Influence of pyrolysis on evaporation and solubility of heavy metals in sewage sludge

O M Larina and V M Zaichenko
Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow 125412, Russia
E-mail: olga.m.larina@gmail.com

Abstract. One of the sewage sludge characteristics is the presence of various pollutant types. This is both pathogenic microflora and chemical pollutants. For example, it is heavy metals. When using the pyrolysis process up to $800 \, ^\circ C$ with thermal cracking of volatile products, as a method of sewage sludge treatment, in addition to synthesis gas a solid residue is formed. It is about 40% by weight of the initial sewage sludge and has an ash content of 58.2% (on dry state). With this amount of ash, the use of solid residue for energy purposes is not appropriate. Such material is subject to disposal. In this connection, the question arises, what proportion of heavy metals remains in the solid residue and goes into syngas. This paper presents the study results of the effects of pyrolytic processing conditions on the behavior of heavy metals in the composition of sewage sludge. The gross content and solubility in neutral and acidic media of heavy metals in the sewage sludge and the solid residue after pyrolysis are determined. The hazard class according to the content of heavy metals of the sewage sludge and the solid residue is calculated.

1. Introduction

The problem of processing sewage sludge is one of the main from the standpoint of improving the environmental situation. European countries have Directive 2008/98/EC of the European Parliament, according to which the methods of recycling and disposal of sewage sludge should be given preference over dumping [1]. By 2020, the share of biodegradable waste to be dumped should not exceed 35% [2]. In Russia, the need to develop technologies for processing sewage sludge at the legislative level is not fixed, but it is obvious that the issue of using organic waste as secondary energy resources should be given priority [3].

Currently, there is a method of two-stage thermal conversion of sludge into synthesis gas, which is based on the pyrolysis of sewage sludge to $800 \, ^\circ C$, followed by thermal cracking of volatile products on ceramics at a temperature of $1000 \, ^\circ C$ [4]. The sewage sludge has one feature that distinguishes it from other types of biomass. In the elemental composition the oxygen content is two times lower than carbon [5]. For other types of biomass, this value does not exceed 1.6 [6]. This difference leads to the fact that the ratio of the volume fraction of $H_2$ to this of CO in the composition of syngas is $2 : 1$ [4], which is the optimal value for the production of methanol [6].

As a result of such treatment, a solid residue is formed, which is 38% from the mass of the initial sewage sludge [4]. The lower calorific value of it is 13.5 MJ/kg, ash content is 58.3%. With such characteristics the main option for further use of such solid residue is dumping.
Table 1. The total content of heavy metals (all values in mg/kg) in sewage sludge from Podolsk waste treatment facilities.

| Metal | Content  | MAC    | APC    | Background |
|-------|----------|--------|--------|------------|
| Cu    | 160 ± 40 | —      | 33–132 | —          |
| Mn    | 120 ± 29 | —      | —      | —          |
| Cd    | 0.64 ± 0.29 | —      | —      | 0.5–2.0   |
| Co    | 1.7 ± 0.7 | —      | —      | 3–15       |
| Ni    | 28.1 ± 9.6 | —      | 20–80  | —          |
| Pb    | 16.2 ± 5.8 | 32     | —      | —          |
| Zn    | 890 ± 230 | —      | 35–220 | —          |

Sewage sludge is characterized by the presence in composition of various kinds of pollutants, among which there are heavy metals. The gross content of heavy metals in the sewage sludge from the Podolsk waste treatment facilities, which was used as a raw material in [4], is presented in table 1.

In Russia, the Ministry of Natural Resources and Ecology controls the gross content of nine heavy metals in the soil. They are Mn, Pb, Cd, Cu, Ni, Zn, Co and Cr. The maximum allowable concentration (MAC) are set for V, Mn and Pb [7]. The approximate permissible concentration (APC) are set for Cd, Cu, Ni and Zn [8]. The standards for Co and Cr are absent, therefore the degree of soil pollution is estimated as fourfold excess of the background level [9].

GOST 17.4.1.02-83 divides metals into hazard classes for soil condition. The most dangerous class (first) includes cadmium, lead and zinc. Cobalt, nickel and copper belong to the second class. Magnesium is third class.

