Enriched Waste Products of Neon-Ferrous Oxidised Quartzites-A Mineral Cement Mixtures Storage/Accumulator

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Abstract: The possibility of obtaining cement mixtures on the basis of enriched waste products of neon-ferrous oxidised quartzes with high physio-mechanical characteristics has been established and the volume of optimum waste dosage of 30% has been determined. The radiographic analysis has shown that in the hydrated cement mixtures containing a quantity of 5 to 30% of waste with the inherent mineral elements in the hydrated cement, there is beta quartz and dicalcinate ferrite. It has been noted that with the waste increase in the cement mixtures the beta quartz content increases. When the microstructure of the hydrated cement mixtures with various dosages of waste was investigated, it was established that the porosity samples decrease with increase in the waste materials. The researched spectral microprobe analysis of the fine layers of the cement mixtures has shown the existence of calcium ferrite spots. It was determined that the waste particles which have been evenly distributed in the volume of cement mixtures are the centres of crystallisation of new growths that leads to increase cement stone durability.

Key words: Enriched waste of neon-ferrous oxidised quartzites · Cement mixtures · Mineral cement mixtures storage/accumulator · New phase component · Microstructure · Physio-mechanical indicators

INTRODUCTION

The technological procedures of iron ore mining and processing industry are directly and inseparably connected to the utilisation of natural resources and the formation of significant amount of various waste products. For example, as a result of production of iron ore and its processing, millions of tons of solid waste products accumulate annually in Russia. Despite their high ecological danger, the dominant method of their reclamation is the surface land placement with the use of platforms as warehousing in the form of technogenic masses. Technogenic masses are characterised by considerable withdrawal of land surface areas and also the negative impact of substance pollution as a result of wind and water erosion on the environmental components that promotes the formation of considerable environmental pollution.

The reduction of the technogenic loads is actually special for territories of intensive technogenesis with local concentration of mining productions and processing industries, particular in the region of Kursk magnetic anomaly. The prominent mining and metallurgical industry of Russia the Mikhailovsky Mining and Processing Integrated Works (Mikhailovsky iron ore mining and processing industry) located in Kursk region, produces about 20% of domestic iron ore raw materials and whose proportion of all-Russian production of pellets [1] accounts for 25%. The main iron ore raw materials of Mikhailovsky Mining and Processing Integrated Works are neon oxidised ferrous quartzites, the contents which were characterised by iron variability connected with magnet (16–30%). These are complicated ores for processing therefore to get high-quality of low pellet contents suitable for direct metal coating in iron ore mining and processing industry a new technology of
enriching magnetite concentrates has been introduced. This is a reverse ion flotation. The waste products of ferrous quartzites to be enriched are stored in residual dump in industrial waste areas one of the largest in area and volume in Russia. The annual volume of residual dump of ferrous quartzites for enrichment account for more than 12 million m³, the volume of residual dump accumulated from the beginning of operation is more than 300 million m³ [2]. Vast residual dumps of industrial waste products generate dust and the most active dust zones are where the wind speed is more than 8 m/s which affects negatively the environment.

It should be noted that currently some enriched waste products of mining productions have already found their application in the industry of construction materials and are successfully used for acquire fine-grained concrete, concrete for road construction, autoclave products, solidification of laying mixtures [3-8]. However, experience of the use of enriched waste products of neon oxidised ferrous quartzites as raw materials for construction materials production is absent. So this provides considerable interest for practical use.

In view of the above-mentioned, it is essential to use enriched waste products of neon oxidised ferrous quartzites, dumped in waste storage places in the construction materials production, particularly in the cement mixtures.

**Technique:** The granulometric analysis of cement particle distribution and waste conducted in the MicroSizer 201 laser analyzer, analytical researches of microstructure samples of the hydrated cements carried out on a raster electronic microscope of TESCAN MIRA 3 LMU through the x-ray microprobe emission, research of processes and products of hydration of cements carried out on x-ray diffractometre DRON-3; tests of cements carried out in accordance with GOST 310.3-76, 310.4-81.

**Main Part:** Currently during the production of construction materials as mineral storage of various natural materials and using waste products of mining and metallurgical recycle, such as slags, scraps, a dust, residual dumps of wet magnetic of ferrous quartzites, technogenic sand etc. [8] are actively used. The experience of the use of enriched waste products of neon oxidised ferrous quartzites as storage for the cements mixtures is absent. For this reason, the research issue for their application possibility has been engaged in. In the near future, the priority attention will be focused on the cement mixtures and composite viscosity [9, 11] that requires conducting theoretical and experimental researches and the establishment of possible use of waste products in the optimisation of compositions of cement mixtures, studying processes of their structurization and physicomechanical properties in the acquisition of cements.

