Sebastian WERLE[1*] and Mariusz DUDZIAK[2]

CHEMICAL ANALYSIS OF QUALITY OF THE DRIED SEWAGE SLUDGE AND SOLID WASTE-PRODUCTS AFTER GASIFICATION PROCESS

CHEMICZNA ANALIZA JAKOŚCI WYSUSZONYCH OSADÓW ŚCIEKOWYCH ORAZ PRODUKTÓW STAŁYCH POWSTAJĄCYCH W PROCESIE ICH ZGAZOWANIA

Abstract: This paper presents the results of chemical analysis of the quality of solid waste products (ash, char coal) obtained during gasification of dried sewage sludge. The sewage sludge originated from two different wastewater treatment systems: mechanical-biological system and mechanical-biological-chemical system with simultaneous precipitation of phosphorus. In both cases, sewage sludge was subjected to anaerobic digestion and dewatering process prior to drying. The gasification of the sewage sludge was performed in the system which is equipped with a fixed-bed reactor using air as the gasifying agent having a temperature of 298 K, and using the amount of the gasifying agent corresponding to the excess air ratio (λ) of 0.18. The ash or char coal were analyzed, among others, for the content of: alkali metals, phosphorous, sulfur, magnesium, calcium and various heavy metals. The obtained results were referred to the composition analyses of inorganic substances present in the fuel before it was subjected to the process of gasification. The influence of heat treatment on the transport of the investigated compounds was studied in the following sequence: dried sludge – gasification – solid waste. Based on the obtained results it was shown that the gasification process promotes migration of certain substances such as zinc or phosphorus from the sludge into the solid phase formed after the heat treatment of the sludge. The potential for further use of the solid by-products generated during the gasification of sewage sludge was presented in the conclusions of the study.

Keywords: sewage sludge, gasification, solid waste products, inorganic compounds

Gasification is considered to be a promising method for the disposal of sewage sludge. This process, apart from a valuable gas fuel, generates solid and liquid waste

[1] Institute of Thermal Technology, Silesian University of Technology, ul. Konarskiego 22, 44–100 Gliwice, Poland, phone: +48 32 237 29 83, fax: +48 32 237 28 72, email: sebastian.werle@polsl.pl

[2] Institute of Water and Wastewater Engineering, Silesian University of Technology, Konarskiego 18, 44–100 Gliwice, Poland, phone: +48 32 237 16 98, fax: +48 32 237 10 47, email: mariusz.dudziak@polsl.pl

* Corresponding author: sebastian.werle@polsl.pl

by-products. The former are generated as a result of the transition of the mineral substance into the solid phase [1–4]. Those solid by-products are primarily ashes, and in special cases also char coal [2]. The formation of char depends on the composition of non-combustible inorganic substances in the sludge resulting in a significant reduction in the characteristic temperatures of ash [5]. Liquid waste products, such as tars, are generated as a result of condensation of the impurities present in the gas.

The parameters of the process the gas produced during gasification of sewage sludges were previously discussed by the authors of the this paper in [5, 6]. The gas produced by the gasification of the sewage sludges originating from various wastewater treatment systems was analysed for the volume fraction of nitrogen, oxygen, carbon monoxide, hydrogen, carbon dioxide and methane. It was determined that the volume fraction of the main combustible components of the gas, i.e. carbon monoxide and hydrogen is greater in the case of the gasification of the sewage sludge which originated from the mechanical-biological wastewater treatment plant operating in the mechanical--biological system as compared to the sludge from the mechanical-biological-chemical wastewater treatment system with a simultaneous precipitation of phosphorus. It was also shown that the parameters of the process gas depend on the process conditions. The most important factors include the amount and temperature of the gasifying agent.

Sewage sludge, apart from energetically favourable compounds, is the source of toxic and hazardous organic and inorganic contaminants. Organic compounds identified in it include [7–10]: dioxins and furans, polychlorinated biphenyls, chlooroorganic pesticides, adsorbed and extracted chloro derivatives, polycyclic aromatic hydrocarbons, phenols and their derivatives, phthalates, sex hormones and others. The group of hazardous inorganic compounds assayed in sewage sludge contains primarily various heavy metals occurring over wide ranges (mg/kg d.m. for raw sewage) [11–17]: arsenic 3–230, cadmium 1–3410, chromium 10–990000, copper 80–2300, nickel 2–179, lead 13–465, zinc 101–49000. Based on this information it can be assumed that sewage sludge gasification by-products can be also contain mentioned above toxic and harmful substances.

