

Utilization of technogenic waste from energy enterprises

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Abstract. The paper shows that the use of nano-additives can reduce the content of harmful impurities in flue gases. It is demonstrated that the waste of the water treatment process of thermal power plants can be used as a cheap and environmentally friendly nanostructured additive to improve the properties of hydrocarbon fuel. If necessary, the effect of carbonate sludge can be enhanced by adding other nanoparticles. The composition and properties of carbonate sludge are presented. The prospectivity of extraction of valuable, rare-earth metals from technogenic wastes generated during combustion of fuel oil at power enterprises is proved. The results of the obtained experimental powder diffractogram of fuel oil ash are discussed.

1 Introduction

One of the directions of modern industrial engineering is the development and optimization of technologies for the application of materials including nanoparticles with sizes up to several hundred nanometers [1-3].

The reactivity of nanoparticles increases as their size decreases below 90 nm.

The addition of nanoparticles to materials leads to significant changes in their properties. Physicochemical and environmental characteristics of nanocomposite materials may also change due to additional structuring of the sample containing nanoparticles.

For industrial and environmental engineering it is relevant to purposefully change the structure and properties of materials by adding certain nanoparticles with the required concentration, which allows to control their composition and properties.

Such an approach has previously been used in several applications of nanoparticles, including improving the properties of diesel fuel.

Addition of small amounts of functional nanoscale structures - engineered nanoparticles of metals, oxides, carbides, nitrides, and carbon nanotubes - to fuel significantly changes the properties of fuel and can even lead to improvement of its physicochemical and environmental characteristics [4-23]. It has been previously determined that the use of functional nanoscale structures changes the structure and properties of fuel oil [18-20].

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Such nano-additives affect the physical and chemical characteristics of fuel oil and reduce the formation of harmful emissions into the atmosphere during its combustion [19-23].

It has been shown in [3, 4, 6, 8, 10-12, 16] that the addition of nanoparticles leads to changes in the properties of fuel as well as other liquid multicomponent systems due to the formation of microheterogeneous nanostructures in multicomponent liquids. Targeted changes in the composition and concentration of introduced nanoadducts will improve the properties of heterogeneous systems.

The advantages of using nanoparticles are obvious. However, despite the positive effects of nanoparticles, the use of some of them in fuel systems can be environmentally harmful [24-29]. The use of nanoparticles leading to changes in the microstructure and properties of composite materials in the desired direction while minimizing environmental damage from their use should be sought. Where appropriate, the synergistic properties of the combined use of different nanoparticles should be utilized to enhance the desired effect.

Anticorrosive additives are added to low-quality liquid fuels to promote the formation of loose deposits in the zone of high-temperature heating surfaces [20]. We have developed an additive based on dehydrated carbonate sludge [20-21], which reduces the viscosity of fuel oil and reduces the content of sulfur oxides in flue gases. Their application [18-20] will improve the properties of hydrocarbon fuels, improve the completeness of fuel combustion and reduce harmful combustion products. It is shown in [21-27] that the best performance can be achieved when carbonate additive is combined with metal nanoparticles and metal oxides.

In [20, 21] it is shown that carbonate sludge, a waste product of the process of chemical water treatment of boiler water at power plants, which is formed in the process of coagulation and liming of river water, can be used as an additive to fuel oil. Additives containing nanomaterials and similar in composition to carbonate sludge are often used to improve the composition of diesel fuel and to bind sulfur oxides in flue gases [20]. Our industrial tests showed that the addition of carbonate sludge to fuel oil at a concentration of up to 0.5 wt. % allowed to reduce its viscosity, hence, to increase the flowability of fuel oil through pipelines and to achieve a significant reduction in sulfur oxide emissions (by 36.5 wt. %) [20-23].

The use of carbonate sludge has improved the physicochemical, operational and environmental properties of fuel and has been effectively used for the treatment of wastewater, gas emissions, in the production of ceramic products, polymer composites and porous materials and others [28-33].

Fuel oil for thermal power plants and boiler houses is the main, emergency, reserve and stoking fuel. Recently, fuel oil is mainly used as a backup for solid and gaseous fuel. Burning fuel oil produces harmful gaseous oxides of sulfur, carbon and nitrogen and solid ash containing valuable metals such as vanadium.

