ECOLOGICAL RISKS REDUCTION IN THE PRODUCTION OF CONCRETE COMPOSITES
Alexandr S. Tutygin, Anna A. Shinkaruk, Arkadiy M. Aisenstadt, Valeriy S. Lesovik
Northern (Arctic) Federal University named after M.V. Lomonosov,
17 Severnaya Dvina Emb., Arkhangelsk, Russia

Abstract
The ecological situation in the North-Arctic region can be improved and the efficiency of interaction in the system “Individual- Material – Environment” can be increased if natural raw materials and environmentally friendly mining wastes are used. If these materials are used, it will be possible to reduce cement consumption and consequently the quantity of harmful wastes in the production of high quality concrete composites.

Key words: natural raw materials, saponite-containing material, thermodynamic criteria, microdispersed materials, composite materials.

1. INTRODUCTION
The development of North-Arctic region in Russian Federation is one of the priorities in Russia development. To improve the ecological situation it is important to apply principles of energy and resources saving, wastes reduction in the production.

The aim of this paper is to examine problems in the production of building materials with the use of mining wastes and in the replacement of clinker cement-constituent with saponite-containing material preserving strength characteristics of concrete at the desired level. Main ecological risks in cement production are the following: energy requirement, solid wastes generation, water consumption, water wastes, etc.

Cement industry is energy intensive as chemical oxidation reaction which is necessary to obtain clinker requires high temperatures. Energy sources are natural gas, petroleum coke, coal or fuel oil. In the process of burning greenhouse gases can appear. In cement production solid wastes appear as well. The wastes such as cement and cement dust are usually considered as unhazardous and major part of them can be reused in the production. Besides there can appear ash from wastes burning utilization of which requires special permission. Water is used for raw material preparation, cooling, dust suppression and machine washing. Water can be received from a water pipe or a local well. When water is taken from a local well, permission is necessary to specify how much water will be collected. In cement production there appears an insignificant amount of waste water. Waste water appears in the process of wet grinding and washing. Slurry, which appears as the result of wetting can accumulate as wastes and require a slurry-treatment plant. Besides wastes from vehicle and production area washing can contain suspended substances and metal impurities. Such water can have high pH level [1].

2. EXPERIMENTAL
Diamond deposit situated 100 km from Arkhangelsk has been developed for the last 12 years. Its wastes are slurry which is stored in a tailing dump. The tailing dump’s storage volume is annually increasing as the speed of sediment settling from the appearing suspension is very low. The sediment is a saponite-containing material (63% of saponite), which belongs to montmorillonite group of clays. Saponite-containing material has a very developed internal face (Fig. 1), which is a very important property to use this material when creating and developing composite materials.

To obtain fine-aggregate concrete of required strength and to reduce cement consumption at the same time it is necessary to apply plasticizers, superplasticizers and various modifying agents.

To obtain fine superconcrete a special composition was developed based on the following components: “Relamix” superplasticizer, CEM I 42.5 cement, quartz fine-grained sand from “Krasnoflotsky-zapad” deposit and mining waste namely saponite-containing material. All the above-mentioned components were grinded to the state from 100 to 500 nm, taking into consideration the model of thermodynamic compatibility the composition for organic-mineral nano-dispersed modifying agent (ONM) was offered where “Relamix” superplasticizer made up 1%, CEM I 42.5 cement made up 10%, qurtz fine-grained sand from “Krasnoflotsky-zapad” deposit made up 85% and a mining waste namely saponite-containing material made up 4%.
Using M.Y. Bazhenov method a composition for fine-aggregate concrete with ONM (1; 2.5; 5; 7.5; 10 and 12.5%) and without it was made.

