Polish Journal of Environmental Studies Vol. 12, No. 2 (2003), 231-237

Modification of the Process of Heavy Metals Immobilization in Wastewater Sludge

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Received: 18 June, 2002
Accepted: 11 September, 2002

Abstract

This paper presents the results of laboratory research on the process of heavy metals extraction from sludge, where heavy metals content exceeds permissible levels. The method of immobilization of heavy metals depends on using the developed technology hygienization process of wastewater sludge (which is pending by patent) to environment utilization. The base of this technology is treatment of municipal wastewater sludge by dust from electrofilters of cement mills with the addition of roasted raw detrital basalt. The modification of this technology involves using the additional unit operation that is followed by extraction of the excessive amount of heavy metals from sludge. The results of heavy metals extraction from wastewater sludge were presented.

Keywords: wastewater sludge, immobilization of heavy metals, organic fertilizer, cement kiln dust

Introduction

Wastewater sludge is part and parcel of the sewage treatment process. It is waste material containing a considerable quantity of pathogenic microorganisms as well as excessive amounts of heavy metals, which occur in the form of various chemical compounds. The sources of sludge contamination are industrial sewage, very often directed to municipal wastewater treatment plants. In big urban agglomerations, the participation of industrial sewage in relation to municipal sewage is greater than in small towns; thus, larger wastewater treatment plants produce larger amounts of sludge containing increased amounts of heavy metals.

A new technology of post-digestion sludge hygienization was elaborated on [1,2]. It allows using the sludge as fertilizer, and fulfills two basic conditions that are imposed on sludge from municipal wastewater treatment plants, namely the elimination of pathogenic microorganisms and immobilization of heavy metals, blocking their leaching at the same time. The essence of this technology is to add cement kiln dust from electrofilters and partly roasted dolomite, along with thermally treated detrital basalt, to wastewater sludge. This allows turning toxic heavy metals into almost insoluble chemical compounds, which decrease the degree of their leaching from the sludge. Moreover, this assures full hygienization of the sludge and allows using thus obtained product as magnesium-sodium organic fertilizer.

This technology, however, underwent modification, the aim of which was to optimize proportions of all added mineral components [3,4] and to try out other waste materials. An attempt to utilize sludge from sodium industry sewage [5] as well as waste material from a slaughterhouse and a meat-processing factory was one of the unit operations extending the possibilities of sludge hygienization.

Further modification of the technology of sludge hygienization involved adding a unit operation based on synthesizing zeolites from EPS fly ashes [6]. The aim of the modification was to enhance immobilization of heavy metals in sludge, and to utilize the ashes. The hygieniza-

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tion process was modified by supplying two components: KOH or NaOH enhancing alkalization of the mixture, and other components enhancing heavy metals immobilization, namely EPS fly ash, partly transformed into zeolites.

Another considered modification of the technology was an attempt to utylize waste phosphogypsum [7] due to:

a) available sulfur content in a sulfate form;
b) available phosphoric acid content;
c) enrichment of the produced fertilizer in phosphoric compounds of non-decomposed phosphorite or apatite;
d) fluorine compounds immobilization;
e) transformation of the fluorine compounds into almost insoluble fluorosilicate compounds and their complexes with natural sorbents.

The improvement of the physical properties of the produced fertilizer has also been a subject of research. When the raw material is post-digestion sludge containing large amounts of polyelectrolytes (e.g. sludge from a centrifugal separator), it is necessary to either apply a screw mixer or to repeat the operation of mixing the sludge with other raw materials many times. The reason for this is that such sludge contains large amounts of water and is characterized by high plasticity. An addition of halloysite simultaneously with cellulose fibrous mass [8] allows us to simplify the mixing process, to decrease water content and to improve utilizable properties of the product. The fibrous mass enhances mechanical strength of soil and boosts its ability to preserve humidity, which makes it easier to deacidificate it in the completely fertilized layer.

All the solutions mentioned above were based on the assumption that wastewater sludge did not contain an excessive amount of heavy metals according to the Regulation of the Minister of Environment Protection, Natural Resources and Forestry from 11 August, 1999 [9].

