Conference Paper

Technogenic Mineral Raw Materials for the Production of Refractories and Ceramics

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Abstract

Chemical–mineral and material–genetic classifications of technogenic mineral raw materials including up to 36 polyphase groups of materials that form the basis of secondary resources suitable for the production of refractories and ceramics after additional processing are proposed. It is shown that technogenic materials of the Urals are cheap multifunctional raw materials and can be used in the production of magnesia-silicate ceramics, carbon- and zirconium-containing high-alumina refractories and cements.

Keywords: classification, secondary mineral resources, composition, recycling, refractories, ceramics.

1. The Urgency of the Problem of Technogenic Wastes

The amount of industrial waste has been growing exponentially over the past 100 years. Over 25 billion tons of only solid technological wastes are produced in the world annually. The third part (>7 billion tons) of this amount are produced in Russia. In the Russian Federation at the beginning of 2013 more than 90 billion tons of production wastes of consumption were accumulated. The area occupied by organized waste disposal zones is more than 400 thousand hectares. Geoecological problems of technogenic wastes are connected not only with environmental protection but directly also with the economic development of the regions. Waste generation is also an indicator of the unsustainable use of natural resources while many of them are on the verge of exhaustion. Therefore the rehabilitation of industrial waste is an urgent natural resource, environmental, geoecological and economic task.

On the one hand waste recycling is an instrument of increasing production efficiency and saving resources and on the other is a natural mandatory condition for restoring of equilibrium in the biosphere as it reduces the burden on ecosystems and increases their
sustainability. In Russia there are various Federal and regional programs whose primary purpose is providing basic conditions for environmentally safe sustainable development of country through the creation of normative, scientific and technological base, i.e. the unified state policy in the sphere of waste management at all levels, ensuring of stabilization and further reduction and elimination of environmental pollution as well as access to savings of natural resources due to maximum involving of secondary waste in the economic turnover. One of the promising directions of the innovation process is the complete recycling of industrial waste within the framework of regional economic complexes. It includes the extraction of valuable and deficit materials (pure oxides, noble, non-ferrous, rare, radioactive and other elements) from industrial waste and the creation of structural and functional materials with high performance properties instead of natural traditional materials and metals. The implementation of this strategy will significantly reduce the consumption of primary natural resources by more than 25 % as well as to solve the issues of raw material security of the country.

Chemical–mineral classification of technogenic refractory and ceramic raw materials. The following classification of technogenic raw materials by chemical and mineral composition are offered.

1. Silica (SiO$_2$ ≥ 90 mass. %).
2. Aluminosilicate (Al$_2$O$_3$–SiO$_2$ system, each oxide 10–90 mass. %).
3. Corundum (alumina, Al$_2$O$_3$ > 90 mass. %).
4. Magnesia (MgO ≥ 90 mass. %).
5. Magnesia–spinline (system MgO–R$_2$O$_3$, where R$_2$O$_3$ = Al$_2$O$_3$, Cr$_2$O$_3$, Fe$_2$O$_3$, Ti$_2$O$_3$, Mn$_2$O$_3$, MgO > ∑ R$_2$O$_3$).
6. Magnesia–silicate (system MgO–SiO$_2$, MgO >50 mass. %).
7. Magnesia–lime (MgO–CaO system at the ratio of components (70:30):(30:70).
8. Lime–silicate system (CaO–SiO$_2$, 65–75 mass. % CaO, 25–35 mass. % SiO$_2$).
9. Lime–aluminate (the system CaO–Al$_2$O$_3$, CaO 8–30, Al$_2$O$_3$ 70–92 mass. %).
10. Lime (CaO ≥ 90 mass. %).
11. Zirconium–containing (the system ZrO$_2$–Al$_2$O$_3$–Cr$_2$O$_3$–CaO–MgO–Y$_2$O$_3$–SiO$_2$–C, ZrO$_2$ ≥ 5 mass. %).
12. Silicon carbide containing (system SiC–Al$_2$O$_3$–SiO$_2$–C, SiC ≥10 mass. %).
13. Carbonaceous system (RO–R$_2$O$_3$–RO$_2$–C, where RO = CaO, MgO, VAO; R$_2$O$_3$ – Al$_2$O$_3$, TiO$_2$, Y$_2$O$_3$, Ce$_2$O$_3$; RO$_2$ – ZrO$_2$, SiO$_2$, TiO$_2$).
14. Nitrogen–containing (system Si–Al–Ti–O$_2$–N$_2$, N$_2$ ≥5 mass. %).
15. Special (borides, nitrides, silicides, REE compounds of various chemical classes, oxycarbides, oxynitrides, etc.).