In this paper, a series of studies aimed at determining the behavior of heavy metals in the two-stage thermal conversion of sewage sludge into synthesis gas were carried out. The gross content and solubility of heavy metals contained in the initial sewage sludge and the solid residue after pyrolysis were determined. The class of hazard according to heavy metal content of the initial sewage sludge and solid residue after pyrolysis was calculated.

2. Determination of the gross heavy metal content in the sewage sludge and solid residue after pyrolysis

To study the behavior of heavy metals in the pyrolysis process, samples of the initial sewage sludge and the solid residues after pyrolysis were taken. The first sample of the solid residue corresponded to a pyrolysis temperature of 250 °C and the mass loss of the raw material of 23%. The second sample of that corresponded to a pyrolysis temperature of 800 °C and a mass loss of 63%. The results of the analyzes are presented in table 2.

To determine the behavior of heavy metal during pyrolysis, it is advisable to compare the data on their content in the solid residue according to results of analysis (tables 1 and 2) and the results of a calculation performed under the assumption that metals do not evaporate from the sewage sludge during pyrolysis (figure 1).

For a mass loss of 23% the calculated and real values of the heavy metal content in the solid residue coincide within the error limits of the method of conducting the study. At this pyrolysis temperature metals remain in the solid residue.

For a mass loss of 63% the calculated values of the copper, manganese, cobalt, nickel and lead contents in the solid residue coincide with the real values within the limits of error. The calculated content of zinc is at the boundary of the error for experimental value, which indicates
Table 2. The total content of heavy metals (all values in mg/kg) in solid residue after pyrolysis at different temperatures.

| Metal | 250 °C | 800 °C  |
|-------|--------|---------|
| Cu    | 200 ± 51 | 380 ± 95 |
| Mn    | 140 ± 36 | 310.0 ± 77.5 |
| Cd    | 0.78 ± 0.36 | < 0.5 |
| Co    | 2.6 ± 1.1 | 5.55 ± 2.33 |
| Ni    | 36 ± 12 | 94.50 ± 24.57 |
| Pb    | 22.2 ± 8.0 | 46.00 ± 16.56 |
| Zn    | 1200 ± 300 | 1950 ± 507 |

Table 3. Melt and boiling temperatures of heavy metals (all values in °C).

| Metal | Melting | Boiling |
|-------|---------|---------|
| Cu    | 1083    | 2595    |
| Mn    | 1244    | 2097    |
| Cd    | 321     | 767     |
| Co    | 1493    | 3100    |
| Ni    | 1452    | 2000    |
| Pb    | 327     | 1737    |
| Zn    | 419.5   | 906     |

its partial evaporation during pyrolysis. The actual cadmium content in the solid residue from pyrolysis at 800 °C is significantly lower than the calculated one. From which it can be concluded that cadmium is evaporated during heating or is carried away by pyrolysis gases. The melting and boiling points of the heavy metals are presented in table 3.

From the data presented in the table, it follows that low-melting metals include cadmium, lead and zinc. At the same time, the boiling point for Zn and Pb is higher than the pyrolysis temperature. Lead, the boiling point of which is much higher than the pyrolysis temperature, according to the results of the analysis, remained completely in the solid residue from pyrolysis. The melting point of zinc is lower, and its boiling point is higher than the pyrolysis temperature. The location of the calculated zinc content value at the error boundary for experimental value may indicate that the process of its evaporation is not intensive enough and the main part of zinc remains in the solid residue. Melting and boiling points for Cd are lower than 800 °C, which leads to the evaporation of a significant part of this metal from the sewage sludge during the pyrolysis process. The results presented in [10] also confirm the fact that cadmium is released during the sewage sludge pyrolysis and the temperature of evaporation start is below 600 °C.