The preliminary research [18] found that the toxic effect of the products produced during sewage sludge gasification depends on both the type of a sample tested (ash, char coal, tar) and sewage sludge used. The research was carried out, using a Microtox® test with *Vibrio fisheri* bacterial strain (luminescence method). Higher toxicity was found in the samples of ash that formed during gasification of sewage sludge, which appeared to be more toxic, than for the sludge of lower toxicity. As for the tar samples, they were all toxic regardless of the sludge gasified. Thus, from the cognitive perspective, the characteristics of such samples in terms of different contaminants which might be responsible for their toxicity are significant.

This paper presents the results of the comparative chemical analysis of the quality of dried sewage sludges and solid waste products (ash, char coal) obtained during the gasification of dried sewage sludge. The investigation of the transport of inorganic substances (alkali metals, phosphorus, sulfur, magnesium, calcium and various heavy metals) in the following sequence: dried sewage sludge – gasification – solid waste, is important both for the assessment of the ecological risks and the potential for their further application (valorization and recovery).

Materials and methods

Two different sewage sludges, which were selected for the study, originated from wastewater treatment plants situated in Poland. Sewage sludge 1 originated from a wastewater treatment plant operated as a mechanical-biological system, and sewage sludge 2 originated from a mechanical-biological-chemical wastewater treatment system with simultaneous phosphorus precipitation. The sludges generated in the wastewater treatment plants are subjected to anaerobic digestion and next after dewatering are dried in a cylindrical dryer on the shelves heated to 533 K (sewage sludge 1) and using hot air of a temperature of 423 K in a belt dryer (sewage sludge 2). In the end, the resulting sewage sludge 1 was in the form of granulate, and sewage sludge 2 was in the form of irregularly cut "noodles" (Fig. 1).

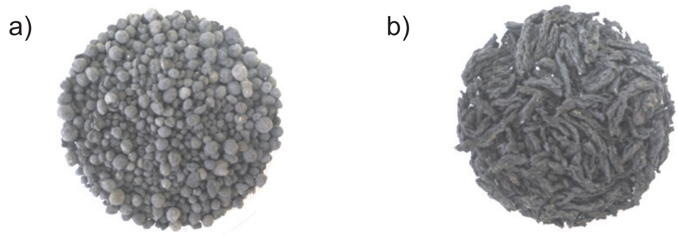

Fig. 1. Sewage sludge analyzed: a) No. 1; b) No. 2

The studied sewage sludges were gasified in the system equipped with a fixed-bed reactor (Fig. 2) using air as the gasifying agent having a temperature of 298 K, and using the amount of the gasifying agent corresponding to the excess air ratio (λ) of 0.18. The applied gasifier was designed as a counter-current system operated under low overpressure generated by an air forced-draught fan. The main element of the installation is the gasification reactor with an inner diameter of d_w = 150 mm and a total height of H = 250 mm. The maximum mass of the feedstock consisting of the dried sewage sludge is m_{pal} = 5 kg. The sewage sludge is introduced into to the reactor from the sludge tank through the top of the reactor. The gasifying agent is introduced through the bottom of the reactor. The fuel moves through the reactor in a countercurrent direction and through the successive zones: drying, pyrolysis, reduction and combustion. The moisture is evaporated in the drying zone. In the pyrolysis zone, the sludge is subjected to thermal conversion into the volatile fractions and the solid form. In the reduction zone, carbon is transformed and carbon monoxide and hydrogen are produced. Those compounds are the main components of the combustible gas produced in the gasification process. Combustion of the remaining solid part occurs in the combustion zone leading to heat production. The produced heat is then used in endothermic reactions occurring in the upper zones. The gasification reactor does not have an automatic fuel feeding system, however, it is not a type of sequencing batch reactor type (termed as 'batch reactor') in which a single batch of fuel is gasified from start to finish. During the measurements, the reactor was fed by an additional amount of