The waste products of neon oxidised ferrous quartzites of Mikhailovsky mining and processing integrated works, dumped in the residual dumps is characterised by high dispersion level which equals to 250sq.m/kg. The analysis of chemical composition of waste products proves that the content of silicate oxide averagely accounts for over 54%, iron oxide more than 41% and the content of the other oxides which are present have insignificant quantities, which determines the possible use as mineral storage in the formation of the cements mixtures (Table 1).

In order to acquire the cement mixtures, the CEM I Belgorod cement 42,5H used the requirements of GOST 31108-2003 which conforms to “All Cements Construction”. Technical specifications of mineral storage were used in the enriched waste of neon oxidised ferrous quartzites of Mikhailovsky mining and processing integrated works (which further is noted as "waste").

Results dispersal of used waste on standard sieves for inert materials are given in table 2.

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**Table 1: Chemical analysis of waste**

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>FeO</th>
<th>p.p.p.</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>54,52</td>
<td>0,48</td>
<td>41,16</td>
<td>1,14</td>
<td>1,12</td>
<td>0,17</td>
<td>0,83</td>
<td>0,58</td>
<td>3,59</td>
<td>2,32</td>
<td>100,00</td>
</tr>
</tbody>
</table>

**Table 2: Dispersal of waste on standard sieve**

<table>
<thead>
<tr>
<th>No sieve</th>
<th>2,5</th>
<th>1,25</th>
<th>0,63</th>
<th>0,315</th>
<th>0,16</th>
<th>0,08</th>
<th>Less than 0,08</th>
</tr>
</thead>
<tbody>
<tr>
<td>The rest on a sieve</td>
<td>-</td>
<td>0,42</td>
<td>7,62</td>
<td>12,36</td>
<td>26,70</td>
<td>52,10</td>
<td>0,80</td>
</tr>
</tbody>
</table>

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Fig. 1: Weight distribution of cement particles and waste products in the sizes: 1–cement, 2 – waste products

Fig. 2: Dependence of the solidity of compression of samples in various terms of solidification from compositions of the mixed cements

The volume density of the waste products equals to 1460 kg/m³. Research of granulometric structure of the waste products and the used cement was carried out through the laser granulometric method (Fig. 1).

For the purpose of analysing the influence and the establishment of optimum volume of introduced waste into the cement, the waste was used in the mixtures in various dosages from 5 to 50%, respectively, varying the cement amount from 95 to 50%. The joint crushing of raw material mixtures in the porcelain mill laboratory to a specific powder level of 300 of m³/kg was carried out. In order to study the physicomechanical characteristics of the cement mixture level of various structure components of cube samples of 30×30×30 mm in size, 3 samples of each structure for various term tests have been formed. Test samples have been carried out between 7 and 28 days of normal solidification period of durability.

The firmness of indicators at compression of the received cements mixtures (Fig. 2) surpasses indicators of cement firmness. At the introduction of waste products into cements by 5%, the durability increases by 15%, at the introduction of waste products from 10% to 20% the durability increases by 22% and at introduction of 30% of waste products durability reaches 85.03 MP that surpasses the durability of cement by 23%. Further increase in the dosage of waste products in the cement by 40% and 50% the firmness at compression of the received cement mixtures falls drastically and this is connected with the overdose of a mineral storage as a result of the dispersal of the composite structures.

The diffractogramme analysis of the hydrated cement indicates that the cement forms various structural components and crystals structures of hydro-silicate calcium, crystallisation tobermorious hydrosilicate CSH (I) calcium – d, [Å] = 9.8; 4.9; 3.07; 2.85; 2.80; 2.40; 2.00; 1.83; portland Ca(OH)₂ - d, [Å] = 4.93; 3.11; 2.63; 1.93; 1.79; 1.69; SASO3 calcium carbonate - d, [Å] = 3.85; 3.35; 3.04; 2.49; 2.28; 2.09; 1.93; 1.87.

In diffractogramme the hydrated cement mixtures with waste product contents in the quantity of 5 to 30%, along with the listed mineral phases of the hydrated cement, the inherent diffraction maximum have been identified of
Fig. 3: Microphotos of surface chips of samples of the hydrated mixed cements at the period of 28 days