Thus, during the pyrolysis of sewage sludge to 800 °C, all heavy metals remain in the solid residue, except cadmium. To reduce the amount of cadmium escaping from the sewage sludge during pyrolysis, the process temperature should be reduced to 500 °C. But in this case it is necessary to control the ratio of the volume fraction of H₂ to this of CO in the composition of the synthesis gas, since, as mentioned earlier, the main goal of the two-stage thermochemical processing of sewage sludge is the production of syngas for methanol synthesis.
Figure 1. Dependence of the content of heavy metals in sewage sludge on the mass loss during pyrolysis.
Table 4. Danger level coefficient of waste component ($W_i$), danger level indicator of waste component in sewage sludge ($K_{0i}$) and in solid residue after pyrolysis at 250 ($K_{1i}$) and 800 °C ($K_{2i}$) as well as in waste at large ($K$).

| Metal and $K$ | $W_i$ (mg/kg) | $K_{0i}$ | $K_{1i}$ | $K_{2i}$ |
|---------------|---------------|----------|----------|----------|
| Cu            | 358.9         | 0.45     | 0.56     | 1.06     |
| Mn            | 537.0         | 0.22     | 0.26     | 0.58     |
| Cd            | 26.9          | 0.02     | 0.03     | 0.02     |
| Co            | —             | —        | —        | —        |
| Ni            | 128.8         | 0.22     | 0.28     | 0.73     |
| Pb            | 33.1          | 0.49     | 0.67     | 1.39     |
| Zn            | 463.4         | 1.92     | 2.59     | 4.21     |
| $K$           | 3.80          | 4.97     | 8.54     |

3. Determination of hazard class on heavy metal content of sewage sludge and solid residue after pyrolysis

The hazard class of the waste is determined by the degree of its possible adverse environmental impact. There are five hazard classes in total. The first class includes extremely hazardous waste. When it is introduced into the soil the ecological system is irreversibly disturbed. The fifth class includes practically non-hazardous waste, the ecological system practically does not suffer when it is introduced into the soil. The calculation of the hazard class was carried out according to the method described in [11].

The hazard class of waste is characterized by an environmental hazard level indicator of $K$. The value of $K$ is calculated as the sum of danger level indicator of individual components of the waste $K_i$. The $K_i$ is calculated as the ratio of the gross waste component content to the danger level coefficient of waste component $W_i$ (mg/kg). The value of $W_i$ for heavy metals is taken from literary sources. Danger level indicator of waste component and waste at large are presented in table 4.

With growth of mass loss both danger level indicator of waste component and waste at large increases. To assign a waste to the fifth class of hazard, it is necessary that the value of the danger level indicator of waste is less than ten (figure 2) [11].

Even with a maximum mass loss, corresponding to a pyrolysis temperature of 800 °C, the solid residue is a waste of the fifth hazard class (according to the experimental method).

4. Determination of the solubility of heavy metals in sewage sludge and solid residue after pyrolysis in aqueous and acidic environments

Organic waste is often dumped into the open air, so all precipitation passes through it. Thus, part of the heavy metals contained in the waste can get into groundwater. In this work, we studied the solubility of heavy metals in neutral and acidic media. Some metals that do not dissolve in a neutral medium can dissolve in acidic. The acidity of the environment was determined by the fact that atmospheric precipitation has a pH < 5.65.

For research, samples of sewage sludge were taken in their original form and after pyrolysis to 800 °C. A water extract was prepared according to [12], the pH of the acid extract was 3.5 [13]. The concentrations of heavy metals in the extracts were determined. The research results are presented in table 5.

The solubility of the heavy metals contained in the initial sludge in a neutral medium (aqueous extract) is higher for all the metals studied than in the solid residue after pyrolysis. The override
Figure 2. Dependence of danger level indicator of waste on mass loss at pyrolysis of sewage sludge.

of solubility for Zn and Pb as the most dangerous of the studied metals is respectively 37 and 7 times. Cadmium also belongs to the metals of the first hazard class, but since it volatilizes during pyrolysis to 800 °C and it was not found in the solid residue (table 2), it is impossible to estimate its solubility. The maximum exceedance of solubility is reached for Ni (106 times) and Mn (88 times). For Cu and Co it is more than 30 times.

To study the solubility of heavy metals in an acidic environment, representatives of heavy metals from different hazard classes with the highest concentration were chosen. They are Zn (first hazard class), Cu (second hazard class) and Mn (third hazard class). The solubility of Zn and Cu contained in the sewage sludge is higher than that in the solid residue after pyrolysis, respectively, 85 and 17 times. At the same time, the acidic environment is most likely in real conditions of dumping, taking into account the acidity of atmospheric precipitation. The solubility of Mn is 2.7 times lower for the sewage sludge than for solid residue. But manganese belongs only to the third hazard class.

