Enrichment of ash and slag waste generated by burning of fuels with additives

Elvira R Zvereva¹, Olga S Zueva¹, Kamil K Gilfanov¹ and Valeria P Tutubalina¹
¹Kazan State Power Engineering University, 420066, Kazan, Krasnoselskaya str., 51, Russia

* Corresponding author: 6elvira6@list.ru

Abstract. The existence of opportunities and prospects for scarce metals extraction from ash and slag waste of high-sulphur fuel oil burning was noted. The volatile ash produced during fuel combustion consisting mainly of metal oxides contains highly toxic substances. Their binding in a zone of burning of fuel is important not only for the purpose of extraction and further use in industry, but also to prevent their harmful environmental impact. It was shown that in the case of petroleum fuel oil an effective way to improve the performance of the fuel while maximizing the adverse environmental consequences of its combustion is to develop new generation effective fuel additives and improve filtration systems for flue gases. It has been established that the use of additives based on carbonate sludge makes it possible to achieve greater binding of metal oxides to non-volatile compounds in the burning zone of the fuel and their reduction in the composition of the emission gases. The mutual using of carbonate additives with the admixture of carbon nanotubes the effect may be even greater. Rational ash and slag waste utilization through the use of their beneficial properties will allow to free occupied areas and reduce environmental damage to the environment.

1. Introduction

The activities of energy industry leads to the emergence of a large amount of mineral ash and slag waste generated during the combustion of liquid and especially solid fuels. Combustion of fuel leads to formation of volatile substances and solid non-combustible waste containing various, including valuable substances. However, toxic compounds are formed in ash and slag waste also, therefore rational waste utilization will make it possible to use the components of ash and slag waste and improve the ecological situation. In Russia a huge amount of ash and slag wastes was formed, requiring close attention in order to process them to improve the ecological situation in the country and to solve production problems related to the fabrication of new materials and products [1].

In Russia, no more than 10% of the total amount of generated waste annually is used as secondary resources for further processing in various industries. In developed countries, 70-95% of ash and slag waste is recycled, and 100% in some Scandinavian countries, for example, in the Netherlands and Denmark. This work is devoted to study of some aspects of controlled change in the composition of ash and slag waste generated during the combustion of fuels with additives with a view to their further use.

2. Features of ash and slag waste

Ash and slag waste from thermal power plants is a technogenic raw material that can be used to extract valuable metals and to manufacture composite materials and products for various purposes. The value of ash is due to its complex chemical composition. In ash waste a large amount of calcium, iron,
aluminium, chromium, nickel, manganese, rare and trace elements compounds are concentrated: vanadium, germanium, gallium. In connection with the natural resources depletion the processing of ash and slag waste in order to extract valuable and noble metals and the further use of waste from their processing could help in implementing a resource-saving policy [2, 3].

Rational multi-stage disposal of ash and slag waste should include measures to maximize the binding of highly toxic substances formed during fuel combustion with solid ash residues suitable for further processing; removal of harmful and valuable components from waste and the subsequent use of neutralized residues in various industries. As valuable features of ash and slag waste it should be noted that they contain noble metals (gold, platinum), rare and trace elements and there are a possibilities of extracting iron-containing magnetic concentrate and secondary coal. Currently there are effective technological solutions that allow high-quality ash and slag waste processing with the aim of extracting from them for example by leaching, gold, titanium, lithium, beryllium, vanadium, tungsten, copper, manganese, zinc, rare earth elements, etc. [4-8].

Measures for ash and slag waste utilization should take into account the inconstancy of the ash composition and its dependence on the type and quality of extracted fuel. Thus the composition and the properties of ash and slag waste as a secondary resource are determined by [9]:
- the type and the features of employed fuel formation (natural factors);
- the features of the fuel combustion process, methods for ash and dust removing (technological factors);
- the storage characteristics of ash and slag waste (environmental factors).

Technological factors may be most manipulated. The employed fuels are natural sorbents containing impurities of many valuable elements including rare metals. When incinerated their content in ash increases many times (100-1000 times) and may be of industrial interest. However some fraction of the valuable elements form volatile compounds and escape into the atmosphere with flue gases. This fraction can and should be minimized. Moreover the metal oxides formed during fuel combustion and emitted through a chimney into environment are highly toxic substances that are harmful to the environment. Therefore the capture of metal oxides is important not only for the purpose of their further use in industry, but also to prevent their harmful environmental impact.

There are several ways to solve the problem of ash and slag waste enrichment while improving the quality of flue gases by trapping metal oxides. Some of them are associated with using of highly efficient methods of burning fuel, improving the design features of boiler furnaces and developing filters that delay some of the harmful emissions. Another simple and cheap way to improve the performance properties of oil and alternative fuels and to perfect the environmental safety of the fuel and energy complex is the special additives introduction into it. Often this method is not only the most affordable, but the only possible.

The use of petroleum fuel oil remains environmentally inappropriate. Therefore the focus should be on improving of performance fuel characteristics while maximizing elimination the adverse environmental consequences of its combustion. Accordingly solutions to the problem should be sought in the development of effective new generation fuel additives and in improvement of flue gas filtration systems. In this work it was shown that use of new generation additives containing nanoparticles allows to achieve greater bonding of metal oxides with nonvolatile compounds in a zone of fuel burning and reduction volatile toxic compounds in the emission gases composition.