So far, there have been no experimental attempts at solving the above problem. The technological concept, which was followed, is based on extraction of the excessive amount of heavy metals from sludge. First, the sludge is acidified. Then, a part of water from the sludge with dissolved heavy metals compounds is removed. In the experiment, the acidifying substance was minced parts of sprouts (*Salix alba L.*). The plant was selected, because it is often used for cultivations where wastewater sludge is applied. Besides, juice from white willow fresh twigs contains, among things, salicylic acid.

A modification of the above-presented technology [1] was proposed. It is based on adding a unit operation involving preliminary acidification of sludge followed by removal of the eluate containing a part of eluted heavy metals. Finally, the sludge undergoes processes of hygienization and immobilization. (Fig. 1)

This paper presents the results of laboratory research on the process of heavy metals leaching from sludge where heavy metals content exceeds permissible levels. Additionally, the results of their elution from sludge after hygienization are described. Adding a unit operation described above modified the hygienization process. In hygienization and immobilization of heavy metals, an alkalizing factor was cement kiln dust from electrofilters containing about 34% weight of calcium oxide, quicklime, and specially prepared detrital basalt was a heavy metals immobilizing factor. Here, detrital basalt functioned as a natural sorbent and ion exchanger having strong affinity to heavy metals and their hydroxides.

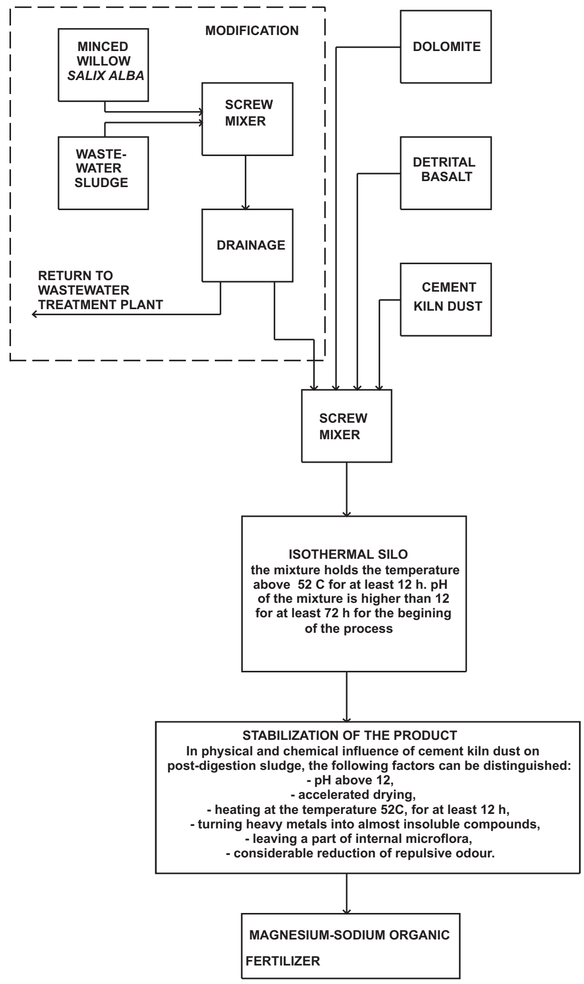

Fig. 1. Scheme of modification of wastewater sludge hygienization.

The measure methodology was borrowed from a paper [5], which examined the process of pasteurization and immobilization of post-digestion sludge from a municipal wastewater treatment plant. Total heavy metals content was established (dissolution in *aqua regia*). It was also checked how much of the dissolved heavy metals was eluted (24h extraction by acetic acid at pH: 4.5).

Experimental

The scope of this experiment concerned the establishment of the degree of heavy metals elution:

1. from raw post-digestion sludge;
2. from mixtures of post-digestion sludge with minced willow twigs;
3. from mixtures of post-digestion sludge after extraction from a mixture containing calcium oxide, cement kiln dust and detrital basalt.