Vanadium belongs to dispersed elements and is practically not found in free form in nature. The main amount of vanadium is contained in ores. For example, vanadium products are obtained from titanomagnetite ores, the content of vanadium oxide in which is 0.14-0.17 %.

The most available vanadium raw materials after iron ores are ash and slag wastes generated during combustion of heavy liquid boiler fuel - fuel oil [42-46].

Vanadium compounds are widely used in metallurgy, chemical technology: as catalysts, for alloying steels, etc. Vanadium compounds are widely used in metallurgy and chemical technology.

A large number of studies have been devoted to the development of methods for utilization of vanadium-containing waste [38-41,44].

In the ash residues from fuel oil combustion, besides vanadium, there are other highly toxic but valuable compounds such as nickel and cobalt, so rational utilization of such

wastes also contributes to increasing their reserves and improving the environmental safety of thermal power plants. Methods of their processing are described in numerous scientific and technical literature [38-47].

The use of carbonate sludge and ash and slag materials contributes to the solution of another environmental problem, namely the utilization of waste generated during water treatment in the processes of liming and coagulation at thermal power plants and boiler houses.

2 Materials

Carbonate sludge from water treatment and ash from the combustion of M100 fuel oil at a thermal power plant were used for the research.

Carbonate sludge was dried to 1% moisture content, ground to particle size not more than 50 microns and consisted of calcium compounds - calcite CaCO_3 and portlandite Ca(OH)_2 , and magnesium compounds - brustite Mg(OH)_2 . The total content of calcium and magnesium compounds in the sludge was at least 80%. It is well known that the chemical composition of carbonate sludge depends primarily on the composition of the source water and coagulants used for water clarification. Iron (or aluminum) salts are mainly used as coagulants. The composition of a sample of carbonate sludge formed in the process of chemical water treatment when using iron salt as a coagulant is presented in Table 1.

Table 1. Chemical composition of carbonate sludge

Mineral part			
Concentration of substances, wt. %			
Cations		Anions	
Ca^{2+}	86,12	CO_3^{2-}	83,22
Fe^{3+}	0,61		
Mg^{2+}	11,82	SO_4^{2-}	6,13
Cu^{2+}	0,07		
Ni^{2+}	0,02	OH^-	9,21
Mn^{2+}	1,15		
Cr^{3+}	0,01	SiO_3^{2-}	1,32
Cd^{2+}	0,09		
Zn^{2+}	0,06	PO_4^{3-}	Less 0,001

The chemical composition of ash generated at combustion of heavy boiler fuel - high-sulfur fuel oil M100, is presented in Table 2 [44].

Table 2. Chemical composition of fuel oil ash [44].

Element	S	Ca	V	Mn	Fe	Ni	Zn	Mo
Content, %	11,5	0,7	18,4	0,1	63,0	5,9	0,2	0,2

3 Methods

Experimental studies of fuel oil ash samples were carried out in the Department of X-ray Structure Research of the SAC Center for Collective Use on the basis of the Laboratory of Diffraction Methods of Research of IOPhKh A.E. Arbuzov. A.E. Arbuzov KazNTs RAS. Powder diffractograms were obtained on Bruker D8 Advance automatic X-ray diffractometer equipped with Vario attachment and Vantec linear coordinate detector. Cu

K α 1 radiation ($\lambda = 1.54063 \text{ \AA}$) monochromatized by a curved Johansson monochromator, X-ray tube mode 40 kV, 40 mA. The experiments were performed at room temperature in Bragg-Brentano geometry with a flat sample.

Processing of the obtained data was performed using the EVA software package [EVA v.11.0.0.3. User Manual. SOCABIM 2005], and the powder diffraction database (ICDD PDF-2, Release 2005) was used. Fragments of the obtained diffractograms are shown in Figures 1-3.

4 Results and Discussion

This paper considers the use of carbonate sludge from the chemical water treatment of thermal power plants as an available and virtually harmless nanostructured material for solving industrial engineering problems to improve the physicochemical and environmental properties of fuels.

