Molybdenum waste usage as thinning agent in concrete production

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Abstract. A comparative analysis of concrete without additives and concrete samples containing molybdenum wastes was carried out. The purpose of the work is to identify the effectiveness of the metallurgical waste influence on the physicomechanical properties of concrete, the transportation from the storage site to the concrete plant, and the substantiation of their application areas. This will solve a twofold problem: to solve the problem of industrial waste (by improving the environmental status on the example of North Ossetia-Alania) and expand the range of additives used in the production of concrete. By conducting laboratory tests the physical and mechanical properties of concrete mixtures are determined. To determine the strength characteristics of concrete samples, the IM-1250M testing machine was used. The tests were carried out under the same temperature and humidity conditions. According to the results of the experiments, the samples with molybdenum-scheelite waste showed a higher result of the physicomechanical properties of concrete. As a result of experimental analysis, the influence of metallurgical industry wastes on the strength characteristics of concrete and water resistance, as well as the safety of their use in concrete mixtures, was determined. The use of waste from the metallurgical industry will save natural material, and at the same time clear large areas of these dumps. The use of waste from the metallurgical industry will save natural material and reduce transportation costs, as there are concrete plants near the dumps, which are economically feasible. Thanks to that use it is possible to clear the large territories of these dumps.

1. Introduction

Modern construction is unthinkable without concrete - concrete has become the main building material. This is due to its cost-effectiveness, manufacturability and basic raw materials accessibility [1].

Concrete consists of a large number of aggregate grains (up to 85% of the volume) bound by a hardened binder. Concrete is a very cost-effective material as cheap natural materials or industrial wastes are used as aggregates for it.

Nowadays, concrete is obtained with a wide variety of physical and mechanical properties [2-3].

The level of the geospheres pollution in the Republic of North Ossetia-Alania remains high despite of the decline in production in the country. Pobedit JSC is one of the main air pollutants emitting a large amount of harmful substances (pollutants - tungsten, molybdenum, cobalt).
The republic has accumulated a huge amount of production waste of I-IV hazard class. These wastes occupy active sections of the urban agglomeration and create a multifaceted negative environmental and economic effect.

The monitoring studies have identified the main pollution factors of the geospheres, including the emission of pollutants from open dumps of metallurgical wastes and concentrate wastes, as well as emissions of metallurgical plants into the atmosphere of the city [4-5]. Thus, further environmental degradation reduces the life potential of the population and can lead to negative demographic indicators. Therefore, the development of technological solutions for the use of secondary resources of scheelite-molybdenum production, the scientific justification of the principles for involving the territories they occupy in economic use and the creation of a mechanism for regulating the ecology of the city agglomeration in Vladikavkaz is an urgent task of the present time [6].

The wastes from the of molybdenum concentrate processing of Pobedit JSC are of the particular interest, their use as additives in the production of concrete [6-7].

In general terms, the technology of the process for producing molybdenum-scheelite wastes is the following: molybdenum concentrates are used as a raw material for the production of pure molybdenum salts, which are processed according to the scheme, including the oxidative roasting, the ammonia leaching of the cinder, the processing of solid ammonia leach residues with hot soda solutions to recover molybdenum. The resulting solid residues of ammonia leaching are dump waste molybdenum production, which, like black dumps, are transported to the dump field. All components containing in the dumps are classified according to SHS 4630-80 dated 4.07.88 as a hazard class II and can be a source of environmental pollution, primarily groundwater, due to leaching by precipitation. The need of development, transportation and methods of waste disposal is obvious [8-9].

2. Methods and materials

The laboratory studies in NCIMM found that the black dumps of the “Pobedit” plant can be used as thinning agents in the production of heavy concrete, with a certain physical and chemical effect on them.

The raw materials for the molybdenum pure salts production are molybdenum concentrates, which are processed according to the scheme, including the oxidative roasting, the ammonia leaching of the cinder, the treatment of solid residues of ammonia leaching with hot soda solutions to recover molybdenum, the resulting solid residues of ammonia leaching, which are molybdenum waste, which are dump waste black dumps taken out to the dump field [10-12].