The composition of the mixtures is presented in Table 1. After preparation of the mixtures of post-digestion sludge with the vegetable material, the sludge was processed in a filter-press.

Fig. 2. displays a system of determining the degree of heavy metals elution. This system was worked out to establish the degree of heavy metals elution from samples by the continuous method in an aqueous dissolvent having selected pH. Contrary to the system described in [5], the measuring vessel was modified, and a sprinkler was applied as it can imitate a natural method of elution.

In contrast to other well-known methods (Table 2), the continuous elution method is based on filtration through an aqueous solution sample having strictly established pH. The model of heavy metals extraction from a solid sample by means of a liquid dissolvent is more similar to natural elution conditions than in the case of other methods compared in Table 2.

In each experiment, pH of the solution was corrected by means of 1 M of NaOH or HCl solution. The extraction was made for post-digestion sludge, OW13 and OW13 B20 in the range of pH: 3.5-7.5. Total content of selected heavy metals was established in the sludge, in cement kiln dust and calcareous dust as well as in mixtures prepared with these substances. The samples were shaken in *aqua regia* for 6 hours, and the final pH did not exceed 1.0. The results are presented in Table 3.

The elution degree was described as the ratio of the heavy metals content in extracts obtained from extraction at fixed pH to the total heavy metals content in a sample extracted by *aqua regia*.

Besides, attempts at eluting heavy metals from samples (of post-digestion sludge, OW12, OW15, OW16, OW13 B10, OW13 B15, OW13 B20, OW15 B10, OW15 B15, OW15 B20, OW16 B10, OW 16 B15, OW16 B20) were made. A weak acid (acetic acid) was applied; pH of the extract was maintained for 24h at the level of 4.5 ± 0.1. The conditions of the experiment were designed

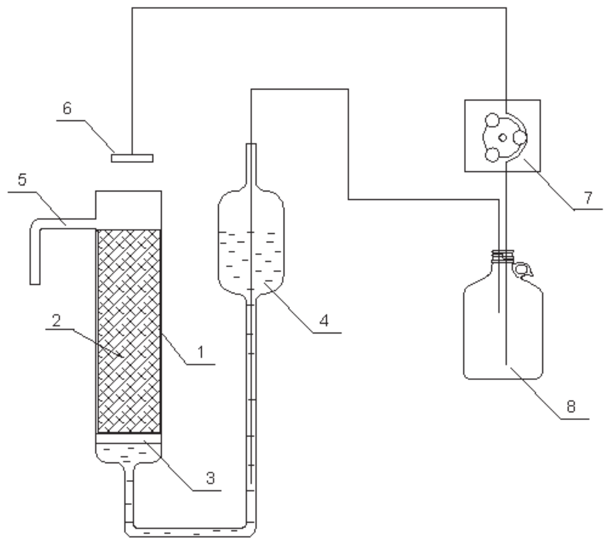

Fig. 2. Scheme of the system used to determine the degree of heavy metals elution from samples using the continuous method. 1 - glass container for eluting, 2 - sludge sample , 3 - glass sinter, 4 - overflow tank, 5 - nozzle, 6 - sprinkler, 7 - peristaltic pump, 8 - solution tank.

Table 1. Comparison of mixtures composition.

Sample symbol	Sample content	Quicklime [% of weight d.m.]	Cement kiln dust [% of weight d.m.]	Detrital basalt [% of weight d.m.]
OW13 B10	OW13 (post-digestion sludge) + quicklime + detrital basalt	15	10	10
OW13 B15	OW13 (post-digestion sludge) + quicklime + detrital basalt	15	10	15
OW13 B20	OW13 (post-digestion sludge) + quicklime + detrital basalt	15	10	20
OW15 B10	OW15 (post-digestion sludge) + quicklime + detrital basalt	15	10	10
OW15 B15	OW15 (post-digestion sludge) + quicklime + detrital basalt	15	10	15
OW15 B20	OW15 (post-digestion sludge) + quicklime + detrital basalt	15	10	20
OW16 B10	OW16 (post-digestion sludge) + quicklime + detrital basalt	15	10	10
OW16 B15	OW16 (post-digestion sludge) + quicklime + detrital basalt	15	10	15
OW16 B20	OW16 (post-digestion sludge) + quicklime + detrital basalt	15	10	20

Table 2. Comparison of standard methods of determining the degree of heavy metals elution from sludge.

