Geotechnical properties of hemihydrate and dihydrate phosphogypsum

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Abstract. The article presents the results of analyses of more than 500 samples of phosphogypsum, which is the waste in the process of phosphorous fertilizers production, consisting of calcium sulfate with admixtures of sulfuric and phosphoric acids, silica and other substances. The characteristics of hemihydrate phosphogypsum (CaSO4·0,5H2O), in which cementation bonds form as the hydration process proceeds, were studied on undisturbed samples taken in 1 and in 6 months, 1, 5 and 10 years after the material was dumped. It is characterized by low strength and insignificant frost-resistance, which is typical for all building materials and products based on gypsum. The cementation bonds have not been formed in dihydrate phosphogypsum (CaSO4·2H2O) and it remains a non-cohesive granular substance in the dump, so its properties were determined by the methods used in a geotechnics for sands and silty soils. The artificially prepared samples with the relative compaction of 0.80, 0.90 and 0.95 were tested. While the obtained values of the internal friction angle, cohesion and hydraulic conductivity were characteristic for fine sands, the compressibility of this material due to the solubility of the particles was substantially higher. The utilization of phosphogypsum as ground material may have limited use, provided that water protection measures are taken and the acids contained in it are neutralized.

1. Introduction
Phosphogypsum is waste in the production of phosphorus fertilizers, which, depending on the raw materials used and the production process, consists of calcium sulfate hemihydrate or dihydrate with admixtures of sulfuric and phosphoric acids, silica and other substances [1, 2]. Every year more than 15 million tons of phosphogypsum in Russia are sent to the dumps [3].

There is some experience in utilization this waste in road construction, for example, as an additive to crushed rock or gravel in the pavement base, where there are no high requirements to the frost resistance [4]. Studies have been carried out on its use in the base of capital type pavement [5, 6]. The effect of this by-product on workability and setting time of the cement mortar was investigated [7].

There are some cases of using the phosphogypsum in the construction of enclosing dams in the storage facilities for industrial waste of chemical industry [8, 9, 10]. As the result of pre-design studies on one of these facilities the recommendations for adaptation of the methods for determining the physical and mechanical properties of this very specific material were given [11]. To assess the possibility of using it in earthquake endangered areas the dynamic properties of dihydrate phosphogypsum were studied [12].

This article presents the results of complex laboratory studies of two types of phosphogypsum (PG), hemihydrate (HPG) and dihydrate (DHPG), as ground material.
2. Materials and methods

HHPG (CaSO\textsubscript{4}·0.5H\textsubscript{2}O) is loose earthy material of white or gray color. It turns into a weak semi–rocky technogenic soil (CaSO\textsubscript{4}·2H\textsubscript{2}O) in the dump as the hydration process goes on and cementation bonds appear. The initial setting time of the PG with water content 30–35 % is from 35 to 40 minutes and the final setting takes from 110 to 120 minutes. At the water content 55–60 %, the initial and final setting time reduces by more than twice. Note that to prevent the loss of crystallized water, the water content of the PG was determined by drying to a constant weight at the temperature of (60 ± 2) °C.

In the DHPG (CaSO\textsubscript{4}·2H\textsubscript{2}O) structural bonds are not formed and it remains a non-cohesive granular substance in the dump. The content of particles smaller than 0.1 mm is from 45 to 85 %; the content of particles from 0.1 to 0.25 mm is from 5 to 25 % and the content of particles larger than 0.25 mm is from 10 to 35 %. Large aggregate inclusions may be present.

The average pH value is usually about 3.0. After 5-10 years the pH increases to 5.5-6.0 due to the impact of atmospheric precipitation. The manufacturers may neutralize the PG with calcium hydroxide [13].

The properties of the HHPG – semi–rocky technogenic soil were studied on undisturbed samples taken from the dump after 1 and 6 months, 1, 5 and 10 years after storage. The samples were taken in the places where the material was not compacted in the process of laying, and was not exposed to the impact of mechanical equipment during storage. In total, 120 samples of HHPG were tested.

