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Method of Dehydration, Moulding, and Processing of Sludge from Thermal Power Plants

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Abstract

The paper examines a facile and efficient method for dehydration of sludge from chemical water treatment of the Surgut Thermal Power Plant using a water-soluble powdered high molecular mass polymer *i.e.* the sodium salt of carboxymethyl cellulose (Na-CMC), as an additive. The integral mass loss and volume loss of samples vary within 70–80 % for 10–15 days when using this method. The optimum amount of the introduced binder is 3–5 % of the mass of the initial sample to obtain dense smooth shaped samples, as established. The data of morphology, structure, phase composition, and particle size in the initial and final products, and also in waste dehydration process are given. Changes in the waste surface during the interaction with Na-CMC accompanied by the formation of hydroaluminates, hydrosulphoaluminates, and hydrosulphoalumoferrite particles with a size of less than 300 nm were recorded. The particles generate a primary alumoferrite frame of a hardening system of coagulation and crystallization structures, as established in a more detailed study. During dehydration and binding processes, it is suggested to dispose of the dry product in the construction industry as an additive for manufacturing cements, foam blocks, foam concretes, in mortars or producing plasters due to the formation of the space frame of iron (III) and aluminium hydroxides. The presence of small amounts of Na-CMC binder will make a positive contribution since it is introduced to reduce setting time when manufacturing construction materials. The results offer prospects for solving environmental issues related to liberating overfilled sludge pits of the thermal power station.

Key words: sludge from thermal power plant, high molecular mass polymer, dehydration, microstructure, alumoferrite frame

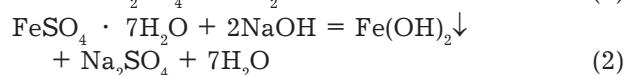
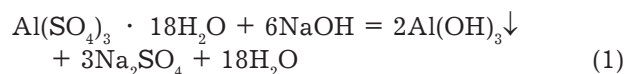
INTRODUCTION

The long and active use of one of the main industrial environmental pollution sources that are thermal power plants (TPP) has exacerbated the environmental situation in the world. Flue gases, thermal pollution, and waste water are the main pollution sources of TPP. Flue gases are completely treated, but even the remaining 1 % has severe adverse effects on the environment. The heat that was not used in the TPP cycle is removed via a graduation tower or a cooling pond into the atmosphere, with the result that the climatic conditions change in this place. And the third type of pollutions is driven by the accumu-

lation of pollutants in sludge pits after chemical water treatment, resulting in the formation of extensive areas and volumes of depositions that are oxidised and spread to the surface of the earth under the influence of water and air. For example, the volumes of unprocessed sludge in two sludge pits on the north side of the Surgut TPP are 36 thousand m³ (by 18 thousand m³ in each). Thus, sludge is one of the volume illiquid outputs of TPP operation. Product composition depends on fuel and reagent type used in chemical water treatment at TPP.

To accelerate precipitation, clarification, and neutralization processes of acid waste water of TPP that contain heavy metal ions aluminium

and iron sulphates are most commonly used as coagulants. The principle of coagulation is one of the common methods of chemical treatment of technical water [1–5]. Precipitated aluminium and iron hydroxides are formed resulting from water treatment:



They entrap salts of heavy metals, fluorine, arsenic, phenol, vanadium, and other impurities from water. Precipitation of poorly soluble compounds sometimes proceeds for a long time and in some cases not completely due to the formation of colloidal precipitates. For this reason, settlers, where sludge of chemical water treatment is accumulated in enormous amounts, are used to continue the neutralization process and separate heavy metal hydroxide precipitates.

