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Comprehensive Saltwater Clearing Technology

Abstract.
One of the major environmental problems at present is the salinization of surface and groundwater sources. Related to the increased discharges of mineralized sewage, this problem can be solved by complex processing. The current study investigates water demineralization with the purpose to create a comprehensive technology for the purification of high-salinity waters with chemical methods and to identify possible ways of utilizing their sediments as the binders or as the components for the binders. Grounded on the results of the study, the technology to apply the sediments in the building industry is proposed. The results of the study evidence that CaO and Na[Al(OH)4] can provide the effective water demineralization.

Key words: *softening, mineralization, sediments, sodium aluminate, lime, gypsum-containing wastes, gypsum binder, concrete.*

1. Background. At present, there are quantitative and qualitative changes in the water resources for a consumer use, occurring due to their intensive exploiting by mankind and the discharge of sewage without previous proper cleaning. A significant amount of pollutants enters the water reservoirs with mine waters [1]. This leads to the increased mineralization found in water sources. The use of such water without proper preparation is impermissible. One of the workable solutions to this problem is the mass-scale implementation of modern comprehensive purification technologies for high-salinity waters. This measure can not only reduce the deficit of fresh water, but also provide proper comprehensive recycling of generated liquid and solid wastes. Therefore, the problem solution for high-salinity water purification is urgent.

2. Research Object and Research Methodology. Considering all above-mentioned we assume it is reasonable to choose the processes of water demineralization as an object for this publication with the purpose to determine the ways of developing a comprehensive technology for the purification of high-salinity waters and subsequently to identify the possible ways of utilizing the sediments as the binders or the components for the binders.

In the reported research, the chemical methods of water purification were used for the water softening and purification from sulphates when they sediment in the form of calcium sulphoaluminate hydrate during water treatment with lime and aluminum-containing coagulants. The water under stirring was treated with the calculated amounts of lime and coagulant. After 3 hours, the sediment was separated and the water in the filtrate was tested for its hardness, sulphate concentration, alkalinity, and pH balance. CO_2 was drafted through the filtrate as long as until pH = 7-8, after that the sediment was separated in the filter, its solution was analyzed for all of the above mentioned parameters.

The degree of softening (Z) and the degree of sulphate recovery from water (A) were calculated by the following formula:

$$Z, A = \left(1 - \frac{H_{res}\left(C_{SO_4^{2-}res}\right)}{H_{in}\left(C_{SO_4^{2-}in}\right)}\right) \cdot 100$$

where H_{in}, $C_{SO_4^{2-}in}$ $C_{SO_4^{2-}in}$ – respectively, the initial hardness and the initial concentration of sulphates; $H_{res.}$, $C_{SO_4^{2-}res}$ $C_{SO_4^{2-}res}$ – respectively, the hardness and the concentration of sulphates in the purified water.

IR spectroscopy and X-ray analysis have been carried out in order to determine the possible directions for utilizing the sediments and to make them serve as the binders or the components of the binders. The analyses have been conducted to study the sediment obtained as a result of chemical softening for the water and the samples have been dried at the temperature of 200°C (drying time was 2 hours).

3. Research Results and Discussion.

3.1. Methods of Water Softening. Various methods have been actively used for water softening: chemical methods [2, 3], ion exchange methods [4], chemicalsediment and electrocoagulation methods [5] and membrane filtration methods [6]. The methods incorporating the application of various reagents are rather widely used due to their cheapness and simplicity plus the possibility of utilizing the precipitated nontoxic sediments.

It is found reasonable to use lime and aluminum coagulants as such reagents [7]. They suggest that the usage of sodium aluminate as a coagulant is convenient when dosing and is characterized by high efficiency in contaminant removal.

3.2. Purification and Sediment Formation. When lime is added to the solution, wherein sulphate concentration reaches 65 mg eq/ dm^3 while its hardness is up to 36 mg eq/ dm^3, calcium sulphate is formed, which partially passes into the sediment. Due to the solubility of gypsum, a significant portion of the calcium sulphate appears in the solution. When sodium hydroxy aluminate is introduced, calcium hydroxy aluminate is formed to produce a complex calcium sulphoaluminate hydrate salt, afterwards it is effectively separated from water. In the alkaline medium, hydrolysis and precipitation of magnesium ions occur. In order to neutralize the alkali to have been formed from sodium hydroxy aluminate and to bind the excess calcium ions, the water was treated with carbon dioxide. Note that in this case pH of the solution decreased from the range of 12.0-12.5 to 7.0-7.5, while the hardness of the solution reduced to 0.29-0.90 mg eq/ dm^3 (refer to Table 1). The efficiency of sulphate recovery increased both with the increase in the consumption of sodium aluminate and with the increase in the consumption of lime. When the dose of lime was higher, the increase in the degree of sulphate recovery was registered along with a slight increase in the alkalinity of water. Such a behaviour evidences that the efficiency of sulphate recovery in this case depends to a large extent on the sediment of calcium sulphate along with the co-sediment of sulphate and calcium aluminate.