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The proposed variant of chemical–mineral classification includes 15 potential groups of secondary resources of inorganic composition which can be used to some extent in the production of refractories and ceramics as the main component of the charge or functional additives. Certainly this classification cannot be qualified as full one of all other chemical classes which are known and currently used in the manufacture of new refractory compounds (partially attributed to the 15th group): chromite (LaCrO₃), complex oxides (Y₃Al₅O₁₂ – yttrium – aluminum garnet), phosphates (AlPO₄, etc.), titanate (CaTiO₃, SrTiO₃, etc.) as well as a number of metals with high melting point (W, Mo, Cr, etc.), there are more than 150 substances. Each group of secondary raw minerals in turn usually contains several technogenic materials each of which has not only sufficient fire resistance but also a set of other valuable properties. According to the modern multifunctional concept any primary (natural and synthetic) or secondary (technogenic) raw material has a set of physical and chemical properties that allow to use it as a raw material in two or more industries.

For example corundum and silicon carbide are not only wear–resistant refractory materials but also high–quality abrasives and ceramics and silicon carbide is also an excellent high–temperature electric heater. Therefore each mineral (inorganic compound) and especially polyphase materials including technogenic is a multifunctional raw material.

Technogenic raw materials of the Urals for the refractories and ceramics production. After the collapse of the USSR in the refractory and ceramic industry of Russia the problems of providing high–quality magnesium, aluminosilicate, high–alumina, zirconium raw materials as well as graphite and chromite sharply aggravated. Many years of experience of the Eastern Institute of refractories (Ekaterinburg) showed that one of the ways out of the raw material crisis is the use of man–made mineral resources. Over the past 90 years more than 20 billion tons of technogenic formations have accumulated in the Ural region; among of which more than 70 % can be recycled as secondary mineral raw materials. The main suppliers of man–made raw materials are mining and metallurgical industries as well as heat and power engineering using solid fuels. Among the many varieties of secondary mineral raw materials besides a refractory scrap of waste linings of thermal aggregates there are a variety of inorganic materials and substances that can be used in the refractory industry. Due to strict fire resistance requirements (at least 1580 °C) only about 1 % of the total secondary mineral resources can be used as raw materials for the refractories production. Approximately 5 % of technogenic wastes are suitable for coarse and fine ceramics production.

Nowadays domestic and foreign industries use for this purpose more than 150 different primary raw materials including more than 100 substances of inorganic composition.
The material composition of raw materials is represented by compounds of various chemical classes: oxides, silicates, carbides, nitrides, elements, phosphates, hydroxides, to a lesser extent borates, sulfates and others. Depending on the origin (genesis) inorganic varieties of raw materials can be combined into three large groups: natural, synthetic and technogenic.

According to Russian Standard no. 28874 refractories are classified into 17 types by the chemical–mineral composition: siliceous, aluminosilicate, alumina, alumina–lime, magnesia, magnesia–lime, lime, magnesia–spinline, magnesia–silica, chromium, zirconite, oxide, carbon, carbide–silica, oxygen–free, sialons and special of complex composition.

Taking into account this standard classification and the availability of accessible raw materials a material–genetic classification of the main (mass) varieties of mineral raw materials used for the manufacture of refractories have been developed (see Table 1). Among the many varieties of natural and synthetic refractory raw materials 12 chemical classes which include 36 groups of natural minerals and artificial compounds are formed. Natural, synthetic and technogenic mineral (inorganic) raw material is represented by silica, silica–alumina, corundum, magnesia, magnesia–spinline, magnesia–silica, magnesia–lime, carbon–, zirconium–, carbide–silica–containing, alumina–lime and oxide (special) materials.

The general characteristics of the main types of technogenic refractory mineral raw materials are given in Table 2.

The most high–refractory industrial materials are represented mainly by substandard dump magnesite, magnesite waste of talc enrichment, fly dust of burning and melting furnaces (caustic magnesite), the disintegration waste and the cortical area of melted magnesia blocks and magnesia products of chemical industry (chlorides, sulfates and carbonates of magnesium).

Substandard chrome ores of Saranovskoye deposit, nonmetallic products of their enrichment, serpentine tailings of talc and asbestos enrichment, cyclone dust of furnaces for dunite production, forsterite–spindle ferroalloy slags and other materials include magnesium–silicate wastes. The total annual growth of such waste is 20 million tons, the reserves in the dumps are more than 4.5 billion tons including wastes from the extraction and enrichment of asbestos is about 4.0 billion tons.

