Industrial Waste as Components of Building Materials

Natalya Fomina*, Irina Pavlova, and Maria Kochergina
Yuri Gagarin State Technical University of Saratov, Polytechnic St., 77, 410054 Saratov, Russia

Abstract. The possibilities of using large-tonnage waste from the Saratov region in the production of building materials are analysed. Waste was investigated: phosphogypsum - waste from the production of mineral fertilizers; steel-making slag, limestone crushing waste, construction waste (crushed concrete). The extraction of strontium and rare-earth metals from phosphogypsum is substantiated, followed by its processing into products that solidify according to the non-hydration principle, or use in the compositions of expanding cements. The development of geopolymer binders of alkaline activation based on steel-making slags is proposed. The introduction of low water demand carbonate cements into construction practice has been substantiated. Limestone crushing waste can be used as a carbonate mineral additive. The processing of crushed concrete waste into crushed stone, coarse sands and finely dispersed additives into cement concretes is considered. Technologies for processing large-tonnage waste in the production of building materials are environmentally sound and economically justified.

1 Introduction

The construction industry is a consumer of a huge amount of resources. We have analyzed world statistics. Cement concrete is produced annually over 20 billion tons, Portland cement is produced over 4 billion tons. It is important that for each ton of cement, at least 1.5 tons of mineral raw materials and 200 kg of fuel are needed. All this is extracted from the bowels of the earth.

The growth of resource extraction and industrial production on a historical scale has an exponential relationship, with a sharp rise in the 20th century. Over the past 200 years, we have dug more from the bowels of the earth than in all previous history.

Waste accumulates as a result of production. A lot of waste can be used to make building materials. Recycling waste into building materials is an effective way to solve many environmental problems.

The purpose of this work is to study the possibilities of using regional waste in building compositions.

* Corresponding author: fominanani@yandex.ru
2 Materials and Methods

Regional waste was investigated:
Phosphogypsum is a waste from the production of mineral fertilizers of the Balakovo branch of PhosAgro Group.
Steelmaking slag is a waste of the production of Balakovo Steel Factory.
Limestone crushing waste - Ershovsky stone quarry, Astek-S.
Construction waste (crushed concrete) generated in a construction laboratory after testing concrete samples.

Chemical analysis was carried out on an X-ray crystal-diffraction vacuum spectrometer "Spectroscan Max GV", using crystal analyzers according to Johann and Johanson LiF (200), C, PET. The equivalent dose of phosphogypsum radiation was determined using a Geiger counter.

We determined the grain size and granulometric composition of the waste by sifting through sieves with mesh sizes: 0.16; 0.315; 0.63; 1.25; 2.5; 5.0; 10.0; 20; 40 mm. Particles less than 0.16 mm in size were analyzed by laser diffraction on a Horiba LA-300.

We determined the strength of large fractions of waste by the index of crushing through the mass percentage of crushed grains after squeezing the sample (separately in dry and in a water-saturated state) in a cylinder 150 mm in diameter under a load of 200 kN.

From phosphogypsum, we made laboratory specimens-beams with dimensions of 40x40x160 mm, which were tested for strength at three-point bending and compression at the age of 2 hours of hardening, as well as after complete drying.

3 Results and Discussion

3.1 Phosphogypsum
For every ton of mineral fertilizers, more than 3 tons of this waste are generated. The volume of the dump in Balakova is measured in tens of millions of tons, and the height of these white mountains is up to 100 meters. Phosphogypsum is 95% calcium sulfate hydrate. According to this indicator, it is an excellent raw material for gypsum binders and products. But there are a number of difficulties. The element composition of the studied phosphogypsum is presented in Table 1.

Table 1. Chemical analysis of phosphogypsum.

| Element | Amount, % by weight |
|---------|---------------------|
| Si      | 0.44731             |
| P       | 1.15762             |
| SO₄     | 55.87095            |
| Ca      | 36.84422            |
| Fe      | 0.39737             |
| Cu      | 0.37635             |
| Sr      | 4.90619             |
| Others  | 1.19054             |
We have established that the radiation background of phosphogypsum is normal. The dose of radioactive radiation from phosphogypsum is less than 0.08 μSv / h, both for old and fresh (a safe level of radiation is considered to be up to 0.2 μSv / h). Phosphogypsum contains residual phosphoric acids and rare earth metals as impurities. Impurities complicate the hardening processes of gypsum binders obtained from phosphogypsum. Therefore, the quality of gypsum products is low [1-3].

Methods of purification and neutralization of phosphogypsum are known. So, in Europe, the Knauf company successfully cleans phosphogypsum and manufactures high-quality gypsum products. Washing and neutralizing phosphogypsum significantly complicates and increases the cost of production. Therefore, in Russia, given the fact that half of the world's reserves of natural gypsum raw materials in our country, phosphogypsum is not in demand by the construction industry.