The unconfined compressive strength was determined on 40×40×80 mm prismatic samples in the air-dry and water-saturated states. The water permeability was studied in triaxial compression devices on cylindrical samples with a diameter of 70 mm and a height of 100 mm at a variable pressure gradient with water supply from bottom to top. To exclude water filtration at the contact with the membrane in the device chamber a pressure of 200 kPa was provided.

The frost resistance of the material was studied on water-saturated cubic 100×100×100 mm samples. The maximum number of cycles of freezing/thawing without destruction of the samples or appearance of damage on their surface was taken as an indicator of frost resistance. The samples were kept for at least 4 hours at the temperature of minus 15 °C and thawed in water at the temperature of 20 °C.

The properties of the DHPG, non-cohesive granular substance, were determined on samples taken from the dump a month after storage. Three types of samples were prepared – with a relative compaction of 0.80, 0.90, and 0.95. Their water content was close to the optimal one that is from 21 to 24 %. Approximately half of the samples were tested at the initial water content, and the remaining samples were saturated with water after loading into the devices. In total 390 samples of DHPG were tested.

The compressibility was studied in oedometers under a load of 12.5, 50, 100, 200 kPa. The consolidation parameters were determined in the same devices with two-way drainage. The load on the samples was applied in one step and it was 25, 50, 100, 200 and 300 kPa. All samples were pre-saturated with water.

The strength characteristics, internal friction angle and cohesion, were determined in the direct shear devices according to the schemes of consolidated–drained and unconsolidated–undrained tests at four values of normal stresses – 50, 100, 200 and 300 kPa. The unconfined compression strength \( c_u \) was determined in triaxial compression devices at three values of the reconsolidation pressure – 100, 200 and 300 kPa.

The hydraulic conductivity was studied in failing head permeability tests. A load of 25, 50, 100, 200 and 300 kPa was applied to the samples.

The shrinkage of water-saturated samples was determined during drying in three steps: in a desiccator with potassium carbonate at room temperature of 20–24 °C, in air at the temperature of 20–24 °C and in a chamber at the temperature of 60 °C.

The swelling was studied in standard devices without vertical load.

The experiments to determine the subsidence were carried out in compression–filtration devices according to the "two curves" scheme at the load on the samples of 25, 50, 100, 200 and 300 kPa. For
every load relative subsidence \( \varepsilon_{su} \), subsidence initial pressure \( p_{sl} \) and relative suffosion compression \( \varepsilon_{sf} \) due to dissolution phosphogypsum in the process of water filtration were determined.

3. Results

3.1 Hemihydrate phosphogypsum

The average values of unconfined compressive strength of the samples in the air–dry and water-saturated states as well as the softening factor equal to their ratio are given in table 1.

| Age, years | Dry UCS, MPa | Saturated UCS, MPa | \( k_{sof} \) |
|------------|--------------|-------------------|---------------|
| 1/12       | 1.3          | 0.5               | 2.6           |
| 1/2        | 1.4          | 0.8               | 1.9           |
| 1          | 1.6          | 0.5               | 2.9           |
| 5          | 0.6          | 0.3               | 2.5           |
| 10         | 0.5          | 0.2               | 2.3           |

As you can see, the strength after dumping gradually increased and after 1 year it reached 1.6 MPa, the water saturation resulted in the decrease of this value up to 0.5 MPa. The further storage in the dump resulted in the strength decrease by several times.

The hydraulic conductivity of HHPG of different ages varies in a rather narrow range: from 0.28 to 0.35 m/day.

The samples of various ages showed extremely low frost resistance: from 3 to 8 cycles (figure 1).

3.2 Dihydrate phosphogypsum

The tests in the Proctor compaction device showed that it is possible to achieve the maximum dry density of the DHPG of 1.37 g/cm\(^3\) at the optimal water content of 23 %, where the water content is determined by drying the samples at the temperature of (60 ± 2) °C (figure 2).
The average values of the compression index for different relative compaction and for two water content values obtained in the tests with an oedometer are shown in Table 2. It is quite natural that when the relative compaction of samples increases from 0.80 to 0.95, the compression index increases by an average of 3.5 times. The water saturation of the samples with the compaction factor of 0.95 did not lead to significant changes in compressibility, but with the factor of 0.80 and 0.90, saturation led to a decrease in the compression index by from 1.2 to 1.8 times.

