HYDROMETALLURGICAL METHOD OF SELECTED METALS RECOVERY FROM SEWAGE SLUDGE ASHES

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Abstract
With the increasing number of new residents attached to the sewerage system, the amount of generated sewage sludge is systematically growing. In line with the restriction placed on landfill waste with a calorific value above 6 MJ/kg introduced on 1 January 2016, the most popular sewage sludge utilization methods are thermal processes and agricultural use. In recent years, there has been increased interest in using thermal sewage sludge utilization methods. The major problem associated with sludge combustion is the enormous amount of by-products, particularly ashes. Due to the specific characteristics, it is necessary to develop new sewage sludge ashes utilization methods in line with economic, law and environmental requirements. Sewage sludge ashes are rich in valuable metals, particularly in zinc, copper and iron. As utilization methods of sewage sludge ashes do not guarantee the metals recovery until now, metals are lost irretrievably. This article presents hydrometallurgical methods of metals recovery from sewage sludge ashes with the use of acid leaching. The aforementioned propositions are beneficial from the economical and environmental point of view because they prevent valuable metals from waste. Additionally, the whole undertaking could contribute to the popularization of sustainable development.

Keywords: sewage sludge ashes, sewage sludge, metals recovery, recycling, hydrometallurgy

1 Introduction

Sewage sludge is a by-product of sewage treatment produced in treatment plants (**Fig. 1**). The amount of generated sewage sludge is systematically growing which is associated with tightening regulations concerning the sewage quality. According to the Central Statistical Office Report [1], 556 thousand Mg municipal sewage sludge was produced in Poland in 2014. A large amount of generated sewage sludge requires new sewage sludge utilization methods in line with environmental, economical and law requirements. In Poland, sewage sludge utilization methods are determined by domestic law, especially Act on Waste of 2012 [2] and Regulation on Urban Sewage Sludge of 15 February 2015 [3]. So far, there have been three dominant sewage sludge utilization methods in Poland: disposal in a landfill, natural use and combustion, among which the most popular was disposal in a landfill. In line with the restriction introduced on 1 January 2016, the landfilling of sewage sludge is forbidden [4]. Due to the banning of sewage sludge storage, its management is a serious problem from the economical and ecological point of view.

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The change of regulations associated with the sewage sludge management led to the development of new sludge utilization methods. In recent years, there has been increased interest in using thermal sewage sludge utilization methods in Poland. According to the Central Statistical Office Report, approximately 30% of generated sewage sludge was burnt in Poland in 2014. In agreement with National Waste Management Plan [5], approximately 60% of generated sewage sludge will be transformed with the use of thermal methods. The main advantages of thermal utilization methods are the reduction of sewage sludge volume and the possibility of energy recovery.

