TECHNOLOGICAL SOLUTIONS OF USING SLUDGE FROM GROUNDWATER DEMANGANATION PROCESSES IN BUILDING MATERIALS

Inna Trus[1], Vita Halysh[1,2], Mariia Tverdokhlib[1]

[1]Department of Ecology and Plant Polymer Technologies
National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute"
37 Beresteiskyi Ave., Kyiv, Ukraine, 03056, inna.trus.m@gmail.com (I.T.); madamtverdohleb@gmail.com (M.T.)
[2]Laboratory of Kinetics and Mechanisms of Chemical Reactions
on the Surface of olids Chuiko Institute of Surface Chemistry
National Academy of Sciences of Ukraine
17 General Naumov St., Kyiv, Ukraine, 03164, v.galysh@gmail.com (V.H.)

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ABSTRACT

The development of solutions for the disposal of waste from water treatment is important from the point of view of reducing its accumulation. In this paper, manganese hydroxide from water demanganization is considered as a component of the cement mixture, which accelerates its hardening. A rational dose of manganese hydroxide sludge for the use in building mixtures is 0.5 - 4.0 %. The research results showed that the desorption of manganese from cement in an aqueous medium is 0.003 - 0.035 mg dm^{-3} in 1 day and 0.005 - 0.041 mg dm^{-3} in 30 days. A technological scheme for the preparation of drinking water from an underground source containing an increased content of manganese and iron ions with subsequent processing of the formed sediments is proposed.

Keywords: hardening time properties of cement, normal density, compressive strength properties, removal of manganese, technological scheme, drinking water.

INTRODUCTION

In Ukraine, water-intensive industries predominate, so providing them with high-quality water is an urgent problem of our time [1 - 3]. Intensive anthropogenic and industrial activity leads to excessive discharge of industrial wastewater and sharp deterioration of water quality [4, 5]. The ingress of heavy metals into surface waters is particularly dangerous, as it negatively affects not only ecosystems, but also the health of the population [6, 7]. Due to the degradation of surface water bodies, groundwater and artesian wells have recently been used to meet water supply needs. Water from underground sources in a significant part of the territory of Ukraine has an increased content of iron and manganese in its composition. In the environment, manganese compounds are most often found in the form of carbonates, sulfates and chlorides, sometimes in combination with humic compounds and phosphates [8]. This is due to the distribution of these elements in the composition of rocks that are in contact with groundwater.

The presence of manganese in water can be both natural and artificial, which affects water quality [9]. Manganese (Mn) is present in natural waters through input from a variety of sources. Manganese can enter water bodies because of natural processes through the decay of geological formations and ores. As a result of industrial production, manganese enters the environment together with wastewater. Fertilizers containing manganese can be used in agriculture, so it gets into the soil and is washed into water sources.

Currently, the problem of water purification from manganese ions is complex and requires the development of effective solutions. Manganese is a necessary biogenic element in normal processes in living organisms, as well as in humans [10 - 12]. However, the purification of natural waters from manganese compounds is vital because of their toxicity and ability to accumulate in living organisms in high concentrations, which can have a negative impact on human health [13, 14].

Increasing the efficiency of water purification when creating new and improving existing water purification technologies will improve the condition of surface and underground waters [15, 16]. There are a significant number of effective methods for removing heavy metals from water [17 - 20]. Today, a wide range of research on manganese extraction from water is presented [21 - 23], including catalytic methods [24]. At the same time, the problem of effective removal of manganese ions from water remains unsolved. This is because manganese ions are removed from water by sorption [24, 25], ion exchange [27], membrane [28, 29] methods are insufficiently effective.

When choosing a method for removing manganese from water, considerable attention is paid to the general chemical composition of water and associated pollutants [30, 31]. The method should also be economically feasible [32]. Sorption, ion exchange, and membrane methods are extremely expensive and characterized by low productivity [33, 34]. Oxidation methods are considered more promising for removing manganese ions from water. Chemical oxidation of dissolved Mn (II) to Mn (IV), followed by its separation as a solid precipitate from the solution is the most promising and expedient. The oxidation method is combined with settling or filtering to achieve maximum effect [35, 36]. Nevertheless, the main and important issue is the further utilization of the formed sediments [37 - 40]. Insufficient knowledge about possible ways of processing or disposal of such sediments determines the necessity of these studies.

Therefore, given the fact that water demanganization waste is toxic, dangerous for the environment, as it can cause significant damage to living organisms, the purpose of the article is to study the possibility of utilization of sediments in the composition of the construction mixture with the determination of their optimal doses and the possibility of further leaching into the environment under the influence of external factors.