### Table 2. Compression index.

| Water content | \( c_s \) at the relative compaction of the samples of: |
|---------------|--------------------------------------------------|
|               | 0.95 | 0.90 | 0.80 |
| \( W_{\text{opt}} \) | 0.06 | 0.09 | 0.19 |
| \( W_{\text{sat}} \) | 0.06 | 0.16 | 0.23 |

The average values of the primary consolidation coefficient \( c_v \) and secondary consolidation index \( c_s \) are shown in Table 3. The secondary consolidation index is given without dividing into three types of samples due to its insignificant variations.

### Table 3. Consolidation factors.

| Load, kPa | \( c_v \), m\(^2\)/year, at the relative compaction of the samples of: | \( c_s \cdot 10^{-3} \) |
|-----------|--------------------------------------------------|------------------|
|           | 0.95 | 0.90 | 0.80 |                     |
| 25        | 5.0  | 4.9  | 2.5  | 1.3                 |
| 50        | 6.3  | 5.6  | 3.3  | 1.6                 |
| 100       | 9.0  | 7.8  | 4.6  | 2.3                 |
| 200       | 12.9 | 8.3  | 5.9  | 2.9                 |
| 300       | 11.2 | 7.4  | 7.2  | 2.9                 |

The average values of the internal friction angle and cohesion are shown in Table 4. The first characteristic when compacting the samples increased slightly by from 1.3\(^{\circ}\) to 3.5\(^{\circ}\). The saturation of the samples with water led to a decrease in \( \varphi \) by from 0.6\(^{\circ}\) to 3.4\(^{\circ}\). The second characteristic is 6 kPa in average. No significant dependence of the strength characteristics on the drainage conditions of the sample was found.

### Table 4. Shear strength.

| Test method | Water content | \( \varphi \), \( \circ \) / \( c \), kPa, at the relative compaction of the samples of: | \( \varphi \), \( \circ \) / \( c \), kPa, at the relative compaction of the samples of: |
|-------------|---------------|--------------------------------------------------|--------------------------------------------------|
|             |               | 0.95 | 0.90 | 0.80 | 0.95 | 0.90 | 0.80 |
| Consolided- | \( W_{\text{opt}} \) | 35.2 | 6.7  | 34.1 | 7.2  | 32.4 | 7.6  |
| drained     | \( W_{\text{sat}} \) | 32.3 | 6.3  | 30.4 | 4.7  | 29.0 | 5.6  |
| Unconsolida- | \( W_{\text{opt}} \) | 32.9 | 6.0  | 32.0 | 5.8  | 29.0 | 7.4  |
| –undrained  | \( W_{\text{sat}} \) | 29.6 | 5.9  | 28.9 | 5.7  | 28.4 | 5.7  |
The average values of the unconfined compression strength $c_u$ are given in Table 5. With the increase in the relative compaction of the samples from 0.80 to 0.95 this characteristic increases by more than 4 times.

Table 5. Unconfined compression strength.

| Reconsolidation pressure, kPa | $c_u$, kPa, at the relative compaction of the samples of: |
|-----------------------------|--------------------------------------------------------|
|                             | 0.95 | 0.90 | 0.80 |
| 100                         | 110.8| 53.0 | 24.4 |
| 200                         | 147.4| 74.0 | 24.6 |
| 300                         | 185.6| 88.1 | 39.5 |

The average values of the hydraulic conductivity are given in Table 6. When the relative compaction increases from 0.80 to 0.95, the hydraulic conductivity decreases by from 2.5 to 4.5 times depending on the load on the samples.

The samples with the compaction factor of 0.95 tend to have a weak swelling and the samples with less compaction does not swell. No shrinkage was observed during drying of the samples.