Currently, processing and technology methods for disposal of waste water of hydraulic ash removal in TPP, however, the main attention is paid to the liberation process of overcrowded sludge pits that occupy enormous territories and to the search for new means of sludge disposal in the construction or other industry. To liberate filled sludge pits a method that suggests introducing into a precipitate an aqueous composition [6] containing water-soluble high-molecular polyethylene oxide, a dispersing agent (salt of alkali or alkaline earth metals), cation electrolyte and an activator (a polyol) is used, herewith, precipitate moisture content for 12 days reaches 68 %. An aqueous composition is prepared in advance and supplied in polyethylene capacities as 25 % gel. The required concentration is obtained directly prior to use in special capacities equipped with a pipeline of solution feed to a mixer. This method allows intensifying sludge drying process, however, it possesses the whole number of disadvantages. Firstly, its realisation requires a large area (sludge beds). Secondly, the final product is impossible to obtain in dry marketable condition. Thirdly, processing technology is fairly complex, as it assumes the use of pre-prepared solutions with specific concentrations.

A sludge treatment method that includes introducing therein a mixture of acrylamide copolymer and the monomer containing a tertiary nitrogen atom and polymer based on acrylic acid amide taken in amounts (by mass) from 3 : 1 to 1 : 1 followed by separation of the solid phase of

precipitate using chamber filter press is also used. Herewith, the average sludge moisture is 76.9 % [7]. The complexity of this technique is driven by the use of an aqueous mixture of two polymers with a specific ratio, and also the need to use a press filter to obtain the dry product. The used methods are complex and characterised by low productivities on sludge processing.

This paper proposes a relatively straightforward and accessible method for sludge processing and liberating therein dry powders of water-soluble high molecular weight polymer [8]. Powdery sodium carboxymethyl cellulose (Na CMC) is used as a polymer. Wet sludge is transferred to a dry solid dense material with the mass loss and volume loss to 80 mass %. The resulting dry product may be further transported for disposal and processing.

EXPERIMENTAL

Sludge from chemical water treatment and water softening of the Surgut TPP (Tumen region) were selected as study objects. They had the following composition, mass %: aluminium hydroxide $\text{Al}(\text{OH})_3$ 60, iron hydroxide $\text{Fe}(\text{OH})_3$ 15, sand 2.5, organic matter of natural origin 2.5, free water 20, according to the passport of hazardous waste of 23 September, 2009 (Fig. 1, a). The composition of the initial sludge was specified using Elan 9000 inductively coupled plasma mass spectrometer (Perkin Elmer). The instrumental relative standard error for impurity elements in semi-quantitative mode TotalQant is normally ± 2 %.

Technical sodium carboxymethyl cellulose (Na CMC, TU 2231-034-79249837-2006, the Combine Kamenskiy FKP) was used to dewater sludge. The salt is an amorphous, fine-grained or fibrous powdery white material with MM of $(30-25) \cdot 10^3$, water soluble, with a density of 1.59 g/cm³. Calcination studies were carried out using Shimadzu DTG – 60/60 H thermoanalyser, QMS 403 Aeolos@ quadrupole mass spectrometer, in which a new concept of capillary conjugation with a thermogravimeter (TG) and synchronous thermal analysis devices (STA is simultaneous measurements of TG and DSC) was realised.

The size and morphology of the resulting samples were analysed using JEOL JSM-6390LA scanning electron microscope (SEM) equipped with JED-2300 energy-dispersive analyser. The phase composition of the samples was identified using Shimadzu LabX XRD-6000 diffractometer.