EXPERIMENTAL

Processing of sludges

Demanganization of water with an oxidation process leads to the formation of a $Mn(OH)_4$ precipitate [41]. The precipitate was separated by filtration, dewatered and disposed of as a component of cement. Sediment with consumption of 0.5 - 4.0 wt. % was mixed with PC I 500-D0 cement. Mixing was performed in a laboratory ball mill for 20 min.

To study the influence of manganese hydroxide consumption on the strength properties of cement samples, normal density, water removal coefficient, time of hardening and compressive strength were studied [42 - 44]. Full design 2^2 was used to study compressive strength of cement samples (Table 1). The effect of sediment consumption (X_1) and time of hardening (X_2) were varied. The values of compressive strength (Y) were investigated. A second-order polynomial (2) also was used:

$$y = 101.67 + 1.0154x1 - 0.035895x2 - 0.0076928x1x2 - - 0.13334x1^2 - 0.0004x2^2 \quad (1)$$

where Y is a response factor compressive strength, b_i are regression coefficients.

Study of manganese desorption from construction mixture

A sample of cement containing manganese hydroxide was placed in a container with distilled water. Water samples were taken after 1 day and 30 days and the content of manganese ions was determined.

The concentration of manganese ions was determined using spectrophotometer at 484 nm [45].

Table 1. 2^2 - factorial design for sediment utilization as a component of cement

Factor	Low level (-1)	High level (1)
Sediment consumption X_1 ,%	0.5	3.5
Time of hardening X_2, day	2	28

Development of a basic technological scheme for the preparation of drinking water with further processing of sediments

Based on the obtained results, a waste-free water demanganization technology is proposed (Fig. 1).

The technological scheme involves the use of water filtration and disinfection with processing of the formed sediments as part of building materials. The proposed method makes it possible to reduce the content of pollutants in groundwater to acceptable standards (Table 2).

RESULTS AND DISCUSSION

Processing of sludges

As a result of the oxidation of manganese ions, a precipitate is formed, which is separated by filtration.

Sediment was added to the cement mixture in the production of type PC I 500-D0 cement. The sediment consumption was from 0.5 to 4.0 wt. %.

It is important to establish the dependence of cement properties on consumption of additional substances. Therefore, the influence of the consumption

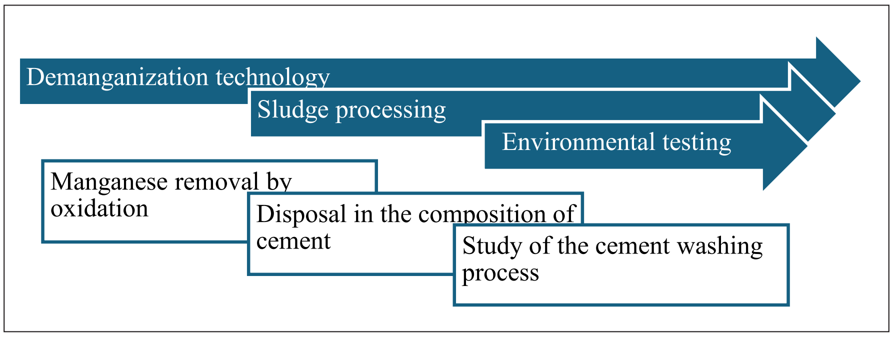

Fig. 1. Complex demanganization technology.

Table 2. Characteristics of water from an underground source.

Indicators, units	Actual value	Normative values according to State Sanitary Norms and Rules 2.2.4-171-10
General mineralization (TDS), mg dm^{-3}	350	$\leq$ 1000.0
Manganese, mg dm^{-3}	1.0	$\leq$ 0.05
Total iron, mg dm^{-3}	2.7	$\leq$ 0.2
Total hardness, mg-eq dm^{-3}	4.6	$\leq$ 7.0
Total alkalinity, mg-eq dm^{-3}	4.2	$\leq$ 6.5
Carbonate hardness, mg-eq dm^{-3}	3.6	is not standardized
Coloration, degrees	30.0	$\leq$ 20.0
Turbidity, mg dm^{-3}	6.5	$\leq$ 1.0
Taste and aftertaste, points	3.0	$\leq$ 2.0
Hydrogen index, pH unit	7.6	6.5 - 8.5
Smell (20°C), points	2.0	$\leq$ 2.0
Smell (60°C), points	3	$\leq$ 2.0
Nitrates (NO^-_3), mg dm^{-3}	2.25	$\leq$ 50.0
Sulfates, mg dm^{-3}	25.8	$\leq$ 250.0
Chlorides, mg dm^{-3}	15.7	$\leq$ 250.0

of manganese hydroxide on the normal density of cement, its hardening time and drainage coefficient was investigated. The results are summarized in Table 3.