3. Materials

Samples of high- sulphur fuel oil brand M100 produced by the Nizhnekamsk oil refinery were taken as boiler fuel. This type of fuel is used in thermal power plants and in boiler rooms as emergency and backup fuel. To improve the physicochemical properties of organic fuels, to increase the efficiency and environmental friendliness of combustion, and to bind volatile compounds, dehydrated carbonate sludge was used. Carbonate sludge is a waste of TPPs chemical water treatment process. Carbonate sludge as a product obtained by chemical precipitation has a complex of specific physicochemical properties, among which should be noted the diverse chemical composition (calcium carbonates, magnesium and
iron hydroxides, aluminium compounds, etc.), as well as its high dispersion and surface activity due to the high porosity arising in the process of water evaporation [10]. As nanoscale additives, multi-walled carbon nanotubes of the Taunit carbon nanomaterial (http://www.nanotc.ru) dispersed in diproxamine (liquid non-ionic surfactant well soluble in oils) were used.

4. Results and discussion

When oil processing organometallic compounds of vanadium, nickel, rare and trace elements are concentrated in the heavy fraction, i.e. in fuel oil and go into ash when at burning [1]. Fuel oil obtained from high-sulphur oil varieties contain the highest concentrations of organometallic compounds [4-7]. Solid fuel oil combustion products are the most affordable raw material for the production of valuable metals after iron ores. On the other hand burning of high-sulphur fuel oils is also characterized by appearance of the greatest amount of harmful emission gases. In order to study the possibilities of binding harmful volatile substances based on organometallic compounds, samples of ash residues of high-sulphur brand M100 fuel oil used at thermal power plants and boilers as emergency and backup fuel were studied. Chemical analysis of ash and slag waste showed that most of them are composed of compounds of iron, vanadium, nickel and sulphur. The chemical composition of ash besieged on the regenerative surfaces of boilers from fuel oil burning is given in Table 1.

| Element | S  | V  | Ni | Ca | Zn | Mo | Cr | Mn | Mg |
|---------|----|----|----|----|----|----|----|----|----|
| Content, % | 11.5 | 18.4 | 5.9 | 0.7 | 0.2 | 0.2 | 0.1 | 0.1 | 0.9 |

Solid and liquid additives are added to highly viscous and sulphurous boiler fuels to improve various properties of fuels. The additives currently used are mainly intended to combat low temperature corrosion. However, environmental degradation requires use of additives that reduce the content of harmful emissions in flue gases.

In matters of additives creation it should be noted that the composition of fuel oil has its own features. It is characterized by the presence of a large number of sulphur compounds and a significant amount of vanadium compounds. Therefore we are not talking here only about the completeness of fuel combustion, i.e. about converting residual hydrocarbons (CH\textsubscript{x}), nitrogen oxides (NO\textsubscript{x}) and carbon monoxide (CO) into harmless nitrogen gas (N\textsubscript{2}), water (H\textsubscript{2}O) and carbon dioxide (CO\textsubscript{2}), but also about the binding of sulphur and vanadium in the combustion fuel zone with the purpose of preventing them from entering into atmosphere. Sulphur and vanadium which are present in fuel oil in the form of various compounds are oxidized during combustion with the formation of oxides which lead to corrosion damage in furnaces and to acid rain in the atmosphere. In addition a high level of sulfur in fuel is one of the factors behind appearance of so-called anthropogenic carbon nanomaterials in the emission gases incoming the atmosphere.

One of the ways to reduce emissions of sulphur compounds can be achieved by adding substances that bind sulfur and vanadium into non-volatile compounds in the combustion zone of fuel. When choosing additives we were guided by the well-known fact that various solid mixtures based on calcium hydroxide, magnesium and some other metals (zinc, copper, etc.) can be effective for binding sulfur in the combustion fuel zone for preventing equipment corrosion. As an additive to boiler fuel we took a finely dispersed fraction of dehydrated water treatment carbonate sludge [10–12]. The development of effective technologies for the use of carbonate sludge has another positive side. To a large extent it would also solve the problem of recycling waste water treatment processing.

Laboratory and industrial tests have shown that the additive in the form of dehydrated carbonate sludge water treatment makes it possible to chemically bind the sulfur contained in fuel oil, which is usually released together with vanadium compounds into the atmosphere during fuel combustion. Due to this, emissions of sulfur oxides and vanadium compounds into the atmosphere are reduced. Industrial tests have shown that the addition of 0.1 wt.% leads to a decrease in emitted sulfur oxides by 36.5 wt. % (analysis of test results of the boiler unit TGM-84B station No. 7, Naberezhnye Chelny). The use of
additives also contributes to the formation of a looser structure of deposits in the zone of high-temperature heating surfaces which reduces corrosion of these surfaces [13].

Thus based on dehydrated carbonate sludge additives developed by us [11, 12] significantly improve the viscosity characteristics of fuel oil and at the same time reduce the content of sulphur oxides in flue gases. Their combined use with additives based on pre-dispersed carbon nanotubes [14, 15] made it possible to create composite fuel with improved properties containing small additives of these substances [16-21]. The use of boiler fuel with developed additives will allow for a more complete combustion of the fuel and more efficient binding of highly toxic substances with solid ash residues suitable for further processing.

5. Conclusion

The existence of opportunities and prospects for scarce metals extraction from ash and slag waste of high-sulphur fuel oil burning was noted in the work. Since a part of the metal oxides formed during fuel combustion are volatile highly, toxic, and harmful to the environment substances, their binding in the fuel combustion zone is important not only for their further use in industry, but also to prevent their harmful environmental impact. It was shown that in the case of petroleum fuel oil an effective way to improve the performance of the fuel while maximizing the adverse environmental consequences of its combustion is to develop new generation effective fuel additives and improve filtration systems for flue gases. It has been established that the use of additives based on carbonate sludge makes it possible to achieve greater binding of metal oxides to non-volatile compounds in the burning zone of the fuel and their reduction in the composition of the emission gases. The mutual using of carbonate additives with the admixture of carbon nanotubes the effect may be even greater. Rational ash and slag waste utilization through the use of their beneficial properties will allow to free occupied areas and reduce environmental damage to the environment.

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