Cement stone, modified by galvanic sludge

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Abstract. The relevance of the research topic stems from the use of multi-tonnage industrial waste in cement systems. One such waste is the sludge resulted from electroplating aluminum alloy products. Galvanic (electroplating) sludge is pasty and unstable in moisture. For this purpose, it was previously dried and then grinded so it could be rationally used. Impact of sludge on technological properties of cement stone and strength properties of cement stone were studied according to standard normative methods. It is shown that galvanic sludge increases the water demand of cement paste. Therefore, the joint effect of naphthalene formaldehyde and polyester carboxylate-based sludges with plasticizing added was studied. Their efficiency depends on the way they are produced. The mixed use of galvanic sludge with plasticizing additives reduces the water-cement ratio by 20-40%, increases the strength of cement stone within the early hardening time by 3 times and in 2 times in the grade age. The phase composition of the modified cement stone was studied using defective thermal analysis. It was established that using galvanic sludge together with plasticizing additives decreases portlandite.

The article can be useful for those recycling the waste in question.

Keywords: cement stone, concrete, galvanic sludge, superplasticizers, waste recycling, hydration.

1 Introduction
There are currently more than 1000 promising technogenic products to be used in the form of secondary raw materials worldwide. Out of those, 700 products are included in the data banks as a subject of use, but only 60 of them are recycled in one way or another. Considering that, researchers constantly give special attention to the use of by-product [1-4].

For example, presently almost all machine-building plants, electrotechnical and other industries of Russia use electroplating production. Galvanic sludge recycling is burdensome for enterprises. That is why the sludges are disposed following the neutralization (transformation into less soluble compounds) 1 [5].

Apart from the well-known global environmental reasons to use the waste as a secondary technogenic raw material instead of natural raw material, there is one of the most important technical and economic factors justifying such use: The matter involves energy and human labor. Therefore, the use of industry-related waste in manufacturing construction materials will inevitably result in economic and environmental effects [6-8].

The only promising method developed in other countries comprising electroplating waste utilization is to use galvanic waste as additives in various construction materials [9-11].

Many works study methods of treating and recycling industrial wastewater sludge, and in particular the galvanic sludge [12-15]. The use of industrial waste in cement systems is of particular interest [16-17].

Thus, special attention should be given to large-tonnage by-products and stable chemical and mineralogical composition wastes.
Based on the above mentioned, the aim of the study is to investigate the sludge of galvanic production [18] and to assess its efficiency in cement systems for the purpose of recycling the sludge while manufacturing concrete and reinforced concrete products.

The obtained research results correlate with the results of other studies [19, 20].

2 Materials and methods

Galvanic sludge (hereinafter GS) is a production waste of aluminum profiles, obtained using anodizing method, is 80% of moisture pasty substance of gray color [18].

The GS chemical composition and the chemical elements contained in it, mg/kg, are given in Table 1 and Table 2, respectively. The particle size distribution if GS paste is given in Figure 1.

Table 1. Galvanic sludge chemical makeup.

| Oxides  | Content in % |
|---------|--------------|
| SiO₂    | 0.61         |
| TiO₂    | 0.01         |
| Al₂O₃   | 55.47        |
| Fe₂O₃   | 0.13         |
| MnO     | <0.01        |
| CaO     | 1.52         |
| MgO     | 1.06         |
| Na₂O    | 1.90         |
| K₂O     | <0.01        |
| P₂O₅    | 0.05         |
| SO₃     | 9.47         |
| PPP/1000* | 29.78      |

*PPP/1000 — Calcination loss at 1000°C

Table 2. Heavy metals, arsenic content (mg/kg).

| Pb     | Ni  | Co  | Cr  | Cu  | Cd  | As  |
|--------|-----|-----|-----|-----|-----|-----|
| <0.01  | 50.2| 92  | 23.6| 27.8| 3.8 | <0.01|

Figure 1. Particle size distribution of galvanic paste sludge (average particle size 70 μm).