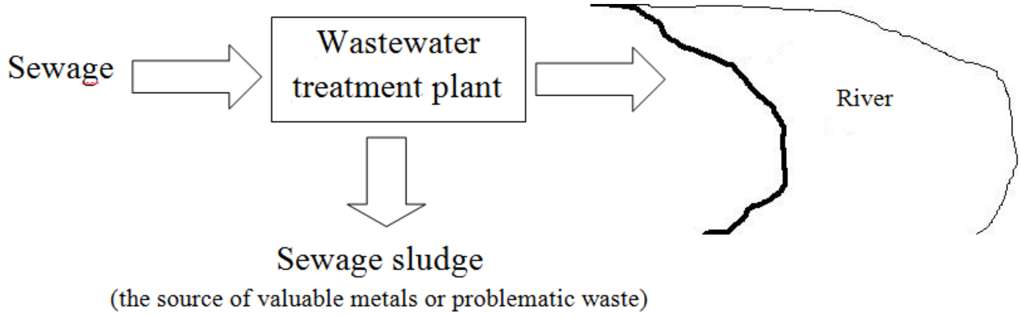

Fig. 1 Sewage sludge management in treatment plants

Sewage sludge burning in fluidized-bed boilers, as an example of best available technology (BAT), results in the production of sewage sludge ashes. It is estimated, that the amount of produced sewage sludge ashes will reach approximately 24÷32 thousand megagrams in 2016 and about 55÷65 thousand megagrams in 2020 in Poland [6]. The increasing amount of produced ashes requires new and effective utilization methods. Recently, more and more produced ashes are processed by means of solidification and used in civil engineering. Both sewage sludge and sewage sludge ashes contain metals, including rare earth elements (REE). Sewage sludge ashes also include the following elements: zinc, iron and copper. The academic research showed that gold accumulated in sewage sludge might have an overall value equivalent to around 360 tons of pure gold [7, 8]. The test performed in U.K. proved that sewage sludge ashes contained platinum metals, including platinum and palladium with a concentration of 600 ppb [9]. Therefore, the metals recovery from both sewage sludge and sewage sludge ashes is necessary from the environmental and economical point of view.

This article presents a solution for zinc and copper recovery from sewage sludge ashes with the use of a hydrometallurgical method. The proposition could be a new technique of sewage sludge management.

2 The characteristics of sewage sludge ashes

Fluidized-bed technologies of sewage sludge combustion result in the production of ashes. In line with Regulation of the Minister of Environment of 9 December 2014 establishing a waste catalog [10], sewage sludge ashes have the following codes: 19 01 06, 19 01 07* and 19 01 14. The properties of aforementioned ashes depend on the quality and quantity of wastewater flowing to a treatment plant.

Typical sewage sludge ashes are characterized by alkaline pH and the high mineralization degree. Additionally, aforementioned by-products comprise the small content of nitrogen and

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the high concentration of phosphorus [11, 12]. Due to the content of phosphorus, sewage sludge ashes might be used in the production of phosphorus fertilizers. Fertilizer production technologies with the application of ashes from sewage sludge combustion are tested in Germany [13]. Sewage sludge ashes are also rich in alkaline elements, particularly in calcium and magnesium. The concentration of aforementioned compounds enables ashes application in agricultural practices. Wierzbowska et al. [14] proved that plant fertilization with use of sewage sludge ashes influenced the intensification of the growth of *Virginia fanpetals* without the risk of soil contamination. However, a detailed tests concerning the physical and chemical properties of sewage sludge ashes are required prior to its agricultural use.

Fluidized-bed combustion does not eliminate the problem associated with the content of heavy metals in sewage sludge ashes. Therefore, combustion by-products are characterized by the different concentration of metals. Białowiec et al. [15] examined the chemical composition of sewage sludge ashes obtained from an incineration plant in Gdynia (Poland) and in Wien (Austria). The results proved a different content of heavy metals in sludge ashes, depending on the country and conditions of ashes storage (**Table 1**). The content of heavy metals is a major factor sustaining sewage sludge ashes agricultural use.

Table 1 The content of heavy metals in sewage sludge ashes according to [15]

Sewage sludge ash	**Heavy metals concentration [mg · (kg d. m.)$^{-1}$]**						
	Cd	**Cr**	**Cu**	**Ni**	**Pb**	**Zn**	**Hg**
Ash from Wien, Austria	2.37	54.5	702.7	111.8	259.20	2331.40	0.074
Ash from Gdynia, Poland	1.18	2.30	370.0	107.0	247.0	7762.00	0.006

d. m. - dry mass

3 Metals recovery from sewage sludge ashes

The metals recovery from waste is essential from the economical and environmental protection point of view. Sewage sludge ashes contain a lot of valuable elements, including REE. Due to the practical application of metals in industry, their mining and transport is a significant problem [16]. It is estimated that the world production of REE is approximately 100 thousand tons and their shortage of supply amounts to several percent [17]. Even though rare earth elements are found in many places in the world, the extraction of metals is not always profitable. Outside of Japan, the recycling of combustion by-products in terms of metals recovery is not applied. Apart from technological and economical reasons, the main barrier preventing metals recovery from ashes is their small content in waste [18]. The research has shown that some combustion by-products might comprise a lot of valuable metals which qualifies them for recovery [19]. Additionally, the content of metals is energetic waste could be higher than in fuel [14]. Regardless of this fact, metals recovery technologies are not used on an industrial scale.