We investigated phosphogypsum as a binder. For this, we heat-treated phosphogypsum at 170 °C to constant weight. From the material obtained, we made compositions of a casting consistency (with a water content of about 60% of the gypsum mass). The strength of the solidified samples did not exceed 3 MPa. We also investigated the possibility of hardening phosphogypsum dihydrate by a non-hydration mechanism [1, 4]. For this, we prepared press powders (with a water content of about 25% by weight of phosphogypsum) and pressed samples. The strength of the samples was 20 MPa after complete drying. These results indicate the promising nature of phosphogypsum as a binder hardening by a non-hydration mechanism.

One of the most promising methods of phosphogypsum utilization, in our opinion, is the extraction of strontium and rare earth metals from it. The purified phosphogypsum is further processed into building products. To date, the implementation of such a project is announced by the Uralchem company, which owns the Voskresensk Mineral Fertilizers plant in the Moscow region.

As for the Balakovo phosphogypsum, attempts are known to build roads using it. We consider this inappropriate, since calcium sulfate is a poorly soluble compound. It should be noted that there are expanding and stressing cements. They are able to increase in volume up to 4%. In conditions constrained by the formwork, the expansion energy goes into self-compacting. You can get durable, frost-resistant concrete, including for road construction. Phosphogypsum can be used in the formulation of such cements.

### 3.2 Steelmaking slag

Another regional industrial waste is the steelmaking slag of Balakovo Steel Factory. The company positions slag as a high-quality graded aggregate for concrete, instead of natural sand and gravel. However, there are difficulties associated with the use of slag in concrete.

Slag really has sufficient strength (grain fragmentation rate 14.7%), normal grain size (the content of lamellar and needle-shaped grains is 7.2%), and satisfactory frost resistance (100 cycles). But the density of the slag is increased, as a result - heavier construction products. Obviously, because of this, transportation, installation, increased loads on the foundations, and so on are more difficult.

We are even more concerned about the stability of the slag structure (3.42%). Steelmaking slags are prone to spontaneous destruction (decay) [5]. Indeed, there are observations of concrete manufacturers - the slag is noticeably crushed by itself even under normal storage conditions. We should note that the calcareous and magnesian slag decays are extended over time. We also had a lot of doubts when we analyzed the chemical composition of the slags (Table 2). A high-quality aggregate for concrete limits the content of iron oxides, manganese, sulfides and sulfates, and reactive silica. By introducing slag into concrete, we run a high risk of getting internal corrosion of concrete, for example,
sulfate or alkali-silicate. Such corrosion processes do not develop quickly, during the operation of the structure.

In our opinion, the development of geopolymer binders (alkaline activation binders) on their basis is a more promising direction for the utilization of steel-making slags. The technology of their production is non-firing. The slag is crushed into a finely dispersed state, which eliminates the danger of its self-decomposition.

| The amount of oxide, % by weight |
|-----------------------------|
| CaO | MgO | SiO₂ | Al₂O₃ | MnO | Fe₂O₃ | FeO | loss of mass on ignition |
| 30.7 | 10.0 | 19.1 | 3.1  | 5.3 | 5.8  | 21.1 | 4.9 |

Here the main difficulty lies in the two-component nature of the system - slag and alkali. We realize that this is more difficult than cement and water. In addition, heating is required for the geopolymers to harden. But as a result, you can get high quality durable concrete with a strength of up to 150 MPa.

We believe that geopolymers in modern construction are a serious alternative to non-ecological and energy-intensive cement.

### 3.3 Limestone crushing waste

Another practically not dangerous, but multi-tonnage regional waste is formed when crushing carbonate rocks - limestone and dolomite. Such waste is formed at all crushed stone quarries in our region.

The Ershovsky stone quarry (Astek-S) waste is a sand-crushed stone mixture with a particle size of up to 10 mm (Table 3). Up to 45% of the processed rock goes to waste. Waste is partially processed - as an aggregate in the compositions of low-grade concrete and mortars, in the compositions of dry building mixtures, as aggregate and mineral flour in asphalt concrete [6-10]. But, nevertheless, waste accumulates in huge quantities, and at least occupies territories and becomes dusty.

| Table 3. Waste particle size distribution. |
|-------------------------------------------|
| Sieve size, mm | Sieve amount, % by weight |
|----------------|--------------------------|
| 5              | 35.6                     |
| 2.5            | 25.6                     |
| 1.25           | 18.7                     |
| 0.63           | 7.8                      |
| 0.315          | 4.5                      |
| 0.16           | 1.9                      |
| pallet         | 5.9                      |

We will focus on one of the most effective ways to dispose of this waste. This is the production of carbonate cements of low water demand [6, 8, 10]. They are obtained by final
grinding of ordinary cements with wastes from crushing carbonate rocks and the addition of plasticizers.