The presented data show that when sediment is added and when its content is increased to 4.0 %, the beginning of hardening time decreases from 42.1 min (for unfilled cement) to 37.0 min. The end of hardening is 139.2 min for a sample of cement that does not contain manganese hydroxide, and 145.3 - 158.9 min for samples with a sediment consumption of 0.5 - 4.0 %.

The value of the drainage coefficient and the normal density of cement do not change with the addition of manganese hydroxide at a rate of 0.5 to 4.0 %. The strength properties of cement samples change slightly from 100.0 % to 103.4 % and from 100.0 % to 102.0 %, both at the age of 2 days and at the age of 28 days, which allows recommending the use of sludge from water treatment in the composition of cement in an amount of no more than 4.0 %.

The compressive strength of cement samples containing sediment was studied, the results are shown in Fig. 2. The effect of sediment consumption on cement compression is described by the following regression Eq. (6):

$$y = 101.67 + 1.0154x1 - 0.035895x2 - 0.0076928x1x2 - 0.13334x1^2 - 0.0004x2^2 \quad (6)$$

Therefore, the sediment formed during

Table 3. Mechanical properties of cement with different content of sediment

Sediment consumption, %	Beginning of hardening, min	End of hardening, min	Normal density, %	Water removal coefficient, %
0.00	42.10	139.20	24.80	4.10
0.50	39.50	145.30	25.35	3.87
1.00	38.70	147.00	25.14	3.91
1.50	37.80	153.00	25.41	3.95
2.00	38.10	157.00	24,93	4.01
2.50	37.40	158.30	24,87	3.99
3.00	37.00	158.90	24,87	3.95
3.50	37.20	157.20	24,91	4.03
4.00	37.00	157.10	24.90	3.99

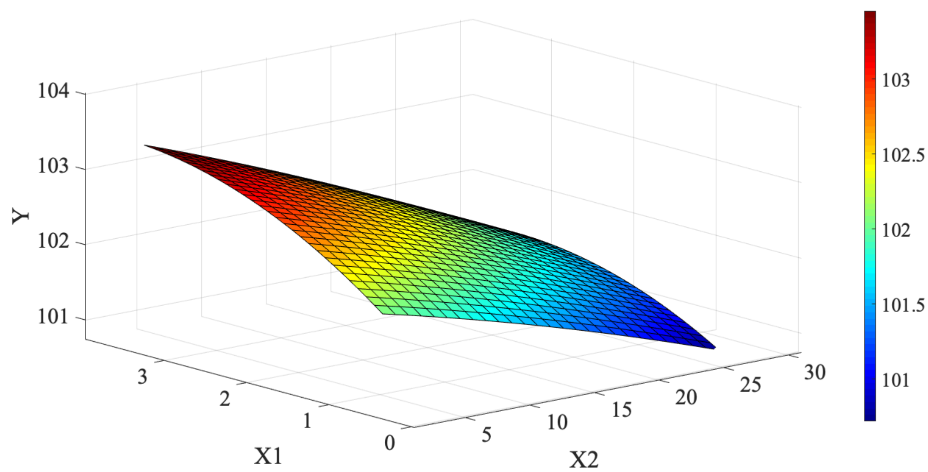

Fig. 2. Effect of sediment application (X1) and time of hardening (X2) on compressive strength of cement samples.

demanganization of water, which is manganese hydroxide, can be used in the production of cement as an additive. Such an additive is able to accelerate the hardening of cement in a certain way.

Desorption of manganese ions from the construction mixture

The main task of processing manganese-containing sediments is to obtain the final product, the properties of which would ensure the possibility of its disposal, or minimize the damage caused to the environment.

A promising measure for the utilization of such sediments is their use as additives in building materials. These additives in building materials improve operational and technical qualities and do not require economic costs for measures aimed at preventing their negative impact on the environment. However, it should be noted that for the disposal of manganese-containing waste for the production of building materials, it is necessary to check the possibility of desorption of manganese compounds into aqueous solutions. Heavy and toxic metals in cement under the influence of external factors can be leached into the environment, thus creating pollution risks for the soil and deteriorating water quality, which requires the development of effective approaches to the management of this issue [46].

Therefore, it is important to study the safety and environmental friendliness of this method in the development of methods of utilization of sediments as part of building materials. Manganese desorption was 0.003 - 0.035 mg dm^{-3} in 1 day and 0.005 - 0.041 mg dm^{-3} in 30 days (Table 4).

