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DETERMINATION OF COMBUSTIBLE SULFUR CONTENT IN SEWAGE SLUDGE

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ABSTRACT

Large amounts of sewage sludge are produced at waste water treatment plants and its disposal is an environmental problem. In this context and in accordance with the European Commission communication on the role of waste-to-energy in the Circular Economy, one of the objectives of Romania Waste Management-Strategy Plan for municipal waste, is incineration of the solid waste in dedicated incinerators, with energy recovery. When the incineration of the sewage sludge with energy recovery is chosen as the final path of disposal, the optimal energy gain, have to be correlated with the limits provided of the legislation in force for the air pollution emissions and with the quantities of the waste which must be minimized. The presence of sulfur in sewage sludge has significant implications in incineration processes due to its transformation at high temperature into SO₂ which is released into the atmosphere, and on the other hand, there is a risk of high-temperature corrosion of the pipes and pumps, depending of the molar ratio 2S/Cl. The paper presents a study on the determination of the technological forms of sulfur and total sulfur in sewage sludge to be incinerated. The results obtained show that the total sulfur is mostly represented by the combustible sulfur which is in a proportion of about 88% and the rest of about 12 % is the sulfur remaining in the ash.

Keywords: sewage sludge, incineration, combustible sulfur, sulfur in ash

INTRODUCTION

The sewage system in urban areas of Romania are unitary, consequently, the waste water are discharged to urban waste water treatment plants. Since the urban areas have unitary sewage systems, after pre-treatment, the industrial wastewater is discharged at urban wastewater treatment plants, the excess sludge being unsuitable for composting and subsequent use for land fertilization. Under the Sewage Sludge Regulations, the owners of wastewater treatment plants are forced to retrofitting the treatment plants, to improve the sewage sludge quality and to ensure the treatment for its stabilization and to find users in agriculture or other fields. If the composition of the sludge does not allow its spreading on land, disposal by incineration or co-incineration must be ensured. At national level, by implementing of infrastructure programs, there are some projects for incineration plants construction dedicated for sewage sludge [1]. These incinerators must offer an optimal energy gain, correlated with limiting of the pollutant emissions and generating a minimum amount of waste which must falls within the pollution limits, set by the Romanian environmental regulations in accordance with the European requirements. [2]. Therefore, when designing and establishing an optimal solution for final disposal of sludge, it is very

important to know the sewage sludge composition. In this context, sulfur content is one of the required parameters with significant implications at incineration processes. During the incineration process, sulfur is released into the atmosphere as SO₂ and dioxins. On the other hand, the recirculated sulfur will increase the gas concentration of SO₂ in the boiler and decrease the C/S ratio of the deposits and ashes, thus producing a less corrosive environment for the super heaters. [3]

The present paper aims to determine the total sulfur content and the sulfur-based technological forms of the sludge resulting from the final dewatering of a sludge treatment line from a municipal wastewater treatment plant in Romania. In addition, the present study looked at the variation of the total sulfur content of the various sludge treatment steps.

EXPERIMENTAL PART

Description of the treatment plant and sampling points.

The sewage treatment plant that was analyzed in this study is composed of two treatment lines as follows: water line (A) and mud line (B). On line (A) of the water is performed mechanical and biological treatment. After mechanical treatment, the fats retained in the grease separators and the sludge from the primary treatment are introduced into the sludge stream (B), to the thickener, for energy recovery. The thickened sludge is stabilized anaerobically by fermentation under conditions of mixing and permanent recirculation at temperatures 36-37°C.

The sludge resulting from the biological treatment grouts is mixed with the sludge from the anaerobic digestion of the primary sludge and the mixture is fed to the dewatering station where a sludge with 36% dry matter is obtained, being proper for final elimination by incineration with energy recovery.

Figure 1 shows the main sludge treatment phases. The representative sampling points for the determination of total sulfur and sulfur forms are highlighted (S1-S4).