	Continuous elution method	JEA method	US-EPA method	Swiss method (initial saturation method)	Swiss method (continuous flow method)	Dutch method
sample preparation	original sample structure	< φ 5 mm	< φ 9,5 mm lub > 3.1 cm^2/g	original sample structure	original sample structure	< φ 125 µm
eluting solvent	deionized water + acetic acid, pH = 4.5	deionized water, pH: 5.8 - 6.3	deionized water + 0,5 N acetic acid < 4 mg/l, pH: 5.8 - 6.3	deionized initially saturated water with CO_2, pH = 4	deionized continuously saturated water with CO_2, pH = 4	deionized water + 1N HNO_3, pH: 5.8 - 6.3
pH quantity	assigned by :1 M NaOH or M HCl	pH = 5	pH = 5	not measured	PH: 4 - 4.5	pH = 4
volume ratio solvent - sample	100 : 1	10 : 1	20 : 1	10 : 1	10 : 1	100 : 1
elution time	24 h	6 h	24 h	24 h	24 h	6 h
filtration	–––	φ 1 µm	φ 0.45 µm	φ 0.45 µm	φ 0.45 µm	φ 0.45 µm
type of mixing	constant circulation	shaking 200 rpm	mixing 200 rpm	mixing 200 rpm	mixing 200 rpm	mixing 200 rpm

Table 3. Comparison of selected heavy metals in samples of materials and their mixtures.

Sample type	heavy metals content [mg/kg d.m.]						
	Pb	Cu	Zn	Cr	Mn	Ni	Cd
post digestion sludge	1200	1650	6750	880	950	740	40.5
OW13 (post digestion sludge after mixing with minced willow twigs in weight proportion 1:3 and draining off)	960	1230	4320	710	735	518	28.7
OW15 (post digestion sludge after mixing with minced willow twigs in weight proportion 1:5 and draining off)	1075	1360	5230	720	784	585	29.5
OW16 (post digestion sludge after mixing with minced willow twigs in weight proportion 1:6 and draining off)	1130	1525	6100	794	840	690	36.7
C cement kiln dust	28.3	21.4	158	31.2	29.2	42.5	31.6
W quicklime dust	14.9	27.3	463	54.2	254	38.9	16.4

to resemble natural conditions of heavy metals elution. The elution degree was described as the ratio of heavy metals content in acetic extracts to heavy metals content in *aqua regia*.

In addition, determination of a number of bacteria, parasites and their eggs was made in a sample of raw post-digestion sludge, as well as in the samples (OW13 B20, OW15 B20, OW16 B20).

Results and Discussion

Fig. 3 shows the results of determining the degree of lead elution from a sludge sample stabilized by quicklime, cement kiln dust and detrital basalt (OW13 B20). The results were compared with a sample of post digestion sludge and an OW 13 sample (post-digestion sludge after mixing with minced willow twigs at a weight ratio d.s. 1:3) in the range of pH: 3.5-7.5.

In this range of pH, the degree of lead elution from a sample of post-digestion sludge is considerable and amounts to from 61% to 43% of weight, decreasing according to pH increase. A much higher elution degree is observed in the case of an OW13 sample: in this range of pH, the elution degree amounts to from 80% to 55% of weight. In the same range of pH, an OW13 B20 sample with an addition of detrital basalt is characterized by the elution degree equal to from 7% to 5.1% of weight.