Residual concentrations in the samples may be influenced by other chemical elements that are part of the cement. After comparing the research results, it can be concluded that the optimally acceptable dose of sediment when added to building mixtures is 0.5 - 4.0 %.

Description of the technological scheme of drinking water preparation

Underground water sources are often used to provide drinking water. Most of the resources have an elevated iron or manganese content.

Water is taken from an underground source and enters the receiving chamber (1), which ensures equalization of water flow and averaging of concentrations of all components. After that, it enters the contact tank (2), where the primary chlorination of water with active chlorine takes place (Fig. 3).

Next, the water enters the catalytic filter (3). This type of filter uses catalytic materials that promote chemical reactions that help remove organic contaminants,

Table 4. Desorption of manganese from cement in a solution of distilled water.

Sediment consumption, %	After 1 day, mg dm^{-3}	After 30 days, mg dm^{-3}
0.00	0.000	0.000
0.50	0.003	0.005
1.00	0.005	0.008
1.50	0.009	0.013
2.00	0.011	0.015
2.50	0.015	0.023
3.00	0.023	0.027
3.50	0.035	0.041
4.00	0.031	0.039

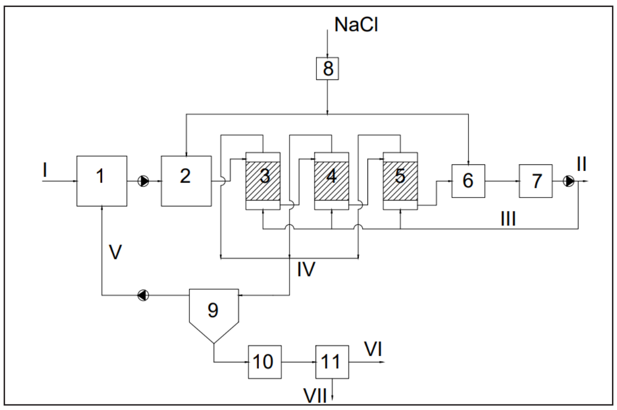

Fig. 3. Technological scheme of preparation of drinking water from an underground source of water supply: 1 - receiving chamber, 2 - contact tank, 3 - catalytic filter, 4 - mechanical filter, 5 - carbon filter, 6 - contact tank, 7 - pure water tank, 8 - electrochlorinator, 9 - clarifier-accumulator, 10 - sludge accumulator, 11 - filter press. I - supply of water for cleaning, II - supply of water to the consumer, III - supply of water for washing, IV - inflow of water with sludge after washing the filters, V - return of water after the settling tank, VI - discharge of filtrate, VII - sludge for processing in the warehouse building materials.

chlorine, iron, manganese, and other harmful substances from the water. A mechanical filter (4) is used to remove the formed sediment from the water.

Then the water enters the carbon filter (5), which can adsorb organic compounds, residual chlorine and other pollutants. The water flows back into the contact tank (6) for secondary chlorination, after which it is collected in (7) - the clean water tank. The use of an electro chlorinator (8) is provided for the generation of active chlorine.

Part of the water from the clean water tank is returned to wash the mechanical, catalytic and carbon filters. After washing the filters, the washing water enters the settling tank-average (9). In which the process of separating solid particles from water takes place. After that, water without a solid phase is pumped into the receiving chamber at the beginning of the technological scheme and goes through the entire path of purification. From the clarifiers, the sediment enters the sludge accumulator (10), after which it is fed to the filter press (11), where the sediment is dewatered, after which the sediment is separated into filtrate and dry residue. The filtrate is discarded, and the dry residue is sent for processing by the proposed method as part of building materials.

CONCLUSIONS

The work established the possibility of using $Mn(OH)_4$ sediment, which is formed during water preparation, in the composition of cement. It is shown that the addition of sediment to the composition of cement with a consumption of 0.5 - 4.0 % does not lead to a change in the water removal coefficient and normal density. As a result of the addition of sediment, the time of the start of hardening is reduced from 42.1 to 39.5 - 37.0 min, and the end of hardening is slightly extended from 139.2 to 145.3 - 157.1 min. The strength properties of cement samples when sediment is introduced at the age of 2 days increase from 100 % to 10.4 %: from 100.0% to 102.0 % at the age of 28 days.

Thus, the physical and chemical characteristics of cement samples was not deteriorated, which makes it possible to conclude about its possible application as additives to the cement with the consumption up to 4.0 %. So, as the results show, the physico-chemical parameters of the cement samples almost did not deteriorate, which allows us to conclude that such sediment can be used as an additive to cement, but with a consumption that does not exceed 4.0 %.

Authors' contributions: *M.T.: methodology, conceptualization; I.T.: investigation, data processing; V.H: literary review, validation*

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