Utilization of final tailings concentration of titano-magnetite ores in Portland cement production

F L Kapustin1,2 and N N Bashkatov1

1Institute of new materials and technologies, Ural Federal University named after the first President of Russia B N Yeltsin, 19, Mira str., Yekaterinburg, 620002, Russia
E-mail: 2f.l.kapustin@urfu.ru

Abstract. When producing iron ore concentrate at Kachkanarsk integrated mining works 2 types of wastes are formed, namely: final tailings of dry magnetic separation (DMS) and final tailings of wet magnetic separation (WMS). Final tailings of wet magnetic separation (WMS) are pulled off or dumped into disposal area up to 45 mln tons annually causing great damages to the environment. These final tailings are finely dispersed materials, their chemical composition is oxides of silicon, aluminium, calcium and iron in general. All this allows to use the wastes under consideration to produce Portland cement clinker replacing clayey and iron components in the raw material mixture completely and limestone partially. The replacement of clay with final tailings of ore enrichment are suitable to manufacture clinker raw material mixture allowing to use two-component raw mix instead of three-component and four-component one thus simplifying the technology of cement production and improving the ecological situation in Sverdlovsk region. The utilization of final tailings for concentration of titano-magnetite ores decreases fuel consumption when burning clinker compared to the traditional compositions. Experimental cement meets all the requirements of the Russian Standard 10178 as to their chemical and physic-mechanical properties and have grade 500.

1. Introduction
Mining industry all over the world is developing approximately 1.5 times quicker than other branches of industry using mineral raw materials. In this case the Russian Federation is not an exception which results in an invariable increase of both mining volumes and raw material enrichment. Therefore, the quantity of technological wastes is increasing, including slimes, final tailings and slags which are to be stored in disposal area. The availability of such dumps including proper activity of integrated mining works and mining beneficitation works (IMW) causes definite damage to environment, namely: air pollution, ground waters and land tenure. There are different suppositions as to utilization of integrated mining works wastes beginning from building materials, and articles manufactured from secondary raw materials for metallurgical industry [1–11].

As the final tailings of ore concentration are fine dense materials firstly, they were supposed to be used as fine aggregates in structural concrete. This was a very successful solution because the concretes produced have higher flowability and place mentability compared to concrete mixtures produced by using quartz sands. Besides the chemical reaction takes place on the border ‘cement-aggregate grain’ to form calcium hydroxilicates with low basility which increases the concretestrength [12]. However, due to this the average strength of concrete density increases in the range of 60 to 250 kg/m³, porosity decreases from 1.87 to 0.83 %, and water adsorption of concrete from 0.78 to 0.19 %.
According to the researches carried out in Ukraine the final tailings from IMW of Krivorozhsky basin containing up to 60–80% of quartz can be used to produce geopolymer binding materials without clinker. The cements in question feature higher durability in sulphatemia, they can be effectively used to produce concretes with up to 50–75MPa [13]. In Novocherkassk polytechnic institute white cement was made delete it on the basis final tailings from Tyrykauzsky IMW which were used both as an aluminosilicate component in the raw materials clinker mixture and as a mineral addition when cement was milled [14].

Kachkanarsky IMW concentration poor titanium-magnetite ores containing up to 16% of iron by using multisteped recycling which results in the formation of large quantity crushed and ground material wastes of two types namely: final tailings of dried magnetic separation (DMS) and final tailings of wet magnetic separation (WMS) [15]. DMS final tailings are the result of crushed rock screening and their grain size is from 10 to 40mm. The particles more than 10mm in size are subjected to wet grinding and further to the first stage of magnetic separation. Then the material passes several stages of grinding and separation. After that WMS final tailings with up to 85% particles from 0.1–1.6mm in size are poured into settling tank. About 45mln tons of similar wastes in the form of slime are produced at IMW annually.

2. Raw materials and methods of investigation

Final tailings of WMS and DMS were used in this research at Kachkanarsky IMW. The mineral composition of DMS final tailings consists of up to 95% pyroxenites, up to 10% plagioclases and not more than 5% gabbro. WMS final tailings consists of up to 80–90% pyroxenes, from 3 to 20% olivines and up to 20% amphiboles. Besides plagioclases, titanomagnetites and ilmenites are also available in their composition as impurities. The chemical composition of final tailings used in experimental research are given in table1.

Table 1. Chemical composition of final tailings from Kachkanarsky IMW.

| Waste type | Oxide content in mass% | others |
|------------|------------------------|--------|
|            | LOI | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO |        |
| DMS        | 0.70 | 47.34 | 12.22 | 11.74 | 18.43 | 6.22 | 3.35 |
| WMS        | 0.68 | 47.51 | 8.15  | 10.30 | 19.99 | 14.06 | 1.47 |

To prepare two-component mixtures limestone from Neviansky and Pashinsky deposit were used (table 2). Four-component raw meal from ZAO Neviansky cementnik and DMS final tailings from OAO Gornozavodsk Cement were used as control contents. To regulate cement setting gypsum anhydride stone from Ergachynsky deposit was used.