"POLIPLAST SP-1" (hereinafter - S-3) superplasticizer is a non-caking powder of brown color, easily soluble in water. Content of active substance in C-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 - MF) superplasticizer is a powder product based on modified polyester carboxylate obtained by spray drying. 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. Properties: high efficiency dispersing agent, reduces shrinkage, effective over a wide temperature range.
The particle size distribution (PSD) was determined using the Horiba LA950 laser particle size analyzer. The procedure is based on scattering and detecting reflected/refracted laser light, red and blue spectra (650 and 405 nm), in accordance with ISO 13320:2020 - Particle size analysis – Laser diffraction methods.

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

Galvanic sludge is a waste with high moisture content (from 40 to 80 %). This will inevitably make it more difficult to introduce the sludge, so it is rational to use it as a powder additive. The sludge was previously subjected to drying and breakage in a laboratory vibration-ball mill. And as a result, 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.

Two ways of introducing the sludge with superplasticizers were considered:
  - 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 [20, 21].

The resulting powders were titled (C-3+GS) and (S-3+GS). It should be noted that when using sludge, the amount of binding sludge decreased by the amount of sludge introduced.

Particle size distribution of pre-dried and ground GS is given in Figure 2.

Figures 1 and 2 show that the particle size distribution curve has shifted from bimodal system into a unimodal system, offsetting to the smaller particle zone. Dried and ground galvanic sludge has a particle distribution from 5 μm to 100 μm with the average particle size being 32 microns.

![Figure 2. Particle size distribution of GS.](image)

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 mixture indices that had both mixed and separate GS and plasticizers injected (Table 3). Earlier it was investigated that the optimal content of GS is equal to 2 % [22, 23] with dosage rates of plasticizers being chosen following the manufacturer's recommendations and the conducted studies.
Table 3. Properties of cement paste while having GS and plasticizers added.

| No. item | Additive          | Dosage rate of plasticizer, % | Normal density, % | setting-up time, hour-min |
|----------|------------------|------------------------------|------------------|----------------------------|
|          |                  |                              |                  | start | end   |
| 1        |                  | -                            | 24               | 2.05  | 3.05  |
| 2        | GS (2 %)         | -                            | 27.0             | 1.00  | 1.55  |
| 3        | (S-3 + GS)       | 0.6                          | 22.3             | 0.48  | 1.05  |
| 4        |                  | 0.8                          | 20.4             | 0.45  | 0.55  |
| 5        |                  | 1.2                          | 19.5             | 0.40  | 0.55  |
| 6        |                  | 0.6                          | 16               | 0.55  | 1.35  |
| 7        | (MF+GS)          | 0.8                          | 14.6             | 1.15  | 2.00  |
| 8        |                  | 1                            | 14.3             | 1.45  | 2.50  |
| 9        | Separate         | 0.6                          | 23.3             | 2.35  | 3.15  |
| 10       | introduction     | 0.8                          | 22.3             | 2.55  | 3.50  |
| 11       | S-3 + GS         | 1.2                          | 21.1             | 3.30  | 4.30  |
| 12       | Separate         | 0.6                          | 18.6             | 3.50  | 5.35  |
| 13       | introduction     | 0.8                          | 17.3             | 4.15  | 6.00  |
| 14       | MF+ GS           | 1                            | 15.2             | 5.50  | 7.25  |

Table 3 shows that GS is more efficient in mixed grinding with superplasticizer. By introducing the sludge into cement paste (S-3 in the amount of 0.8 % + GS) and (MF in the amount of 0.8 % + GS) we reduce water demand by 20 % and 14.6 %, respectively, relative to the non-additive composition. However, the considered superplasticizers change drastically the cement and GS setting-up time with these two dilution agents injected. Not only does superplasticizer S-3 increase the concentration, it reduces the setting-up time as per the "decaying" curve, and the effect of the hyperplasticizer Melflux 2651F on this indicator is seen in the curves with minimum dosage rate of 0.6 %. In particular, introducing the S-3 in the amount of 1 % reduces the early setting-up time to 0.5 hours, and the late setting-up time to 0.65 hours; the higher the dosage rate of Melflux 2651F the longer the setting-up time is (at 1 % up to the initial values). The discovered synergy effect of the joint effect of the GS and both plasticizers on the cement paste setting-up time is very interesting and practically important. It requires further experimental study in an expanded combination of GS and S-3, GS and Melflux concentrations using the experimental planning or chemometry methods.