Table 1 shows the initial labeling of the concentrate supplied to the “Pobedit” plant.

| Table 1. Concentrate labeling. |
|-------------------------------|
| Label | Mo | SiO₂ | As | Sn | Pb | Cu |
| CL-1  | 50 | 5    | 0.07 | 0.07 | 0.07 | 0.5 |
| CL-2  | 48 | 7    | 0.07 | 0.07 | 0.07 | 1   |
| CL-3  | 47 | 9    | 0.07 | 0.07 | 0.85 | 2   |

The chemical composition of one of the groups is shown in table 2.
### Table 2. Chemical composition, %.

| № group | Phys. Weight, g | % H₂O+oil dry weight, g | Weight in terms of 52% | Weight in terms of 100% | % number of seats | Mo | W | Fe | SiO₂ | CaO | K | Na | Cu |
|---------|----------------|--------------------------|------------------------|------------------------|---------------------|-----|---|----|------|-----|---|----|----|
| 90, 5   | 10.00          | 5.0                      | 9457.0                 | 9665.0                 | 4899.0              | 8.0 | 0.9 | 8.0 | 9.0   | 3.0 | 8  | 1   | 0.2|
| 5       |                |                          |                        |                        |                     |     |     |     |       |     |    |     |    |

The raw material composition meets the environmental safety requirements.

The molybdenum concentrate is fired to convert the molybdenum sulfide to oxide, into a compound readily soluble in ammonia water.

The main reaction that occurs during firing:

\[
\text{MoS}_2 + 3.5\text{O}_2 \rightarrow \text{MoO}_2 + 2\text{SO}_2 + 2666 \text{cal.}
\]

The chemical composition of wastes is shown in table 3.

### Table 3. Chemical composition of Mo cinders.

| Component     | Dumps from cinder leaching | Dumps after cleaning solutions from TM |
|---------------|---------------------------|---------------------------------------|
|               | content. %                | component | content. %      |
| MoO₃          | 1.5-30                    | Mo gen.  | 2.5-3.0        |
| MoO₂          | 0.1-0.3                   | Mo gen.  | 0.7-1.0        |
| MoS₂          | 0.2-0.8                   | Cu       | 30.50          |
| CaO           | 0.5-2.5                   | Fe       | 12.4           |
| CaSO₄         | 2.0-10.0                  | S        | 15.0           |
| FeO           | 1.5-12.0                  |          |                |
| Ca(OH)₂       | 13.3                      |          |                |
| CaMoO₄        | 4.9                       |          |                |
| Fe₂O₃         | 3.0-24.0                  |          |                |
| SiO₂          | 11.0-27.7                 |          |                |
| CuO           | 0.86                      |          |                |
| Co₂O₃         | 0.47                      |          |                |

The resulting dumps are stored in an open area, which leads to environmental pollution due to meteorological parameters and the chemistry of the process, reacting with oxygen in the air. While exposed to atmospheric precipitation, waste decomposes, which affects the release of large amounts of sulfur and carbon dioxide.

All components contained in the dumps are classified according to BCR 4630-80 of 07/04/88. to hazard class 2 and can be a source of environmental pollution, first of all, groundwater, due to leaching by precipitation. Landfill storage sites do not have shields or watertight devices against solutions contaminated with harmful impurities, so the soil under the waste and groundwater are saturated with numerous environmentally hazardous components. The material composition indicates the presence of migratory activity of metals, both in cationic and in anionic form and, therefore, the active possibility of their transition to ground and underground waters. One can expect hydrolysis of ferrites, calcium, aluminum, sodium silicates with the formation of alkaline solutions, as well as the oxidation of sulfide components, leaching of the anionic forms of tungsten and molybdenum chemisorbed on iron hydroxides, etc.
Granulometric waste with a particle size of 0.25-0.05 mm is added to the main raw material for the manufacture of concrete, as thinning agents.

Pre-selected composition 1m^3 without additional concrete mix grade M350:
- cement 380 kg
- sand 780 kg
- crushed stone 1100 kg
- water 1601

While conducting the experimental researches, we used:
- Portland cement PC 500 (Voronezh branch of Eurocement Group JSC);
- Crushed stone of fractions of 5-20 mm was used as a large aggregate (LLC PROGRESS RSO-Alania);
- sand with a fineness modulus Mk = 2.8 (LLC PROGRESS RSO-Alania) was used as a fine aggregate.

To confirm the conformity of the declared brand of cement with the specified manufacturer, the activity of cement was determined in the following order:
1. According to GOST 30744-2001, the normal density of the cement paste (31%) was determined using a Vika device.
2. Three beam samples were made 160 × 40 × 40 mm (GOST 310.5-88 “Cements. Test methods”) with subsequent determination of bending and compression strength, and the cement activity was determined using the accelerated method on its contract on the Cement-Forecast device, equal to R28 = 51 MPa. After 28 days, the samples of the beam stored in water were tested for bending and compression. The average strength value R28 = 49.4 MPa of six samples corresponds to a cement grade of 500.

