Transformations, threats and the bond of chlorine in the processes of burning the wastes

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Abstract. The aim of the study was to present the possibility of reducing the emission of HCl to the atmosphere and the possibility of limiting the formation of PCDD/F in the technologies of incineration of waste fuels and incineration of animal waste. Waste fuel and animal biomass were burned in a two-stage system i.e.: Io-gasification and IIo-combustion of gas products of gasification. As part of the implementation, the reduction of HCl emissions to air was investigated when Ca(OH)₂ was added as an additive to the fuel from waste. Ca(OH)₂ bonded HCl releasing into the gas space in the combustion process. HCl binding in the combustion chamber not only limited its emission to the atmosphere. Its elimination also limited the possibility of creating PCDD/F. In case of animal waste, HCl was captured with CaO produced from the decomposition of bone material (hydroxyapatite). The efficiency of this process was low. It was thus necessary to remove it in the built-in exhaust purification plant.

1 Introduction

This Municipal, industrial waste and agricultural biomass have a chlorine load in their composition. It is an element, that during their thermal transformation causes difficulties in exploitation of boiler devices and a threat of emission of harmful substances into the atmosphere. Due to the lack of the possibility of its elimination from waste or biomass, the problem of counteracting these threats is still valid. Biomass is mainly a chlorine carrier in inorganic combinations [1,2]. In the waste, chlorine, in addition to mineral calls (mainly NaCl), is mostly present in organic compounds, e.g. PVC, PVDC [3,4]. The nature of the chlorine binding determines the behavior of this element in the boiler furnace, i.e. the method, speed and the form in which it is released from the combustible material. Combustion of fuel containing the composition of organically or inorganically bound chlorine, causes serious operational disturbance [5,6]: (i) the reduction of the softening temperature of ashes due to the presence of alkali and heavy metal chlorides, (ii) high temperature chlorine corrosive degradation of structural steel boiler furnace elements.

It is also the cause of excessive emission of HCl and PCDD/F - harmful and toxic to the environment [7,8]. The combustion process is usually incomplete and not entire. This results in the presence of combustible products in the gases - including hydrocarbons. These hydrocarbons (mainly aromatic) are precursors of the formation of dioxane and furans. If chlorine compounds are present in the fuel, the chlorinating agent is liberated at high temperature during combustion. The simultaneous presence of precursors for the formation of dioxins and furans, together with the chlorinating agent, result in the formation of PCDD/F. Even the smallest amount of chlorine in the combustion chamber can lead to the formation of these toxic compounds - mainly in de novo processes [9]. [10] were studying formation of PCDD/F increased with increasing chloride content in the feed, and appeared to correlate it with the chlorine content in the fly ash. The catalysts for the formation of PCDD/F in the combustion of fuels and wastes are heavy metals, including Fe and Cu, as confirmed in the studies [11].

The issue presented in this paper is a part of the authors experience in the implementation of low-emission waste incineration, with particular emphasis on the reduction of HCl emissions. The study focused on the combustion of animal waste and waste fuels in two-stage combustion technologies. Animal waste was disposed of by gasification in the Io installation - a rotating chamber. The Io waste incineration plant was stationary with a stepped cell in which the gasification process was performed. Io both installations were equipped with an Io gas burning chamber. The research was aimed at capturing HCl with lime sorbent directly in the reaction chambers. HCl binding in the combustion chamber limits its emission to the atmosphere. It also affects the formation of toxic PCDD/F (from precursors or in de-novo processes).
2 Experimental setup

Materials and Methods

2.1 Fuel properties of the waste fuel

Studies included fuel formed from industrial wastes. This fuel is produced by grinding to desired granulation such waste as: paper, cardboard, foils, textiles, plastic wrap, tape, cables, cleaning rags or tires. Tables 1-3 show the fuel and the physicochemical properties - PN-EN-ISO 18134-2:2015-11; PN-EN-ISO 9029:2005; PN-ISO 1171:2002 and chlorine gram fraction was denoted in compliance to Polish Standard PN-ISO 587/2000, HHV - PN–ISO 1928:2002. Elemental composition of the flammable substance—carbon (C), hydrogen (H), nitrogen (N), sulfur (S) has been determined with the use of elemental analyzer CHNS, model 2400, series II by Perkin Elmer.