Copper is a metal which can be eluted from a sample of post-digestion sludge quite easily (Fig. 4). However, the elution degree decreases from 77% to 34% of weight according to pH increase from 3.5 to 7.5. The addition of minced willow twigs (OW13) increases the elution degree, but its value decreases from 92% to 50% of weight

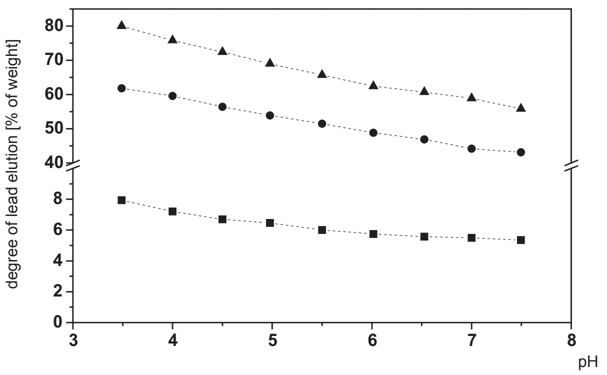

Fig. 3. Comparison of the degree of lead elution from a sample of sludge stabilized by quicklime, cement kiln dust and detrital basalt OW13 B20 with a sample of post-digestion sludge, and from a sample of OW13 (post-digestion sludge after mixing with minced willow twigs at weight ratio d.m. 1:3).
▲ - OW13, ● - post-digestion sludge, ■ - OW13 B20.

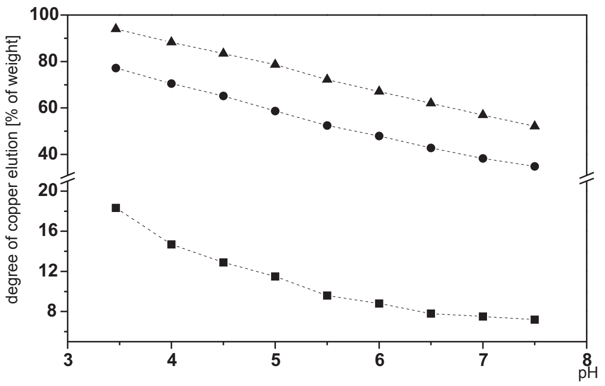

Fig. 4. Comparison of the degree of copper elution from a sample of sludge stabilized by quicklime, cement kiln dust and detrital basalt OW13 B20 with a sample of post-digestion sludge, and from a sample of OW13 (post-digestion sludge after mixing with minced willow twigs at weight ratio d.m. 1:3).
▲ - OW13, ● - post-digestion sludge, ■ - OW13 B20.

in the range of pH: 3.5-7.5. An addition of detrital basalt (OW13 B20) changes this; changes of the elution degree are considerably smaller and amount to from 19% to 7% of weight. Paper [5] presents similar results of the elution degree of copper (from 20% to 10% of weight in the range of pH mentioned above) determined in samples of post-digestion sludge with a 12% addition of detrital basalt.

Zinc can be very easily eluted from post-digestion sludge samples (from 90% to 72% of weight) as well as from an OW13 sample (from 96% to 75,7 % of weight) in the range of pH: 3.5-7.5 (Fig. 5). The OW13 B20 sample with an addition of detrital basalt in this range is characterized by the elution degree equal to from 11% to 3.5% of weight.

In the case of chromium (Fig. 6), a similar shape of curves illustrating the dependence of the elution degree on pH change was registered. For a post-digestion sludge sample, the elution degree decreases from 63% to 55% of weight in the range of pH: 3.5-7.5. In the same range of pH for an OW13 sample, the decrease amounts to from 70% to 61% of weight, whereas in the case of an OW13 B20 sample, the elution degree of chromium decreases from 11% of weight to 4.5% of weight.

Table 4 presents the results of determining heavy metals elution degree by means of acetic acid (like in US-EPA method) from post-digestion sludge and from sludge samples stabilized by calcareous dust, cement kiln dust and an addition of detrital basalt. The pH value of the extraction solvent was lowered to 4.5 (US-EPA method takes pH: 5.8-6.3) in order to sharpen the experiment conditions. In all prepared samples, the lowest heavy metals elution degree was achieved at 20% of weight of detrital basalt content (OW13 B20, OW15 B20, OW16 B20). The degrees of heavy metals elution from these samples increase in the direction OW13 B20 < OW15 B20 < OW 16 B20. This phenomenon was caused by the change of heavy metals content in samples of post-digestion sludge after mixing with minced willow twigs. The content of heavy