<table>
<thead>
<tr>
<th>Number of ranges</th>
<th>Elements, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>40 weight. %</td>
<td>27,0</td>
</tr>
<tr>
<td>[Å], micron</td>
<td>1,2</td>
</tr>
<tr>
<td>41 weight. %</td>
<td>11,2</td>
</tr>
<tr>
<td>[Å], micron</td>
<td>1,3</td>
</tr>
<tr>
<td>43 weight. %</td>
<td>8,8</td>
</tr>
<tr>
<td>[Å], micron</td>
<td>1,4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number of ranges</th>
<th>Elements, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>49 weight. %</td>
<td>22,4</td>
</tr>
<tr>
<td>[Å], micron</td>
<td>0,7</td>
</tr>
</tbody>
</table>

beta quartz – d, [Å] = 4,25; 3,35; 2,45; 2,28; 2,23; 2,12; 1,975; 1,813; 1,668; 1,656 and double calcium ferrite 2CàΕFe O _2_ 3, [Å] = 7,148; 5,242; 3,898; 3,696; 3,056; 2,799; 2,714; 2,68; 2,609; 2,456; 2,356; 2,189; 2,082; 1,949; 1,903; 1,884; 1,847; 1,746; 1,669.

Comparing the diffractogramme of the cement mixtures to the various waste components, it should be noted that the increase in the waste products leads to the increase contents in the compositions of beta quartz.

In order to confirm the formation and existence in the composite structures of a of dicalcinate ferrite 2Sao·Fe O, a microprobe analysis of the chip surfaces of the hydrated cement mixtures has been carried out (Fig. 3). The quantitative distribution of basic elements in the sample sections of the hydrated cement mixtures is presented in Table 3.

The spectral analysis shows that in the spot ranges no 41, there are 49 the calcium ferrite, proving that at combined grinding of particles of cement and waste there is micro-chemical activation. It is obvious that the processes occurring during firm substance crushing the process connected with destruction of natural or technical minerals the intensity is proportional to size of mechanical impact on the material. For crystals the development of destruction leads to the beginning of an amorforisation of the surface layers, accompanied simultaneously by increase in their chemical activities. During grinding of minerals and as a result of substances destruction there is a formation of non-compensated atomic links on the surface of particles of the dispersions capable of chemical interaction. According to results of various researches [11-13], at combined grinding of components mixtures there is a possibility of solidification reactions between parts of solid substances.

The obtained results of researches prove that mechanical chemical activation of the particles of the cement mixture, resulting in combined grinding of waste products and cement. Researches of microstructures of
chip surfaces of samples of the hydrated cements mixtures under the electronic microscope raster of Tescan MIRA 3 LMU have revealed the distinctions in their microstructures.

Within 28 days the cement stone is presented by the dense gloved mass consisting hydrate formations of the cement in an amorphous and crystal form with initial grain nuclei of a clinker and pores various sizes. From a considerable increase of ×3000 to ×50000 (Fig. 4) the microstructure of cement stone represents layers of separate blocks formed from separate grain scales which in turn, consist of fine spherical switches in the whole material mass indicating various sizes and outlines.

Research of the microstructure of the hydrated cement mixtures during the period 28 days has shown that the created matrix has hardened viscous materials homogeneously on the waste products of the mineral storage compared to the formation of insignificant quality of substrates, porosity, calcium hydrosilicates are formed.

With the increase in the waste products, a more dense structure of the composite is formed with intensive porosity increase as well as the formation of the dense helicoid mass consisted of hydrant formations of cement in amorphous and crystal forms with the nuclei of relic particles of clinker and various porosity sizes have been formed which distinctly is observed in Fig. 5-7.

As a result of crystallisation of new formations into pores, increase of the last is observed and as a result, there is a reduction of stone porosity as a whole. It has been established that the porosity of samples decreases
with increase in the waste products. It is clearly visible that parts of the waste of various degree of dispersion are covered with the hydrant products. Thus, the smallest grains of waste products act as the centres of crystallisation of new formation that leads to increase in cement the stone durability.

**CONCLUSION**

During the combined grinding of component mixtures there are possibilities for the solidification formation reactions between their particles which prove that mechanical chemical activation of particles of cement mixtures have been created.

Research of microstructure of the cement mixtures samples received has shown that with increase in the waste product components, there is a more dense material structure that has been formed with a more obvious increased porosity.

It has been established that the porosity of samples decreases with increase in the waste contents. The particles of the waste products which have been evenly located in volume of mixed cements, act as the centres of new crystallisation formations that leads to increase of durability of cement stone.

As a result of the researches carried-out the possibility of obtaining cement mixtures with high physicomechanical characteristics on the basis of enriched waste neon oxidised ferrous quartzites has been established and the optimum dosage of waste products equal 30% has been defined.
Conclusions: The use of enriched waste products of neon oxidised ferrous quartzites allows obtaining cement mixtures with high physicomechanical indexes. Thus, the expensive power-intensive clinker will allow the use of technogenic raw materials rationally and solve an important environmental problem on recycling of the enriched neon oxidised ferrous quartzites occupying big warehousing areas, harmfully influencing the environment and health of the people.

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REFERENCES