Table 1. Fuel properties fuel formed from industrial wastes

| Element                  | value | moisture (%) | inflammable fraction [%dry m | flammable fraction [%dry m | HHV [MJ/kg-dry m] | LHV [MJ/kg-dry m] |
|--------------------------|-------|--------------|-------------------------------|-------------------------------|------------------|------------------|
| HCl content in the exhaust gas without the contribution of lime sorbents added to the fuel-extensively discussed in papers [12].

Table 3. Elemental composition of the fuel from wastes supplemented with PVC recycle granules [%].

| Addition of PVC [%] | value fuel from wastes 1 | value fuel from wastes 2 | value fuel from wastes 3 | value fuel from wastes 4 |
|---------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| Cl [%]              | 63.90                    | 63.83                    | 63.75                    | 63.60                    |
| H [%]               | 7.60                     | 7.59                     | 7.59                     | 7.57                     |
| N [%]               | 3.55                     | 3.53                     | 3.52                     | 3.58                     |
| S [%]               | 1.26                     | 1.25                     | 1.25                     | 1.24                     |
| O [%]               | 23.17                    | 23.19                    | 23.20                    | 23.25                    |

2.2 Fuel properties of animal waste

Chlorine in animal waste is associated with alkali metal chlorides KCl, NaCl. Hydrogen chloride is formed in the high temperature environment of the combustion chamber (Iio) in an indirect way. Substrates belonging to the waste gases are NaCl(g), KCl(g), SO2, H2O and O2.

The study included slaughterhouse waste (tripe, fat, bones, feathers, sludge, slush, bristles, blood), meat and bone meal. Each time the waste came from another supplier (Table 4). The heat of combustion is determined using the LHV calorimetry technique. If the tested material is animal waste, it creates great difficulties in applying the calorimeter bomb to tests. It is very difficult to obtain a representative and homogeneous sample. As the results in Table 5 show, the LHV for particular types of waste are very diverse. In addition, the caloric content of the same type of waste with each supply varies greatly. This creates big difficulties, not only analytical but also technological.

For the purpose of the study, the fuel from wastes was grained successively with admixture of recycled polyvinyl chloride PVC. Therefore, a number of fuels different in gram share of chlorine were obtained (Table 3) [12].

Only the type of chlorine, which was in addition to the recycled PVC was clearly defined. Obtained model fuel was mixed with different amounts of limestone sorbent Ca(OH)2, in order to reduce the mobility of chlorine in the gasifier chamber. Limestone sorbent was in the form of a fine powder. Then the gasification of the fuel from wastes 1-4 was carried out. In these processes, concentrations of basic gas products or hydrogen chloride were measured. HCl emission measurement results were converted into relative emission (Φ), which is the ratio of HCl content in the exhaust gas to the initial

\[ CaO + 2HCl → CaCl2 + H_2O \] (1)
However, the efficiency of HCl capture in high temperatures (1100-1200°C) is low, which is extensively discussed in papers [13].

Table 4. Results of the first series of research on calorific value

| Type of sample | Moisture [%] | Sulfur S [%] | LHV [MJ/kg] |
|----------------|--------------|--------------|--------------|
| MBM            | 5.5          | 0.3972       | 23.24        |
| Sediment       | 61.9         | 0.0071       | 10.28        |
| Bones          | 46.1         | 0.0071       | 8.46         |
| Tripes         | 66.0         | 0.0064       | 22.98        |
| Bristles       | 66.1         | 0.7202       | 10.39        |
| Feather        | 64.4         | 0.6943       | 22.65        |
| Tripes 2       | 738          | 0.0080       | 6.89         |
| Fat            | 2.9          | 1.3860       | 39.06        |
| Bones 2        | 56.5         | 0.1019       | 7.16         |
| Slush*         | 48.6         | 0.1096       | 28.31        |
| Bristles 2     | 75.1         | 0.6421       | 9.73         |
| Feather 2      | 65.5         | 0.5142       | 85.76        |
| Sediment 2     | 66.2         | 0.0046       | 17.07        |
| Blood          | 20.2         | 0.3768       | 21.08        |
| MBM 2          | 6.0          | 0.4860       | 19.09        |

*Sample described as slush contained 2 layers: at the bottom-slush, on the top-fat. The bottom layer was taken for studies.