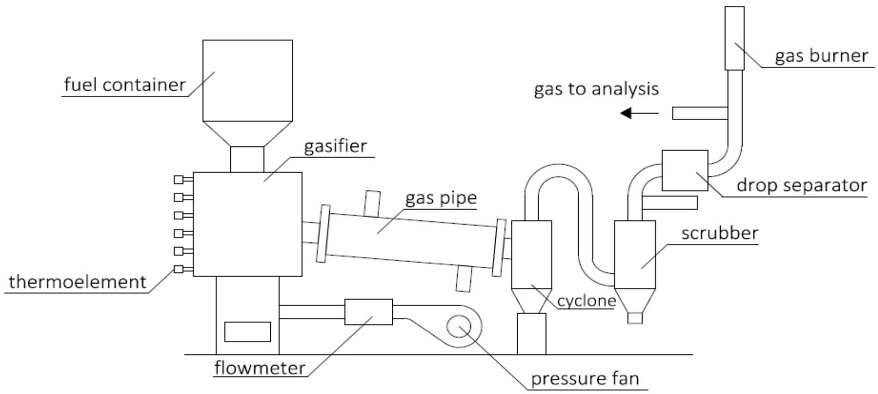

Fig. 2. Fixed bed installation

fuel by ejection of successive baffles located in the fuel tank. This was aimed to maintain the operating conditions, which would be similar to the conditions occurring in the industrial installation. The rate of fuel gasification allowed for manual addition of a specified amount of granulates/noodles, which occurred periodically when the air supply was stopped. This temporary suspension of the air supply was not found to significantly lower the internal temperature of the gasifier. After refueling, and reintroducing the air, the gasifier was restarted. The observed decrease in the internal temperature of the reactor was mainly caused by the imbalance of the system upon the addition of the fuel.

The effect of the gasification parameters on producer gas yield, its composition and calorific value in particular, are discussed in detail in [5, 6]. As far as the by-products are concerned (Fig. 3), the gasification of sewage sludge 1 produced both ash (taken from the ash-pan) and char coal (taken from the inside of the reactor), while sewage sludge 2 produced ash only. Char coal existing in the case of sewage sludge number 1 was caused by the composition of the inorganic, non combustible substance in sewage sludge which can decrease fusion temperatures of ash [5].

Chemical analysis of the quality of the dried sewage sludge and the solid products formed in the process of gasification included an assessment of the content of the primary elements (carbon, hydrogen, nitrogen, chlorine, fluorine, sulfur, and oxygen), alkali

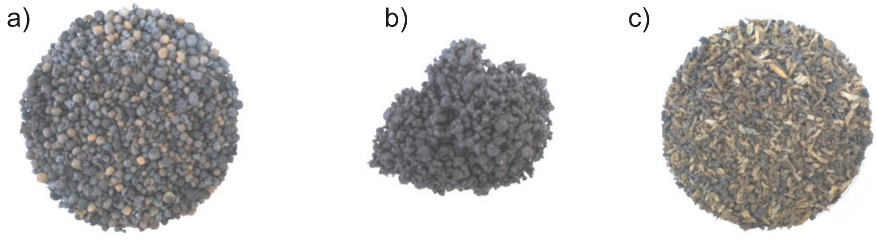

Fig. 3. By-products of sewage sludge gasification: a) ash and b) char coal from sewage sludge no 1 and ash c) from sewage sludge 2

metals, phosphorus, magnesium and calcium (mineral elements) as well as selected heavy metals. The content of the primary elements was determined automatically by IR analyzer. On the other hand, the content of mineral elements and heavy metals in the test samples was determined by means of absorption or plasma spectrometry.

In the previous studies the following parameters of the sewage sludges subjected to the gasification were determined: moisture content, volatile substances and ash content, heat of combustion and calorific value. The content of moisture, volatile substances and ash were determined by gravimetric method described in these standards: PN-EN 14774-3:2010, EN 15402:2011 and EN 15403:2011, respectively. In contrast, the heat of combustion was determined by calorimetric method, and the calorific value was calculated using the mass fractions of the main elements in the sample. The determined sludge properties are shown in Table 1

Table 1

Sewage sludge properties

Analysis and test feature		Sewage sludge	
		No 1	No 2
Proximate analysis, [%] (as received)*	Moisture	5.30	5.30
	Volatile matter	51.00	49.00
	Ash	36.50	44.20
Ultimate analysis, [% d.m.]	C	31.79	27.72
	Cl	0.22	0.03
	F	0.013	0.003
	H	4.36	3.81
	N	4.88	3.59
	O (by difference)	20.57	18.84
	S	1.67	1.81
Mineral components contents, [% d.m.]	Ca	10.87	16.02
	K	1.34	0.77
	Mg	2.10	1.37
	Na	0.56	0.73
	P	9.07	6.19
Heavy metal contents, [mg/kg d.m.]	As	4.19	3.94
	Cd	6.47	3.24
	Cr	180.53	584.53
	Cu	495.30	183.16
	Hg	0.99	0.96
	Ni	103.67	18.90
	Pb	119.30	59.97
	Se	9.84	1.70
	Zn	920.90	991.20
Calorific value [d.m.]*	HHV, MJ/kg	14.05	11.71
	LHV, MJ/kg	12.96	10.75

* Based on the works [5, 6].

