Cement stone, modified by chemical water treatment sludge

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Abstract. Chemical treatment of municipal and industrial wastewater is becoming increasingly common in the world, resulting in sludge formation. But only a small fraction of the waste is disposed of. Therefore, the issue of the potential use of these wastes in making construction materials is vital.

This paper examines the possible use of multi-tonnage industrial waste, in particular, sludge of chemical water treatment (SHVO) produced by combined heat and power plants in cement systems. Sludge of chemical water treatment is a pasty mass unstable in moisture. For this purpose it is advisable to pre-dry this waste until it becomes a fixed-mass, and then grind it. The impact of SHVO on the technological properties of cement paste and strength properties of cement stone was studied. The article shows that the introduction of SHVO into cement paste increases its water demand. The joint effect of naphthalene formaldehyde and polyester carboxylate-based sludge with additives was studied. Their efficiency depends on the way they are produced. The use of sludge with superplasticizers reduces binding agent consumption by 7.5% without loss of strength properties and reduces porosity of cement stone.

It was established that the introduction of SHVO into cement systems changes the physiography of newgrowths.

Key words: cement stone, concrete, sludge of chemical water treatment, superplasticizers, waste recycling, hydration.

1 Introduction

Every day industrial enterprises generate a large amount of industry-related waste during production process. But only a small part of it, no more than 15%, are disposed of in one way or another [1, 2]. Basically, enterprises store wastes in piles. This contributes to an environmental problem [3]. The use of industry-related raw materials instead of natural raw materials is the most urgent technical and economic task. The matter involves energy and human labor.

Chemical treatment of municipal and industrial wastewater is becoming increasingly common in the countries of the European Union, Asia, America and Russia. As a result, the amount of wastewater sludge increases daily [4-6]. Waste dumping of these types of sludge is prohibited in most countries because of the high content of heavy metals [7].

Today, there are various ways to dispose of these types of waste. For example, we studied a possible use of wastewater sludge generated by incineration plants as a secondary source of phosphorus. According to the legislation of the European Union, this is a sensitive issue because of the phosphorus removed from waste being a critical raw material [8].

The production of construction materials is an attractive area for the utilization of industry-related waste, in particular sludge. To date, the construction industry uses a very small proportion of sludge, although technologically they are the most “prepared” products because they are highly dispersed.
There are studies on the use of sludge: for the production of building ceramics [9]; as a aggregate in asphalt mixtures while constructing road pavements [10] and in cement concrete [11]; as an alternative fuel and raw material for producing cement clinker [12]; as chemical additives in cement concrete [13, 14]. Technical and economic efficiency of the SHVO use is shown in all works.

Experimental studies on the use of ash resulted from burning chemical water treatment sludge while manufacturing cement mortars and concrete with cement partial replacement were carried out in the works [15, 16]. This study used wastewater sludge from the Zagreb Wastewater Treatment Plant. The study shows that the introduction of ash resulted from burning the sludge into cement systems within 10% does not affect the strength properties. The data obtained are consistent with the results of other studies [17].

The study shows the efficiency of water treatment plants sludge application. These plants use aluminum salts in cement systems as the main coagulant. The impact of powdered sludge on mechanical properties of cement concrete is considered. It was revealed that the replacement of cement in concrete by 6% in the prepared SHVO allows to reach concrete compressive resistance and tensile strength higher than that of the non-additive composition when breaking.

Special attention should be given to large-tonnage by-products and stable chemical and mineralogical composition wastes. One of such wastes is the sludge of chemical water treatment from thermal power plants stored in large quantities in sludge reservoirs or in industrial landfills. The study of this sludge is relevant. For example, one combined heat and power plant's sludge pits accumulate about 5 thousand tons of sludge which has no further use every year. The sludge is then taken away on a dump further contributing to an ecological problem.

Based on the above mentioned, the aim of the study is to investigate the sludge of CHP chemical water treatment and assess its efficiency in cement systems.

The results of the research are consistent with other works [19-21].

2 Materials and methods
Chemical water treatment sludge (SHVO) is a carbonate paste-like waste of CHP generated as a result of lime treatment and water coagulation. Phase composition and physical properties of sludge are presented in Tables 1 and 2. The particle size distribution of SHVO paste is given in figure 1.