Technogenic aluminosilicate raw materials are represented by a large group of kaolin and alumina–containing materials, namely high-alumina waste of chemical industry catalysts, overburden and coal enrichment waste (clay + coal), fly ash of thermal power plants and rotary kilns for alumina and fireclay burning, sludge waste of electrocorundum of abrasive production, high–alumina ferroalloy alumothermic slags, aluminum–containing...
TABLE 1: Classification of the main types of refractory raw materials (authors’ work).

| Refractory type, system (composition, mass. %) | Genetic varieties of raw materials |
|-----------------------------------------------|-----------------------------------|
| Siliceous SiO₂                               | Natural                          |
|                                               | Quartzite, marshalite, quartz sand|
|                                               | Synthesized                      |
|                                               | Silica glass SiO₂(lechatelierite), glass fiber SiO₂|
|                                               | Technogenic                      |
|                                               | Microsilica, slurry quartzite    |
| Aluminosilicate                               |                                  |
| Al₂O₃–SiO₂ and corundum Al₂O₃                  | Natural                          |
| ∑(Al₂O₃+SiO₂) > 70                            | Quartzite, marshalite, quartz sand|
|                                               | Synthesized                      |
|                                               | Tubular corundum, melted corundum: white, normal, doped. Melted Mullite. Aluminosilicate fiber|
|                                               | Technogenic                      |
|                                               | Slurry corundum, pyrophyllite, alumina fly dust, catalysts wastes of organic synthesis, secondary refractories, aluminio-thermal slags, aluminosilicate ash|
| Magnesian MgO>85                              | Natural                          |
|                                               | Magnesite, brucite, hydromagnesite, huntite, bishofit|
|                                               | Synthesized                      |
|                                               | Periclase: sintered, melted, magnesium|
| Magnesia–spinel                               |                                  |
| MgO–Cr₂O₃, MgO–Al₂O₃, MgO–FeO–Al₂O₃            | Natural                          |
|                                               | Magnesite, chromite, Chromespinelides: magnnochromite, aluochromite, ferro chromicitte, chromite|
| Magnesia–silica                               | Synthesized                      |
| MgO–SiO₂, ∑(MgO+SiO₂) ≥ 60                    | Periclase–chromite: sintered, melted. Spinel: sintered, melted. Hercinitis. Melted chromium alumina spinelid|
| Magnesia–lime                                 | Technogenic                      |
| MgO–CaO MgO≥CaO                               | Fly dust from kilns (caustic magnesia). Substandard brucite and magnesite|
| Carbonaceous C+RO+RO₂+RO₂, C=4–40             |                                  |
|                                               | Natural                          |
|                                               | Graphite, shungite, anthracite, quartz|
|                                               | Synthesized                      |
|                                               | Artificial graphites, technical carbon. Mixes with MgO, Al₂O₃, spinel ZrO₂, SiO₂ etc.|
|                                               | Technogenic                      |
|                                               | Graphite spell, oven electrodes, secondary refractories, wastes of electrodes graphitizing|
| Zirconium–containing ZrO₂–SiO₂                |                                  |
|                                               | Natural                          |
|                                               | Baddeleyite, zircon|
|                                               | Synthesized                      |
|                                               | Baddeleyite: sintered, melted, bakor|
| Silicon–carbide–containing SIC                |                                  |
|                                               | Natural                          |
|                                               | Quartz, shungite, graphite, coal|
|                                               | Synthesized                      |
|                                               | Silicon carbide: green, black, silicified graphite|
| Alumina–lime, CaO=8–30, Al₂O₃–CaO              |                                  |
|                                               | Natural                          |
|                                               | Limestone, chalk, bauxite|
|                                               | Synthesized                      |
|                                               | Bonit, high alumina cement, alumina cement|
| Oxide special ROR₂O₃, RO₂                      |                                  |
|                                               | Natural                          |
|                                               | Beryl, cassiterite                |
|                                               | Synthesized                      |
|                                               | BeO, Cr₂O₃, Y₂O₃, SnO₂            |
|                                               | Technogenic                      |
|                                               | Secondary refractories and ceramics|

etching solutions of nonferrous metallurgy and synthesis of organic compounds (phosphates, alcohohlates of aluminum, etc.). The total annual growth of these materials in the region is 500-600 million tons.
Substandard and slurry quartzite, silica fume dust from production of crystalline silicon and silicon ferro–alloys (up to 98 % SiO₂) and very large–scale quartzite (substandard) and quartz waste of refractory and mining industries and other materials are included in the group of technogenic high–silica materials.