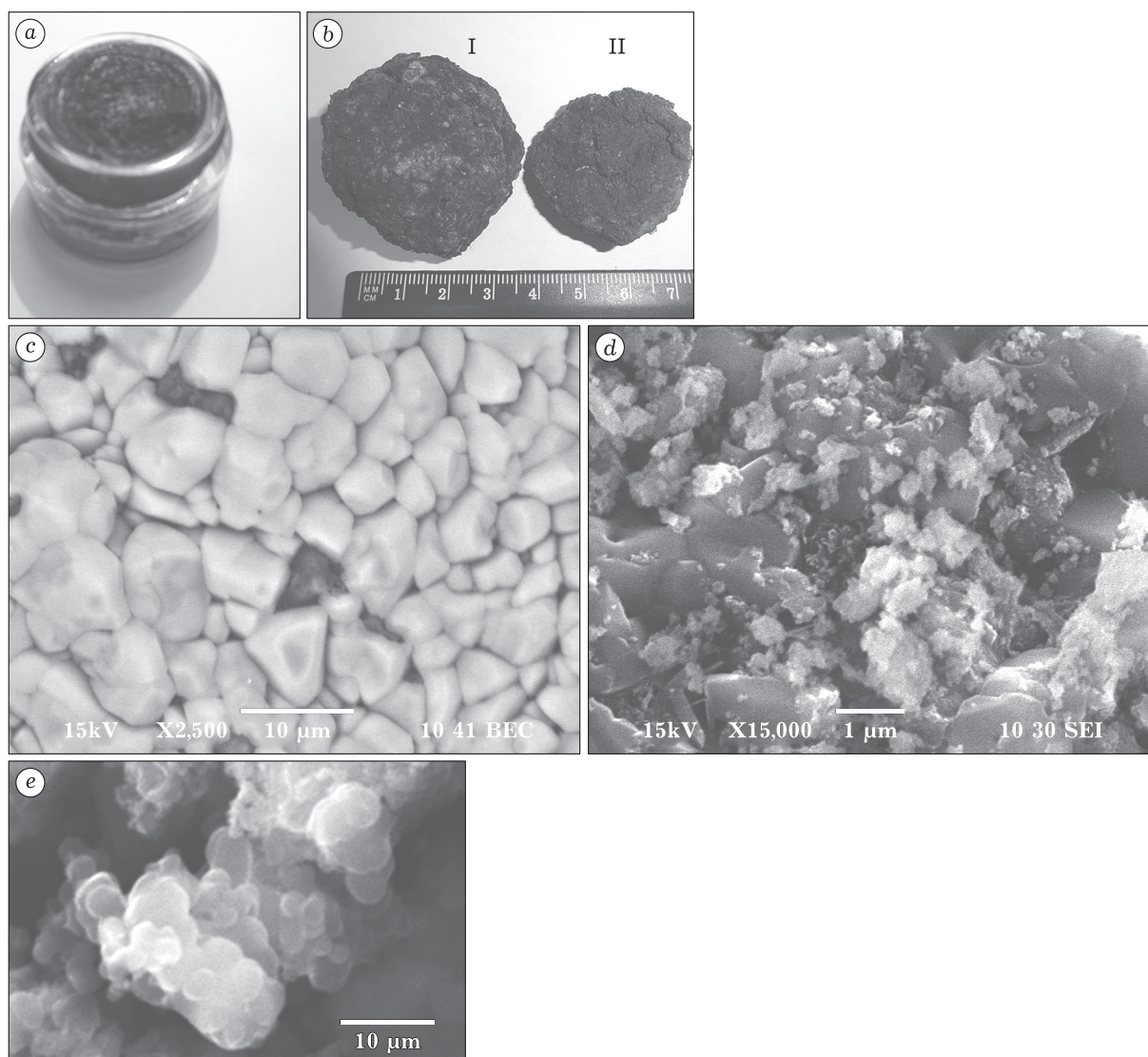


Fig. 1. Electronic image: initial sample of sludge from the thermal power plant (TPP) with moisture content to 80 % (a); general views of sludge samples (I – 2 % Na-CMC, air-drying for 20 days, room temperature; II – 17 % Na-CMC, 15 days, room temperature) (b); initial sludge from TPP, air drying for 5 days at room temperature (c); sample with Na-CMC 5 %, air drying for 5 days at room temperature (d); forming the alumoferrite frame of nanoparticles (e).

RESULTS AND DISCUSSION

The main part of sludge consists of aluminium hydroxide (60 %) that is formed in the neutralization of acid waste water initially into a colloidal solution of $\text{Al}(\text{OH})_3 \cdot n\text{H}_2\text{O}$ as a white voluminous gelatinous precipitate that is almost insoluble in water and of amphoteric nature (Fig. 2, a). Aluminium hydroxide changes its amphoteric nature for the poorly crystalline structure of $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ with time on long storage in sludge pits under the influence of the environment. The presence of $\text{Fe}(\text{OH})_3$ (15 %) provides sludge with red colour, high dispersion, and caking and clumping abilities. Thus obtained precipitates saturated with water are poorly filtered (quickly choke or “silt” filters), settle slowly, easily roiled

during water discharge after settling. In the latter case, “secondary” water pollution happens, therefore, such precipitates are difficult to re-lease from the water [9].