Table 2. Chemical composition of raw materials.

| Materials | Oxide content in mass% | Modula |
|-----------|------------------------|--------|
|           | LOI | SiO₂ | Al₂O₃ | Fe₂O₃ | CaO | MgO | SC | n | p |
| Limestone of Neviansky deposit | 41.59 | 2.79 | 1.98 | 0.89 | 52.02 | 0.41 |
| Limestone of Pashinsky deposit | 39.35 | 6.22 | 1.99 | 1.01 | 50.11 | 0.81 |
| Raw meal | 32.86 | 14.18 | 3.84 | 3.25 | 43.73 | 1.21 | 0.91 | 2.00 | 1.18 |
| Raw slime | 34.87 | 13.72 | 3.56 | 2.79 | 42.79 | 1.62 | 0.94 | 2.16 | 1.28 |

Chemical composition of raw materials and mixes were determined by Russian State Standard 5282 ‘Cements and materials of cement production. Methods of chemical analyses’. Calculation of the raw materials content was done according to generally accepted methods for the saturation coefficient $SC = 0.94$, the raw mix was milled to specific gravity of 300m²/kg to produce clinker from laboratory and plant mixes briquettes were prepared which were burnt in the muffle kiln at 1450°C and is other mic availability for 30 minutes. The physic-mechanical properties of the experimental and control
cements were determined in accordance with Russian Standard 310 ‘Cement. Methods of testing’ and the results obtained were compared with Russian Standard 10178 ‘Portland cement and Slag Portland cement. Technical conditions’.

3. Results of experiments and discussion

The chemical composition of WMS final tailings from Kachkanarsk IMW is characterized by stability of the same order kind as for the raw materials used in cement industry. However, their chemical and mineral compositions vary considerably from the IMW final tailings of the south-western part of Russia and Kazakhstan, tested as raw materials to produce cement clinker [14, 16]. Kachkanar final tailings are characterized by high content of CaO, MgO, TiO₂ and SiO₂ and differ from the closest to their content final ore tailings of Sokolovo-Sarbysky deposit. It is found that the raw mixtures produced by using final tailings of Kachkanarsk IMW and limestones from Neviansky deposit are characterized by higher silicate modulus, but Pashinsky raw mixtures are characterized by higher silicate modulus (n) too and lower value of Al₂O₃ modulus (p) (table 3). Besides the latter contain the higher quantity of MgO which requires additional tests of cements as to the uniformity of volume changes when MgO expands.

| The origin of limestone | Components content, mass% | Modula | MgO quantity in clinker, mass% |
|------------------------|---------------------------|--------|-------------------------------|
|                        | limestone | final tailings | SC    | n  | p  |               |
| Neviansky              | 75.05     | 24.95          | 0.94  | 2.15 | 1.19 | 5.62         |
| Pashinsky              | 80.03     | 19.97          | 0.94  | 2.38 | 1.13 | 5.04         |

Taking into account that the raw meal used at ZAO Neviansky cementnik contains 79.36% of limestone, but the raw slime from OAO Gornozavodsk cement consists of 85.57% of carbonate content, the use of the final tailings from Kachkanar IMW allows not only to exclude clayey and iron components, but also to decrease limestone consumption in the two-component mixtures. And availability of CaO in the final tailings bound in silicates will contribute to fuel consumption reduction which is used for the clinker formation processes.

The research of the raw mixtures sintering showed that CaO₅ assimilation in the experimental mix using Neviansky limestone is taking place approximately in the same way as when the burning of the plant free lime (CaO₅) occurs in spite of high silicate modulus and raised quantity of MgO (table 4). The considerable content of CaO₅ in the mix under study after burning at 950°C explains the acceleration of the limestone decarbonization when final tailings concentration is available. The tested raw mix using the limestone from Pashinsky deposit has shown a smaller quantity of CaO₅ during burning at all temperatures compared to the raw slimes from OAO Gornozavodsk cement that acknowledges the improvement of clinker burnability when WMS final tailings are introduced.

