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SHORT COMMUNICATION

Determination of metal content in sewage sludge and sewage sludge ash to find opportunities to use them in the construction industry

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ABSTRACT

Sewage sludge management is becoming an increasing problem in developed and developing countries. Due to their physicochemical properties (mainly high content of heavy metals) a safe method of utilization is sought. Considering environmental protection, energy recycling, reduction in use of the raw materials and the possibility of immobilization hazardous substances, the use of ashes in building materials becomes a very good way of utilization. Both unprocessed sewage sludge and ashes after their thermal utilization can be used in the construction industry. Before using sediments and ashes, it is necessary to analyze the content of heavy metals, because they can have a negative effect, for example, on cement-stabilized products. The purpose of this work was to determine selected metals (Cd, Cu, Ni, Pb, Zn, Cr, Mg, Mn, Fe) in the primary, dehydrated, digested, excess sludge and ash after his incineration to check and compare heavy metal content. The obtained data can be used to optimize the production process of cement products that contain sewage sludge at differ form, and confirm the environmental safety of proposed approaches.

***Keywords*:** sewage sludge, sewage sludge ash, heavy metals, sewage sludge management

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1. INTRODUCTION

Many countries are struggling with the increasing production of sewage sludge. Newer and more ecological methods of it processing are applied, moving away from e.g. direct application to land while technologies related to recycling or energy recovery are introduced. One of the modern solutions is the incineration of sewage sludge in fluidized bed furnaces. [1]. In European Union countries, about 10 million tons of dry matter (DM) of sewage sludge are produced. The largest producer of sewage sludge in the EU is Germany (they produce approx. 2 mln t DM) [2], [3]. For Asian countries, China produces around 6.25 mln t DM of sewage sludge [4]. In Japan, the amount of produced sludge is approx. 2.2 mln t DM [5]. In U. S., in 2004, 6.5 mln t of sewage sludge were produced (DM), where more than half of were used to improve the quality of the soil [6]. In countries where sewage management is not developed (some countries in Africa, Asia or Latin America), sewage or sewage sludge is not usually utilized or treated and mostly goes to septic tanks or directly to surface waters [7]. It is worth noting that the laws regarding the management of sewage sludge are becoming more and more stringent and the overall production of sewage sludge is constantly increasing, which makes it necessary to manage with efficient techniques. Many countries, in order to eliminate potentially harmful effects on the environment, limit or prohibit the use of unprocessed sludge. An example of a modern and environmentally friendly way of sewage sludge management is incineration.

Sewage sludge can be successfully processed thermally, in particular as regards mono and co-combustion. Prior to the incineration, it is necessary that the sludge should have a low moisture content (usually 10%). If sewage sludge has a low calorific value (caused by e.g. high moisture content), it is possible to combust it with other fuels or waste. [8]

Thanks to sewage sludge incineration, it mass is reduced to 70% with the simultaneous neutralization of toxic substances. It causes that incineration is becoming an increasingly used technique of sludge utilization and in EU countries, nearly 22% of sewage sludge is incinerated. Significant amounts of ash usually containing much higher heavy metal content compared to sewage sludge (converted into DM) becomes another problem and at the same time the main disadvantage of this utilization technique [1].

Considering environmental protection, energy recycling, reduction in use of the raw materials and the possibility of immobilization hazardous substances, the use of ashes in building materials becomes a very good way of utilization [9]. In the literature can be found applications sewage sludge ash as an addition to cement [10], a substitute for fine aggregates (e.g. sand) [11] or additive in fired bricks [12].

In the construction industry, it is also possible to use raw or pre-stabilized sewage sludge in some products and also may prove to be an alternative technique of utilizing both raw sludge and ashes after incineration. The presence of raw sludge in construction products, even in small quantities, reduces the strength of end products. However, in the literature it can be found attempts to make mortars and concretes [13], concrete bricks [14], ceramic products [15] or lightweight aggregate [16] with the addition of raw sewage sludge.

The purpose of this article is to present the results of tests comparing the content of metals in sewage sludge coming from different parts of the plant's technological line and in ash obtained by thermal utilization dewatered sewage sludge. The comparison of the results is aimed at confirming the thesis that ashes constitute a completely different type of waste and the obtained data will allow to estimate which sludge is most suitable for use in construction.

Selected elements (Cd, Cu, Ni, Pb, Zn, Cr, Mg, Mn, Fe) were determined in primary, dehydrated, digested, excess sludge and ash after incineration dehydrated sewage sludge to check and compare its content. The obtained data can be used to optimize the production process of cement products that contain sewage sludge at differ form, and confirm the environmental safety of proposed approaches.