2.4 Animal waste combustion

As in the case of industrial waste fuel, a two-step process of thermal destruction of animal waste is being observed. In the first stage I° gasification was carried out at a temperature of 650-700°C. In the second stage II°, in the secondary combustion chamber, at a temperature of 1100°C-1200°C, gaseous and solid products of gasification were burned. The study was conducted in a full technical scale. Loading capacity of waste was 1000kg/h. Fat and meat-and-bone meal constituted fixed caloric input ensuring autothermal combustion. Therefore, for combustion of the mentioned mass flow of waste was consumed 200kg/h of fat and 100kg/h of flour were used. At the same time, in the combustion chamber, thermal decomposition of bone material to CaO was taking place.
the waste heat exchanger (steam generator) at the temperature of 200-180°C, and then emitted into the atmosphere through the system of multicyclones, exhaust fan, a bag filter and a chimney. The installation worked continuously. Secondary air blown into the secondary combustion chamber, in each case of the test, was carried out for 1.5 hours, continuously adjusting the performance of the fan 7 (Fig. 2) [13].

Measurements of exhaust components emissions were made in a continuous manner, by means of exhaust gas analyzer system produced by Environment SA (MIR-IS and Grab HIT 52M models).

3 Results and discussion

Combustion of waste and fuels from waste creates many operational difficulties. Chlorine introduced into the boiler furnace with fuel (and especially such as waste) plays a key role in corrosive processes. In the high-temperature atmosphere of the boiler, chlorine corrosion is a threat to its steel structural elements, screens, superheaters or evaporators. To assess the risk of chloride corrosion based on the fuel composition, the so-called fuel chloride corrosion indicator is used. Chlorine released from the fuel mass affects the deposition of pollutants (fly ash) and slag on heat exchange surfaces. In order to avoid adverse phenomena during the combustion process in the form of agglomeration of the bed, the formation of wastes on heated surfaces, the ash fusing temperature should be higher than the temperature in the furnace during fuel combustion [14]. Waste (and fuel from waste) is therefore a difficult fuel, as their combustion or co-combustion with coal requires prevention of these unwanted processes, which significantly hinders the trouble-free exploitation of boilers.

The presence of chlorine or hydrogen chloride in the gas atmosphere of the boiler (burning waste or fuels formed from waste laden with a chlorine charge), may result in the formation of toxic PCDD/F. Chlorine in the chlorination reaction of phenols (intermediate products of decomposition of flammable substances), causes the formation of chlorophenols according to the reaction C₆H₆OH (in fuels) + Cl₂ → chlorofenols - precursors to the formation of PCDD/F [15]. The high temperatures of the chamber limits the processes of chlorophenols formation, and then their condensation on volatile dust. Thus, it inhibits the formation of PCDD and PCDF. The intense formation of PCDD/F in boiler conditions is significantly affected by the temperature in the convection part of the boiler, which may fall below 700°C. This favors the local chlorophenol condensation processes, which in turn leads to the formation of PCDD/F.

It is important to learn about chlorine transformation in waste incineration processes (present in waste in various chemical forms), and then its effective elimination of the combustion chamber from the gas phase.

3.1 Fuel from waste

During the studies, the scale limit of the mobility of chlorine liberating from the fuel in the gasifier chamber was set. Breakdown of the combustible substance during heating of fuel Pas-R leads to release of chlorine in the form HCl, which is easily released from the PVC, already in the temperature above 180°C. The liberated HCl, on the grill gasifier was bound by calcium sorbent. The higher the temperature, the more the binding of HCl did not keep the rate of its release from PVC. The resulting calcium chloride CaCl₂ underwent partial decomposition at elevated temperatures, releasing HCl again, but the higher the temperature, the faster the process. The obtained experimental data and specific functional dependencies enable: (i) selection of the percentage addition of Ca(OH)₂ for fuels with different proportions of chlorine gram share (according to the desired concentration of HCl in the flue gas); (ii) determination of the maximum addition of PVC, which can be loaded to fuel formed from waste; (iii) concluding on the binding efficiency of chlorine in the fuel combustion using calcium sorbents.