The research has shown that Portland cement produced by grinding of experimental clinker with a 5 % addition of gypsum-anhydride stone has physic-mechanical properties close to cements made of plant mixtures (table 5). However, they have a shorter period of setting and higher compressive strength. Experimental cements meet the Russian Standard 10178 requirements, as their properties and for ZAO Neviansky cementnik plant Portland cement has 500 grade as to strength, but for OAO Gornozavodsk Cement Portland cement in question has 400 grade.

| The cement | Mixture type | CaO₅ content, mass % after burning at temperatures°C | 950 | 1150 | 1250 | 1350 | 1400 | 1450 |
|------------|--------------|---------------------------------------------------|-----|------|------|------|------|------|
| Neviansky cementnik | plant | 26.0 | 24.0 | 11.0 | 3.7 | 2.8 | 0.9 |
|                | experimental | 32.0 | 21.0 | 7.0  | 3.0 | 2.5 | 0.8 |
| Gornozavodsk Cement | plant | 28.0 | 26.0 | 18.0 | 2.6 | 2.1 | 0.6 |
|                | experimental | 28.0 | 17.0 | 13.0 | 2.0 | 1.6 | 0.5 |
Table 5. Physic-mechanical properties of Portland cement.

| Cement plant | Charge type | Fineness of grinding, % | Normal thickness of cement paste, mass% | Setting times, hours-minutes | Compression strength after 28 days, MPa |
|--------------|-------------|-------------------------|----------------------------------------|-----------------------------|---------------------------------------|
|              |             | beginning               | ending                                 | bending strength            | compressive strength                  |
| Neviansky    | plant       | 4.8                     | 31.7                                   | 2-10                        | 3-15                                  | 6.9                                    | 47.9                                  |
| cementnik    | experimental| 9.7                     | 28.0                                   | 1-55                        | 2-50                                  | 6.8                                    | 49.6                                  |
| Gornozavodsk | plant       | 5.5                     | 34.6                                   | 1-29                        | 5-47                                  | 6.6                                    | 43.5                                  |
| Cement       | experimental| 8.4                     | 29.3                                   | 1-08                        | 4-30                                  | 6.4                                    | 44.1                                  |

With the aim to confirm the lab research results at Nizhnetagilsky cement plant proof-production tests were carried out to obtain Portland cement by burning two-component mixture consisting of limestone and DMS final tailings the chemical composition of this two-component mixture is given in table 1. The five-component raw mixture containing 78.9% in mass of limestone, 18.3% of clay, 1.6% of sand, 0.7% of blast furnace granulated slag and 0.5% of pyrite cinder was used to burn clinker at the plant in the traditional manner. The experimental slime consisted of 74.0% of limestone and 24.5% of final tailings.

The preparation of the raw material slime was done according to the technology accepted at the plant with chemical composition correction in vertical basins and storage of finished slimes in the horizontal basin 4270m³ of experimental slime have been prepared with characteristics shown in table 6. The recording of the rotary kilns work to burn plant slime were fixed within 24 hours and the experimental slime recording were fixed for 34 hours. The productivity of the rotary kilns for clinker burning was determined by means of slime consumption calculation taking into account its moisture and mass losses when calcining takes place.

Table 6. Composition and properties of raw material slims.

| Raw material slims | Modula SC | n | p | Sieve residue No02, mass% | Humidity, mass% | LOI, mass% |
|--------------------|------------|---|---|---------------------------|-----------------|------------|
| Plant              | 0.91       | 1.81 | 1.00 | 1.4                       | 36.0            | 34.54      |
| Experimental       | 0.91       | 1.99 | 1.04 | 1.3                       | 30.7            | 30.89      |

When carrying out the experiments it was established that the productivity of the raw mills grinding either slime does not differ. Feeding the kilns with experimental slime was supported on the same level and the level was not changed when the common mixture was burnt, but at the same time the productivity concerning clinker burning increased due to less moisture and mass losses on calcining. So, the kiln productivity with Ø3.6 by 127m in size has increased by 30% and the kiln with Ø3.6 by 150m in size increased by 11% and the specific fuel consumption decreased by 21.4% for the former and by 12.5% for the latter one. The difference in the results of the kiln work while burning clinker is apparently takes place due to carry-over of dust. It is quite possible that while introducing the experimental slime into the short kiln the ablation of material increases because of poor work of the chain curtain. The increase of speed and temperature of the kiln gases caused by gaseous fuel consumption growth when burning the mixture and also vacuum or rarefaction in dust chamber could contribute to this too. As to the long kiln these indicators decreased when two-component slime was used. The working parameters of the kiln with Ø3.6 by 150m are given in table 7.
Table 7. The indicators of the kiln with $\varnothing3.6$ by 150 m dimentions to burn clinker.

| Indicators                        | Raw material slims |
|----------------------------------|--------------------|
|                                  | plant              | experimental     |
| t° of off-gases                  | 247                | 269              |
| Vacuum in dust chamber, Pa       | 820                | 795              |
| Fuel consumption, m³/h           | 5465               | 5428             |
| Productivity as to clinker       | 26.8               | 30.4             |
| Specific fuel consumption, m³/tclinker | 203.7            | 178.3            |