The chemical composition of sludge from the Surgut TPP (Table 1) was specified using an inductively coupled plasma mass spectrometer. The former is in agreement with the content of the main elements of technogenic wastes, according to the technical passport. The initial sludge contains 78.67 % of free and hydrated moisture (Fig. 3, a), as established using Shimadzu thermal analyzer. There is a sharp jump up related to the release of water vapor to the gas phase during free water evaporation, and then slow removal of hydrated moisture happens from 200 to 350 °C. Small amounts of CO_2 (at temperatures of 300–

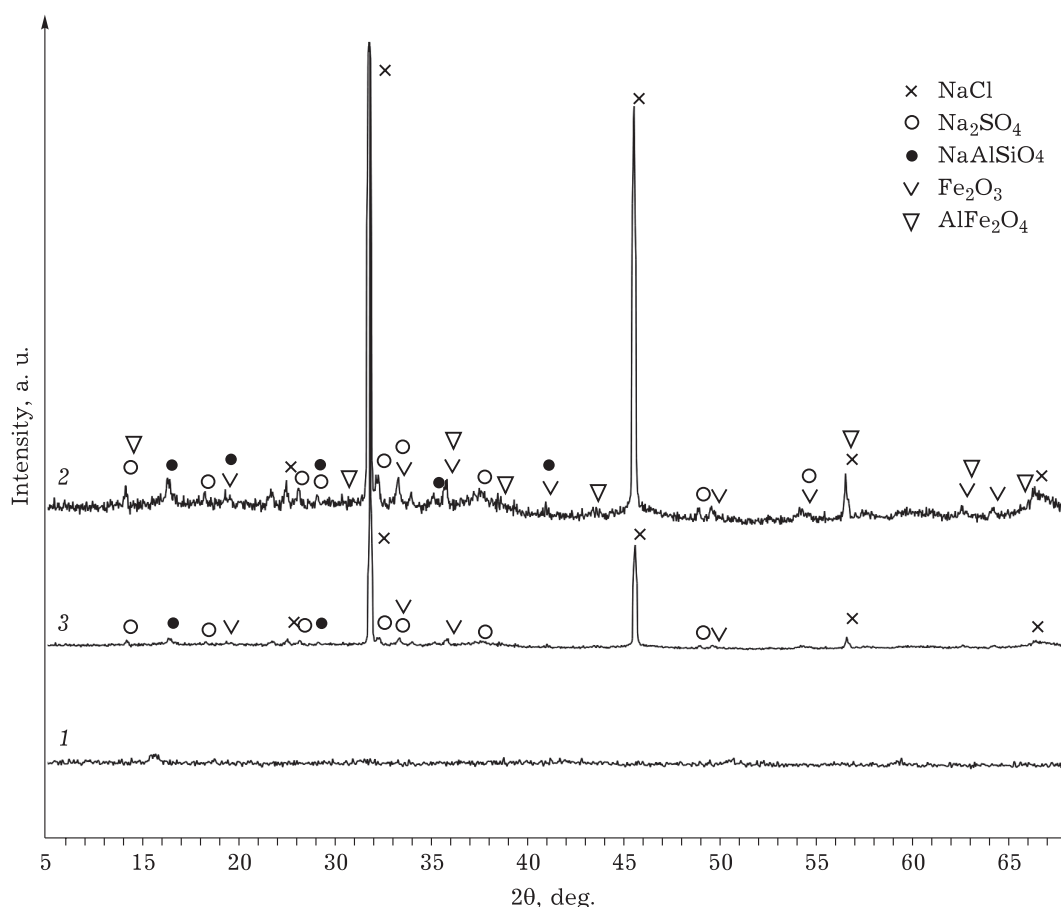


Fig. 2. Diffraction patterns of processes of dewatering sludge from TPP: initial slurry from TPP (a), air drying, room temperature; dross T = 900 °C, exposure time is 60 min (b); sludge from TPP with 5% Na-CMC, air-drying for 15 days at room temperature (c).

