Physical and Mechanical Properties of Fine-Grained Concrete Produced using Water Purified by Natural Adsorbents

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The main part of drinking water consumption falls on powerful industrial facilities, however, the requirements for water used in technological processes are much lower than for drinking water. This work has shown that water contaminated with sulfates, after purification with natural adsorbents, comes up to the requirements of the standard. Determination of the initial and residual concentration of the pollutant in the solution was carried out through the control of electrical parameters, the so-called conductivity method. The purified solutions were used for the production of fine-grained concrete and the strength of the finished products was determined on the 28th day of hardening. The suitability of such solutions for use in the concrete industry was established not only from the point of view of suitability according to standards but also from the point of view of ensuring the required strength.

Introduction

Lack of clean drinking water is one of the most acute problems facing humanity [1]. Limnetic waters are only 2.5% of the total amount of water that exists on our planet. More than half of this volume is represented by glaciers and snowcaps of the mountains. That is, humankind can use only 1% of all limnetic water resources on the planet [2].

One of the problems of lack of water resources is the uneven distribution of water resources throughout the globe.

It's not only a natural process, but the result of human activity. The main reasons are:

• the greenhouse effect associated with global warming

• annual population growth

• improper use of natural resources

According to statistics, 3300-3500 km^3 of water is consumed annually around the globe [3]. Most of this huge amount (about 70%) goes to agriculture. The pulp and paper and chemical industries, non-ferrous and ferrous metallurgy cannot do without water, it is necessary to meet the household needs of the population. Given the water cycle in nature, its consumption is much higher than recovery [4, 5].

Even in the construction industry, water has many requirements. Many methods of water purification are known, but the main methods of determining its suitability for use in concrete are regulated by European standards. The water should also conform to either the chemical requirements or the requirements for setting time and compressive strength and not cause corrosion of the fittings. Sewage, swamp and peat water are not allowed for the preparation of concrete and mortars, care of concrete and washing of aggregates.

Much attention in these norms is paid to water recovered from processes in the concrete industry. This concerns detergents (any foam should disappear within 2 minutes), colour (the colour shall be assessed qualitatively as pale yellow or paler) and odour (no smell, except the odour allowed for potable water and a slight smell of cement and where blast furnace slag is in the water, a slight smell of hydrogen sulphide). Requirements for other pollutants are the same regardless of the origin of the water resource. For example, oils and fats should be no more than visible traces, no suspended matter, and pH $\geq$ 4.

Water not conforming to one or more of the requirements described above may be used only, if it can be shown to be suitable for use in concrete, inaccordance with next requirements. The initial setting time obtained on specimens made with the water shall be not less than 1 hour and not differ by more than 25 % from the initial setting time obtained on specimens made with distilled or de-ionised water. The final setting time shall not exceed 12 hours and not differ by more than 25 % from the final setting time obtained on specimens made with distilled or de-ionised water. The mean compressive strength at 7 days of the concrete or mortar specimens, prepared with the water, shall be at least 90 % of the mean compressive strength of corresponding specimens prepared with distilled or de-ionised water.

The chloride content of the water expressed as Cl^- shall not exceed the levels given in **Table 1**.

Table 1. Maximum chloride content of mixing water

End use	**mg/L**
Prestressed concrete or grout	500
Concrete with reinforcement or embedded metal	1000
Concrete without reinforcement or embedded metal	4500

Sulfates often enter water sources together with wastewater as a result of incomplete purification from detergents, surface-active substances, as well as from industries where sulfuric acid is used in technological processes. Such water is not suitable for consumption, but it can be used for technical needs. Given the lack of drinking water, technical water can be used for technological processes in other industries, in particular, concrete production. The chemical composition of water must meet the requirements of EN 1008:2002 standards. Exceeding the content of Cl^- ions;

SO_4^{2-} affects setting time, mechanical characteristics and contributes to corrosion of fittings [6].

The sulphate content of the water expressed as SO_4^{2-} shall not exceed 2 000 mg/L

In the first instance, qualitative tests for sugars, phosphates, nitrates, lead and zinc may be carried out. If the qualitative tests show a positive result, either the quantity of the substance concerned shall be determined or tests for the setting time and compressive strength shall be performed [7].

If chemical analysis is chosen, the water shall conform to the limits given in **Table 2**.

Table 2. Maximum content according to requirements for harmful substances in water used for concrete

Substance	mg/L
Sugars	100
Phosphates; expressed as P_2O_5	100
Nitrates; expressed as NO_3^-	500
Lead; expressed as Pb^{2+}	100
Zinc, expressed as Zn^{2+}	100

Every year, the resources of natural waters for commercial and drinking purposes are reduced due to uncontrolled, usually the discharge into natural reservoirs of insufficient or untreated wastewater after a variety of technological processes. As a result, natural waters are increasingly used for production needs, which in some indicators do not meet the standards, having previously carried out purification, which makes it possible to bring the water composition to normal. The purpose of this work is the process of water purification by known cost-effective methods and methods of rapid monitoring of purified water quality. These measures make it possible to use unfit for drinking or wastewater after technological processes [8].