Results and discussion

The comparison of the tested sewage sludges allow for conclusion that sewage sludge 1 has higher calorific value than sewage sludge 2 (Table 1). This was confirmed by the study of gas composition and its calorific value presented in [5–7]. The primary contamination of the tested sewage sludges by inorganic substances varied in terms of mass fraction of individual elements, including heavy metals (Table 1, Fig. 4 and 5). For example, the content of three (potassium, magnesium, phosphorus) of the five tested mineral elements (calcium, potassium, magnesium, sodium, phosphorus) was higher in sewage sludge 1 than in sewage sludge 2. Also, in the case of heavy metals, it was observed that the content of seven (arsenic, cadmium, copper, mercury, nickel, lead, selenium) of the nine analyzed heavy metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium, zinc) was higher in sewage sludge 1 than in sewage sludge 2. The total content of heavy metals in the sewage sludges was, however, similar and was equal to 1841 mg/kg d.m. for sewage sludge 1 and 1848 mg/kg d.m. for sewage sludge 2. It is noteworthy that sewage sludge 2 had 3-fold higher chromium concentration as compared to sewage sludge 1, which could cause its toxicity. This phenomenon was described previously in [18].

As it was mentioned above, two types of solid by-products are produced in the case of the gasification process for sewage sludge 1, this is, ash and char coal. Based on the results of chemical analysis it was determined that the mass fraction of phosphorus and calcium in the generated solid products was greater than for the sewage sludge sample prior to the heat treatment, with the greatest accumulation observed in the char samples (Fig. 4a). A similar trend was observed in the case of sewage sludge 2 and the ash produced during gasification of this sludge (Fig. 4b). Similar effects are given in paper [19] which points out that phosphorus concentration in the ash formed after sewage

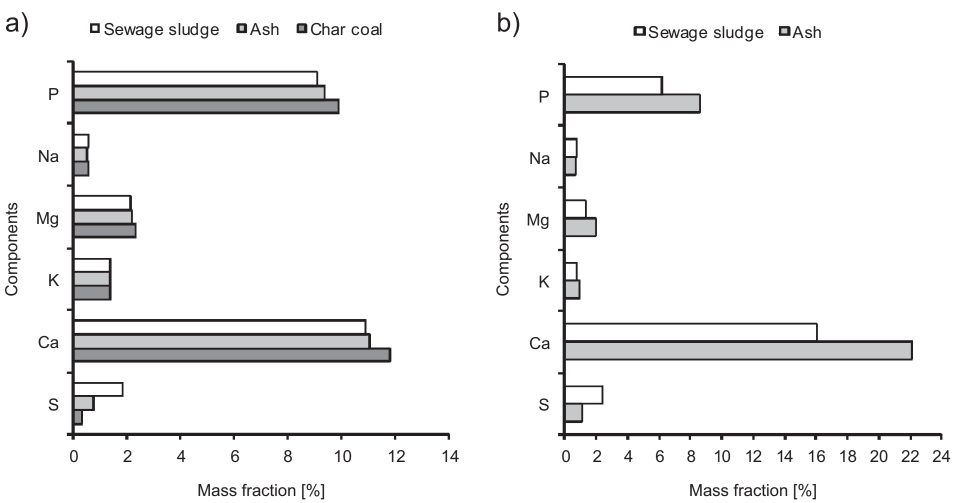

Fig. 4. Mass fraction of the selected components in sewage sludge a) No. 1; b) No. 2 and in solid waste gasification products

sludge gasification increased from 14.1 mg/kg d.m. to 20.6 mg/kg d.m. (an increase by 68 %).