In order to recover zinc and copper from sewage sludge ashes, hydrometallurgical methods with the application of acid leaching might be suggested (**Fig. 2**). The main advantages of metallurgical extraction are the lower energy consumption in comparison with pyrometallurgical methods and the higher purity of obtained products. The proposed method of zinc and copper recovery from sewage sludge ashes is a complex process, which is characterized by a relatively small amount of residual waste. Firstly, by-products of sewage sludge combustion are shredded and ground by means of a ball mill. Secondly, shredded ashes are sifted with the use of sieves. The aforementioned process enables the separation of fractions which are insufficiently shredded. Afterwards, such obtained sewage sludge ash has to undergo flotation, thickening and filtration processes so as to obtain metals condensate containing zinc.

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Zinc condensate obtained in this way undergoes the appropriate hydrometallurgical method which is based on acid leaching with low pH. As leaching solution, sulfuric acid containing iron ions (III) is recommended. The process of metals recovery is undergone on the bed in temperature below 100°C. In order to intensify the acid leaching, artificial mixing might be applied. The product of the aforementioned process is a pulp which undergoes the multi-step filtration process with downstream washing. In this way, obtained sludge could be used as a fertilizer in agricultural practices. The additional advantage of acid leaching with the use of sulfuric acid is the possibility of regeneration of leaching solution. For the regeneration of sulfuric acid, biochemical methods with the use of microorganisms, such as *Thiobacillus Ferroxidans*, might be applied.