Experimental part

Materials and methods

This research used cements CEM I-42,5 produced by PJSC Podilskyi Cement (Kamianets-Podilskyi, Khmelnytskyi region of Ukraine) got from the clinker of the normalized mineralogical composition (mass %: C_3S – 59,7; C_2S – 18,5; C_3A – 6,6; C_4AF – 11,9). According to physico-mechanical parameters listed in **Table 3**, cement CEM I-42,5 meets the requirements of EN 196-1.

Table 3 Physical and mechanical properties of the cement

Specific surface A m^2/кg	The sieve residue 008, mass %	Setting time, min		Compressive strength at age, days (MPa)		
		initial	final	2	7	28
340	1,6	160	250	20,5	38,5	52,4

Bulk density was 1140 kg/m^3.

According to EN 196-1 natural quartz sand with fineness modulus, M_f = 1.53 was used. Besides, it characterized a bulk density, which consists of 1420 kg/m^3 and a voidness of 45.8%. The specific surface of the sand used is 15.3 m^2/кg.

Clinoptilolite from the Sokyrnytske deposit (the southwest part of the Transcarpathian internal trough) was used for the research. The mineral rock composition was as follows: clinoptilolite 60–90%, quartz and feldspar 6–7%, clay minerals 2–6%, plagioclase 2%, smectite 7%. The chemical composition of zeolite included (wt.%): SiO_2 - 70.21; Al_2O_3 - 12.27; Fe_2O_3 - 1.2; FeO - 0.55; TiO_2 - 0.14; MnO - 0.073; P_2O_5 - 0.033; K_2O - 3.05; Na_2O - 1.77; SO_3 - 0.10; and (CaO+MgO) 10.604. The composition of clinoptilolite corresponded to the following formula:

$$0.2Na_2O \cdot 0.26K_2O \cdot 0.43CaO \cdot 0.2MgO \cdot \cdot 9.57SiO_2Al_2O_3 \cdot 0.09Fe_2O_3$$

Shungite from the Zazhogino deposit was used for the research. It belongs to the II category of black shungites, one of the youngest categories of this mineral. Carbon content consists of 35-80 %, density - 1.98 g/cm³, porosity - 3.2 %. The main element carbon is partially contained in the form of fullerene, which determines its specific properties. The nature of shungite is still unclear despite its more than a century-long study by scientists. However, it is often compared with clinoptilolite [9].

The physico-mechanical tests of samples were carried out according to the European standards, covering the determination of limits of compressive and bending strengths of fine concrete by using test beams. The samples of 4×4×16 cm size containing silica sand of 75 wt % were prepared at w/c ratio of 0.28. The samples were tested by using a hydraulic press P – 50.

The X-ray analysis of the samples was carried out according to the method of powder on a DRON-2.0 diffractometer and CuKα radiation. The thermal analysis aimed at identifying the temperatures at which changes in physical conditions of the samples or their chemical compositions can be observed.

The thermal analysis of clinoptilolite and shungite samples was performed using the Q-1500 derivatograph of the Paulik, Paulik and Erdey system at the temperatures from 20 to 800 ^{0}C. The samples were analyzed dynamically at the heating rate of 10°/min in air. The weight of the samples was equal to 500 mg. To carry out the X-ray phase and thermal analyses, the samples were crushed in a mortar until they fully penetrate through sieve No.008.

Determination of water pollutants was performed by the standard conductometric method that is designed for rapid studies of concentrations of substances that affect the conductivity of a liquid of multicomponent solutions. This method allows determining the concentration of a single controlled substance in a multicomponent fluid, using a single measured value of the specific conductivity at a predetermined in laboratory frequency of the electromagnetic field [10].

Results and discussion

For the treatment of non-concentrated effluents, the adsorption method is promising, where activated carbon is used as a sorbent, but its high cost and low sorption capacity to absorb pollutants led to the search for new, cheaper and more common materials with high mechanical strength and large pores that can purify water to concentrations regulated by standards. Such natural materials are clinoptilolite (zeolite) and shungite.

The X-ray diffraction patterns of shungite and zeolite are shown in **Figure 1**.