![Figure 1. Particle size distribution of chemical water treatment paste sludge (average particle size is 60 μm).](image-url)
### Table 1. Phase composition.

|          | CaCO₃, % | MgCO₃, % | SiO₂, % | CaSO₄·2H₂O |
|----------|----------|----------|---------|------------|
|          | 96       | -        | 1       | 2          |

### Table 2. Physical Properties.

|                           | True density, kg/m³ | Bulk density, kg/m³ | Humidity, % | Specific surface, g/cm² | Average particle diameter, µm |
|---------------------------|---------------------|---------------------|-------------|-------------------------|-------------------------------|
|                           | 2,71                | 0,65                | 40-60       | 8400                    | 40                            |

“POLYPLAST SP-1” (hereinafter S-3) superplasticizer is a mixture of polymer compounds neutralized by sodium hydrate of different relative molecular weight obtained by naphthalene sulphis acids condensation with formaldehyde and technical lignosulphonates, non-caking powder of brown color easily soluble in water. Content of active substance in S-3 expressed as dry product is not less than 69%, ash content is not more than 38%, pH (2.5%-th water solution) is 7-9, and water content is not more than 10%.

“MELFLUX 2651F” (hereinafter referred to as MF) superplasticizer is a powder product obtained by spray drying based on modified polyester carboxylate. Technical data: in the form of yellowish powder; bulk density is 400—600 g/l; loss when heated up is 2.0 %weight; 20% solution at 20°C, has pH = 6.5-8.5.

The particle size distribution (PSD) was determined using the Horiba LA950 laser particle size analyser. The procedure is based on scattering and detecting reflected/refracted laser light of red and blue spectra (650 and 405 nm), in accordance with ISO 13320:2020 - Particle size analysis – Laser diffraction methods. Size determination is based on Mi’s theory of dispersion.

Complex thermal analysis was carried out using “DERIVATOGRAF” Q1500D updated device when heated in open platinum crucibles with the same samples of 140 mg at a speed of 10 deg/min over the temperature range of 20-1000°C. The intensity of the corresponding reflexes and the accompanying loss of mass served as a basis for quantitative determination of the phase. The results were processed in comparing the obtained peaks with the benchmark.

Technological properties of cement paste and strength properties of cement stone are tested out according to standard normative methods.

### 3 Results

Sludge of chemical water treatment is a waste with high moisture content (up to 40%). Introduction of sludge into cement in its original form is not possible, so it had to be pre-dried and ground using laboratory vibration-ball mill. The introduction of finely dispersed products into cement paste leads to increased water demand, so plasticizing additives should be used. These studies used naphthalene formaldehyde superplasticizer – S-3 and polycarboxylate superplasticizer – MF.

SHVO was introduced into cement together with superplasticizers in two ways:
- the first way is a separate introduction of ground sludge and superplasticizer;
- the second way is a mixed grinding of dried sludge with plasticizer. In so doing, while grinding the sludge, superplasticizer serves as a grinding intensifier [22, 23].

The resulting powders were titled S-3+SHVO and MF+SHVO. It should be noted that when using sludges the amount of binding sludge was decreased by the amount of sludge introduced.

Figure 2 shows the particle size distribution of the SHVO.

Figures 1 and 2 show that the particle size distribution curve has shifted from a polymodal system into a bimodal system, offseting the curve to the smaller particle zone. At the same time, the average particle size decreased from 60 µm to 21,8 µm.
Figure 2. The particle size distribution of chemical water treatment sludge with specific surface of 12000 cm²/g.

The obtained additives were introduced into the cement mixture, following that the main technological and physico-mechanical properties of the mixture and stone were determined. The obtained results were compared with the parameters of the compositions into which SHVO and plasticizers were introduced separately (table 3, 4). Following the manufacturer's recommendations were chosen using dosing rate of SHVO of 7.5%, and dosing rate of plasticizers and on the basis of the studies carried out.

Table 3. Composition, normal density and setting-up time of cement paste.

| Composition No. | Cement, g | S-3+ SHVO, g | SHVO, g | S-3, g | Water, ml | NG, % | Setting-up time, h-min |
|-----------------|-----------|--------------|--------|--------|-----------|-------|-----------------------|
|                 |           |              |        |        |           |       | beginning | end                 |
| 1               | 400       | -            | -      | -      | 116       | 29    | 3-00      | 4-10                |
| 2               | 370       | 1.6+30       | -      | -      | 130       | 32    | 3-00      | 5-30                |
| 3               | 370       | 3.2+30       | -      | -      | 118       | 29    | 4-40      | 5-30                |
| 4               | 370       | -            | 1.6    | 30     | 122       | 31    | 4-10      | 5-10                |
| 5               | 370       | -            | 3.2    | 30     | 111       | 28    | 5-10      | 6-50                |