Also in the case of heavy metals it was shown that their concentration was higher in the ash and char coal samples than in the sludge samples (Fig. 5a–d). This observation was valid for seven (arsenic, cadmium, copper, mercury, nickel, lead, selenium) of the nine analyzed heavy metals (arsenic, cadmium, chromium, copper, mercury, nickel, lead , selenium, zinc) regardless of the type of sewage sludge. Similar conclusions were drawn by the authors of paper [12] who found an increase in the concentrations of

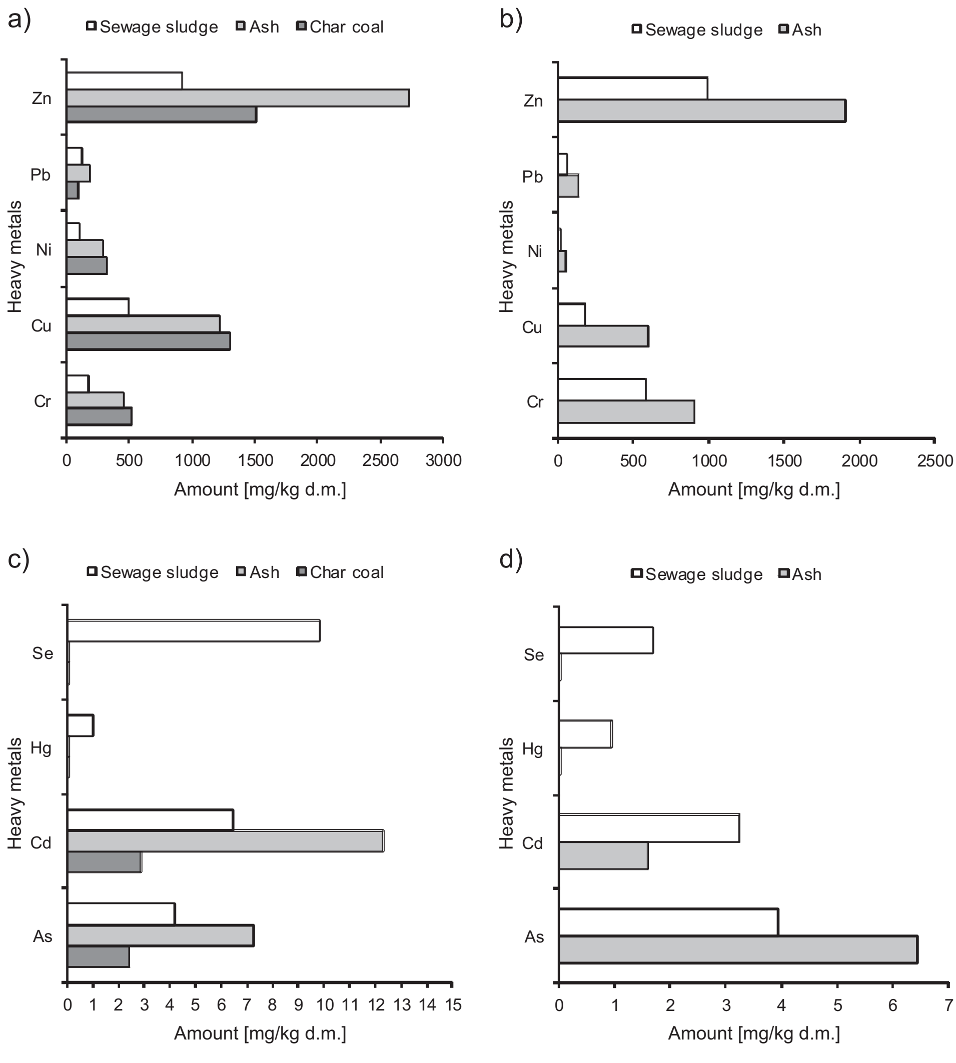

Fig. 5. Amount of the selected heavy metals in sewage sludge and in solid waste gasification products (no 1 – a and c, no 2 – b and d)

cadmium (from 0.93 to 1.67 mg/kg d.m.), chromium (from 80.82 to 247.95 mg/kg d.m.), copper (from 580.36 to 922.14 mg/kg d.m.), lead (from 78.27 to 125.09 mg/kg d.m.) and zinc (from 402.09 to 637.50 mg/kg d.m.) in sewage sludge and ash samples after gasification. The difference was observed, however, in the extent of accumulation of the heavy metals in the solid products. For example, in the case of the zinc concentration in the samples of the ash generated in the gasification process it was observed that it increased 2-fold for sewage sludge 2, and 3-fold for sewage sludge 1.