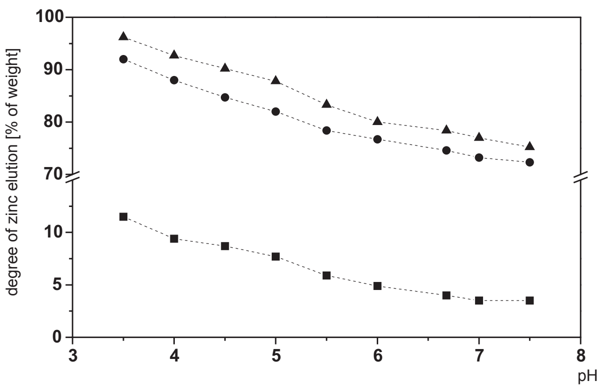

Fig. 5. Comparison of the degree of zinc elution from a sample of sludge stabilized by quicklime, cement kiln dust and detrital basalt OW13 B20 with a sample of post-digestion sludge, and from a sample of OW13 (post-digestion sludge after mixing with minced willow twigs at weight ratio d.m. 1:3).
▲ - OW13, ● - post-digestion sludge, ■ - OW13 B20.

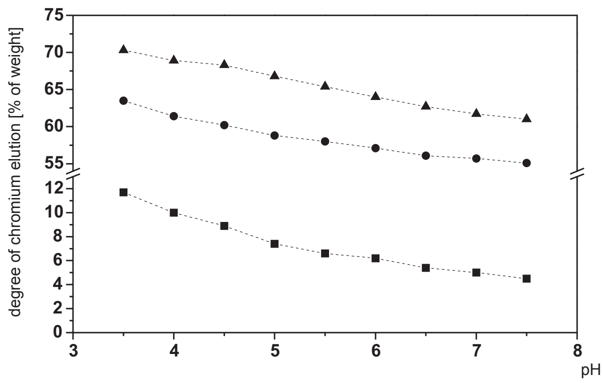

Fig. 6. Comparison of the degree of chromium elution from a sample of sludge stabilized by quicklime, cement kiln dust and detrital basalt OW13 B20 with a sample of post-digestion sludge, and from a sample of OW13 (post-digestion sludge after mixing with minced willow twigs at weight ratio d.m. 1:3).
▲ - OW13, ● - post-digestion sludge, ■ - OW13 B20.

Table 4. Degree of heavy metals elution from samples (extraction by acetic acid at pH: 4.5 ± 0.1).

Sample type	degree of heavy metals elution [% of weight]						
	Pb	Cu	Zn	Cr	Mn	Ni	Cd
post-digestion sludge	56.4	71.5	84.7	61.6	63.4	43.8	57.3
OW13	78.3	83.4	90.2	68.3	68.7	48.7	65.3
OW15	72.4	79.2	88.4	66.9	66.1	45.0	62.6
OW16	65.8	75.6	87.3	65.7	65.3	44.9	59.3
OW13 B10	7.5	14.5	10.2	12.3	16.8	13.6	8.6
OW13 B15	6.9	13.2	9.4	11.5	14.2	10.7	7.1
OW13 B20	6.7	12.9	8.7	8.9	13.9	9.3	5.5
OW15 B10	8.8	19.6	15.9	17.3	25.8	22.9	21.1
OW15 B15	8.5	18.2	13.4	14.1	24.0	19.2	17.2
OW15 B20	7.8	15.8	10.3	12.8	17.4	16.8	14.3
OW16 B10	9.6	23.7	17.2	22.1	26.3	27.9	29.8
OW16 B15	9.3	21.5	15.3	18.7	23.6	25.4	26.1
OW16 B20	8.4	18.5	13.8	15.1	20.3	22.3	23.6

Table 5. Comparison of the results of determining the number of bacteria, parasites and their eggs in a hygienization process with sanitary requirements for sludge.