Considering cement and ONM as a whole the concrete composition was calculated in the following order:

1. Energy of mixed cement was determined ($R_k$):

$$R_k = K_R \cdot R_{Ц} = 0.95 \cdot 52.6 = 49.97$$

2. water-cement ($\frac{В}{Ц}$) ratio is calculated to obtain desired concrete strength:

$$\frac{В}{Ц} = А \cdot \frac{R_м}{R_Ц + 0.8 \cdot А \cdot R_Б} = 0.75 \cdot \frac{50}{35 + 0.8 \cdot 0.75 \cdot 50} = 0.47$$

3. The volume of entrained air is determined ($ВВ$), l:

$$ВВ = 81.8 - 16.6 \cdot М_кр + 0.7 \cdot (М_кр)^2 = 81.8 - 16.6 \cdot 1.6 + 0.7 \cdot (1.7)^2 = 55.603$$

4. The consumption of mixed cement is calculated ($Цсм$) according to formula:

$$Цсм = \frac{1000}{1/p_{см} + \frac{В}{Ц} + \frac{n}{ρ_П}} = \frac{1000}{1/1.4 + 0.47 + 2.26/1.65} = 450.46 \text{ kg/m}^3$$

5. overall consumption of water is calculated:

$$В = Цсм \cdot \frac{В}{Ц} = 450.46 \cdot 0.47 = 215 \text{ l/m}^3$$

Water proportion to be increased in an overall water consumption is calculated according to the following formula:

$$B = Πсм \cdot (1/\rho_{см} + Π/п/\rho_П) = (1000)/(1/1.4 + 0.47 + 2.26/1.65) = 450.46 \text{ kg/m}^3$$
\[ V_d = (V_H - H_G) \cdot N = -0.71 \] (8)

where \( V_H \) – water requirement of micro filling agent (relative value);

\( H_G \) is normal cement consistency which is accepted as 0.25 per unit quantity;

\( N \) is the proportion of filling agent per 1m³ of concrete in kg.

7. sand consumption is calculated, kg/m³:

\[ \Pi = n \cdot \Pi_{cw} = 3.70 \cdot 450.46 = 1670 \text{ kg/m}^3 \] (9)

8. average density of fine-aggregate concrete with micro filling agent is calculated, kg/m³:

\[ \rho_c = \Pi + N + B + \Pi = 446 + 4.46 + 215 + 1670 = 2335.46 \text{ kg/m}^3 \] (10)

**Fig. 2.** Sand-cement ratio graphs, where the given flow (\( P_K \)) and workability (\( Y \)) depend on water-cement ratio [165].

**Fig. 3.** \( n \)-value adjustment graph, where \( n \) depends on sand size fineness: 1 – \( M_k = 2.5 \); 2 – \( M_k = 1.5 \); 3 – \( M_k = 0.75 \)

5. Cement (\( \Pi \)) and filling agent (\( H \)) consumption is determined (kg/m³) in mixed cement:

As the result the composition of fine-aggregate concrete was made calculated per 1m³: cement – 446 kg; ONM – 4.46 kg; water – 215 l; sand – 1670 kg.

Calculated composition of fine-aggregate concrete with various ONM content made it possible to prepare test samples to prove the conclusions made about concrete strength properties improvement.

Grade of concrete was determined according to all-union state standard (GOST) [2] after the 70x70x70 mm samples were tested by destructive load. Such samples can be used to determine strength properties of fine-aggregate concrete not containing coarse aggregate. The samples were made from concrete mix and tested after curing for 28 days in normal conditions. A number of samples in a mode was accepted as equal to six.
Concrete mix was poured and consolidated into molds and each sample was graded. The curing process was made in normal thermal and moisture conditions. 24-hours strength of concrete was determined using the above mentioned method according to standards. [2]. Fig. 4 and 5 show the photographs of samples with main and test composition before and after the tests by destructive load.

Fig. 4 – Photography of concrete samples before tests: a – without a modifying agent; b – with 1 % ONM

Fig. 5 – concrete samples after tests by destructive load: a – without a modifying agent; b – with 1 % ONM.

Super concrete samples were tested according to all-union state standard (GOST) after 28-days strength development. The obtained results are given in Table1.

Fig. 6 shows an example test log for samples tested by destructive load. Fig. 7 shows parameters of concrete samples with main and test composition.