The most common are refractory calcium–containing materials which are dolomite and limestone piles, self–disintegrated ferroalloy refining slags, bauxite (red) and nepheline sludges, lime–aluminate (aluminate–thermic) ferroalloy slags, fly ashes of furnaces for dolomite and lime burning. Graphite spel of blast furnace production, graphite and silicon carbide wastes of metallurgical, chemical and ceramic industries are of interest from the group of carbon–containing waste for the refractory industry. The most valuable among them are used oxide– lining.

In addition to the traditional use of non–metallic components the use of refractory technogenic materials for the production of refractories, ceramics, cements and other more high–tech and expensive products is technically and economically more effective as cheap raw materials for the construction industry. It can quickly got the economic effect and return on investment especially during the recycling of technogenic wastes in the refractory and ceramic industry.

| Types and sources of secondary raw materials | Material composition (base) | Mineral (phase) composition | Stocks (order) [tons] | Possible use                          |
|---------------------------------------------|-----------------------------|----------------------------|----------------------|--------------------------------------|
| Magnesian                                   |                             |                            |                      | Periclase refractories                |
| Dumping brucite                             | Brucite, magnesite          | MgO(OH), MgCO₃, CaMg(CO₃)₂ | n·10³                |                                      |
| Substandard magnesite                       | Magnesite, dolomite         | MgCO₃, CaMg(CO₃)₂          | n·10⁵                | –                                    |
| Dolomite dumps                              | Dolomite, calcite, clay     | CaMg(CO₃)₂, CaCO₃         | n·10⁷                | –                                    |
| Talc–magnesite waste                        | Magnesite, hematite, chloride| MgCO₃, Fe₂O₃              | n·10⁴                | Filling powders                       |
| Magnesian fly dust                          | Periclase, magnesite        | MgO, MgCO₃                |                      | Magnesia refractories and cements     |
| Chloride and carbonate magnesia wastes      | Bischofite, carnallite, hydromagnetic | MgCl·6H₂O₂, KCl·MgCl₂·6H₂O | n·10⁴ | Periclase refractories and concretes |
| Magnesian secondary refractories            | Periclase, impurities       | MgO, CaMgSiO₄, Ca₃SiO₄, MgFe₂O₄ | | Basic refractories                    |
| Aluminosilicate and alumina-containing      |                             |                             |                      |                                      |
| Types and sources of secondary raw materials | Material composition (base) | Mineral (phase) composition | Stocks (order) [tons] | Possible use |
|---------------------------------------------|----------------------------|-----------------------------|----------------------|-------------|
| Alumothermic slags                           | Calcium aluminates, spinel, corundum | CaO·Al₂O₃, CaO·2Al₂O₃, CaO·6Al₂O₃, MgAl₂O₄ | n·10⁷           | High alumina cement |
| Sludge wastes of electrocorundum             | Corundum, iron α–Al₂O₃, α–(Al,Cr)₂O₃ | n·10³           | High alumina refractories |
| Aluminosilicate ashes of heat power engineering | Aluminosilicate glass Al₂O₃·3SiO₂, Fe₂O₃, Fe₂O₄ | n·10⁷           | Chamotte lightweight refractories |
| Pyrophyllite–containing rocks                | Pyrophyllite, quartz Al₂O₃·4SiO₂·H₂O, SiO₂, Fe₃O₄ | n·10³           | Chamotte |
| Aluminosilicate secondary refractories       | Mullite, glass –                   | –                        | –                        |
| Dust from fireclay kilns for alumina production | Kaolinite, metakaolinite, alumina Al₂O₃·2SiO₂·2H₂O, Al₂O₃·2SiO₂, Al₂O₃ | n·10⁵           | –                        |
| **Magnesia-silicate**                        | **Serpentine, brucite** 3MgO·2SiO₂·2H₂O, Mg(OH)₂ | n·10⁷           | Forsterite refractories and steatite ceramics |
| Tailings of chrome ore enrichment            | **Tailings of asbestos enrichment** – 3MgO·2SiO₂·2H₂O, Mg(OH)₂ (Mg,Fe) (Cr,Fe,Al)₂O₃ | n·10⁹           | Steatite ceramics |
| Substandard chrome ore                       | Chromite, serpentine 3MgO·2SiO₂·2H₂O | n·10⁶           | Chrome–forsterite refractories |
| Tailings of talc enrichment                  | Talc, magnesite, chloride 3MgO·4SiO₂·2H₂O·X | n·10⁴           | Forsterite refractories |