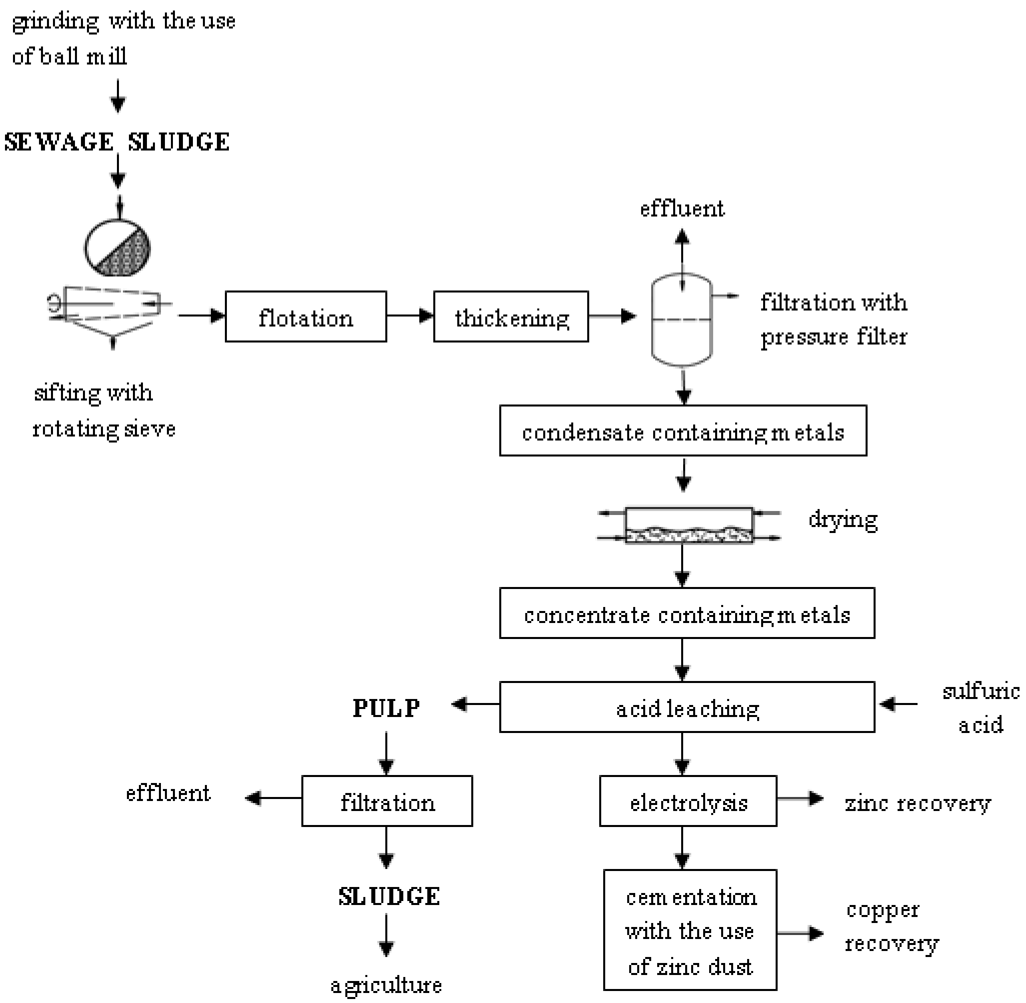

Fig. 2 Scheme of metals recovery from sewage sludge ashes

From the filtrate obtained in leaching, zinc is recovered by means of electrodes. Additionally, it is also possible to recover copper from the solution obtained after the filtration process. The

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copper might be recovered by means of cementation with the use of zinc dust. From the cementite obtained after cementation, the copper recovery might be possible.
Zinc and copper leaching from sewage sludge ashes could be improved by the use of ultrasounds (**Fig. 3**). The application of ultrasounds enhances the convection motion and increases the contact area between a solid and liquid in order to improve the effectiveness of the process. The use of ultrasounds could increase the metals recovery by several percent.