500 °C), N₂, and O₂ (to 400 °C) were recorded in the gas phase, in addition to water vapours, (see Fig. 3, b). The quantitative phase gas composition is as follows, according to calculations, %: H₂O 92.30, CO₂ 7.13, N₂ 0.21, O₂ 0.36. Sample mass is completely stabilized in 500–600 °C temperature range.

Studies on air calcination of sludge were carried out in a laboratory muffle electro furnace (Nabertherm, HT 08/16) in 500–900 °C temperature range for 1 h using heating and cooling rate of 10 °C/min. After calcination, dross is obtained; its composition has been studied using X-ray

TABLE 1

Spectral chemical composition of TPP sludge

Elements	Content, mass %	Elements	Content, mass %	Elements	Content, mass %
Al	2.5	P	<0.001	Ga	0.0003
Fe	1.2	K	<0.001	Ni	0.0002
Si	0.05	V	<0.001	Pb	0.0001
Na	0.04	As	<0.001	Nb	0.0001
Zn	0.04	Se	<0.001	La	0.0001
Mg	0.02	Br	<0.001	Li	0.0001
Mn	0.007	Mo	<0.001	Ca	0.0001
Cu	0.006	B	<0.001	Au	<0.0001
I	0.006	Ag	<0.001	Sb	<0.0001
Ba	0.0015	Ti	0.0009	In	<0.0001
Sr	0.001	Te	0.0009	Sn	<0.0001
Cr	0.001	Ce	0.00025	U	<0.0001

phase analysis (see Fig. 2, b). Samples consist of iron oxides (076-4579) and sodium aluminosilicate (NaAlSiO_4 , 052-1342), aluminium ferrite (AlFeO_4 , 089-7408), and sulphate Na_2SO_4 (074-2036), as established after calcination in air. Dross mass is 8 % of the initial sample mass. The elemental chemical sample composition is as follows, mass %: Al 56, Fe 18, Si 12, Na 6, admixture phases (containing S, Cl, K, Ca, P, etc.) 8. Thus, sludge pits can be liberated simply by sludge combustion and 8 kg of dross will remain from 100 kg of sludge, and 80 kg – from 1 ton. However, in addition to the main components, there is chlorine in the spectral map of the main element distribution by a sample obtained using energy-dispersive analysis (Fig. 4). The element is contained as admixture organics of natural origin in the amount up to 2.5 % (chlorides in the initial sludge – to 67 mg/dm³). To determine the amount of generated dioxin chemical analysis in special accredited laboratories is required, furthermore, it is known that combustion of technogenic products may have harmful effects on the environment and future generations of humanity.

As mentioned above, water-soluble high molecular weight polymers are most commonly used to bind water. This work used Na-CMC (sodium salt of carboxymethylcellulose) for sludge dewatering and moulding. Figure 5 presents the dependencies of a change in the mass and volume of the samples on the amount of the introduced polymer and drying time. It can be seen that the samples are completely stabilized by mass and