| The olivine concentrates from enrichment     | Olivenite, calcite (Mg,Fe)₂[SiO₄]₂, CaCO₃ | n·10⁴           | –                        |
| Slag of carbon ferrochrome                   | Forsterite, spinel Mg₂[SiO₄]₂, Mg[Al,Cr]₂O₄ | n·10⁵           | Forsterite–spinel refractories |
| **Zirconium-containing**                     | **Baddeleyite Corundum Glass Baddeleyite Corundum mullite** ZrO₂(mon) Al₂O₃, ZrO₂(mon) ZrO₂(cub) | n·10⁵           | Bakor Spinel High alumina refractories and special ceramics |
| Bakor producers from linings of glass kilns  | Products scrap of production in continuous casting machine Scrap of corundum–mullite–zirconium products | –                        | –                        |
| Dusts of silicon alloys                      | Amorphous silica SiO₂ | n·10⁵           | Siliceous masses |
| Quartz wastes of enrichment of kaolin, clay ores etc. | Quartz, clay SiO₂, Al₂O₃·2SiO₂·2H₂O | n·10⁴           | Monolithic lining |
| Types and sources of secondary raw materials | Material composition (base) | Mineral (phase) composition | Stocks (order) [tons] | Possible use |
|---------------------------------------------|-----------------------------|----------------------------|----------------------|--------------|
| Pyrophyllite wastes                         | Quartz, pyrophyllite, pyrite| SiO₂, Al₂O₃·4SiO₂·xH₂O, FeS₂| n·10⁶               | –            |
| Quartz–mica wastes                          | Quartz, muscovite           | SiO₂, K₂(OH)₂·(AlSiO₄)n | n·10⁶               | –            |
| Wastes of molding earths ( sands)           | Quartz, cristobalite, glass, iron | SiO₂, Fe₃Fe₂O₄ | n·10⁴               | –            |
|                                               |                             |                            |                      |              |
| **Lime-containing**                          |                             |                            |                      |              |
| Fly dust from kilns for lime and dolomite firing | Lime, periclase, dolomite | CaO, MgO, CaMg(CO₃)₂ | n·10⁴               | Lime–periclase refractories |
| Dolomite dumps                              | Dolomite, limestone         | CaMg(CO₃)₂, CaCO₃         | n·10⁷               | –            |
| Samoraspadowaiaseysa fefferspolawne shlaki | Calcium orthosilicates     | γ –Ca₂(SiO₄)₃, Mg₃Al₃O₁₀ | n·10⁵               | Lime–silicate refractories |
| Steel–rifying slags                         | The aluminates of calcium   | Al₂O₃·CaO, 12CaO·7Al₂O₃   | n·10⁴               | –            |
| Electro-thermophosphoric slags              | Wollastonite, anortite      | CaSiO₄, CaO·Al₂O₃·2SiO₂   | n·10⁴               | Slag–forming mixes |
| Bauxite and nepheline slurries              | Calcium silicates, calcite, hemmate, aluminates | Ca₃SiO₄, CaCO₃·Fe₂O₃·NaAlO₂ | n·10⁶               | –            |
| Lime and dolomite slurries                  | Slaked lime, brucite        | Ca(OH)₂, MgO, Mg(OH)₂     | n·10⁵               | Lime–periclase refractories |
| **Carbonaceous**                            |                             |                            |                      |              |
| Scrap of oxide–carbon refractories          | Graphite, periclase, corundum, spinel | C, Mg₂Al₂O₅, Mg₃Al₂O₄ | n·10³               | Oxide–carbon refractories |
| Graphite spell                              | Graphite, iron, slag        | C, α–Fe                   | n·10³               | Carbonaceous refractory |
| Wastes of electrodes graphitizing           | Graphite, carborundum       | C, SiC, SiO₂               | n·10⁴               | Carbide–silicon refractories |
| Slurry carborundum                          | Silicon carbide, iron       | SiC, α–Fe                 | n·10³               | –            |
| Silicon carbide kapseli                     | Silicon carbide, glass      | SiC, SiO₂                 | n·10²               | Carbonaceous refractory |
| Electro cinders of electrolysers            | Graphite, carbon             | C_car, C_amor              | n·10²               | –            |

**2. Conclusion**

A variant of chemical–mineral classification of technogenic mineral raw materials including 15 groups of secondary mineral resources suitable for the production of refractories...
and ceramics after additional processing is offered. The secondary mineral resources primarily of the Urals region are considered. The estimated total reserves of these raw materials in the Ural region exceed 140 million tons.

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