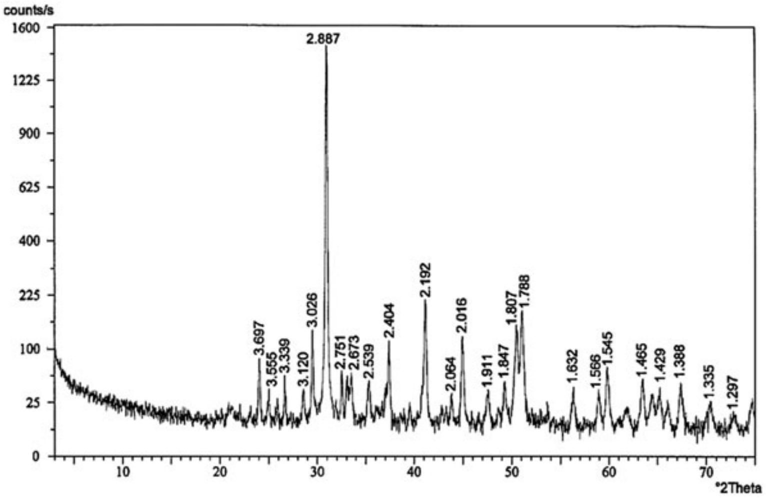

Fig. 1. XRD patterns of post-flotation waste sample.

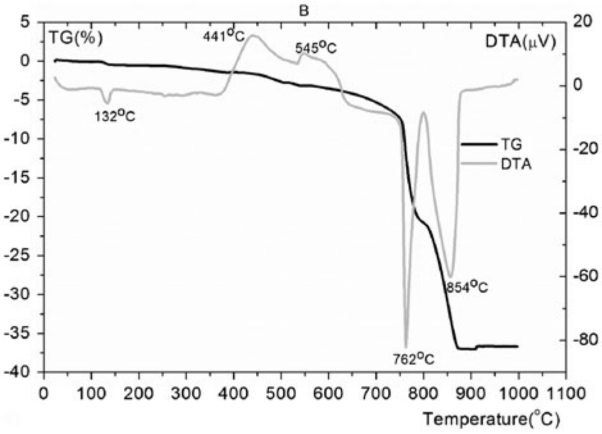

Fig. 2. TG/DTA curves of flotation waste from the lead–zinc industry.

iron, zinc, and lead. There was a lack of any of these phases or their quantities were far below the sensitivity of the X-ray reflections.

The results of thermal analysis of tested material is shown in Fig. 2.

Endotherm on the DTA curve with a maximum at 132°C indicates the presence of bassanit (in case of gypsum it would be bisected endotherm). DTA curve shape in the range of 400–600°C reveals a strong exotherm, while a very small weight loss (on TG curve), suggesting the presence of iron sulfides. At the temperature interval from 600 to 900–920°C the TG curve reveals two asymmetric, overlapping effects of weight loss, accompanied by similar in shape endotherm (maximum in 762 and 854°C) observed in the DTA curve. This course of the curves shows the thermal decomposition characteristic of dolomite.

The dolomite waste is characterized by the grain composition shown in Fig. 3.

The examined material is finely grained—grains < 63 μm constitute almost 77%, wherein more than 17% of this class was having a grain size of 1 μm. Grain roughness coefficient calculated according to the formula A.Hazena was $U = 4.5$, which indicates a uniform particle size.

$$U = \frac{d_{60}}{d_e} \tag{1}$$

where U—coefficient of graining non-uniformity; d_{60}—alternate diameter, mm; and d_e—effective grain size, mm.

Particle size distribution of waste is very advantageous because of the possibility of a self-sealing layer which is built from them, a large development of the ultrafine particles leads to an equilibrium chemical reaction on the phase boundary of grain solution.

Three series of the investigations on sorptive capabilities of post-flotation dolomites were carried out according to the procedure described in chapter 2. Used initial concentrations (C_0) and the measured equilibrium concentrations (C_k) for Zn, Pb, and Cd ions are shown in Table 3.