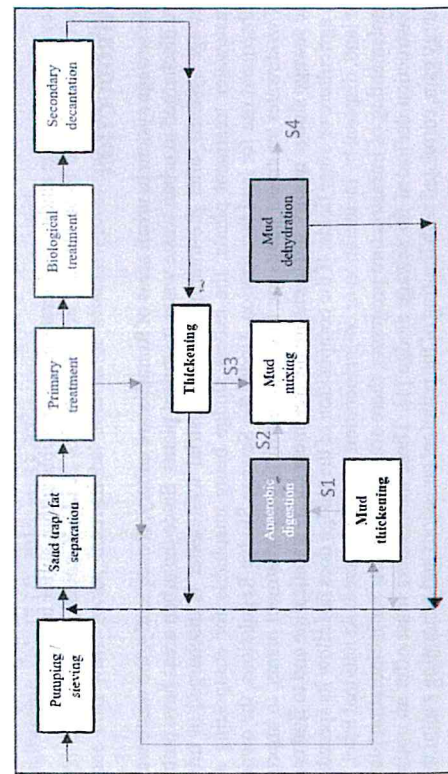


Figure 1 – Flows of the sewage treatment plant

Because one of the objectives of this paper was to study the variation in total sulfur content in different stages of mud treatment on line B and taking into account the technological flows presented above, the following sampling points were established: (S1) and (S2) - represents the sludge before and after anaerobic digestion (S3) is representative of the thickened sludge and (S4) is the sampling point for the mixture of biological sludge and digested dehydrated sludge prior to discharge by incineration.

As a consequence, samples related to this sampling point were also characterized in terms of sulfur forms, namely fuel sulfur (S_c) and sulfur ash (S_A) correlated with total sulfur (S_T). In order to obtain the sulfur (S_c) and (S_A) technological forms, it was necessary to experimentally determine the chemical forms of sulfur, namely total sulfur (S_T), sulphate sulphate, S_{SO4} and mineral sulfur (S_M). With the results obtained, sulfur sulphide (S_S) and organic sulfur (S_O), which are representative of fuel sulfur calculation, can be calculated using the following formulas (1) and (2):

$$S_S = S_M - S_{SO4} \quad (1) \quad S_O = S_T - S_M \quad (2)$$

The sulphate concentration is the sulfur form that burns in the ash, and as a result it can be considered that the experimentally determined sulfate sulfur remains ash in the combustion processes. From a technological point of view, total sulfur is the sum of the fuel sulfur (S_c) and the sulfur in the ash (S_A) and is calculated by the formula (3), [4]:

$$S_T = S_c + S_A \quad (3)$$

Samples preparation.

Sample preparation consists first of all, in homogenization after having been dried in oven at 105°C, using Heratherm OMH 100-S equipment up to obtain the constant mass of sample. Further, milled samples with a Vibratory Disc Mill Retsch RS 200 and screened through a sieve with the size <200 µm. Samples prepared in this way were kept sealed plastic bottles at a temperature of 20 °C until the time of analysis [5].

Figure 2 shows images of the mud samples before and after processing.

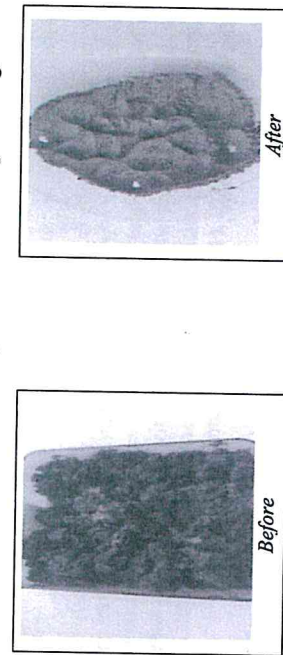


Figure 2 – images of the mud sample before vs. after processing.

Another stage of sample preparation involves the use of suitable methods for the extraction of total sulfur (S_T), sulfur sulphate S_{SO4} and mineral sulfur S_M. Thus, for the Total Sulfur (S_T), the Eschka method and the calorimetric pressure bomb method were used in the presence of oxygen. Sulfur sulfate S_{SO4} and mineral sulfur S_M were extracted by digestion in acids and heating.

The methods used are described in the following:

- **Eschka method:** in a platinum melting pot, mix 1 g of sample and 4 g of Eschka mixture. Samples were burnt at 800 °C in a Notherm B 150 oven. Residues burned from the platinum melting pot and washings were discharged into a 400 ml Berzelius glass. The obtained suspension was treated with concentrated hydrochloric acid to completely dissolve the of the burned residue. The interferences were eliminated by adding ammonia and filtering the solution through medium porosity paper. Have resulted 4 samples (S1), (S2), (S3), (S4) x 5 replicates [4].