Water treatment wastes are practically non-toxic as they belong to the fifth class of hazard [21]. However, their storage in sludge dumps leads to alienation of large areas that could be used rationally. The use of water treatment product as an additive makes it possible to utilize this production waste and reduce environmental damage from energy enterprises.

The researches on studying the composition of ash residues of fuel oil and proposed methods of extraction of valuable metals from them.

We have shown that addition of carbonate sludge to heavy hydrocarbon boiler fuel in concentration up to 0.5 wt. % leads to decrease of its viscosity, improvement of combustion process and decrease of sulfur oxide emissions (by 36.5 wt. %) into the environment. Carbonate sludge used as a fuel additive different high specific surface area, has a heterogeneous structure of its microparticles. The specific surface of dehydrated carbonate sludge powder is $13.07 \pm 0.06 \text{ m}^2/\text{g}$ [20-23].

One of the ways to change the physical and chemical properties of fuel in the necessary direction is directed modification (enrichment) of carbonate sludge, by adding, for example, salts of certain metals. In the process of chemical precipitation, the added salts, just like the original salts, will first be deposited in the form of nanoparticles, and then will create bulk conglomerate structures of more complex composition. In liquid media, the conglomerate structures of enriched carbonate sludge will partially disintegrate into smaller nanostructured formations that change the properties of heterogeneous systems, which can be used to target the properties of fuel systems.

Ash residues obtained by combustion of fuel oil with carbonate sludge as an additive in the amount of 0.1 % were investigated by X-ray diffraction methods.

Figure 1 shows the powder diffractogram for the initial untreated sample. The experiment was performed in a standard PMMA cuvette. The presence of a significant amount of iron in the investigated sample leads to the occurrence of intense fluorescence scattering, which arises when the sample is irradiated with "copper" radiation by an X-ray beam with a wavelength of 1.5418 \AA generated by an X-ray tube with a copper anode.

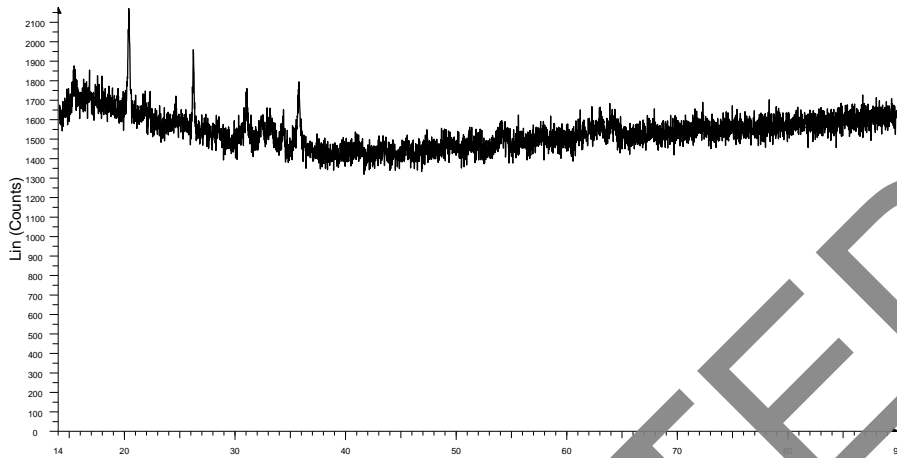


Fig. 1. Experimental powder diffractogram of an untreated ash sample

In the course of the study, the ICDD PDF-2 powder diffractometry database was searched, and the multicomponent nature of the sample, i.e. the presence of several crystalline phases, was detected.

It was found that the magnetic phase of the analyzed substance constitutes more than half of the sample mass. To separate the sample into magnetic (iron-containing) and non-magnetic phases, dispersion of the sample in aqueous medium, intensive stirring to suspension and separation of the magnetic part with the help of a strong neodymium magnet were used.

A powder diffraction experiment was performed for each of the separated phases of the sample (Figs. 2 and 3).