Table 4. Composition, normal density and setting-up time of cement paste.

| Composition No. | Cement, g | MF + SHVO, g | SHVO, g | MF, g | Water, ml | NG, % | Setting-up time, h-min |
|-----------------|-----------|--------------|--------|-------|-----------|-------|-----------------------|
|                 |           |              |        |       |           |       | beginning | end                 |
| 1               | 400       | -            | -      | -      | 116       | 29    | 3-00      | 4-10                |
| 2               | 370       | 0.8+30       | -      | -      | 133       | 33    | 3-40      | 6-50                |
| 3               | 370       | 2+30         | -      | -      | 138       | 34    | 3-40      | 7-10                |
| 4               | 370       | -            | 0.8    | 30     | 123       | 31    | 4-00      | 7-10                |
| 5               | 370       | -            | 2      | 30     | 109       | 27    | 4-30      | 9-00                |
As can be seen from table 3, the use of the (S-3+SHVO) additive obtained by mixed grinding does not reduce the mixture water demand in comparison with the composition with no additives. It is only the separate use of SHVO and S-3 in the amount of 0.8% of the cement mass that allows reducing water demand by 4%. At the same time, the latest setting-up time is observed.

As can be seen from Table 4, the use of the (MF+SHVO) additive obtained by mixed grinding does not reduce the mixture water demand in comparison with the composition with no additives. It is only the separate use of SHVO and MF in the amount of 0.8% of the cement mass that allows reducing water demand by 4%. At the same time, the setting-up time is observed to slow down, the setting-up time completes in nine hours after gauging, which is five hours later than in the composition with no additives.

Thus, it is possible to reduce the water demand of the SHVO only by introducing sludge powder and any type of superplasticizer separately.

Impact of SHVO and various plasticizing additives on strength (table 5, 6), allows determining the effectiveness of these modifiers added to the cement mixture. The studies were carried out with the normal density cement.

**Table 5.** Composition of cement mixture and strength properties of cement stone on day 1, 7 and day 28.

| Composition No. | Cement, g | S-3+ SHVO, g | SHVO, g | S-3, g | Water, ml | Strength of cement stone, MPa |
|----------------|-----------|-------------|---------|--------|-----------|-------------------------------|
|                |           |             |         |        |           | 1 day | 7 days | 28 days |
| 1              | 400       | -           | -       | -      | 116       | 29,42 | 52,00 | 75,00  |
| 2              | 370       | 1,6+30      | -       | -      | 130       | 13,78 | 37,54 | 53,97  |
| 3              | 370       | 3,2+30      | -       | -      | 118       | 21,86 | 43,31 | 60,23  |
| 4              | 370       | -           | 30      | 1,6    | 122       | 18,31 | 43,00 | 57,48  |
| 5              | 370       | -           | 30      | 3,2    | 111       | 21,59 | 59,17 | 73,93  |

Table 5 shows that the additive obtained by mixed grinding (s-3+SHVO) is ineffective. It decreases the cement stone strength throughout all the hardening periods. It is only the separate use of 0.8% of SHVO and S-3 of the cement mass that produces a proportional strength relative to the control composition, while slowing down the strength development on the first day of hardening.

**Table 6.** Composition of cement mixture and strength properties of cement stone on day 1, 7 and day 28.

| Composition No. | Cement, g | MF+SHVO, g | SHVO, g | MF, g | Water, ml | Strength of cement stone, MPa |
|----------------|-----------|------------|---------|-------|-----------|-------------------------------|
|                |           |            |         |       |           | 1 day | 7 days | 28 days |
| 1              | 400       | -          | -       | -     | 116       | 29,42 | 52,00 | 75,00  |
| 2              | 370       | 0,8+30     | -       | -     | 133       | 20,57 | 39,96 | 54,50  |
| 3              | 370       | 2+30       | -       | -     | 138       | 20,47 | 43,38 | 57,17  |
| 4              | 370       | -          | 30      | 0,8   | 123       | 30,84 | 52,16 | 65,2   |
| 5              | 370       | -          | 30      | 2     | 109       | 34,88 | 62,82 | 78,2   |
Table 6 shows that the additive obtained by mixed grinding (MF+SHVO) is ineffective. It decreases the cement stone strength throughout all the hardening periods. It is only the separate use of SHVO and MF in the amount of 0.8% of the cement mass that increases the cement stone strength by 19, 21 and 5% on day 1, 7 and 28 in comparison with control composition.