Determining the percentage of PVC additive for fuels, we can decide of the scale limit of HCl emissions, depending on the percentage addition of Ca(OH)₂ to the fuel (Fig. 3) where Φ is the ratio of HCl content in the exhaust gas to the initial content of HCl in the exhaust gas without calcium additives to the fuel. This emission decreases linearly, with the rate of decline being the greater, the bigger the addition of PVC to fuel.

![Image](https://example.com/image)

Fig. 3. The dependence of relative concentration of HCl in the wet exhaust gas from the sorbent addition Ca(OH)₂ to fuel from wastes 1-4.

Linear relationships: 1, 2, 3, 4 correspond to the consumption of sorbent in cases where the percentage of fuel from waste additive PVC was respectively 0%, 0.5%, 1%, 2%. Experimentally determined characteristics allow selection of Ca(OH)₂ amount for fuels containing different amounts of PVC. These characteristics make it possible to model the fuel formed in such a way, as not to exceed the specified emission of
HCl. Thus, it is possible to make an optimal choice for the treatment of exhaust gases installation. Furthermore, Fig. 3 shows, that fuels with higher content of PVC, thus chlorine in the combustible material, are characterized by greater susceptibility to the calcium sorbent activity, than those with less fuel recyeclate.

In Fig. 4 HCl concentration referred to gram relationship is shown: Ca(OH)$_2$/Cl, CaO/Cl and Ca/Cl, in which calcium contained in the fuel and sorbent Ca(OH)$_2$ was recalcualted to form an oxide and elemental. The results are therefore hypothetical. This relationship allows to evaluate the potential use of the sorbent, e.g. in the form of CaO, wherein to this use the same range of HCl concentrations is attributed, which corresponds to the application of the sorbent. It follows that the CaO sorbent can more effectively bind the HCl in the exhaust gas than Ca(OH)$_2$.

3.3 Animals waste

The increase in the concentration of HCl in the flue gases is due to the presence of potassium and sodium sulfatizing reaction, affecting simultaneously reduction in SO$_2$ concentration. It is indcated by the results presented in [13]. The formation of HCl may also be promoted by secondary processes of HCl formation from Cl$_2$.

Fig. 5 illustrates HCl concentration changes as a function of the percentage share of oxygen in the exhaust gas. It can be seen that most of the measuring points is in the range of high HCl concentrations, of 40-80 mg/Nm$^3$. The data presented in Fig 5 initially indicate that with the increase of the oxygen content, we may have to deal with the Deacon reaction in the process: 4HCl + O$_2$ $\rightarrow$ 2Cl$_2$ + 2H$_2$O. The condition for the occurrence of this reaction is the presence of fly ash, which in this case form deposits on the tubes of the waste heat exchanger, where the temperature may fall to 400°C. Two-stage combustion technologies are characterized by relatively high emissions of fly ash when compared to other technologies e.g. grate technologies, which promotes intensification of the deposition on the tubes of the heat exchanger.

After cleaning the tubes in the waste heat boiler (after removal of deposits from the walls of the tubes), in conditions of excess air - oxygen saturation (> 12% O$_2$ in gases), there was no decrease in the concentration of HCl in the flue gas (Fig.6). This may indicate that in the absence of sediment, which catalyze the oxidation of HCl, Deacon reaction does not occur. This is a process which negatively affects the stability of heating surfaces (superheating, Cl$_2$ diffusion) and the heat exchange efficiency decreases.

![Fig. 5. HCl = f(%O$_2$)](image_url)

![Fig. 6. HCl = f(%O$_2$) – after removal of sediments](image_url)