CaO dose, mg eq/ dm³	Na[Al(OH)$_4$] dose, mg mole / dm³	Extraction degree of ions SO_4^{2},%	Softening Degree, %
166	10.83	77.8	98.4
166	13.00	79.5	99.3
166	16.25	87.1	99.2
231	10.83	83.4	97.5
231	13.00	86.3	99.3
231	16.25	87.4	99.2

Table 1. Effect of Reagent Doses on the Purification Efficiency (Solution Processing with Lime, Sodium Hydroxy Aluminate and Carbon Dioxide)

The sediments, which are formed during the water purification and softening for various purposes, are said to be classified as industrial wastes. Moreover, the industrial wastes include the wastes from the chemical industry, the construction business, power engineering and metallurgy.

For the research, the IR spectroscopy and the X-rav analvsis have been carried out and their results are shown in Fig. 1 and Fig. 2.

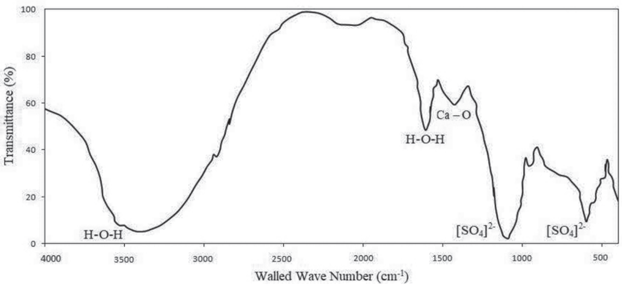

Figure 1. The IR Spectrum Visualized: the Sediment Formed when Water Softening with the Reagents.

The graph of the IR spectrum indicates that the sediment contains sulpho compounds, namely sulphates, calcium compounds and water of crystallization. The presence of the crystallization water and of the sedimen which after the precipitation passed through the drying stage at the temperature of 200°C leads to the conclusion that calcium sulphate hemihydrates is within the composition of the sediment.

The X-ray structural analysis does not clearly determine that very modification of calcium sulphate (dihydrate or hemihydrate) which is present in this sediment. However, the diffractogram identifies magnesium hydroxide and calcium sulphoaluminate hydrate.

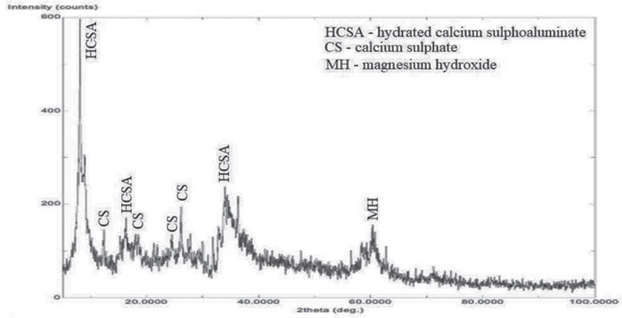

Figure 2. Sediment Diffractogram (the Sediment Formed during Chemical Water Softening)

Thus, the quantitative relationship of the sediment formed during the water softening via chemical reactions is represented by the rates of calcium sulphate, magnesium hydroxide and sulphoaluminate hydrate.

The wastes based on various modifications of calcium sulphate (gypsum-containing wastes) have found wide application in the construction industry. In general, there are about 50 types of gypsum-containing wastes, but only a small number of them has acquired practical significance (phosphogypsum, desulphogypsum). Regarding some wastes, there are extensive scientific studies on the methods for their processing and utilization, but they have not been introduced into industry (vitamin gypsum, citrogypsum).

3.3. Prospects for Utilization in the Construction Industry. We find it rational to make a brief review on gypsum-containing wastes that are used in the construction industry and on the lists of the problems arising from their utilization and processing.

3.3.1. Phosphogypsum in Cement Manufacture. The first substance to draw your attention is phosphogypsum, a waste product of phosphoric acid extraction, consists of hemihydrate gypsum, anhydride, or a mixture thereof plus admixtures.

In the process of phosphoric acid production, it is generated as much as 4.3-5.8 tons of phosphogypsum per 1 ton of phosphoric acid depending on the type of raw materials and the technology adopted. The phosphogypsum is mainly discarded in Ukraine on the dumping sites located on the territory of the Ukrainian regions as follows: Sumy onlast, Vinnytsia oblast, Rivne oblast and Lviv oblast [8].

Currently, two practices are mostly applied worldwide with respect to phosphogypsum: dumping into water bodies (rivers, seas) and storing on land. With storage in dry without preliminary neutralization, phosphogypsum releases on average 10 g of fluorine per ton of the waste into the air while approximately 10% of phosphogypsum is washed out by atmospheric precipitations. Therefore, phosphogypsum requires proper storage in special facilities maximally isolated from water bodies. Neutralization with lime milk is a strongly advised procedure for phosphogypsum before storage in storehouses [9].