Based on the results from Table 3, we evaluated the sorption activity (A_{Me}) for every tested metal as follows:

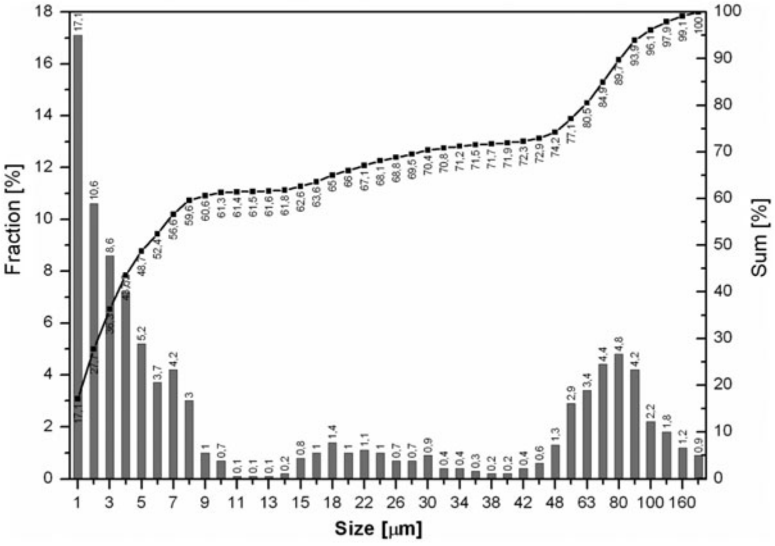

Fig. 3. Decomposition of grain categories for dolomite post-flotation waste.

Table 3
Changes in the concentrations of metal ions during static sorption

	Concentration of metal ions (mg/L)						
	Zn		Pb		Cd		
Series No.	C_0	C_k	C_0	C_k	C_0	C_k	pH after sorption
1	50	14.30	20	0.19	5	0.46	7.78
	25	6.30	10	0.18	2.5	0.22	7.81
	10	4.00	4	0.15	1	0.14	7.80
	5	2.47	2	0.14	0.5	0.08	7.79
2	50	14.90	20	0.18	5	0.39	7.82
	25	6.00	10	0.14	2.5	0.20	7.80
	10	2.07	4	0.14	1	0.14	7.78
	5	1.64	2	0.14	0.5	0.11	7.76
3^*	50	10.50	–	–	–	–	7.76
	25	4.90	–	–	–	–	7.75
	10	3.30	–	–	–	–	7.77
	5	2.42	–	–	–	–	7.79

Note: C_0—initial concentration, C_k—equilibrium concentration, 3^*—the series of investigations on solutions with Zn^{2+} ions only.

$$A_{Me} = V\frac{C_0 - C_k}{m}\ \mathrm{mg/g} \tag{2}$$

where V—solution volume, L; C_0—initial concentration of metal ions, mg/L; C_k —equilibrium concentration of metal ions, mg/L; and m—sorbent mass, g.

The calculated values of sorption activity vs. initial concentration are depicted as points in graphs shown in Figs. 4–6.

The statistic analysis of the results indicates strong linear correlation between the sorption activity A_{Me} and the initial concentration C_0. No significant dependency between the sorption activity of the tested metals and the way of sorbent preparation in particular series was observed. From the third series, which was carried out in order to find how the activity of zinc sorption depends on the presence of other metal ions in the solution, it follows that only for highest initial concentrations the sorption activity is greater if no other metal ions are present. The sorption activity observed for each series is strictly connected with the initial concentration of the solution. Analyzing the percentage of sorbing for particular metals, one can notice that sorption activity was lowest for zinc, and sorption percentage increases as the metal concentration in the solution grows (Table 4).

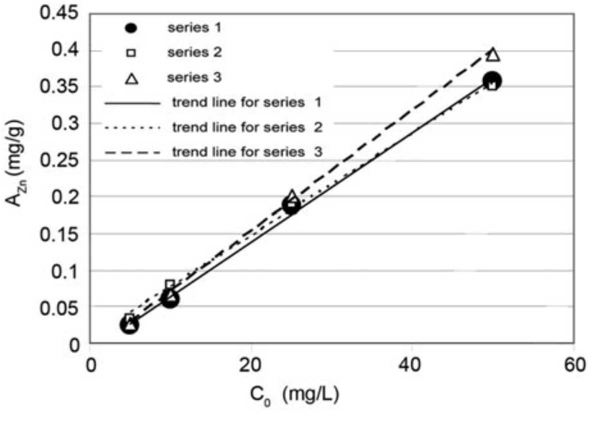

Fig. 4. Sorption activity for zinc vs. initial concentration of the solution.

