Nature raw materials of Russian Primorsky Krai for concrete

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Abstract. The paper presents the evaluation of the raw materials of Primorsky Krai, used in the concrete manufacture. It was revealed that the region has all the necessary natural materials capable of ensuring the release of the concrete with the highest technical indicators.

1. Introduction

The minimize of transportation cost of natural raw materials is essential for both an economic point of view and an environment one in the building materials production. In this case, it is scheduled to use the local materials in the construction industry. Accordingly, the study of natural geological reserves of Primorsky Krai is an actual scientific task. The paper considers the presence in Primorsky Krai of the natural raw materials which are need for production of the most common structural composite material - concrete.

Primorsky Krai is a part of the Far Eastern Federal District of the Russian Federation. About four-fifths of the territory is a mountain system of Sikhote-Alin stretching from north-east to south-west. The plains and the lowlands are only about one-fifth of the territory. A variety of known minerals deposits is in the Primorsky Krai territory to date: tin, tungsten, lead, zinc, copper, silver, gold, boron, fluorite, rare earth elements, titanium, bismuth, indium, iron, manganese, various construction materials, vermiculite, zeolites, collectible, facing and building stones, natural raw materials for stone casting and expanded clay, perlite, cement raw materials, porcelain, stone, various coals, and a number of other materials (Figure 1) [1-4].

2. Raw materials for the Portland cement production

Spassk cement is the largest in the Russian Far East plant of the construction industry. Its design capacity of 3.6 million tons per year was surpassed in 1988. Today, it produces the cement of different brands as well as the clinker for related businesses. However, the volume of construction, much less than the 25 years ago, is not allowed to return to the record results.

Portland cement clinker - the main component of cement – is a product of roasting before sintering the fine homogeneous raw mixture of limestone and clay or some materials (marl, blast furnace slag, etc.). It is seen as the pre-emptive content of the highly basic calcium silicates in the clinker, when burning.

The cement clinker quality can be characterized by:
- the individual oxides content of chemical composition;
- the numerical values of the modules, expressing the ratio between the number of main oxides as a percentage;
- the clinker microstructure, size and configuration of mineral crystals;
- the main content of clinker minerals.

Figure 1. Geological map of Primorsky Krai.

The clinker quality is the most important parameter of cement quality.

3. Limestone

A limestone, sometimes dolomitic of terrigenous and terrigenous-siliceous rocks, has interlayers horizon of up to 100-150 m that was crushed together in compressed (sometimes overturned) folds, sometimes in overturned folds in sublatitudinal and NW-trending. There is developed lens limestone
in Bamburovo deposit and Barabash deposit in Laoelin-Grodekovsk terrane in Southwest Upper Primorye. The Sikhote-Alin system limestones are stacked olistoliths and landslide plate in the Jurassic and Early Cretaceous olistostromes. They are characterized by reef facies of Carboniferous-Permain and Late Triassic age Tauhinsk terrane - in Natalinskoe, Sankin Klyuch, Frolovskoye, Kuznetsovsk, Nikolaev, Nowitzkoe, Vysokiy Utes and other deposits. They can participate in the scalyst-thrust structures and olistostrome strata in Spassk terrane. There are deposits of limestone Dlinnogorskoe, Malye Klyuchi, Spassky and Prokhorovka; those of dolomites - Buk-Prokhorovka, Lipovetsky and Pervomayskoye. Group limestone deposits in the area of Spassk are the foundation of the cement industry of the region. They are used for production of lime as building stones and dolomites - as a raw material for glazes.

It should be noted that limestone is not an only raw material for the production of cement clinker, but can be additionally introduced into the cement composite binder for cement economy and impartion additional characteristics for cement stone. In our studies [5-6], limestone mineral powders of Dlinnogorskoe deposit (production by "Spasskement") are used for the design of composite binding materials. The mineralogical composition of applied micro filler has the following minerals: organogenic limestone, dolomitic (2-25%), crystalline, variegated with glauconite grains (up 20%), with a few small voides leaching. There is a presence of phosphate (2-3%) and single grain quartz. Physical-mechanical properties and the chemical composition are shown in Tables 1, 2.

**Table 1.** Mineral powder physical-mechanical properties

| №  | The name of indicators | Unit of measure | Indicator |
|----|------------------------|----------------|-----------|
| 1  | Volume weight          | g/cm³          | 2.59      |
| 2  | Porosity               | -              | 1.37      |
| 3  | Water absorption       | %              | 1.64      |
| 4  | Abrasion               | g/cm³          | 0.97      |
| 5  | Factor softening       | -              | 0.85      |
| 6  | Frost-resistance       | -              | F25       |

**Table 2.** Mineral powder chemical composition

| CaO  | MgO  | SiO₂  | Al₂O₃ | Fe₂O₃  | TiO₂  | LOI  |
|------|------|-------|-------|--------|-------|------|
| 44.21| 2.57 | 7.49  | 3.33  | 0.24   | 0.24  | 38.71|

Mineral powder X-ray diffraction results are shown in Figure. 2.

**Figure 2.** Mineral powder X-ray diffraction results.
According to the above-mentioned data, the limestone mineral powder complies with GOST 52129-2003.

4. Fine aggregate for concrete
There are large deposits of granite in Primorsky Krai. Accordingly, macro fillers of various fractions remain after granite processing. They can be used in the production of concrete [7-9]. In the papers [5-6], the crushed granite from Wrangel deposit was used for fine-grained concrete (Tables 3,4).