2. SUBSTRATES CHARACTERIZATION

Sewage sludge is a mixture with a high degree of hydration, which includes microorganisms (also pathogens) as well as organic and inorganic substances. Sewage sludge is rich in easily absorbable organic matter, N, P, Ca, K, Mg, Zn and a number of micronutrients. This makes it a good fertilizer and material that improves soil quality. The limitation in the use of sewage sludge for soil purposes is, among others high content of heavy metals, which increases particularly when thickening / dewatering sludge, which often means that it cannot be used in this way. The most common toxic heavy metals in sewage sludge are: Cu, Cd, Cr, Hg, Ni and Pb. The content of these heavy metals vary and depend on the type of wastewater and treatment technology. The fermented sludge may contain less iron or aluminium ions than the one that has been dehydrated due to use coagulants [15], [17].

The combustion process allows for the conversion of organic carbon to CO_2, water vapour and other volatile substances. Solid residues, i.e. ash and dust, are separated from the flue gas stream and require further utilization. Figure 1. presents an example diagram of a sewage treatment plant equipped with sewage sludge incinerator. Before the sludge is burnt, it is thickened and then dewatered using belt press. For the auto-thermal combustion of sludge, its moisture content must be approx. 28-33 wt %. If this value is higher, the sludge should be incinerated with other auxiliary fuels. The combustion process itself is carried out in a fluidized bed furnace, where, thanks to waste gases, the sludge is first dried and then burned at the temperature of approx. 750 °C. The ash and dust from the flue gas stream is extracted using bag filters, electrostatic precipitators or cyclones, then goes to a wet scrubber where the flue gas is cleaned with acidic or alkaline solutions and if necessary with active carbon. The resulting scrubber sludge can also be a hazardous waste and is stored in a landfill.

The efficiency of exhaust cleaning from solids is 95% - 99%, which means that the total production of ash in countries using thermal methods of sludge utilization (U.S., EU, Japan) is about 1.7 million tonnes / year. The composition of the ash may vary depending on the type of sludge being incinerated and the used cleaning technology, but in principle the main oxides in ash and dust are Si, Al, Ca, Fe and P. Volatile metals such as Hg, Cd, Sb, As and Pb are well absorbed on the surface of ash particles and are also present in it [19], [20]. Comparison of metal content in sewage sludge and sewage sludge ash are given in Table 1.

As mentioned, both raw sludge and ashes after incineration can be used in building materials. The properties of these materials are influenced by, among others the presence of heavy metals, carbon and other organic substances, therefore a detailed analysis of the substrate is necessary before proceeding with the chosen application technique. It may seem that the content of heavy metals after thermal utilization will only increase due to weight and volume reduction. This estimation may turn out to be wrong, as the differences between the composition of ashes, dusts and sewage sludge are noticed. Such differences were presented by the D. Marani et. al. [20]. Raw or dewatered sludge should therefore be treated completely differently compared to dust and ash after its thermal utilization.