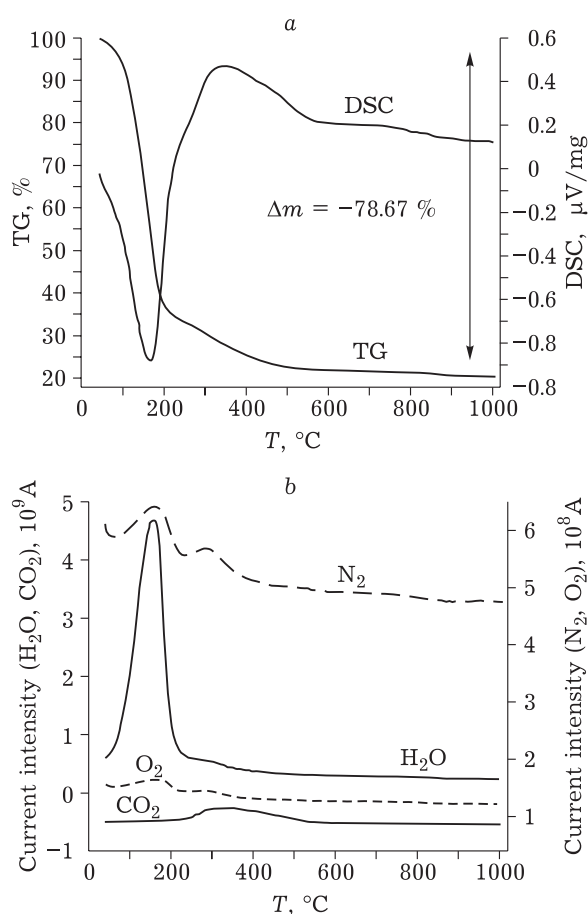


Fig. 3. Thermal analysis of the gas phase of a slurry sample from TPP.

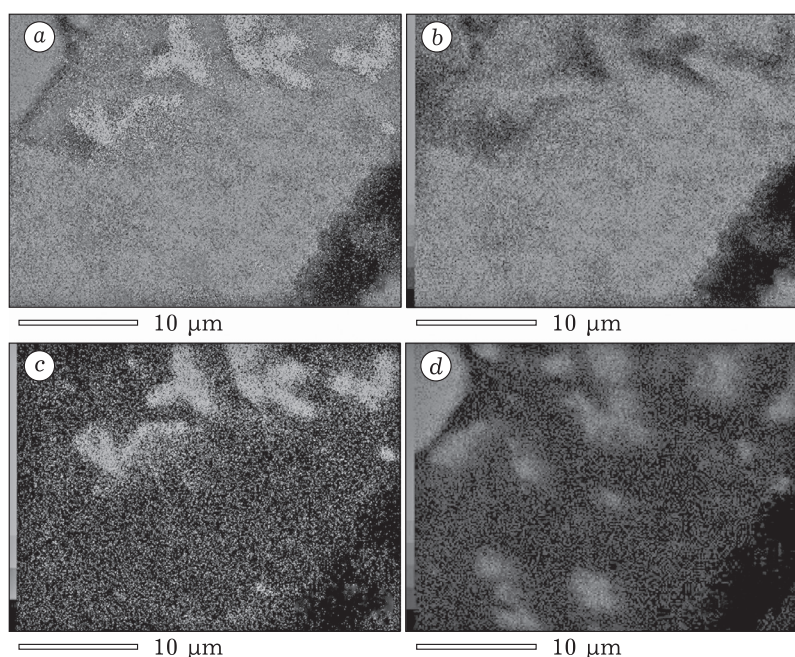


Fig. 4. Distribution of the main components, such as Al (b) Fe (c), Cl (d) along a sludge sample in the spectral map (a).

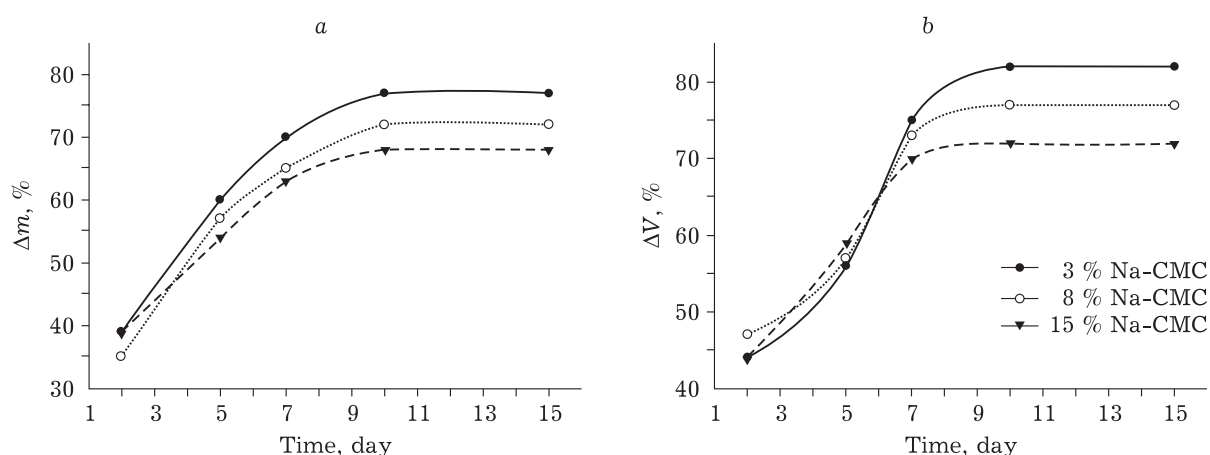
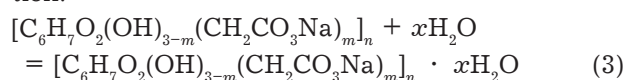