- **Calorimetric Bomb Method:** 1 g of the sample was decomposed into a calorimetric bomb at 30 atm pressure in the presence of oxygen. We use Parr 6200 calorimeter. After decomposing the sample, the bomb was washed with distilled water, including cover and electrodes, and the washings were transferred into a 400 ml Berzelius glass. To remove possible residues, the solutions obtained were filtered through medium-porosity filter paper. Finally resulted 4 samples (S1), (S2), (S3), (S4) x 5 replicates, [6], [7].

- **Sulfur sulphate extraction (S_{SO4})** by digestion with hydrochloric acid: 10 g of the sample was weighed into 250 ml Berzelius glasses. Digestion was performed by addition of 20 ml of HCl, 10% and heating on the thermostatic hotplate at 80 °C.

The digested samples were filtered on medium-porosity filter paper and the filter was subsequently washed with warm water until the acid reaction disappeared (check with methyl-orange indicator). In that situation, result 1 sample (S4) x 5 replicates.

- **Extraction of mineral sulfur (Ms) by digestion with HNO₃:** 1 g of sample was weighed into 250 ml Berzelius glass and 100 ml of 20% HNO₃ was added. The samples were kept under gentle boiling for 50 minutes, and after cooling. Were filtered on medium porosity paper which was subsequently washed with warm water until the acidic reaction disappeared (check with methyl-orange indicator). To the filtered solutions were added a few drops of bromine water and evaporated to dryness to remove nitric acid. The resulting residues were wetted with 37% HCl and evaporated again to dryness. 3 ml of HCl and 100 ml of distilled water were added and boiled for a few minutes. In that situation, result 1 sample (S4) x 5 replicates of the mineral sulphur.

Remove interferences for the last two methods described above was similarly done for both sulphate and mineral sulfur. To the samples was added 1 g of ammonium chloride, 2-3 drops of bromothymol blue and ammonia. Samples were boiled for 5 minutes, and filtered through qualitative paper which was subsequently washed with hot water until the chlorine ion disappeared [4].

Determination of sulfur content.

The quantification of the total sulfur content and of the sulphate and mineral sulfur forms was achieved by gravimetric method. Thus, aqueous sulfate anion solutions were evaporated to 200 ml on the thermostatic hot plate, acidified with hydrochloric acid, and 10 ml of 10% BaCl₂ solution was added under continuous stirring. The samples were maintained on a hot plate at 70 °C for 1 hour. After cooling, filtered blue filter paper without ash, and washed with warm water until the chlorine ion disappeared in the filtrate. The sulfur content was calculated by the formula (4):

$$S = \frac{(P - B) \times 13,73}{W} \quad (4)$$

Where:

P = mass of barium sulphate in the analyzed samples;

B = mass of barium sulphate in blank sample;

W = sample mass analyzed;

All the results obtained are related to the dry matter content.

RESULTS AND DISCUSSIONS

Total sulfur content.

The results obtained for the total sulfur content in samples taken (S1), (S2), (S3) and (S4) using the Eschka methods and the calorimetric method are summarized in Table 1 and graphically represented in Figure 3.

Table 1 – Total sulfur content in samples, sampling points (S1), (S2), (S3) and (S4).

S1	Total sulfur, (% dry matter),						
	Eschka method		Calorimetric bomb method				
	S2	S3	S4	S1	S2	S3	S4
0.54	0.86	1.04	1.07	0.54	0.85	0.99	1.02
0.69	0.84	1.20	1.18	0.67	0.82	1.18	1.15
0.72	0.83	1.23	1.20	0.70	0.80	1.20	1.18
0.56	0.82	0.96	1.10	0.56	0.82	0.96	1.09
0.54	0.94	1.16	1.13	0.54	0.88	1.06	1.07