Thus, the solid residue after pyrolysis to 800 °C is more suitable for dumping than the sewage sludge. It has a lower solubility of heavy metals in neutral and acidic medium so it is a waste with a lower degree of negative effect on the environment.
Table 5. Solubility of heavy metals in acidic and aqueous environments (the concentration in extract).

| Raw material       | Metal | Content (mg/kg) | Acidic (mg/l) | Aqueous (mg/l) |
|--------------------|-------|-----------------|---------------|----------------|
| Sewage sludge      | Cu    | 160             | 0.52          | 0.255          |
|                    | Mn    | 120             | 0.0018        | 0.145          |
|                    | Cd    | 0.64            | —             | 0.0001         |
|                    | Co    | 1.7             | —             | 0.0275         |
|                    | Ni    | 28.1            | —             | 0.445          |
|                    | Pb    | 16.2            | —             | 0.013          |
|                    | Zn    | 890             | 0.94          | 0.27           |
| Solid residue      | Cu    | 370             | 0.03          | 0.008          |
| (800 °C)           | Mn    | 330             | 0.0048        | 0.00165        |
|                    | Cd    | < 0.5           | —             | 0              |
|                    | Co    | 5               | —             | 0.0008         |
|                    | Ni    | 69              | —             | 0.0042         |
|                    | Pb    | 44              | —             | 0.0023         |
|                    | Zn    | 2000            | 0.011         | 0.00735        |

Table 6. Gross heavy metal content in solid residue after pyrolysis at 500 °C.

| Metal | Content (mg/kg) |
|-------|-----------------|
| Cu    | 310 ± 80        |
| Mn    | 350 ± 90        |
| Cd    | 1.7 ± 0.5       |
| Co    | 5.7 ± 2.4       |
| Ni    | 66 ± 23         |
| Pb    | 43 ± 16         |
| Zn    | 1820 ± 500      |

5. Behavior of heavy metals at two-stage thermal pyrolysis conversion of sewage sludge to syngas at 500 °C

Experimental studies of the two-stage thermal conversion of sewage sludge to syngas at 500 °C were carried out on a laboratory-scale setup the scheme and description of which are presented in [4]. The purpose of this experimental study was to investigate the behavior of cadmium in the composition of sewage sludge at pyrolysis to 500 °C and to determine the ratio of the volume fraction of H₂ to this of CO in chemical composition of the synthesis gas.

According to the material balance, the solid residue is 45% of the initial sewage sludge mass. The results of analyzes on the gross heavy metal content in solid residue after pyrolysis to 500 °C are presented in table 6. The solid residue after pyrolysis to 500 °C also belongs to the fifth hazard class of the waste (see figure 2), since the value of the danger level indicator, calculated similarly to the method presented in section 3, is 8.52.

According to the data presented in figure 3, cadmium completely remains in the solid residue after pyrolysis to 500 °C (the corresponding mass loss is 56%). Thus, all heavy metals that are
Figure 3. Dependence of the cadmium content in sewage sludge on mass loss during pyrolysis.

Table 7. Characterization of syngas obtained as a result of two-stage pyrolysis conversion of sewage sludge at 500 °C.

| Composition (vol%) | Calorific value (MJ/m³) | Specific volume yield (m³/kg) |
|-------------------|-------------------------|-----------------------------|
| H₂, CO, CO₂, CH₄, NO₂, H₂S, SO₂ | 13.6 | 0.56 |

controlled by the Ministry of Natural Resources and Ecology of the Russian Federation remain inside the solid residue and it can be argued that the synthesis gas is completely free from heavy metal vapors.

Characteristics of syngas obtained as result of the two-stage thermal conversion of sewage sludge at a temperature of 500 °C are presented in table 7.