The principle ways how phosphogypsum can be effectively utilized are focused on manufacturing gypsum binders from it. The appropriate technologies have been developed and introduced for obtaining gypsum binders, they are based on semi-aqueous gypsum of α-modification, β-modification and anhydrite. Moreover, phosphogypsum is used as a mineralizer in the raw mix for cement production and as a substitute for natural gypsum within the compositions of additive-free type I cement. Among the countries wherein these technologies are applied, it is important to highlight Japan, China, Germany, France, Russia and South Africa. However, in quantitative terms, these technologies utilize approximately 15% of the global phosphogypsum; the remaining 85% is stored in specially designated places [10].

3.3.2. Desulphogypsum Abundance to be Solved. The next substance to address is desulphogypsum, a waste by-product that is formed during the purification of flue gases from sulphur compounds to have formed during coal combustion at thermal power plants. There are wet and dry techniques for the gases purification along with those engaging lime and limestone, but they result in desulphogypsum formation.

The product resulting from dry desulphurization with limestone is a finely dispersed mixture that contains fly ash, calcium carbonate, calcium oxide, calcium hydroxide, sulphite and calcium sulphate. As a result of the wet method of flue gas desulphurization, the various modifications of calcium sulphate, calcium hydroxide and calcium carbonate are predominantly formed [11].

Nowadays, the process of introducing flue gas desulphurization systems is at the initial stage in Ukraine. The system of dry desulphurization is applied at the Kurakhivska thermal power plant while the system of semi-dry desulphurization is used at Trypilska thermal power plant. However, most thermal power plants in Ukraine simply emit flue gases into the atmosphere, in particular, the annual emissions of SO_2 into the atmosphere amount up to about 1.5 million tons [12].

The utilization issues have mainly touched the problems of furnace waste generated from thermal power plants. Thus, in Ukraine, furnace waste is used in road construction. Since there are no systems for wet flue gas desulphurization in Ukraine, there is no experience of desulphogypsum utilization either. The world leader in desulphogypsum utilization is Japan, which has introduced the technologies for the production of plaster and gypsum wallboards from desulphogypsum [13].

3.3.3. Prospective for Vitamin Gypsum and Citrogypsum. A sulphuric-acid bath when neutralized with calcium hydroxide in the process of vitamin A production generates vitamin gypsum, which is mainly represented by calcium sulphate dihydrate. The experience gained by Belgorod State Technological University named after V. G. Shukhov confirms that vitamin gypsum can be processed into the gypsum binders [14].

The production of citric acid also adds to the gypsum-containing waste dumping as it releases the by-product of citrogypsum generally in the amount of 3.8-5.7 tons of the waste per 1 ton of citric acid. Citrogypsum is not only gypsum slurry but it also includes mycelium and calcium citrate filtrate. This gypsum is mainly represented by its hemihydrate and anhydrous modifications. Today's Ukraine just discard but does not further use either gypsum slurry or other wastes of citric acid production. However, there are scientific searches conducted on the methods to utilize citrogypsum and they show that this by-material can be successfully processed into the gypsum binders or the articles made from gypsum, in particular, decorative ones [15].

3.4. Threatening Ratio and the Solutions. Nowadays, only a few kinds out of the 50 types of gypsum-containing waste have actually been used. The main deterrent factors for the gypsum-containing waste to be widespread are high humidity, significant variations in their chemical compositions, the presence of harmful impurities, radioactivity, the need for complex or expensive equipment for preparing waste into secondary raw materials, and the economic inexpediency of processing waste, compared to their natural comparable substances. The most influential deterrent factor could be named is varying chemical composition of gypsum-containing waste.

We analyze both the technologies currently applied and the scientific researches concerning the issues of waste utilization and this has allowed us to identify the ways how gypsum-containing wastes could be processed and utilized, in particular, their sediments, which are formed during the chemical purification of water. Additionally, it is worth noting that gypsum, natural gypsum stone and gypsum binders have a wide application inherently: they are the activators of slag hardening, the components for expanding additives and a component of mixed binders. Thus, gypsum-containing wastes, in particular, the sediments formed during the chemical purification of water, can be utilized as follows: 1) as a raw material for the production of the gypsum binders and the articles made from them, mainly plasters and gypsum boards; 2) as mineralizers within the raw mix for cement production; 3) as replacers for natural gypsum stone in cements; 4) as the components of expanding cements; 5) as the activators for hardening slag cements and cements with active mineral additives; 6) as the components for the production of gypsum cement-pozzolanic binders.

Thus, the sediments that are formed during the chemical softening of water are widely used in the construction industry. In this case, the chemical way of water softening followed by reclamation of the sediments in the compositions of binding materials is able to develop a low-waste technology for water demineralization.

4. Conclusions

It has been established that with the use of lime, sodium hydroxide aluminate and carbon dioxide, one can achieve both effective water purification from sulphates and effective water softening at its high alkalinity values, which depend on the total sulphate, on sodium hydroxy aluminate consumption and on the sodium sulphate content in water. The sediments that are formed as a result of water purification can find wide application as the gypsum binders, the components of various types of cement and mixed binders.

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