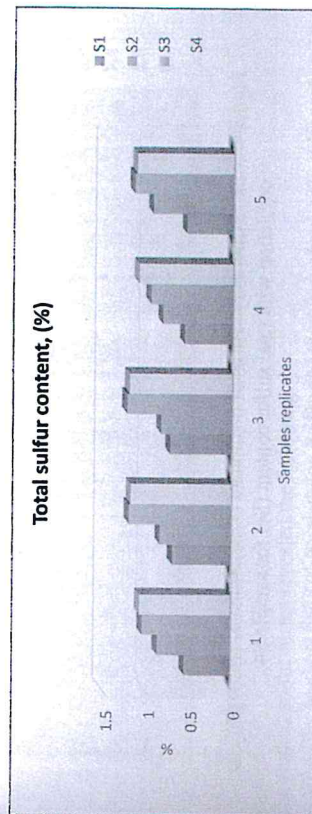


Figure 3 – Total sulfur content (S1), (S2), (S3) and (S4)

The obtained results highlight the following:

- the total sulfur content obtained by two different methods of sample processing is similar, its variation being within the uncertainty range of the methods;
- there is a significant increase in total sulfur content after the anaerobic digestion step. According to literature data, the increase in the total sulfur content expressed in (% d.m.) can be explained by the destruction of the organic material during anaerobic digestion and association with the release of biogas. If the sulfur is not releasably as H₂S in biogas, its concentration in the sludge increases. Sulfur retention in mud may be due to the

presence of iron that binds sulphides and therefore leads to black insoluble precipitations of FeS or FeS₃ [8]. Consequently, the concentration of H₂S released in biogas and the sulphide concentrations remaining in the digested mud depend very much on the technological process.

Chemical forms and technological forms of sulfur in the mud proposed for incineration.

The results obtained experimentally for S sulphate and mineral sulfur content in the sample (S4) are centralized in Table 2 and represented graphically and Figure 4, in accordance with the total sulfur content.

Table 2 – The results obtained for sulfur chemicals forms for sample (S4)

Total sulfur (S _T) (%, d.m.)	Mineral sulfur (S _M) (%, d.m.)	S sulphate (S _{SO4}) (%, d.m.)
1.07	0.87	0.14
1.18	0.91	0.16
1.20	0.93	0.18
1.10	0.79	0.15
1.13	0.91	0.13

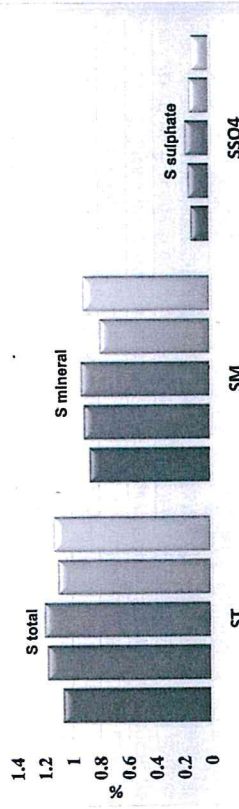


Figure 4 – Experimentally results of S sulphate (S_{SO4}), mineral sulfur (S_M), in correlation with total sulfur content (S_T) for sample S4

With the results obtained experimentally for S sulphate (S_{SO4}) and mineral sulfur (S_M), the sulfur sulphide (S_S) and organic sulfur (S_O) forms were calculated to estimate the sulfur for combustion. For calculations, formulas (5) and (6) were used and the results are centralized in Table 3.

Table 3 – Concentrations of sulfur sulfide (S_S) and organic sulfur calculates (S_O)

Sulfur sulfide (S _S) (%, d.m.)	Organic sulfur (S _O) (%, d.m.)
0.73	0.20
0.75	0.27
0.74	0.27
0.64	0.31
0.78	0.22

The technological forms of sulfur are represented by the sulfur content of fuel, sulfur content from ash and total sulfur. Fuel sulfur (S_c) is the amount of sulfur capable of burning and therefore consists of sulfur sulfide (S_s) and organic sulfur (S_o). Sulfur content in ash (S_A) is the amount of sulfur left in ash after combustion of fuels and was estimated by formula (6). Total Sulfur [S_T] represents the total amount of sulfur in the fuels. The estimation of the technological sulfur forms was based on formulas (5) and (6). The results are centralized in Table 4 and represented graphically in Figure 5.