Thus, the GS can be used as a hardening agent. To assess the hardening kinetics, mixtures with (GS+S-3) and (GS+MF) added were considered.

Table 4. Mixtures and strength properties of modified cement stone.

| Number of mixture from item Table 3 | Cement, g | Water, ml | S-3, % | S-3, %+ GS, % | Melflux, % | Melflux, %+ GS, % | Compressive strength, MPa |
|-------------------------------------|-----------|-----------|--------|---------------|------------|------------------|----------------------------|
|                                     |           |           |        |               |            |                  | 12 hours | 16 hours | 1 day | 28 days |
| 1                                   | 500       | 120       | -      | -             | 0.24       | 14.9             | 27.1     | 38.2     | 86    |
| 3                                   | 500       | 100       | 0.6    | -             | 0.21       | 31.1             | 41.1     | 50.9     | 102   |
| 4                                   | 500       | 95        | 0.8    | -             | 0.20       | 37.7             | 45       | 54.1     | 108   |
| 5                                   | 500       | 95        | 1.2    | -             | 0.20       | 36.2             | 44.0     | 52.8     | 109   |
| 6                                   | 500       | 92        | -      | 0.6           | 0.17       | 40.8             | 48.1     | 55.3     | 146   |
| 7                                   | 500       | 89        | -      | 0.8           | 0.16       | 43.7             | 52.7     | 56.7     | 163   |
| 8                                   | 500       | 84        | -      | 1             | 0.16       | 32.1             | 49.2     | 57.2     | 180   |
Table 4 shows that the optimal plasticizer content is 0.8 % of the cement weight. It should be noted that the strength of all the mixtures with an additive is 3 times greater than that of non-additive mixture. Thus, according to the efficiency criteria, adding the plasticizer and GS is an accelerator class.

Four endothermic effects, accompanied by weight reduction were recorded on thermograms (Figure 3, Figure 4) of hydrated portland cement at the age of 1 day of hardening.

A large and wide endothermic effect in the temperature range of 75-200 °C is associated with the removal of adsorbed water from gel-like hydration products, such as: calcium hydrosilicates, hydrated calcium aluminates, hydrated calcium sulfoaluminates. The narrow endothermic effect in the temperature range of 430-480 °C characterizes the dehydration of calcium hydroxide.

**Figure 3.** Thermogram of hydration products of portland cement stone in 1 day of hardening.

**Figure 4.** Thermogram of hydration products of portland cement stone with S-3 and GS in 1 day of hardening.
Thermograms of hydrated cement with superplasticizer S-3, and a complex additive contain the above endothermic effects. However, their peak values and temperature intervals differ from that of the original cement. For example, when introducing S-3 and GS the effect value characterizing dehydration of calcium hydroaluminates and calcium hydrosulfoaluminates decreases.

The data obtained are consistent with the results of other studies [24].

4 Discussion
1. The possible use of multi-tonnage industrial waste of galvanic sludge in cement systems to be added as a hardening accelerator is shown.
2. The efficiency of galvanic sludge depends on the way the sludge is introduced into the cement system. For rational use, pasty and sludge unstable in moisture was previously dried and then grinded.
3. The synergistic effect of the joint effect of the GS and both plasticizers added on the cement paste setting-up time was revealed. By introducing S-3 in the amount of 1 % we reduce the early setting-up time to 0.5 hours, and the late setting-up time to 0.65 hours. When introducing Melflux 2651F in the amount of 0.6 % of the cement mass, the early setting-up time reduces to 0.9 hours and the late setting-up time reduces to 1.55 hours. When increasing the dosage rate of Melflux 2651F, the setting-up time increases up to the initial values.
4. By introducing mixed ground S-3 in the amount of 0.8 % and GS; MF in the amount of 0.8 % and GS into the cement paste we reduce water demand of cement paste by 20 % and 14.6 % respectively, relative to mixture without additive composition.
5. GS effects cement hydration products, reducing portland's share at the age of 28 days.

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