Table 3. Granite aggregate mineral composition

| Name of rock | The mineral content, % by weight |
|--------------|---------------------------------|
|              | feldspars | quartz | biotite |
| Granite      | less 65   | 25-30  | 5-10    |

Table 4. Granite aggregate chemical composition, %

| Name of rock | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | FeO | MnO | MgO | CaO | Na₂O | K₂O | H₂O | P₂O₅ | CO₃ |
|--------------|------|------|-------|-------|-----|-----|-----|-----|------|-----|-----|------|-----|
| Granite      | 70.18| 0.39 | 14.47 | 1.57  | 1.78| 0.12| 0.88| 1.99| 3.48 | 4.11| 0.84| 0.19 | 0.25|

Taking into account the fact that granitic rock has a different background radiation, it was necessary to determine the specific activity of natural radioactive nuclei $A_{\text{eff}}$ of the material. The authors measured specific activity of radium $^{226}\text{Ra}$ - $A_{\text{Ra}}$, of thorium $^{232}\text{Th}$ - $A_{\text{Th}}$, of potassium $^{40}\text{K}$ - $A_{\text{K}}$. Then they were summed according to the formula: $A_{\text{eff}} = A_{\text{Ra}} + 1.31A_{\text{Th}} + 0.085A_{\text{K}}$ for obtaining the value of $A_{\text{eff}}$. The test results by the spectrometric complex "USC Gamma Plus" are shown in Table 5.

Table 5. Determination of specific activity of natural radioactive nuclei of crushed granite

| The name of indicators | Unit of measure | The measurement result (A) |
|------------------------|----------------|--------------------------|
| Activity $^{40}\text{K}$ | Bq/kg          | 322±78                   |
| Activity $^{232}\text{Th}$ |                | 19.5±5.7                 |
| Activity $^{226}\text{Ra}$ |                | 21.63±5.43               |

In accordance with Table 5, the effective activity is 73 ± 10 Bq / kg. This broken stone applies to the first class of materials (less than 370 Bq / kg) in accordance with GOST 30108-94 "Building materials and elements. Determination of specific activity of natural radioactive nuclei". This material can be used for all kinds of construction works. The sand from Razdolnensky deposite was used in addition to broken stone. Its grain structure and physico-mechanical properties are shown in Tables 6, 7.

The grain composition and the grain size value module of sand №1 relate to fine additions with a high content of pulverulent impurities, so using this type of sand is uneconomic. Sand №2 is referred to medium sands and meets all the performance requirements of GOST 8735-88 [5-6].

5. Basalt
There are large deposits of basalt in Primorsky Krai. Basalt is the basic igneous rock. It is used as a raw material for the concrete aggregates, as a basalt fiber production (for producing thermal insulating materials), as a stone casting powder and acid, as well as a filler for concrete. It is of interest to use the
basalt fibers from local raw materials for concrete reinforcement [10-12]. Table 8 presents the chemical composition of the Primorsky basalt.

| Table 6. Determination of sand grains composition |
|-----------------------------------------------|
| Sample number | Content of coarse-grained impurities, % | Residues on sieve, % | Granulometric composition | Sieve sizes, mm | Gradation factor |
|----------------|---------------------------------------|-----------------------|--------------------------|----------------|-----------------|
|                | ab. 10 mm | ab. 5 mm | 2.5 | 1.25 | 0.63 | 0.315 | 0.16 | <0.15 |
| 1              | -         | -       | partial | - | 0.5 | 11.5 | 62.0 | 23.5 | 25 | 1.8 |
| 2              | -         | -       | full    | - | 0.5 | 12.0 | 74.0 | 97.5 | 100 |

| Table 7. Sand physical-mechanical properties |
|---------------------------------------------|
| Sample number | Bulk density, kg/m³ | Real density, kg/m³ | Void volume, % | Content, % | organic particles |
|----------------|----------------------|----------------------|---------------|------------|-------------------|
| 1              | 1220                 | 2630                 | 53.6          | 1.0        | lighter than standard |
| 2              | 1343                 | 2630                 | 48.9          | 0.5        | lighter than standard |

| Table 8. Basalt chemical composition |
|--------------------------------------|
| Type of raw materials | SiO₂ | Fe₂O₃ | FeO | Al₂O | MgO | CaO | K₂O+Na₂O | Other |
| Basalt Primorsky         | 49.5 | 14.06 | 12.45 | 6.00 | 9.80 | 3.35 | 4.49 |

6. Coal ash
It is of interest to study the composition and the origin of the fly ash of Primorye thermal power plants for additives in a composite binder. The type of coal burned affects ash characteristics [13-15]. The basic fuel of Vladivostok thermal power plant was fixed Pavlovsky lignite from incision Chihez field. Pavlovsky lignite is grade "B". It is grossly dense and is dark brown in color which is dominating matt gloss (sometimes semi-mat). The coal structure is streak-striped and lenticular-striped. The original plant material is dominated by the remains of the coal woods stem, leaf and parenchyma bark. The composition is dominated by coal vitrinite (80-99%). Brown coal is mined by the open method. Main characteristics of the coal for the first stage of the calorific value are 2920 kcal / kg; moisture content is 41%; ash content is 8.8%.

7. Water
Concrete manufactures are using the technical water by State Unitary Enterprise "Primorsky Vodokanal" which meets the requirements of GOST 23732-2011 "Water for concrete and mortars. Specifications" for mixing binders. The water does not contain harmful impurities or contains a limited amount of them from the viewpoint of corrosion of the cement stone. Vladivostok tap water has pH = 6.52. Total water hardness is 0.41-0.60 mg-eq / l [16-19].
8. Conclusion
Thus, Primorsky Krai has all the necessary natural reserves for the efficient production of concrete. In particular, it is possible to use local raw materials in concrete:
- Spassky Portland cement CEM I 42.5N;
- riddled crushing of granite rubble from Wrangel deposit
- enriched sand from Razdolensky deposit;
- limestone from quarry Spassky;
- fly ash from Vladivostok TPP and Artem TPP;
- water from local water pipelines.

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