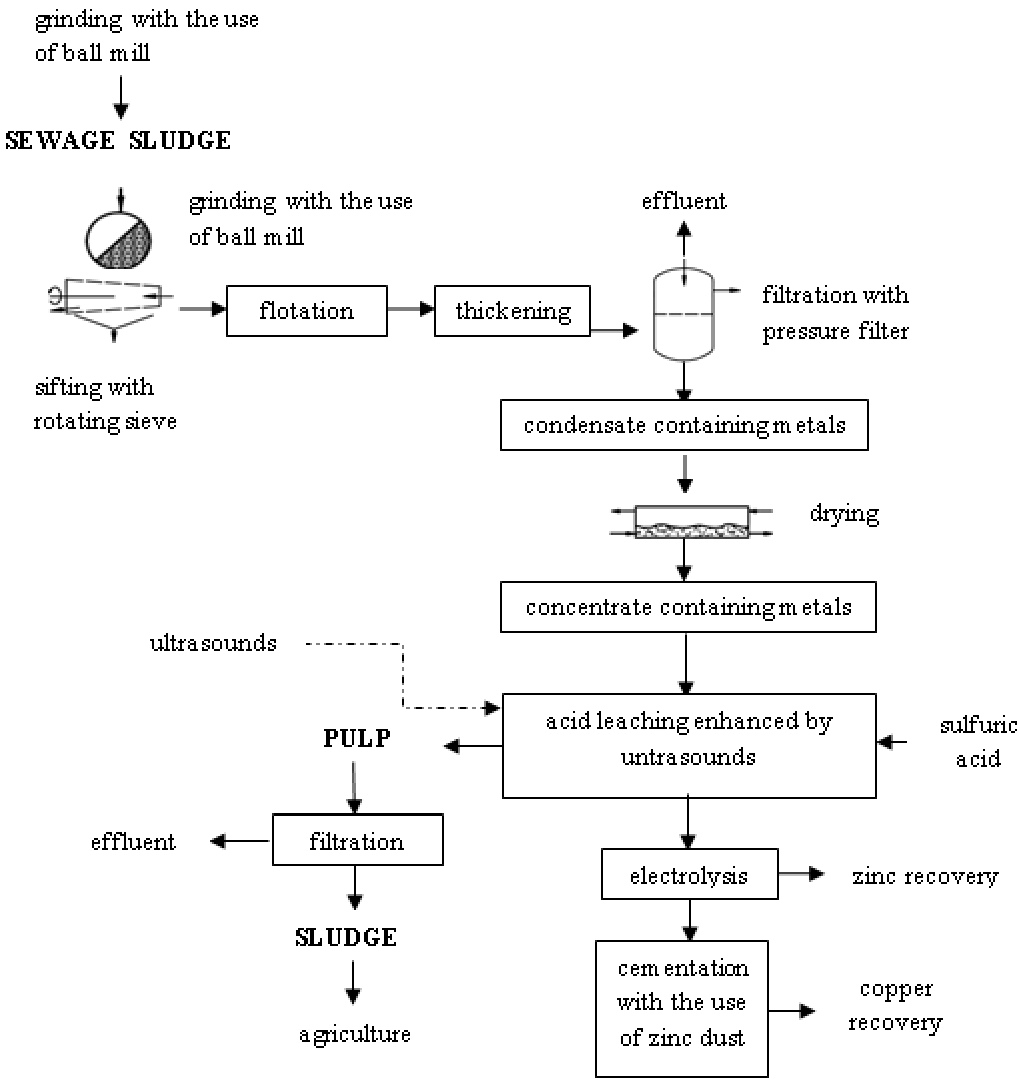

Fig. 3 Scheme of metals recovery from sewage sludge ashes with the application of ultrasounds

Another suggestion of copper recovery was shown in **Fig. 4**. The proposed method involves two-step leaching from metal concentrate. At the beginning, sewage sludge ashes are shredded and sieved, just as in the first proposed method. After mechanical grinding, properly prepared combustion by-products undergo flotation, thickening and filtration in order to achieve metal condensate. After drying under temperature in the range of 100÷150°C, the concentrate containing copper is obtained. The zinc recovery from concentrate includes two-step leaching with the use of sulfuric acid and iron ions (III). From the obtained filtrate, zinc is recovered on the platinum electrodes. The final product of the aforementioned process is sludge which has undergone the multi-step filtration process. As a result, the product obtained in filtration could be used as a fertilizer in agriculture. As a result of the proposed method, the content of copper is reduced significantly which is advantageous from the environmental point of view. Leaching solution might be regenerated by means of anode methods.