Fig. 5. Mass (1) and volume (2) of samples versus Na-CMC content and drying time.

volume for 10–15 days; herewith, the losses of sample mass reach 75 %, and of sample volume – 80 %. The degrees of change in viscosity and humidity of the samples were determined depending on drying time. Samples containing 0.06 g/cm^3 (15 mass %) Na-CMC had polymer concentration after drying 35 %. It has also been found that when using binders in amounts of less than 3%, more fragile and friable samples that require a longer time for binding and complete dehydration are obtained (see Fig. 1, b, I). If the amount of the binder exceeds 15 %, drying time reduces from 2 to 5 days, the resulting samples are denser but they are inferior to those with 3 % Na-CMC content and require high reagent consumption (see Fig. 1, b, II). The optimum amount of the introduced binder should be 3–5 % of the initial sludge mass, as demonstrated by the carried out studies. Sodium chloride and sulphate begin to crystallize in the first place, as established using XPA in the dehydration process of the samples. Afterwards, the beginning of the formation of iron oxide and sodium aluminosilicate phases has been recorded (see Fig. 2, c). Thus, a dry, dense product mainly consisting of solid phases of sludge with losses in mass and volume up to 70–80 % for 10–15 days has been obtained.

The use of dry powders of a hydrophilic high molecular weight polymer as an additive allows quickly transferring a pasty hydrated suspension into the solid and dry condition without using additional equipment, *e.g.* press filters. This result is driven by polymer dissolution in sludge moisture and intense water evaporation through a polymer film. The process is accompanied by the chemical interaction of Na-CMC and water by the reaction:



The viscosity of Na-CMC – $x\text{H}_2\text{O}$ system depends heavily on x value; Na-CMC is able to draw out significant amounts of water from inner sludge layers and evaporate it into the air due to this interaction. We have managed to record sludge changes during the interaction with Na-CMC. Figures 1, b and c demonstrate sludge surface without the binder and with the introduced one (10 %), respectively. Both samples are air dried at room temperature for 5 days. Thus, the polymer acts as a conductor pulling out water from the slurry and introducing it to the gas phase. A dispersed particle system that generates the space frame of coagulation and crystallization structures is formed resulting from dehydration as far as sludge samples slow harden (see Fig. 1, e). The entire dehydration process from the initial hydrogen-containing sludge to the final dewatered, dry product can be traced in Fig. 1. One can see resulting low-basic hydroaluminates, hydrosulphoaluminates, hydrosulpho-alumoferrites, and other compounds with sizes less than 300 nm during a more detailed study. The resulting primary alumoferrite frame of the hardening system will allow widely using the dried product in the construction industry as additives for manufacturing cements, foam blocks, foam concretes, mortars or manufacturing plasters. As a result, reinforced concrete products will only strengthen due to the alumoferrite frame. The presence of a small amount of a binder has a positive effect since Na-CMC in manufacturing building materials is introduced to reduce the setting time.

CONCLUSION

A new method of dehydration and binding the main phases of sludge into the dry product that may be further transported with a view to its pro-

cessing and disposal has been developed. Mass and volume losses of the resulting sample reach 80 % of the initial indicators. Thus, the realization of this method opens up prospects on liberating overfilled sludge pits in any thermal power plant (TPP), regardless of the chemical content of sludge.

The composition of the initial technogenic waste that is sludge from the Surgut TPP has been explored. A change in its properties, morphology, and structure during dehydration and moulding processes has been studied. The amphoteric frame based on iron (III) and aluminium hydroxides is formed, as established during the dehydration process. Routes of further processing of sludge and its use in the construction industry have been outlined.

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