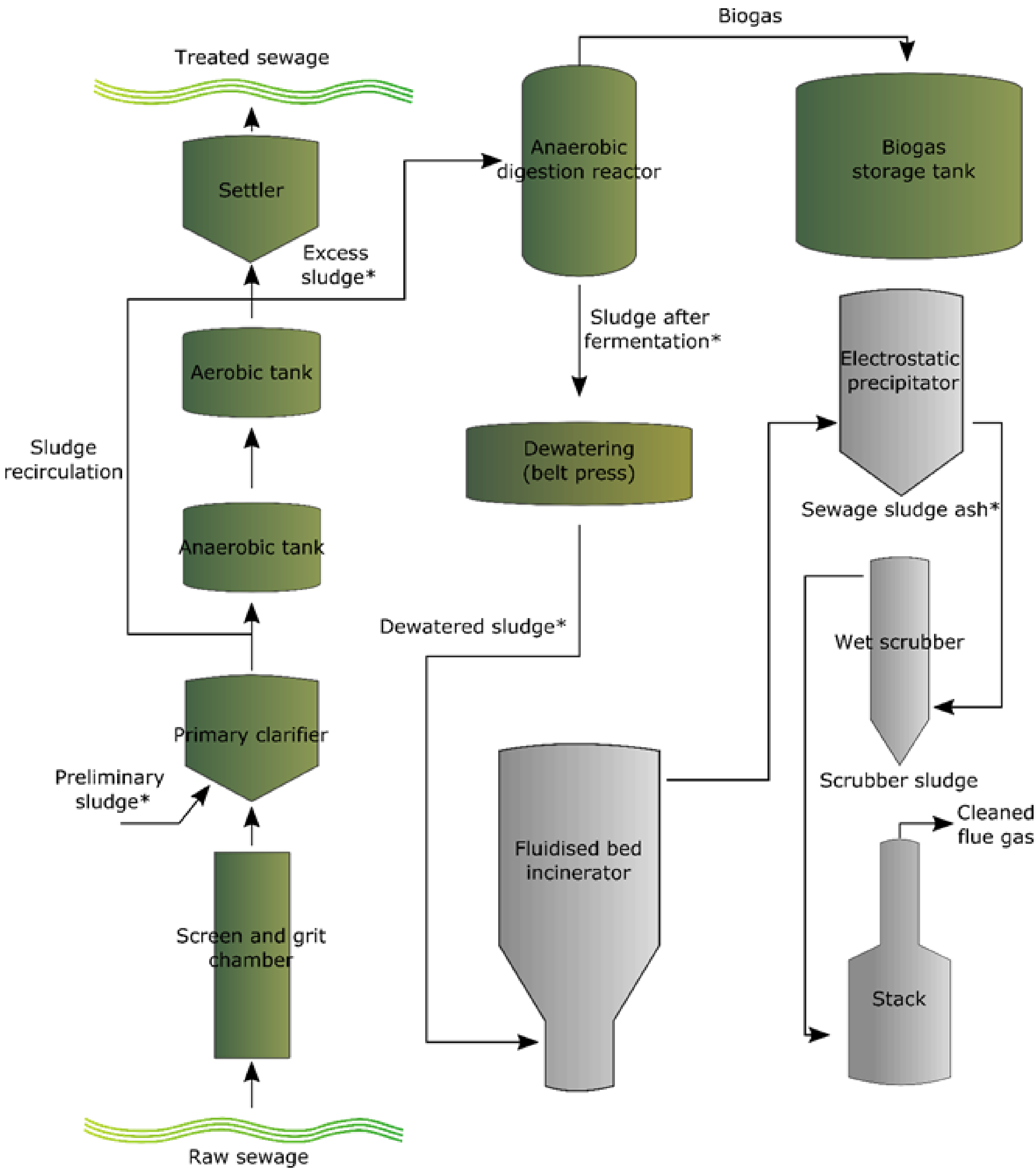

Figure 1. A simplified scheme of a sewage treatment plant equipped with sludge incinerator (*-sampling) [18], [19].

Table 1. Comparison of the content of elements in sewage sludge and sewage sludge ashes.

Sample / Element	Municipal sewage sludge [21]	Municipal sewage sludge [22]	Dewatered sewage sludge [20]	Sewage sludge ash [23]	Sewage sludge ash [24]	Sewage sludge ash [25]
Cd [mg/kg DM]	2.78	-	14-23	14	15	18
Cu [mg/kg DM]	433	57	262-599	2483	1503	1826
Ni [mg/kg DM]	621	15	36-53	621	112	228
Pb [mg/kg DM]	126	171	104-137	720	1175	344
Zn [g/kg DM]	2.0	0.21	2.8-4.2	7.1	2.8	3.0
Cr [mg/kg DM]	856	325	240-650	2636	172	585
Mg [g/kg DM]	-	8.1 ± 1.9	5.0-6.0	-	-	13.0
Mn [mg/kg DM]	-	208 ± 24	75-98	-	474	1149
Fe [g/kg DM]	-	27.3 ± 2.9	6.0-7.0	-	35.3	75.7

3. MATERIALS AND METHODS

Samples of ashes from sludge and sewage sludge (primary sludge, dehydrated sludge, sludge after fermentation, excess sludge) were collected from one of the wastewater treatment plants in Gdansk, Poland. In order to determine the content of metals in the samples, their dry masses were first determined. For this purpose, about 2 g of each sludge was weighed, placed in a porcelain crucible and dried at 105 °C to constant weight. Each analysis was done with three repetitions.