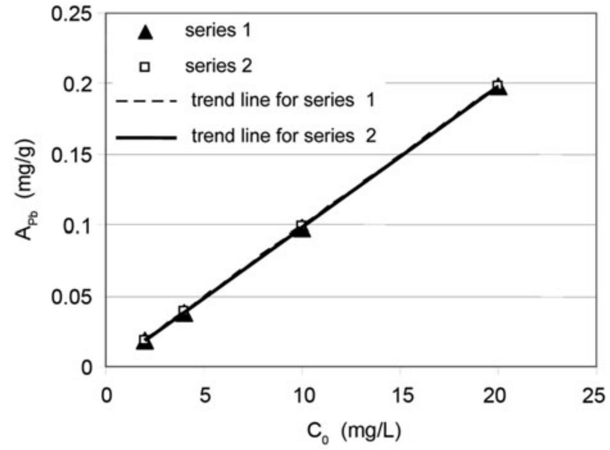

Fig. 5. Sorption activity for lead vs. initial concentration of the solution.

The changes that occur are of a chemical reaction on the phase boundary with removal of solid products of the reaction and continuous regeneration of the

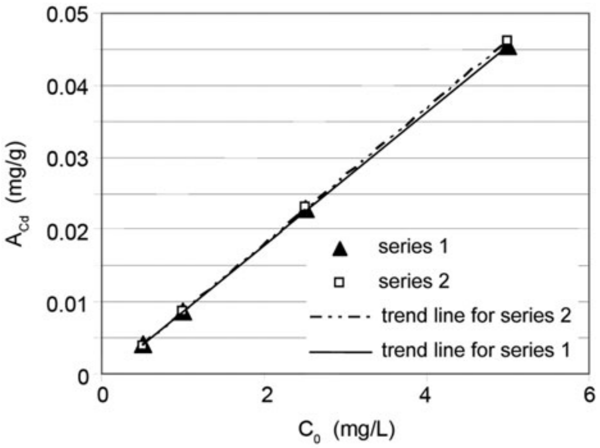

Fig. 6. Sorption activity for cadmium vs. initial concentration of the solution.

surface of waste grains, as it was confirmed by the studies of other authors [23–27]. Ordering ions according to the increasing sorptive activity Zn–Cd–Pb indicate that the reason for eliminating ions from the solution cannot be precipitating hydroxides only since in that case, as follows from their solubility products, the order would be Cd–Zn–Pb [28]. However, if the carbonates precipitation occurred only, which is highly likely in the investigated environment, the elimination of ion would be in the order of carbonates solubility products (Table 5) of these metals Zn–Pb–Cd.

It seems that all of these mechanisms with variable part for each ion cause an almost complete removal of metals from solutions in contact with the post-flotation waste.

For the reasons mentioned above with the elimination of metal ions in solutions, the hydrolysis (in the presence of CO_3^{2-}) leading to alkaline carbonates precipitation should be added [29–31]. In the case of zinc and lead compounds, alkaline carbonates are the most durable compounds in natural conditions as

Table 5
Carbonates solubility products of Cd, Pb, and Zn

Metal carbonates	$t(K)$	K_r
Cd CO_3	298	2.5×10^{-14}
Pb CO_3	298	1.5×10^{-13}
Zn CO_3	298	6×10^{-11}

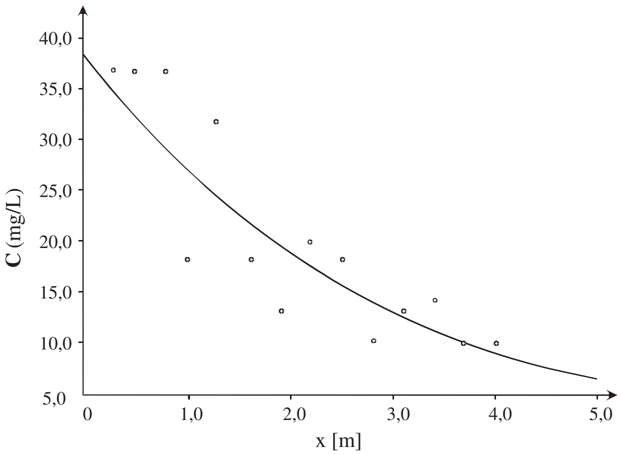

Fig. 7. Zinc concentration vs. depth of infiltration.