Production of cements with mineral additives is a worldwide trend. Cement production is responsible for 2.5 billion tons of carbon dioxide emissions annually. Therefore, the more mineral additives in the cement, the more environmentally friendly and less energy intensive the cement.

The use of carbonate waste as additives is also associated with their availability and good grindability. Most importantly, the possibility of chemical interaction of finely ground carbonates with cement has now been proven [6, 9].

Projects for the introduction of carbonate cements are already being implemented in Tatarstan. In our opinion, such binders will soon become the main product of the cement industry.

3.4 Construction waste (crushed concrete)

Construction waste can be effectively disposed of by the same principle. They are formed during the demolition of old objects. Most of these are concrete and brickwork scrap. The volume of construction waste generation is very impressive - annually up to 17 million tons in Russia. Most often they are used in road construction [11-12]. But the return to the production of concrete and reinforced concrete structures is more effective, since they have an affinity for the cement matrix.

Some characteristics of crushed concrete scrap are presented in Table 4.

| Sieve size, mm | Sieve amount, % by weight | Grain fragmentation rate, % | Size module |
|---------------|--------------------------|----------------------------|-------------|
|               |                          | dry | water-saturated |              |
| 10 - 20       | 48.2                     | 14.0| 14.5            | -            |
| 5 - 10        | 27.9                     | 20.8| 21.7            | -            |
| 0.16 - 5      | 19.7                     | -   | -               | 2.9          |
| < 0.16        | 4.2                      | -   | -               | -            |

In our opinion, it is most expedient to fractionate crushed concrete scrap [13]. Then use material larger than 5 mm as a coarse aggregate in ordinary concrete. The sand fraction should also be dispersed, and material larger than 0.63 mm should be used to coarse fine-grained sands. Particles less than 0.63 mm in size should be crushed in mills together with plasticizing additives to a specific surface area of about 400 m² / kg and used in cement concrete compositions as an active mineral additive.

4 Conclusions

Appropriate ways of processing regional waste in construction are:

1. Extraction from the mass of phosphogypsum up to 5% of strontium and rare earth metals. Subsequent processing of calcium sulfate dihydrate into a building block made by compression pressing, which provides hardening by a non-hydration mechanism, with a compressive strength of products up to 20 MPa.
2. Development of composite expanding cements with phosphogypsum content up to 25% by weight.

3. Development of geopolymer binders of alkaline activation based on steelmaking slag.

4. Development of carbonate cements of low water demand, by regrinding fine fraction (up to 0.63 mm) of limestone crushing screenings (up to 20% by weight) together with Portland cement and plasticizing additive.

5. Crushing and fractionation of construction waste into crushed stone (fraction larger than 5 mm), mineral chips (0.63-5 mm) and finely dispersed additives (up to 0.63 mm) into cement concrete.

References
1. V.V. Belov, A.F. Buryanov, V.B. Petropavlovskaya, Modern effective gypsum binders, materials and products (2007)
2. E. Saadaoui, N. Ghazel, Ch. B. Romdhane, N. Massoudi, Int. J. Environmental Studies (2017)
3. Yu.G. Meshcheryakov, S.V. Fedorov, Fundamental research, 6, 273 (2015)
4. X. Huang, X. Zhao, Sh. Bie, Ch. Yang, P - ESEM, 31, 970 (2016)
5. K.M. Voronin, D.D. Khamidulina, S.A. Nekrasov, I.S. Trubkin, Building materials, 12, 71 (2017)
6. V.V. Belov, S.L. Subbotin, P.V. Kulyaev, Building materials, 3, 25 (2015)
7. V.I. Golik, O. N. Polukhin, O.Z. Gabarev, Dry building mixtures, 5, 14 (2014)
8. I. Ya. Kharchenko, D.A. Bazhenov, Building materials, 5, 48 (2018)
9. L.O. Larsen, V.V. Naruts, Magazine of Civil Engineering, 8, 76 (2016)
10. Yu.V. Pukharenko, T.V. Kharitonova, Bulletin of Civil Engineers, 4(69), 121 (2018)
11. M.V.A. Florea, H.J.H. Brouwers, Cement and Concrete Research, 53, 278 (2013)
12. N.M. Krasinikova, E.V. Kirillova, V.G. Khozin, Building Materials, 1-2, 56 (2020)
13. N.N. Fomina, M.M. Polyanskiy, E3S Web Conf, 97, 8 (2019)