Sample type	*coli* titre	*Clostridium perfringens* titre	*Salmonella* spp.	Eggs of *Ascaris lumbricoides* and *Trichocephalus trichiura*	number of vegetative bacteria in 1g of sludge
raw post-digestion sludge	0,0001 g	0,0001 g	not registered	A 38/100g T 27/100g	180,000,000
OW13 B20	>> 1g	>> 1g	not registered	dead	20
OW15 B20	>> 1g	>> 1g	not registered	dead	5
OW16 B20	>> 1g	>> 1g	not registered	dead	5
permissible quantity according to an MOŚZNiL regulation from 7. 07. 1986	no less than 0,01	-----------	not detectable	up to 10 in 1 l	
permissible quantity according to an Institute of Medicine of Village in Lublin	no less than 0,01	no less than 0,001	not detectable	up to 10 in 10 kg sludge	

metals decreases according to the increase of the willow addition (heavy metals content decreases in direction OW16 < OW15 < OW 13, Table 3). The change results not only from diluting the sludge mass with the vegetable addition, but also from dissolving part of chemical compounds of heavy metals in water included in the sludge, additionally acidified by acids of vegetable origin. Then, the solution is removed from the mass of the sample. This fact is confirmed by the results of heavy metals elution according to pH of the solution (Figs. 3-6). In each case, the degree of heavy metals elution from samples of post-digestion sludge (mixed with vegetable material) was higher in comparison with the degree of heavy metals elution from raw post-digestion sludge.

A comparison of the results of determining the amounts of bacteria, parasites and their eggs (Table 5) in raw sludge and samples of sludge stabilized by lime dust and cement kiln dust with the addition of detrital basalt (OW13 B20, OW15 B20, OW16 B20) proves that hygienization of post-digestion sludge is achieved and

Table 6. Comparison of heavy metals content in wastewater sludge and cement kiln dust with appendix (the amount of heavy metals in wastewater sludge for non-industrial purposes) to the regulation of the Minister of Environmental Protection, Natural Resources and Forestry from 11 August, 1999.

Metal	Sample type				Concentration of heavy metals in mg/kg dry substance of sludge not greater than:		
	post-digestion sludge [mg/kg d.m.]	OW13 [mg/kg d.m.]	OW15 [mg/kg d.m.]	OW16 [mg/kg d.m.]	in agriculture, for soil recultivation for agricultural purposes and for composting	for soil recultivation for agricultural purposes	for cultivation of plants intended for compost production and for vegetable fixation of soil
Lead (Pb)	1200	960	1075	1130	500	1000	1500
Cadmium (Cd)	40.5	28.7	29.5	36.7	10	25	50
Chromium (Cr)	880	710	720	794	500	1000	2500
Copper (Cu)	1650	1230	1360	1525	800	1200	2000
Nickel (Ni)	740	585	518	690	100	200	500
Mercury (Hg)	n.a.	n.a.	n.a.	n.a.	5	10	25
Zinc (Zn)	6750	4320	5230	6100	2500	3500	5000

n.a. - not analyzed

fulfills the requirements of the above-mentioned Polish sanitary regulations [9, 10].

Post-digestion sludge used in the experiments being the subject of this paper did not fulfill the requirements for sludge as far as heavy metals content is concerned (Table 6).

The degree of heavy metals elution from a sample of post-digestion sludge (pH: 4.5) is high. Introducing vegetable material – white willow – enhanced the elution effect. The choice was not accidental. White willow is often cultivated on soils fertilized with wastewater sludge. It was observed that white willow could absorb considerable amounts of heavy metals. It seems that it is possible to start a cultivation, the aim of which would be production of vegetable material to influence heavy metals content in wastewater sludge. Now, however, there are no proposals to solve the problem of sludge containing excessive amounts of heavy metals [11]. So far, only burning the sludge or storing it in waste dumps have been suggested.

Results of the research show that the technology of wastewater sludge hygienization [1] can be also applied in different versions of solutions for heavy metals immobilization in wastewater sludge excessively contaminated by heavy metals. The technology can be equally well applied even before storing the sludge in waste dumps.

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