Table 4
Efficiency of metals removal as a function of their initial concentration in the solution

	Zn		Pb		Cd	
Series	C_0	% (percentage of sorbing)	C_0	% (percentage of sorbing)	C_0	% (percentage of sorbing)
1	50	71.4	20	99.05	5	90.8
	25	74.8	10	98.2	2.5	91.2
	10	60.0	4	96.25	1	86.0
	5	50.6	2	93.0	0.5	84.0
2	50	70.2	20	99.1	5	92.2
	25	76.0	10	98.6	2.5	92.0
	10	79.3	4	96.5	1	86.0
	5	67.2	2	93.0	0.5	78.0
3*	50	79.0	–	–	–	–
	25	80.4	–	–	–	–
	10	67.0	–	–	–	–
	5	51.6	–	–	–	–

Note: *—the series of investigations on solutions with Zn^{2+} ions only.

hydrozincite and hydrocerussite. In simple terms, the hydrolysis reaction equations can be written:

$$3Ca^{2+} + 3CO_3^{2-} + 2H_2O + 3Pb^{2+} + 3SO_4^{2-} \leftrightarrow \underbrace{Pb_3[CO_3]_2(OH)_2}_{\text{hydrocerussite}} + 3SO_4^{2-} + 2H^+ + 3Ca^{2+} + CO_3^{2-} \quad (3)$$

$$5Ca^{2+} + 5CO_3^{2-} + 6H_2O + 5Zn^{2+} + 5SO_4^{2-} \leftrightarrow \underbrace{Zn_5[CO_3]_2(OH)_6}_{\text{hydrozincite}} + 5Ca^{2+} + 5SO_4^{2-} + 3CO_3^{2-} + 6H^+ \quad (4)$$

In order to confirm the phenomenon of metal removal on a bed of dolomite in the sorption and to determine changes in water infiltrating into the settling tank of post-flotation waste, the research *in situ* of changes, the concentrations of zinc ions in the samples taken from various depths were carried out. The concentration of zinc ions in the analyses was examined because the prior laboratory survey had indicated that sorption activity for zinc was the lowest among the tested metals. The concentration of zinc ions occurring in the moisture of the samples was evaluated under the assumption that in the eluats there were ions which had not been adsorbed on the surface of the solid phase of the sample. The concentration became

$$C = 38.75 \exp(-0.362x) \quad (5)$$

where C—zinc concentration (mg/L) and x—depth of solution infiltration down the tank (m).

The result of the analyses and curve (5) are shown in Fig. 7.

The results obtained allow one to conclude that a dolomite waste layer of the depth of 5 m reduces zinc ion concentration about six times. High concentration of zinc ions observed in superficial layer is connected with the process of digesting metal-carrying minerals because of the access of oxygen introduced with air and water. In deeper layers, the processes of sorption and precipitation of metal ions dominate since hydrolysis causes alkalization of infiltrating rain waters and releasing CO_3^{2-} ions into them. The observed decrease of zinc concentration in the solution migrating between grains of the waste consists in inhibiting the processes of digesting metal-carrying minerals and metal sorption on the dolomite which is the main constituent of the waste.

4. Conclusions

The investigations on sorptive capabilities of Zn–Pb ore post-flotation waste indicate that it could be used as the subsoil in dumping sites for hazardous wastes with heavy metals. The fineness and high sorption capacity for heavy metal ions are the main features of post-flotation wastes. In addition, the wastes are accumulated selectively above ground or in subsurface tanks of thickness much greater than required in order to eliminate heavy metal ions from the infiltrating waters. Thus, one can say that a thick layer of this fine-grained material is a mechanically indestructible perfect sealing as well as a barrier eliminating soluble forms of heavy metals from infiltrating solutions.

In comparison to traditional technologies based on mineral barriers with plastic foils, the proposed dumping technology has the following advantages:

(1) durability of the construction throughout a long time span,
(2) ability of self-sealing,
(3) efficiency and solidity in the regions being subject to deformation,
(4) low expenditure of implementing protections and
(5) low costs of exploitation.

In building the new type of dumping site, one can use flotation waste at the place of their accumulation (in tanks) as well as by forming them in a barrier in new locations, keeping the thickness which insures suitable operating efficiency.

The effectiveness of this method of dumping hazardous waste is practically confirmed by solutions used in the plant processing accumulator scrap "Orzeł Biały" SA in Bytom (Poland) according to the patent [12]. The plant dumps the slag from lead smelting in Dörschl furnaces into inactive settling tanks for flotation waste created several dozen years ago. Dumping hazardous waste on the surface of the tank caused no changes in the content of leakage waters taken in the girdling ditch.

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