Table 6. Hydraulic conductivity.

| Load, kPa | $k$, m/day, at the relative compaction of the samples of: |
|-----------|--------------------------------------------------------|
|           | 0.95 | 0.90 | 0.80 |
| Without load | 0.091 | 0.165 | 0.431 |
| 25         | 0.063 | 0.119 | 0.182 |
| 50         | 0.056 | 0.096 | 0.146 |
| 100        | 0.056 | 0.089 | 0.138 |
| 200        | 0.056 | 0.074 | 0.112 |
| 300        | 0.039 | 0.055 | 0.104 |

The indicators of subsidence during permeating with water: relative subsidence $\varepsilon_{sl}$, initial pressure of subsidence of $p_{sl}$ and relative suffosion compression $\varepsilon_{sf}$, due to the dissolution of the test material during water filtration, are shown in Table 7. When the relative compaction increases from 0.80 to 0.95, the relative subsidence and suffosion compression decrease by 14-37 and 2.7-4.5 times, respectively.

Table 7. Subsidence and suffusion.

| Relative compaction | $\varepsilon_{sf}$ $\cdot 10^{-2}$ under load, kPa | $p_{sl}$, kPa | $\varepsilon_{sf}$ $\cdot 10^{-4}$, under load, kPa |
|---------------------|--------------------------------------------------|--------------|-------------------------------------------------|
| 0.95                | 0.1     | 0.3     | 0.3     | 0.3     | >300   | 0.4     | 1.3     | 1.6     | 1.7     |
| 0.90                | 0.2     | 0.3     | 0.7     | 2.0     | 2.7     | 0.6     | 1.1     | 1.8     | 2.0     | 2.1     |
| 0.80                | 3.5     | 3.7     | 4.3     | 4.4     | 4.9     | <25     | 2.2     | 2.8     | 3.5     | 4.6     | 5.8     |

4. Discussion

4.1 Hemihydrate phosphogypsum

The density of natural gypsum stone is usually from 2.20 to 2.40 g/cm$^3$ [14, 15]. The density of the studied samples is on average 2 times less than that of natural gypsum and is 1.20 g/cm$^3$, further as it stays in dump it decreases to 0.92 g/cm$^3$ as a result of chemical and mechanical suffosion [16]. These processes cause a decrease in the strength of the phosphogypsum during its long stay in the dump [17]. If during the first year the material gained strength, then later its strength decreased and after 10 years
it reached values from 0.2 to 0.5 MPa, which are 4 times lower than the minimum grade of gypsum binder [18].

The suffosion processes did not lead to an equally significant change in water permeability as the hydraulic conductivity. The permeability of this material is about the same as that of fine sands.

A distinctive feature of the HHPG, in addition to low strength, is the almost complete absence of frost resistance, which is characteristic for all building materials and products based on gypsum binder [19].

4.2 Dihydrate phosphogypsum
The material under study, compacted to a relative compaction of 0.95, can be attributed to medium-deformable soils, and with less compaction it can be attributed to highly deformable soils. Moreover, if water saturation of samples with a relative compaction of 0.95 practically did not affect the compressibility, then for samples with a lower initial density this led to a rapid increase in deformations.

The obtained values of the consolidation parameters are typical for highly deformable soils, which is most likely due not to the slow removal of water from the pores or the creep of the matrix, as in clay water-saturated soils, but to the dissolution of particles.

As it turned out, the DHPG has the values of friction angle and cohesion characteristic for fine sand, and, as with these soils, these values are weakly dependent on the test conditions.

According to the value of unconfined compression strength, the DHPG with the relative compaction of 0.95, 0.90 and 0.80 refers to soils of high, medium and low strength, respectively [20].

The DHPG with the relative compaction of 0.95 has a weak swelling and the one with a lower initial density did not swell. No shrinkage was observed at any sample density. The DHPG is characterized by subsidence and suffosion compression. Prolonged filtration of water through its massive will lead to the development of suffosion sediment.

5. Conclusions
The comprehensive laboratory studies of the geotechnical properties of phosphogypsum have shown that this material can have only limited use as ground material, for example, in the construction of the roads with low traffic and the enclosing dams on industrial landfills, as well as in situ waste remediation, etc.

It is recommended to fill the dihydrate phosphogypsum with the relative compaction of at least 0.95, which will allow reducing its water permeability and achieving the maximum possible values of deformation and strength characteristics.

To form a massive of hemihydrate phosphogypsum with the maximum values of strength the time of its transportation from the facility shall not exceed the 40 minutes.

When using this chemical industry waste, its susceptibility to chemical suffosion should be taken into account, as well as the need to neutralize the acids contained in it.

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