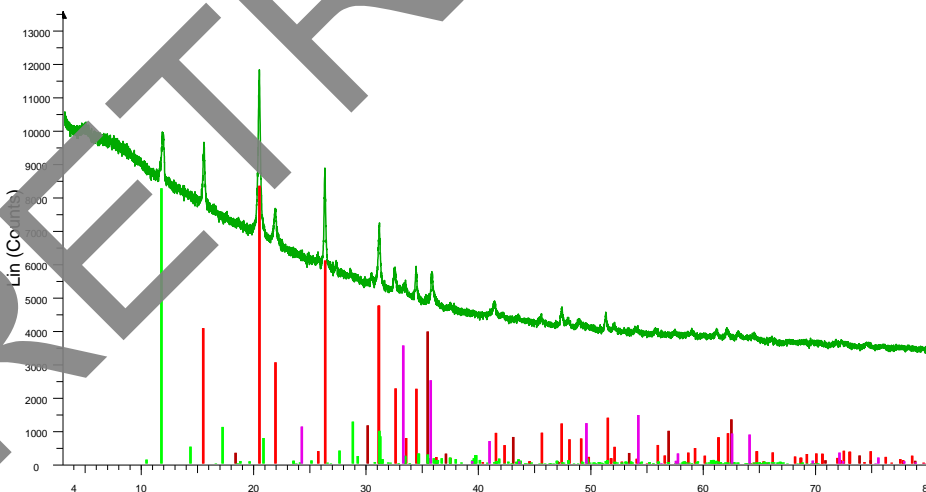


Fig. 2. Experimental powder diffractogram for non-magnetic phase

The predominantly non-magnetic phase 1 is a mixture of several crystalline phases, mainly consisting of the crystalline form of vanadium oxide V_2O_5 , (code No. 01-070-8747). Also present in small amounts are gypsum $CaSO_4(H_2O)_2$, (code No. 01-076-1746),

hematite Fe_2O_3 (syn, code #01-089-8104), and magnetite Fe_3O_4 (syn, code No. 01-089-3854).

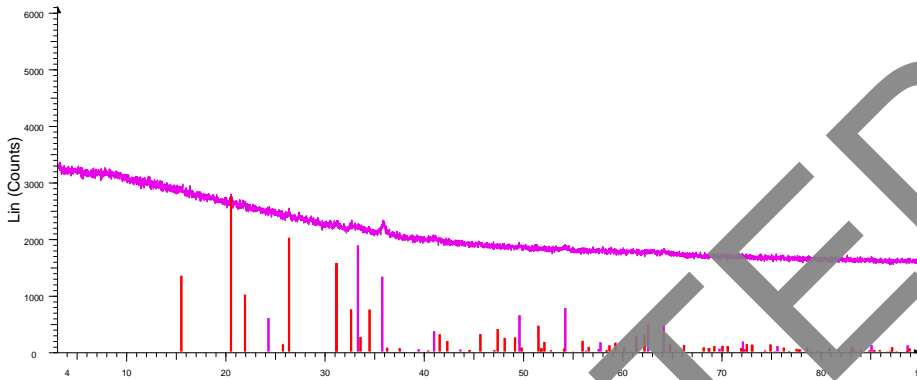


Fig. 3. Experimental powder diffractogram for the magnetic phase.

The red vertical bars in Fig. 3 shows the positions of interference peaks for the crystal form of vanadium oxide V_2O_5 , (code No. 01-070-8747); green vertical dashes show the positions of interference peaks for gypsum $\text{CaSO}_4(\text{H}_2\text{O})_2$, (code No. 01-076-1746); purple vertical strokes positions of interference peaks for the crystalline form of iron oxide Fe_2O_3 (hematite), syn (code No. 01-089-8104); maroon vertical strokes positions of interference peaks corresponding to the crystalline form of iron oxide Fe_3O_4 (magnetite), syn (code No. 01-089-3854). A powder diffraction experiment for magnetic phase 2, predominantly iron-rich, was performed using a Ni filter to attenuate the fluorescence background. This phase was found to contain a small amount of crystalline vanadium oxide V_2O_5 , (code No. 01-070-8747) and an amorphous component. The large amount of iron-containing components in the sample leads to the preservation of the fluorescent background on the diffractogram, but the concentration of the phase allowed us to identify the observed peaks as corresponding to Fe_2O_3 iron oxide (hematite, syn., code No. 01-089-8104) [44].