Six samples of the experimental and plant clinkers have been chosen during proof-production tests. The samples of the experimental clinker possessed fairly close modula characteristics but differed from the plant clinker with higher quantity of MgO (table 8). Besides in 2 samples of the experimental clinker with $SC=0.93$ the CaO content was 1.46 and 2.39%, but in the rest contents the CaO content did not exceed 1%. Insufficient degree of burning of some experimental clinkers can be caused by high kiln productivity when the raw slime was burnt which consisted of final tailings and shortage of fuel necessary to burn these experimental clinkers. When $SC$ of the experimental clinker is on 0.91, level the better burnability of the clinker is provided and accordingly the place. The plant and experimental clinkers with rationing CaO content have an activity about 50.0 MPa, but the raised quantity of CaO the activity decreases down to 44.1MPa.

Table 8. Modula characteristics and activity of clinkers.

| Clinker   | Modula | MgO quantity in clinker, mass% | Compression strength after 28 days, MPa |
|-----------|--------|--------------------------------|----------------------------------------|
|           | $n$    | $p$                            |                                        |
| Plant     | 0.91   | 1.81                           | 0.95                                   | 1.64 | 50.6 |
| Experimental | 0.91−0.93 | 1.99–2.08                    | 0.98−1.12                            | 3.82–4.32 | 48.8–49.0 |

4. Conclusion
The final tailings of titanium-magnetite ores concentration form in considerable quantity as aluminosilicate component of Portland cement raw mixture. But iron component is to be excluded from it. By using the final tailings in the composition of the two-component mixture allows to simplify the technology of the raw slime preparation to reduce its moisture and fuel consumption when burning clinker and also to raise the productivity of the rotary kiln which is confirmed with the proof-production tests.

References
[1] Makarov D V, Melkonyan R Y, Suvorova O V and Kumarova V A 2016 Perspectives of the use of the industrial wastes to obtain ceramic binding materials Mining info-analytical bulletin 5 pp 254–81
[2] Gafarova N E 2016 Application of shell rock into monolithic building International journal of applied fundamental research 6 pp 630–2
[3] Sverguzova S V, Starostina I V, Fomina E V, Porozhnuk L A, Denisova L V and Shykhiev I Y 2016 Obtaining of decorative plaster mixes by using final tailing to enrich ferric quartzites Herald of Technological University 1923 pp 144–8
[4] Melkonyan R G 2016 Ecological problems of the use of technogenic raw materials in the production of silicate materials Mining info-analytical bulletin S1 pp 499–510
[5] Krasheninnikov O N, Belogurova T P, Latshuk V V and Puk A A 2007 Overburden rocks of Colsky peninsula deposit and getting broken stone on its base Ecology of industrial production 1 pp 64–73
[6] Belogurova T P and Krasheninnikov O N 2004 Utilization of overburden rocks of Hybinsky apatite-nepheline deposits in building Building materials 7 pp 32–5

[7] Absatarov S H, Loktionov S V and Fedorovsky U A 2007 Manufacture of crushed stone from overburden rocks at Lebedinsky IMW Mining journal 7 pp 56–58

[8] Chen Jia, Chen Tiejun and Zhang Yimin 2012 Vanadium tailings for high performance ceramsite synthesis Metal Mine. In Chinese 1427 pp 161–5

[9] Zengxiang Lu and Meifeng Cai 2012 Disposal methods in solid wastes from mines in transition from open-pit to underground mining Procedia Environmental Sciences 16 pp 715–21

[10] Zhou Lianbi 2007 Investigation and practice on mining land rehabilitation and ecological reconstruction in China Nonferrous Metals 259 pp 90–4

[11] Vyborov S G and Silin A A 2012 Perspectives of dump rocks as aluminium raw materials Ukraine coal 5 pp 31–7

[12] Chuprunenko E V and Larionova Z M 1976 Investigation of aggregates interaction with cement Stone from Dnepropetrovsk IMW Scientific works of Belgorod Technological Institute of binding materials 21 pp 24–30

[13] Shevchenko O, Chehov V and Mysin V 1973 Slags lime clinkerless cement Binding materials and constructions 5 pp 20–1

[14] Florova R I 1975 Utilization of wastes from integrated mining works to produce cements Scientific works of Novocherkask polytecnik Institute 312 pp 87–8

[15] Prokofieva V V, Bozhenov P I, Syhachev A N and Eremmin H Ya 1986 Utilization of products to enrich iron in the building on the North (Leningrad: Stroyizdat) [In Russian]

[16] Sylumanov A T 1986 Binding materials made of industrial by-products (Moscow: Stroyizdat) [In Russian]