As shown in the figure 1 carbon (**C**) and silica (**SiO_2**) are the main shungite components (b), while the phase composition of the zeolite is represented by three components (a): the same silica (**SiO_2**), corundum (**Al_2O_3**) and hematite (**Fe_2O_3**)

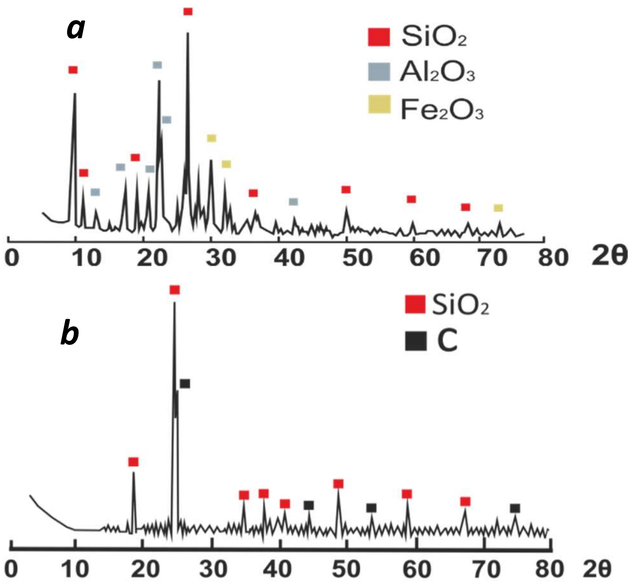

Figure 1. X-ray diffraction patterns: a – zeolite, b – shungite.

Thermal analysis can be used to define the rock's mineral composition. The thermal analysis data can vividly show the nature of mineral-bound water. In addition, the influence of various factors on the structure and chemical composition can be investigated by the nature of the water loss when heated.

Thermolysis of the clinoptilolite samples included four stages (**Figure 2**). At the first stage, the physically adsorbed moisture is released at the temperatures of 20 to 203°C. This process is followed by a rapid mass loss of the samples and a deep endothermic effect that appears on the curve of differential thermal analysis (DTA).

The second stage of thermolysis in the temperature range from 200 to 410°C fits with the discharge of structured water that is coordinately linked with the mineral exchangeable cations. This process is followed by the gradual mass loss of samples along with a change to the character of a rising region of the DTA curve. The third stage of thermolysis happens at the temperatures of 400 to 580°C. It demonstrates a release of isolated water molecules being localized on the mineral's surface due to water bonds with the OH groups. The process is also accompanied by the appearance of a shallow endothermic effect in the DTA curve.

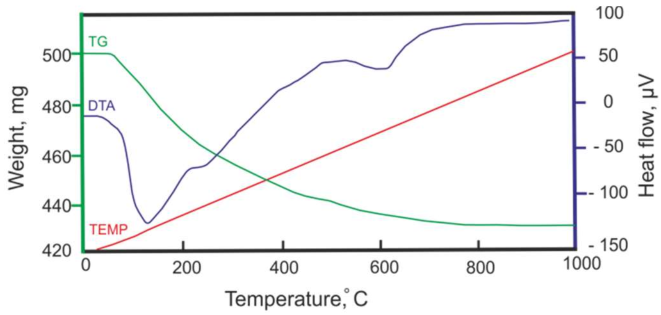

Figure 2. Thermogram of the zeolite

At the fourth stage in the temperature range of 508–800°C, one can notice the surface dehydroxylation followed by the liberation of OH groups being chemically bound with the surface. The process ends up with the destruction and amorphization of the clinoptilolite crystalline structure. A strongly endothermic effect appears in the DTA curve.

Thermolysis of the shungite samples includes three main stages (**Figure 3**).

At the first stage, the physical and chemical adsorbed moisture is released at the temperatures of 20 to 600°C. This process is followed by a slow mass loss of the sample and a deep endothermic effect that appears on the DTA curve of differential thermal analysis DTA.

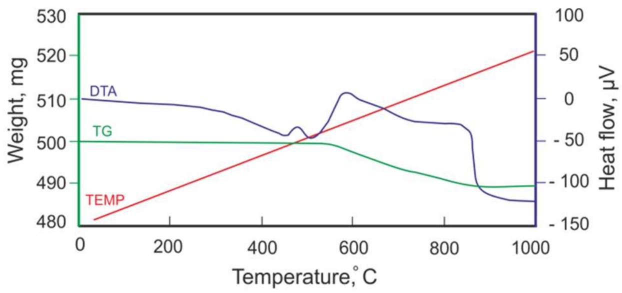

Figure 3. Thermogram of the shungite

At temperatures from 600°C to 850°C, the carbon transformed to CO_2, and rapid weight loss was observed. After 900°C weight loss stabilized.

Analysis of TG curves of both samples confirms the content of bound moisture. However, in clinoptilolite this content is higher. This may be due to the existence of internal channels and pores in clinoptilolite [11].