For the laboratory research, we needed a concrete mixture with a volume of 0.005 m^3, because sizes of special laboratory forms are 100x100x100 mm [13-16].

Therefore, the concrete mix composition for 0.005 m^3 is shown in table 4:

| concrete type                  | cement (kg) | sand (kg) | crushed stone (kg) | water (kg) | molybdenum (kg) |
|-------------------------------|-------------|-----------|--------------------|------------|-----------------|
| without additives             | 1.9         | 3.9       | 5.5                | 0.8        | -               |
| With the addition of molybdenum 15% by weight of cement | 1.9         | 3.9       | 5.5                | 0.8        | 0.285           |
| With the addition of molybdenum (5%) with a decrease in the mass of cement | 1.805       | 3.9       | 5.5                | 0.8        | 0.095           |

Figure 1 shows the process of the components preparation for the concrete mixture with molybdenum waste additives.
Mixed up the concrete we layed it layer-by-layer in molds with the compaction and vibration according to GOST 10180-2012, Figure 2.

**Figure 1.** Process of concrete mixture components preparation with molybdenum waste additives.

**Figure 2.** Concrete mixture with the addition of molybdenum waste in the form.
Figure 3 shows the destruction of a concrete sample during testing (with the addition of molybdenum waste 15%).

![Figure 3. A concrete sample destruction on a testing machine.](image)

3. Research results
The strength of concrete consists of measuring the minimum effort required to destroy specially made concrete samples under static loading with a constant rate of rise of the load, and then calculating the stresses under these conditions.

The test was carried out in accordance with GOST 10180-2012 "Methods for determining the strength of control samples." The strength of control samples and samples with additives was determined at 7 and 28 days of hardening under normal conditions.

7-day compressive strength test results for concrete samples are shown in Table 5.

| Type of Concrete | Size of Samples (cm) | Weight of Sample (g) | Density (g/cm³) | Collapsing Load, ts | Strength, kgf/cm² | Average Strength, kgf/cm² | Concrete Class on Compression |
|------------------|----------------------|----------------------|-----------------|---------------------|-------------------|--------------------------|----------------------------|
| Without Addition | 10 10 10             | 2484                 | 2.48            | 41.09               | 390.36            | 391.13                   | B40                        |
| With the addition of molybdenum 15% by weight of cement | 10 10 10 | 2506 | 2.506 | 41.25 | 391.9 |
| 10 10 10 | 2502 | 2.502 | 41.22 | 391.59 |
| 10 10 10 | 2512 | 2.512 | 41.82 | 397.29 | 394.44 | B40 |
| With the addition of molybdenum 15% by weight of cement | 10 10 10 | 2494 | 2.494 | 35.43 | 336.6 | 347 | B40 |
addition of molybdenum (5%) with cement diminishing

28-day compressive strength test results for concrete samples are shown in Table 6.

Table 6. 28-day compressive strength test results for concrete samples.

| type of concrete | sizes of samples, cm | Weight of sample, g | Density, g/cm³ | Collapsing load, ts | Strength, kgf/cm² | average strength, kgf/cm² | concrete class on compression |
|------------------|----------------------|---------------------|----------------|--------------------|-------------------|--------------------------|-----------------------------|
| without addition | 10 10 10             | 2480                | 2.48           | 58.7               | 557.6             |                          | B40                         |
|                   | 10 10 10             | 2500                | 2.50           | 58.93              | 559.8             |                          |                             |
| With the addition of molybdenum 15% by weight of cement | 10 10 10             | 2502                | 2.50           | 59.74              | 567.5             | 563.45                   | B40                         |
| With the addition of molybdenum (5%) with cement diminishing | 10 10 10             | 2490                | 2.49           | 50.61              | 480.8             |                          |                             |
|                   | 10 10 10             | 2468                | 2.46           | 53.74              | 510.5             | 495.65                   | B40                         |

4. Conclusion
As a result of laboratory and technological tests of concrete samples with the addition of thinning agents, the concrete mixture became more workable, its density and strength showed the higher result. The use of metallurgical waste as additives allows you to save natural material, the transportation costs and at the same time to clear the areas of urban agglomeration, which solves the urgent environmental problem. We consider it appropriate to use the molybdenum wastes for improvement the ecological state of North Ossetia-Alania territory.

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