The presence of heavy metals in solid products generated during the gasification of sewage sludge has a potential impact on their use or disposal. It is commonly known that one of the main obstacles to agricultural use of sewage sludge is the high content of heavy metals, which can be transferred from sludge to the soil environment causing pollution [15]. This rule will also apply to the feasibility assessment of the application of sewage sludge gasification by-products. Taking into consideration the increase of the concentration of heavy metals in solid products formed during the gasification of sewage sludge, which was evidenced by the presented results, it should be noted that there is an ecological risk associated with this type of waste. It is mainly due to the presence of chromium. This was confirmed by the results of toxicity tests for these samples, which were presented in previous studies [18].

The analysis of heavy metals contamination of by-products and sewage sludges subjected to gasification allows for assumption that the generated process gas will be only slightly contaminated by these substances. Most of the inorganic substances initially present in the sludge gasified in a fixed-bed reactor accumulate in the solid by-products generated during the process. For this reason, the sewage sludge gasification technology (implemented in a fixed-bed reactor) is competitive with other methods used for this purpose. Because of that, for example, during combustion of sewage sludge in a fluidized bed boiler a higher concentration of heavy metal is observed in the fly ash than in the so-called bottom ash [20], which consequently causes the possibility of the emission of these pollutants into the environment.

The authors suggest that further research should concentrate on the recovery of phosphorus from solid products (ash and char coal) formed during the gasification of sewage sludge e.g. through leaching phosphorus from ash or sinter with mineral acids. The application of ash resulting from gasification to the sorption of toxic and hazardous compounds (e.g. heavy metals) from different sewage is also worth considering. Similar research has already been carried out, using dried sewage sludge [21, 22].

Conclusion

Based on the results of the study it was shown that the gasification process promotes migration of certain inorganic compounds, such as zinc or phosphorus from the sludge into the solid phase formed after the heat treatment of the sludge. This phenomenon depended both on the type of solid by-product (ash, char) and the used sludge. Taking this into consideration, the future research direction is to study the recovery of phosphorus from solid products generated during the gasification of sewage sludge, for example, by leaching of phosphorus from the ash or char by mineral acids. On the other hand, this study evidenced large accumulation of heavy metals, mainly chromium, in the analyzed solid by-products. This indicates the ecological threat posed by this type of waste, which can potentially be toxic. However, it can be attempted to use the gasification ash for the sorption process of toxic and hazardous compounds (e.g. heavy metals) from various kinds of wastewater.

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[1] Instytut Techniki Cieplnej
[2] Instytut Inżynierii Wody i Ścieków
Politechnika Śląska w Gliwicach

Abstrakt: W pracy przedstawiono wyniki analiz chemicznych jakości stałych produktów odpadowych (popiół, spiek) uzyskanych podczas zgazowania wysuszonych osadów ściekowych. Osady ściekowe pochodziły z dwóch różnych układów oczyszczania ścieków, tj. mechaniczno-biologiczny i mechaniczno-biologiczno-chemiczny z symultanicznym strącaniem fosforu. W obu przypadkach przed procesem suszenia osady ściekowe poddawano fermentacji i odwodnieniu. Proces zgazowania osadów ściekowych prowadzono w instalacji wyposażonej w reaktor ze złożem stałym przy użyciu powietrza jako czynnika zgazowującego o temperaturze 298 K oraz stosując ilość czynnika odpowiadająca stosunkowi nadmiaru powietrza (λ) 0,18. Analiza obejmowała ocenę zawartości w popiele, czy też spieku m.in. metali alkalicznych, fosforu, siarki, magnezu, wapnia, a także różnych metali ciężkich. Otrzymane wyniki odniesiono do analiz składu substancji nieorganicznej występującej w paliwie przed poddaniem go procesowi zgazowania. Przeanalizowano wpływ obróbki termicznej na transport badanych związków na drodze: wysuszony osad ściekowy – proces zgazowania – stały produkt odpadowy. Na podstawie wyników badań wykazano, że proces zgazowania promuje migrację niektórych związków, jak na przykład fosforu czy też cynku z osadu ściekowego do fazy stałej powstałej po obróbce termicznej tego osadu. We wnioskach pracy przedstawiono również potencjalne możliwości dalszego wykorzystania stałych produktów ubocznych powstających podczas zgazowania osadów ściekowych.

Słowa kluczowe: osady ściekowe, zgazowanie, stałe produkty uboczne, związki nieorganiczne