To determine the adsorption properties of the studied natural materials used ordinary drinking water and a model solution obtained by adding to drinking water suitable for mixing concrete, a known amount of sodium sulfate.

A model solution of a known concentration of 2500 mg/L (in terms of sulfate ions) was defended in closed beakers under the same conditions, with the same amount of each tested adsorbent (1 kg of adsorbent was ground until complete passage through a sieve with mesh size 0315). After 1 day, the concentration of SO_4^{2-} in the solutions after purification was determined by the titrimetric method and it was found that for the solution of shungite purification it was 1812 mg/L, and clinoptilolite - 1548 mg/L.

Checking the sorption capacity of selected natural materials was carried out by the conductometric method. It allows rapid control of the quality of purification of water from pollutants.

The electrical properties of all 4 solutions were studied: standard, model and after purification with each adsorbent.

The offered electric method is a method of rapid control of the content of multicomponent liquids and is based on the measurement of values of complex conductivity (active component) at multifrequency influences of an electromagnetic field [12].

Figure 4 shows the frequency dependences that illustrate and confirm the possibility of using the measured values of the admixture to control the concentration of the controlled substance in the liquid.

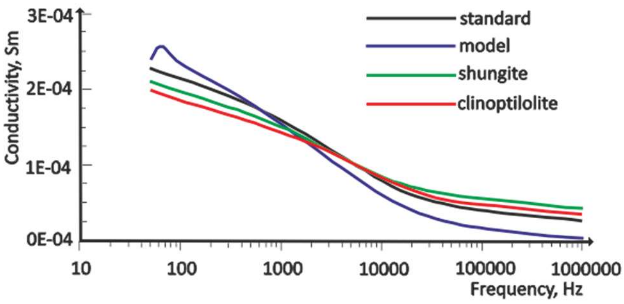

Figure 4. Dependence of the active component of conductivity on the frequency of the signal

For example, at the selected frequency of 100 Hz, the value of the electrical index for the model solution is greater than for the standard, because it has a larger number of charged particles - charge carriers. Figure 4 shows that the conductivity of the solution purified with shungite is 2.09 • 10^{-4}Sm, and the conductivity of the solution purified with clinoptilolite is 1.93 • 10^{-4}Sm. This suggests that clinoptilolite is a more effective adsorbent than shungite for this type of pollutant. The results of the proposed electrical method are fully correlated with the previously described titrimetric and thermogravimetric analyzes.

The purified solutions were used for mixing fine-grained concrete to test the effect of water-dissolved sulfates on the strength of the products. It is known from various sources that sulfates can chemically react with hydration products of clinker minerals and substances contained in concrete. The formation of new chemical compounds as a result of such reactions, especially crystal hydrates, can lead to a significant increase in their volume, which in most cases results in the formation of cracks and subsequent destruction of concrete [13].

Three types of samples were formed: 1 - mixing water was drinking water, for 2 used a solution purified by shungite, for 3 - a solution purified with clinoptilolite. The results are shown in **Table 4**.

Table 4. The influence of water pollutants content amount on the physical and mechanical properties of concrete

Age, (days)	Bending/compressive strength of samples (MPa)		
	1	**2**	**3**
1	3.0/9.7	3.5/10.6	3.2/10.2
7	7.3/32.4	7.7/37.4	7.5/35.1
14	8.3/38.6	8.3/38.2	8.1/37.6
28	10.1/40.8	9.6/39.5	9.9/40.2

In general, a slight plasticizing effect was observed for samples 2 and 3 (ease of laying increased). Concerning strength characteristics, on the 1st and 7th day of hardening these samples were characterized by an accelerated set of strength, compared with 1. However, on the 28th day of hardening, the difference of strength of all samples was within 3% and was about 40 MPa.

These results again indicate that the water purified by the studied natural adsorbents is suitable for use in the concrete industry.

Conclusions

With the help of natural materials such as shungite and zeolite it is possible to purify contaminated water to values claimed according to the requirements of the standards. This is due to the features of their structure. In this case, zeolite is a more effective cleaner from our chosen type of pollutant than shungite.

Analysis of methods for determining the content of contaminants showed that the classic titrimetric is more durable and resource-intensive. Simpler, faster, and at the same time reliable is the electric method, where the values of the active component of conductivity for solutions with different values of the content of dissolved substances are measured at one frequency. The greater the value of conductivity, the higher the concentration of solute pollutant. The results obtained by the electric method are fully consistent with the titrimetric data.

At the same time, we see a correlation with static physical and mechanical tests. Fine-grained concrete, mixed with a solution with a higher concentration of sulfite ions in the initial stages of hardening is characterized by a faster set of strength, which can be explained by the appearance of additional crystallization centers, but by 28 days this trend weakens. The compressive strength of all samples is approximately 40 MPa with a deviation of ± 3%.

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