Thus, the obtained strength results are consistent with the data on water demand.

In addition to the cement stone strength, the porosity has some impact. Thus the impact of sludge based additives on porosity was investigated. The study results of the cement stone porosity and density are presented in tables 7, 8.

**Table 7.** Composition of cement mixture and structural indicators of cement stone on day 7 of hardening.

| Composition No. | Cement, g | S-3+ SHVO, g | SHVO, g | S-3, g | Water, ml | Total porosity, % | Density, g/cm³ |
|----------------|-----------|--------------|---------|--------|-----------|------------------|----------------|
| 1              | 400       | -            | -       | -      | 116       | 25,11            | 2,16           |
| 2              | 370       | 1,6+30       | -       | -      | 130       | 28,74            | 2,07           |
| 3              | 370       | 3,2+30       | -       | -      | 118       | 27,32            | 2,15           |
| 4              | 370       | -            | 30      | 1,6    | 122       | 24,27            | 2,12           |
| 5              | 370       | -            | 30      | 3,2    | 111       | 23,42            | 2,16           |

The use of SHVO and S-3 aimed at modifying the structural parameters of cement stone, as shown in table 7, when introduced separately, reduces total porosity by 3 and 7 per cent while adding plasticizer at a dosing rate of 1,6 and 3,2 g respectively.

**Table 8.** Composition of cement mixture and structural indicators of cement stone on day 7 of hardening.

| Composition No. | Cement, g | MF+SHVO, g | SHVO, g | MF, g | Water, ml | Total porosity, % | Density, g/cm³ |
|----------------|-----------|------------|---------|-------|-----------|------------------|----------------|
| 1              | 400       | -          | -       | -     | 116       | 25,11            | 2,16           |
| 2              | 370       | 0,8+30     | -       | -     | 133       | 27,73            | 2,00           |
| 3              | 370       | 2+30       | -       | -     | 138       | 24,19            | 2,00           |
| 4              | 370       | -          | 30      | 0,8   | 123       | 21,43            | 2,06           |
| 5              | 370       | -          | 30      | 2     | 109       | 23,23            | 2,17           |

The use of SHVO together with Melflux plasticizer is also effective when introduced separately, as can be seen in table 8. At a MF dosing rate of 0.8 g, total porosity is reduced by 14% as compared with the control composition.

Thus, the efficacy of the SHVO sludge is dependent on the way it is introduced with the plasticizer. The use of sludge with superplasticizers reduces binding agent consumption by 7.5% without loss of strength properties and reduces porosity of cement stone. The type of superplasticizer does not affect the values.
The phase composition of newgrowths was studied using the differential thermal method (figure 3). This made a complete analysis of the sludge impact on the cement stone hydration.

**Figure 3.** Thermogram of hydration products of Portland cement stone with no additives on day 1 and day 28 of hardening.

**Figure 4.** Thermogram of hydration products of Portland cement stone with SHVO sludge on day 1 and day 28 of hardening.

As can be seen from figure 3 and figure 4, by introducing the SHVO sludge changes the physiography of newgrowths both on day 1 and on day 28 of hardening. SHVO introduced on the first day increases the amount of calcium hydrosilicates and decreases the proportion of portlandite on day 28.
Discussion

1. The possible use of chemical water treatment sludge (SHVO) of heat and power plants (CHP) in cement systems as an active mineral additive was shown.

2. It was revealed that the efficiency of the chemical water treatment sludge depends on the way it was introduced into the cement system. The sludge was previously dried and then ground so it could be rationally used. It was established that the SHVO is effective when separately introduced with superplasticizer, as mixed introduction increases water demand.

3. The use of sludge with superplasticizers reduces binding agent consumption by 7.5% without loss of strength properties and reduces porosity of cement stone by 7%.

4. The introduction of SHVO with superplasticizers into cement paste slows down the setting-up time to 9 hours. This effect will be positive when concreting monolithic mass, as it will help to avoid temperature deformations. The setting-up processes can be controlled by the amount of sludge introduced.

5. Introducing SHVO has an impact on cement hydration products. Thus, the amount of calcium hydrosilicates increases on day 1 of hardening, the proportion of portlandite decreases by day 28.

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