$$S_c = S_s + S_o \quad (5) \quad S_T = S_{Sc} + S_A \quad (6)$$

Table 4 – Combustion sulfur concentrations calculates for sample S4

Total sulfur (S _T) (%, d.m.)	Sulfur for combustion (S _c) (%, d.m.)	S sulphate (S _{SO4}) (%, d.m.)
1.07	0.93	0.14
1.18	1.02	0.16
1.20	1.01	0.18
1.10	0.95	0.15
1.13	1.00	0.13



Figure 5 – Technological form of sulfur concentrations for sample S4

The studied sulfur forms revealed the following:

- total sulfur is about 88% of combustion sulfur and therefore about 12% sulfur sulphate.
- combustion sulfur is predominantly made up of sulfur sulphide (approximately 65%) and organic sulfur (approximately 35%).

CONCLUSIONS

The presence of sulfur in sewage sludge has significant implications in incineration processes due to its transformation at high temperature into SO₂ which is released into the atmosphere, and on the other hand, there is a risk of high-temperature corrosion of the pipes and pumps, depending of the molar ratio 2S/Cl.

In the present study the variation of the total sulfur content (S_T) in various stages of treatment of a sludge at a municipal wastewater treatment plant was analyzed, after which the technological forms of sulfur combustible (S_c), sulfur from ash (S_A) and total sulfur

(S_T) in the sludge obtained after the dehydration step in order to achieve the elimination by incineration.

Considering the values obtained for the total sulfur content in the sludge treatment stages, these have revealed a significant increase of the total sulfur content after the anaerobic digestion step (sample S₂), which can be explained by the fact that anaerobic digestion takes place the destruction of organic material associated with the release of biogas.

For the estimation of the sulfur technological forms, experimental determination of the chemical forms of sulfur sulfate (S_{SO4}) and mineral sulfur (S_M) was necessary. With the obtained results the sulfur sulphide (S_S) and organic sulfur (S_O) forms, necessary for the estimation of the sulfur for combustion, were calculated. Sulfur from ash (S_A) was calculated as the difference between total sulfur (S_T) and combustion sulfur (S_C). From the results obtained, it is observed that the total sulfur in the sample is represented by approximately 88% sulfur for combustion and 12% sulfur sulphate.

ACKNOWLEDGMENTS

This work was carried out through the "Program Nucleu", financed by the Ministry of Research and Innovation, project code: PN 16.25.01.13.

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ECONOMY OF PACKAGING AND WASTE FROM PACKAGING ON THE EXAMPLE OF THE WOOD INDUSTRY

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ABSTRACT

In recent years, the packaging market has become an important element of the economy of many countries. Its growing importance is associated with rapid industrial development, globalization, free transfer of goods and growing demand from consumers. Customer requirements affect the growing demand for more functional, colorful, light, flexible, ecological and environmentally safe packaging. Currently, the packaging has become an element that in many cases determines the demand for a given product. In particular, this applies to households. Industrial packaging is also a very important part of the packaging market. In most cases, their task is to adequately protect the product during transport.

In recent years, Poland has become one of the largest producers of various types of packaging in Europe. This industry is equipped with modern means of production and uses the latest technologies. The dynamically developing industry favours the production and sale of an enormous amount of packaging for the domestic and European market. However, this production results in a huge amount of waste that has a negative impact on the natural environment. That is why Poland, as a member state of the European Union, was obliged to conduct an effective policy against excessive packaging waste.

The article characterizes the global packaging market and the waste generated from it. Waste management from packaging was discussed, focusing in particular on waste from industrial packaging. In the group of industrial waste, wooden and wood-based packaging is of great importance and it should be used and reused as much as possible. Legal conditions, apart from various economic aspects are of great importance in the process of waste management. For this reason, the analysis of legal acts regulating the waste management market was presented in this work. Based on the acquired data, structural analysis of the waste, with particular reference to wood waste, was made. This article also presents data from one of the companies dealing with the production and management of waste from wooden packaging. The obtained data show that the management of waste from wooden packaging can be economically viable and very beneficial for the natural environment.

This work should be treated as a voice in the discussion on the protection of the natural environment and improve the environmental awareness of the society. Currently, all types of waste are a big economic and social problem. For some industries this particular problem may be an important barrier to their development.

Keywords: packaging, waste, economy, recycling, wood industry