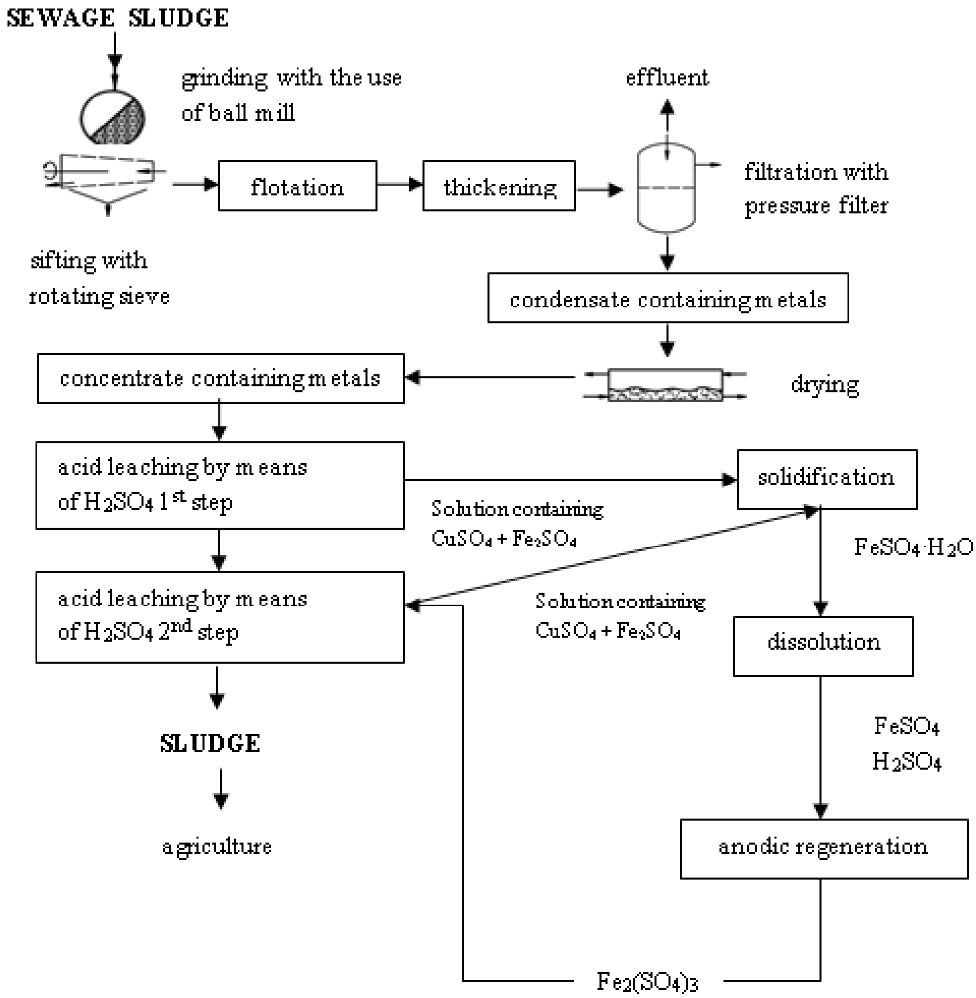

Fig. 4 Scheme of copper recovery from sewage sludge ashes

4 Summary

With the increasing number of new residents attached to a sewage system, the amount of produced sewage sludge is systematically growing. In Poland, the sewage sludge management is

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a relatively new field of waste management called “in statu nascendi”, the standards of which have not been recognized yet, and requires the implementation of new solutions in the field of sewage sludge. So far, the most popular method of sewage sludge utilization was disposal in a landfill. In line with the restriction placed on landfill waste with a calorific value above 6 MJ/kg which was introduced on 1 January 2016, the agricultural use and thermal methods are mostly applied.
In Poland, there has been increased interest in using thermal sewage sludge utilization methods. According to the **Central Statistical Office** Report, approximately 30% of generated sewage sludge was burnt in Poland in 2014. The main problem associated with sludge combustion is the enormous amount of ashes which have to be managed in line with economical, law and environmental requirements. According to the waste hierarchy, produced waste should be recycled or reused as much as possible. Recently, sewage sludge ashes have been used in the construction and ceramics industry. Research is also conducted in order to apply aforementioned waste as a fertilizer in agricultural practices.
Sewage sludge ashes are rich in valuable metals, particularly in zinc, copper and iron. The research has shown that some combustion by-products might comprise precious metals which qualify them for recovery. As utilization methods of sewage sludge ashes have not guaranteed the metals recovery until now, metals are lost irretrievably. An alternative solution for traditional sewage sludge ashes utilization methods could be metals recovery from combustion by-products. In order to receive precious metals, hydrometallurgical methods with the application of acid leaching might be used. Even better results could be obtained with the use of ultrasounds during leaching. From the obtained filtrate, zinc and copper are recovered on the platinum electrodes by means of the electrolysis process. Additionally, leaching by-products might be applied as a fertilizer in agricultural practices. The proposed scheme could be a new method of metals recovery from sewage sludge ashes. The aforementioned proposition is innovative and has never been applied before.
Hydrometallurgical methods might play an important role in sewage sludge management. Due to the limited metals deposit and demand for sewage sludge utilization, metals recovery is economically justified. Acid leaching of metals is a promising alterative for other sewage sludge utilization. Additionally, metals recovery from sewage sludge ashes enables the implementation of European programs: “Zero Waste Programme for Europe” and “Horizon 2020” [20]. Additionally, metals recovery from sewage could indicate the appropriate waste management strategies.

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