Fig. 7 shows the effect of SO$_2$ concentration on the formation of HCl for the O$_2$ content in the exhaust gases from 6 to 16% (according to the oxygen test carried out in the experiment). As has the conducted test cycle shown, reduction of the SO$_2$ in the flue gas causes and increase of HCl to a maximum value of about 80-90 mg/Nm$^3$, corresponding to the O$_2$ content in the flue gas of approx. 11 to 13%. In the further step to increase the flow of air (up to a content of O$_2$= 12-16%) we note a
The downward trend of HCl, due to the initiation of Deacon reaction on the surface of the waste heat boiler exchanger. The observed phenomenon suggests that in the secondary combustion chamber, at a high temperature, the process of HCl formation by sulfatizing (NaCl)\(_2\) and (KCl)\(_2\) occurs. These process conditions may create reactions of molecular chlorine Cl\(_2\) formation and secondary processes of hydrogen chloride. It should be noted that the high concentration of SO\(_2\) in the gaseous combustion products (approx. 1600 mg/Nm\(^3\)), related to low O\(_2\) share in the exhaust gas) is due to a relatively high sulfur content of animal waste for disposal. Phenomena that occur at high temperature in the secondary combustion chamber (with the participation of reactive CaO) do not affect the HCl emission reduction, on the contrary, the concentration of HCl increases. This process is accompanied by a decrease in the concentration of SO\(_2\). Dependence disclosed during the animal biomass incineration (rich in alkali metal chlorides) HCl = f(SO\(_2\)) shown in Fig. 7, requires a testing research in laboratory scale. It seems that such research can significantly bring closer qualitatively and quantitatively the processes of forming gaseous environment during the combustion of biomass rich in alkali chlorides.

![Fig. 7. HCl = f(SO\(_2\)) for O\(_2\) = 16-6%](image)

### 4 Conclusions

Fuels from waste and biomass waste contained chlorine. Chlorine was bound in various combinations. In the process of burning waste, gaseous forms of chlorine are released. The fumes, which are contained in their composition and are emitted to the atmosphere, pose a threat to the environment. In addition, the presence of chlorine HCl, Cl\(_2\)) in the gas phase of the combustion chamber results in the formation of toxic PCDD/F. PCDD/F are produced by the precursor reaction or by de novo synthesis. It is therefore desirable to remove the chlorine gas forms and to bind them in the combustion chamber.

In an experiment conducted in a full technical scale, the capture of HCl intensively proceeded in case of combustion of fuel from waste rich in chlorine. The process of HCl capture with lime sorbent [Ca(OH)\(_2\)] was ran in the furnace, mainly in its first stage (I\(^\circ\)), i.e. on the grill of the gasifier. On the gasifier grate the fuel was fed, with different Cl and limestone sorbent Ca(OH)\(_2\) share. Dechlorination process proceeded more intensively for fuel with a high percentage of the element Cl i.e. fuel with a large addition of recycled PVC. For example, with the fuel from wastes 4, where the proportion of Cl = 0.86, dechlorination of gaseous products was intense - the process was of about double the efficiency. Fuels with lower rate of Cl (0.69%, 0.61%, 0.52%)- dechlorination process was less intense with the same amount of lime sorbent added.

During the two-stage combustion of animal waste, the presence of reactive waste lime sorbent CaO, does not produce significant results in the dechlorination process. In general, HCl formed in the oxidizing zone (T = 1100-1200°C) due to sulfatizing of pairs NaCl(g) and KCl(g), does not react with highly reactive CaO, which in turn arises from the decomposition of bone material. It should be noted that the proportion of CaO in the secondary combustion chamber is high and the ash content is approx. 35 - 45%. At the same time CaO is actively involved in the flue gas desulfurization. Looking for a way to dechlorinate waste gases, the share of air in the combustion process was increased. Firstly, we noted the growth of HCl formed by sulfatizing alkali chlorides, and then in the share of O\(_2\) in the flue gases, from 12 - 16.5% followed by a rapid decline of HCl. That is, this process could take place under conditions typical for the Deacon reaction, on volatile dusts polluting the heating surfaces of the heat exchanger. This phenomenon was confirmed after cleaning the heat exchanger of mineral deposits. The share of HCl in the flue gas, regardless of the O\(_2\) share, was determined at a constant maximum level.

The analysis of results shows that much better ecological effects, as regards to the emission of HCl, are obtained in the case of two-stage combustion of fuel from waste, i.e. gasification of fuel and afterburning of synthesis gas in a secondary combustion chamber. In case of fuels formed from waste with a high proportion of Cl, the method of HCl capturing from gaseous products of combustion described in the paper (dechlorination), can be successfully implemented. In case of animal waste (because of the nature of the chlorine binding – mineral), the dechlorination process in a two-stage furnace is practically meagre.

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