Currently, technologies have been developed and used to utilize technogenic wastes from industrial enterprises in order to extract valuable rare earth elements from them [44].

The results of the studies have shown that fuel oil ash consists of a complex of useful elements: vanadium, manganese, iron, nickel, zinc and molybdenum, etc., so these technogenic wastes are valuable raw materials. The low content of elements found in fuel oil ash in nature, their high cost in the world market allow us to make a reasonable conclusion about the expediency of deep extraction of valuable elements from technogenic wastes of power engineering enterprises. Rational utilization and industrial production of useful products on the basis of large-tonnage processing of CHPP wastes is limited by the lack of economically efficient and environmentally safe technologies.

We propose a technology of ash and slag waste processing with subsequent extraction of useful metals [44].

Preliminary ash and slag waste is divided into fractions, from which are further extracted products of underburning, iron oxides, microspheres and microdisperse components, consisting mainly of silicon, aluminum, vanadium oxides. The ash is subjected to screening, where it is broken down into fractions, products of underburning are removed. Further, ash and slag wastes with coarseness not more than 0.5 mm are directed to magnetic separation (magnetic field voltage should be not more than 100 kA/m) for separation of iron oxides. The magnetic fractions are passed through the first helical

separation to produce a higher quality iron concentrate. The tailings are deslimed and sent to the second screw separation, where the light fraction represents aluminosilicate concentrate, and the heavy fraction is sent to the concentration table for extraction of valuable metals [44].

Further processing of slags is carried out in order to extract useful metals from them by extraction, sorption processes, methods of gravitational and electrolytic precipitation, etc.

Ash and slag waste processing can be carried out by oxidative roasting with table salt or sylvinite; oxidative roasting with soda; chlorination; ash leaching [44].

Various methods of extraction of valuable rare-earth metals from ash and slag materials consist in their chemical treatment after combustion of fuels with various chemical reagents. The main method of ash waste processing is their stripping with acid reagents, primarily mineral acids.

The method of leaching of metals and rare earth elements from fuel ashes with solutions of nitric, sulfuric or hydrochloric acids in concentration from 50 to 300 g/l at different ratio of solid and liquid phases and temperature from 18 °C to 90 °C is known. Up to 80 % of valuable elements were extracted. As disadvantages of this method it should be noted high energy costs and environmental hazard of the method, due to the use of high concentrations of strong mineral acids [45].

It is known leaching of ashes with different concentrations of hydrochloric acid, in the temperature range up to 80 °C [46]. It was possible to achieve concentrations of extraction of elements Sc - 84 mg/l, Y - 91 mg/l. The disadvantage of the method is unecological method - the use of highly concentrated hydrochloric acid solutions.

The method of extraction of elements from pyritic ore in different media is also known [47].

The remaining part of ash and slag materials can be used for production of concrete products and materials for road and cement industries. The advantages of this method are that it is possible to create products with rather high indices of frost resistance (-300 F and less), low water absorption (less than 5 %), certain architectural forms and stable properties. The method of vibro-pressing allows to produce various building materials from paving slabs to wall stone.

5 Conclusion

The paper shows that the use of cheap and practically harmless nanosized additives allows to improve the physical and chemical properties of fuel, increase the environmental safety of CHPs by reducing the content of sulfur oxides in flue gases. Data on the composition and properties of the fuel carbonate additive are given.

The results of powder diffractogram of magnetic (iron-containing) and non-magnetic phase of ash obtained at combustion of high-sulfur fuel oil are presented.

The paper shows the existence of promising ways of extraction of deficient metals from ash and slag wastes generated at combustion of fuel oil and deposited on the regenerative surfaces of boilers.

The method of complex processing of ash and slag wastes of power enterprises with the subsequent extraction of rare and useful elements from it is offered. The extracted valuable and rare-earth metals can be, first of all, demanded in the electrical complex, at metallurgical, machine-building, ferroalloy and other industrial enterprises.

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