Since most of the heavy metals are bound in the organic part of the sewage sludge, it is not necessary to digest the silica contained in the samples. Determination of pseudo total metal concentration consisted in weighing about 1g of each type of sample into a special vessel (teflon bomb) and subjecting them to wet pressure mineralization using microwave energy (the Anton Paar Mineralization system, model Multiwave GO). Aqua regia was a dissolving mixture and the mineralization was carried out for 1.5h with a maximum temperature of 150 °C. The obtained solutions were quantitatively transferred into 25 ml graduated flasks and made up to volume with deionized water. Atomic absorption spectrometry with flame atomization (GBC SCIENTIFIC EQUIPMENT model SensAA) was used to determine elements such as: Cd, Cu, Ni, Pb, Zn, Cr, Mg, Mn, Fe. Each measurement was repeated three to four times for uncertainty calculation.

Using the dry mass values of the samples and the concentration of heavy metals in the mineralized samples, the content of heavy metals calculated per kg DM of the sample was calculated. The results are shown in Table 2.

4. RESULTS AND DISCUSSION

On the basis of the test results, it can be concluded that the content of heavy metals (Cu, Cr, Pb, Ni) in individual sewage sludge samples were similar. More visible differences can be registered for other metals. It is related to various steps of the technological process which sediments are subjected. At some stages of the purification, additives are used, which are responsible for the removal of some substances from wastewater (e.g. nutrients). In the case of dewatering, Fe and Al salts are used, which are coagulants. In addition, alkali (e.g. $Ca(OH)_2$) is often used to remove P. This also causes the precipitation of Mg or Zn salt ($Mg(OH)_2$, $Zn(OH)_2$). For this reason, dehydrated sludge has often higher Fe, Mg or Zn content, which is apparent in the results shown in Table 2.

Table 2. The main elements present in sewage sludge and sewage sludge ash. [mg/kg DM].

Sample / Element	Preliminary sludge	Dewatered sludge	Fermented sludge	Excess sludge	Sewage sludge ash	LOD*
Cd	6.189 ± 0.093	10.88 ± 0.15	<LOD	<LOD	6.19 ± 0.19	1.8
Cu	186.0 ± 9.4	269 ± 12	230 ± 11	257 ± 13	722 ± 34	-
Ni	<LOD	<LOD	<LOD	<LOD	34.1 ± 3.5	5.0
Pb	<LOD	<LOD	<LOD	<LOD	48.0 ± 6.5	6.8
Zn	129.0 ± 3.5	1216 ± 47	110.4 ± 3.2	188.9 ± 5.9	1918 ± 67	1.9
Cr	<LOD	<LOD	<LOD	<LOD	96 ± 51	24
Mg**	0.660 ± 0.18	8.2 ± 1.9	0.85 ± 0.19	2.4 ± 0.57	28.6 ± 6.6	-
Mn	<LOD	208 ± 24	<LOD	14.3 ± 1.2	548 ± 61	5.8
Fe**	2.07 ± 0.22	27.1 ± 2.9	2.23 ± 0.24	6.65 ± 0.94	54.4 ± 6.3	-

*- Limit of detection (LOD)
**- g / kg DM

In the case of ashes, a significant reduction in volume and mass should cause about 10 times higher heavy metal content than in the substrate subjected to incineration. Analysis of the test results, however, indicates that differences in the content of elements do not depend directly on the reduction of the volume of deposits during combustion. This is probably caused by different sizes of ash particles that are able to adsorb metals on their surface. Different granulometric ash fraction may vary considerably composition (especially in terms of heavy metals) [20]. Small differences in individual sludge can also be caused by temporary changes in the composition of sewage.

5. CONCLUSIONS

Sewage sludge management in Europe and the world is a serious problem related to the amount and negative impact of unprocessed sewage sludge. Both sewage sludge at various stages of purification and sewage sludge ashes after thermal utilization can be considered as a potentially attractive substrate in the construction industry. The elemental composition of both sludge and ashes is similar to the cement constituents, which gives the possibility of pro-ecological use. Ashes can also contribute to the pozzolan reaction. The presence of heavy metals can affect the rate of binding of manufactured products and the possibility of leaching them from finished products causes that monitoring and thorough analysis of the composition is required.

In Europe, an increase in the production of excess sewage sludge is observed due to restrictive legal requirements and constantly developing purification technologies. One of the best and more often used methods is incineration, thanks to which the volume of sludge is reduced while producing sterile ash. The disadvantage of the method is the production of ashes and dusts, the composition of which is variable.

The elemental composition of sewage sludge (based on DM) is different than the ashes and at the same time it is impossible to predict the content of heavy metals in the ash based on the analysis of sludge only. The analysis of metals only in sewage sludge is insufficient, it can be used to qualitatively determine the metals that are likely to be present in the ashes.

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