To evaluate initial modulus of elasticity there was marked an area with direct proportion on stress-strain dependence diagram (fig.6).
Fig. 6. Destructive load test log: diagram of strength for concrete with main composition, 28-days strength.
Fig. 7. Functional dependence of average concrete strength on concrete samples age

Table 1. The results of fine concrete samples tests

<table>
<thead>
<tr>
<th>Composition index</th>
<th>Mixed cement, kg/m³</th>
<th>Fine sand, «Krasnoe floksy-zapad»</th>
<th>Water, l/m³</th>
<th>ONM, %</th>
<th>SCM, %</th>
<th>Fine sand and 1% SCM agent</th>
<th>Slump of concrete cone (O.K.), sm</th>
<th>Average concrete density, kg/m³</th>
<th>Compression strength, R_u, MPa, 28 days</th>
<th>Prism strength, R_p, MPa, 28 days</th>
<th>Concrete grade, В</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>446</td>
<td>1770</td>
<td>210</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>2330</td>
<td>46.3</td>
<td>31.2</td>
<td>35</td>
</tr>
<tr>
<td>2</td>
<td>446</td>
<td>1770</td>
<td>215</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
<td>2336</td>
<td>65.7</td>
<td>40.3</td>
<td>50</td>
</tr>
<tr>
<td>3</td>
<td>446</td>
<td>1770</td>
<td>215</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
<td>2345</td>
<td>71.4</td>
<td>55.7</td>
<td>55</td>
</tr>
<tr>
<td>4</td>
<td>446</td>
<td>1770</td>
<td>215</td>
<td>5</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>2353</td>
<td>73.7</td>
<td>63.8</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>446</td>
<td>1770</td>
<td>221</td>
<td>7.5</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
<td>2360</td>
<td>82.2</td>
<td>65.7</td>
<td>55</td>
</tr>
<tr>
<td>6</td>
<td>446</td>
<td>1770</td>
<td>229</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>6.8</td>
<td>2380</td>
<td>74.2</td>
<td>58.4</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
<td>446</td>
<td>1770</td>
<td>242</td>
<td>12.5</td>
<td>-</td>
<td>-</td>
<td>6.7</td>
<td>2400</td>
<td>73.1</td>
<td>57.5</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>446</td>
<td>1770</td>
<td>215</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>6.8</td>
<td>2340</td>
<td>53.3</td>
<td>37.8</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>446</td>
<td>1770</td>
<td>215</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>6.8</td>
<td>2343</td>
<td>51.9</td>
<td>37.5</td>
<td>40</td>
</tr>
</tbody>
</table>

ONM – organic-mineral nanodispersed modifying agent
SCM – saponite-containing material
S+SCM – a modifying agent with an optimum ratio of fine sand (96%) and saponite-containing material (4%)

Strength properties of high quality fine concrete can be increased from 46.3 MPa to 82.2 MPa if 7.5% ONM is added.
Thus it has been proved that high quality fine concrete can be obtained if composite mixed cement, ONM from raw materials of the Arkhangelsk region as well as mining wastes, close-packed arrangement of modifying agent and “Relamix” superplasticizer are used.

Samples were examined on Sigma VP SEM. As the result good quality photographs were received and accurate analytical results for fine concrete with close-packed arrangement \( (R_{сж}=82.2 \text{ MPa}) \) and for concrete without ONM \( (R_{сж}=46.3 \text{ MPa}) \) were obtained (fig. 8,9), which proved that particles in concrete structure are practically consolidated and regularly distributed.

In the hydration of cement and ONM there is observed regular distribution of hydration products in a composite (fig. 8 and 9).

3. CONCLUSIONS

The examination of microstructure showed that optimization of structure formation process is possible if ONM based on saponite-containing waste from diamond treatment plant is used. Its combined action includes: 1. plasticizing on the concrete mix preparation stage; 2. fluidal composition control; 3. binding of CaO which is emitted in alite hydration process producing hydrated calcium silicate of second generation on the stage of new growth synthesis.

![Fig. 8. Microphotography of fine concrete without ONM](image-url)
ACKNOWLEDGMENT

1. Studies were conducted on the equipment of Unique stands and installations "Physical Chemistry of Surface of nanodispersed systems"

2. This work was supported by the Russian Federal Target Programme “Research and development on priority directions of scientific-technological complex of Russia in 2014 - 2020 years”

REFERENCES