The synthesis gas has a calorific value suitable for use in the process of generating thermal energy. The ratio of the volume fraction of H₂ to this of CO is 2.1 : 1, which indicates the applicability of syngas for methanol synthesis. The presence of CO₂, CH₄ and NO₂ that are not involved in the reactions has a positive effect on methanol synthesis. The methanol production reaction is exothermic and, as a result, difficult to control. The presence of ballast gases will help heat dissipation and simplify the maintenance of the required temperature. At low ratio
of the volume fraction of CO$_2$ to this of CO the degree of CO and H$_2$ conversion are decreased significantly. So with an increase in the ratio of the volume fraction of CO$_2$ to this of CO from 0.1 to 0.4, the degree of conversion are grown from 34% to 47% [14]. Syngas is heavily polluted with sulfur compounds. They cause poisoning of copper-containing catalysts, participating in methanol synthesis [15]. For further use of such syngas, purification of syngas is necessary.

6. Conclusion

Studies of the gross heavy metal content in the composition of sewage sludge and solid residues after pyrolysis at 250, 500 and 800 ºC, the solubility of heavy metals in the sewage sludge and solid residue after pyrolysis at 800 ºC in a neutral and acidic environments are carried out. The hazard class of waste for sewage sludge and the solid residue after pyrolysis at 500 and 800 ºC is calculated. It is shown that syngas obtained as result of the two-stage thermal conversion of sewage sludge at a temperature of 500 ºC has the ratio of the volume fraction of H$_2$ to this of CO of 2 : 1, which is optimal for subsequent methanol synthesis. Synthesis gas needs to be purified from sulfur-containing compounds. The solid residue formed at pyrolysis to 500 ºC is 45% by mass of the initial sewage sludge and contains all the heavy metals that were part of the initial sludge. At the same time, the solid residue has the same hazard class, and the solubility of heavy metals in neutral and acidic environments is 10–100 times lower than that in the initial sewage sludge. Thus, the solid residue is waste with a lower degree of negative environmental impact than the original sewage sludge.

References
[1] 2008 Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on Waste and Repealing Certain Directives Official Journal of European Communities vol L312 pp 3–30
[2] 1999 Council Directive 1999/31/EC of the European Parliament and of the Council of 26 April 1999 on the Landfilling of Waste Official Journal of European Communities vol L182 pp 1–19
[3] Belyaeva S and Korotkova E 2013 Water Supply and Sanitary Technique 4 5–9
[4] Larina O and Zaichenko V 2018 J. Phys.: Conf. Ser. 946 012034
[5] Larina O, Sinelshchikov V and Sychev G 2017 J. Phys.: Conf. Ser. 774 012137
[6] Sheldon R 1987 Chemicals from Synthesis Gas (Dordrecht: D. Reidel Publishing Company)
[7] Onishchenko G G 2006 Health Standards 2.1.7.204106 Predel’no Dopustimyye Kontsentratsii Khimicheskikh Veshchestv v Pochve (Moskva)
[8] Onishchenko G G 1995 Health Standards 2.1.7.020-94 Oriyentirovochno Dopustimyye Kontsentratsii Tyazhe-lykh Metallov i Mysh’yaka v Pochvakh (Moskva)
[9] Vodyanitsky Yu 2012 Eurasian Soil Sci. 3 308–75
[10] Stammbach M, Kraaz B, Hagenbucker R and Richarz W 1989 Energy Fuels 3 259–66
[11] Order of the Ministry of Natural Resources of the Russian Federation of June 15, 2001 No. 511 On Approval of the Criteria for Assigning Hazardous Wastes to the Class of Hazard to the Environment
[12] Prozhornina T I 2009 Praktikum po Kursu Khimicheskoi Analiz Poch. v (Chast I) (Voronezh: Izdatel’skiy Tsentr Voronezhskogo Gosudarstvennogo Universiteta)
[13] Pinaeva A V 2006 Migratsiya ionov tyazhelykh metallov v pochve pri zakhoronenii osadkov stochnykh vod gal’vanicheskogo proizvodstva Thesis (Tolyatti: Ulyanovsk State Technical University)
[14] Kozyukov Ye A, Krylova A Yu and Krylova M V 2006 Khimicheskaya Fizicheskaya Pirochlennoy Gaza (Moskva: MAI)
[15] Karavayev M and Leonov V 1984 Tekhnologiya Sinteticheskogo Metanola (Moskva: Khimiya)