KnE Materials Science
TECHNOGEN-2019
IV Congress "Fundamental research and applied developing of recycling and utilization processes of technogenic formations"
Volume 2020

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.

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Published: 31 December 2020

Publishing services provided by Knowledge E

Selection and Peer-review under the responsibility of the TECHNOGEN-2019 Conference Committee.

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 a 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 ($SiO_2 \geq 90$ mass. %).

2. Aluminosilicate (Al_2O_3–SiO_2 system, each oxide 10–90 mass. %).

3. Corundum (alumina, $Al_2O_3 > 90$ mass. %).

4. Magnesia ($MgO \geq 90$ mass. %).

5. Magnesia–spinline (system MgO–R_2O_3, where R_2O_3 – Al_2O_3, Cr_2O_3, Fe_2O_3, Ti_2O_3, Mn_2O_3, $MgO > \sum R_2O_3$).

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_2O_3, CaO 8–30, Al_2O_3 70–92 mass. %).

10. Lime ($CaO \geq 90$ mass. %).

11. Zirconium–containing (the system ZrO_2–Al_2O_3–Cr_2O_3–CaO–MgO–Y_2O_3–SiO_2–C, $ZrO_2 \geq 5$ mass. %).

12. Silicon carbide containing (system SiC–Al_2O_3–SiO_2–C, $SiC \geq 10$ mass. %).

13. Carbonaceous system (RO–R_2O_3–RO_2–C, where RO – CaO, MgO, VAO; R_2O_3 – Al_2O_3, TiO_2, Y_2O_3, Ce_2O_3; RO_2 – ZrO_2, SiO_2, TiO_2).

14. Nitrogen–containing (system Si–Al–Ti–O_2–N_2, $N_2 \geq 5$ mass. %).

15. Special (borides, nitrides, silicides, REE compounds of various chemical classes, oxycarbides, oxynitrides, etc.).

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 ($LaCrO_3$), complex oxides ($Y_3Al_5O_{12}$ – yttrium – aluminum garnet), phosphates ($A1PO_4$, etc.), titanate ($CaTiO_3$, $SrTiO_3$, 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 been 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 industryies use for this purpose more than 150 different primary raw materials including more than 100 substances of inorganic composition.

DOI 10.18502/kms.v6i1.8056

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 in to 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		
	Natural	Synthesized	Technogenic
Siliceous SiO_2	Quartzite, marshalite, quartz, opal, diatomite, quartz sand	Silica glass SiO_2 (lechatelierite), glass fiber SiO_2	Microsilica, slurry quartzite
Aluminosilicate Al_2O_3–SiO_2 and corundum Al_2O_3 $\sum(Al_2O_3+SiO_2) > 70$	Refractory clay, kaolin, topaz, kyanite, andalusite, sillimanite, bauxite, iron–poor, quartz sand	Tubular corundum, melted corundum: white, normal, doped. Melted mullite. Aluminosilicate fiber	Slurry corundum, pyrophyllite, alumina fly dust, catalysts wastes of organic synthesis, secondary refractories, alumino–thermal slags, aluminosilicate ash
Magnesian $MgO \geq 85$	Magnesite, brucite, hydromagnesite, huntite, bishofit	Periclase: sintered, melted, magnesium	Fly dust from kilns (caustic magnesia). Substandard brucite and magnesite
Magnesia–spinel MgO–Cr_2O_3, MgO–Al_2O_3, MgO–FeO–Al_2O_3	Magnesite, chromite. Chromespinelides: magnochromite, alumochromite, ferro chromicotite, chromite	Periclase–chromite: sintered, melted. Spinel: sintered, melted. Hercinitis. Melted chromium alumina spinelid	Chromia–alumina catalysts of petrochemical industry, carbon ferrochromium slags (silicate–spinel)
Magnesia–silica MgO–SiO_2 $\sum(MgO+SiO_2) \geq 60$	Dunite, olivinite, serpentine, talc, talcum magnesite	Dolomite: sintered, melted. Dunite: sintered, melted. Forsterite: sintered, melted	Slags of ferrochrome, wastes of talc flotation and chrome ore enrichment
Magnesia–lime MgO–CaO $MgO \geq CaO$	Dolomite, dolomitized magnesite, limestone, chalk, etc.	Dolomite: sintered, melted	Kiln fly dust, carbide sludge $Ca[OH]_2$
Carbonaceous $C+RO+RO_2+RO_2R_2O_3$ C=4–40	Graphite, shungite, anthracite, quartz	Artificial graphites, technical carbon. Mixes with MgO, Al_2O_3, spinel ZrO_2, SiO_2 etc.	Graphite spell, oven electrodes, secondary refractories, wastes of electrodes graphitizing
Zirconium–containing ZrO_2–SiO_2	Baddeleyite, zircon	Baddeleyite: sintered, melted, bakor	Secondary refractories
Silicon–carbide–containing SiC	Quartz, shungite, graphite, coal	Silicon carbide: green, black, silicified graphite	Wastes of electrodes graphitizing ($SiC+SiO_2$)
Alumina–lime, CaO=8–30, Al_2O_3–CaO	Limestone, chalk, bauxite	Bonit, high alumina cement, alumina cement	Alumothermic toxins
Oxide special RO, R_2O_3, RO_2	Beryl, cassiterite	BeO, Cr_2O_3, Y_2O_3, SnO_2	Secondary refractories and ceramics

etching solutions of nonferrous metallurgy and synthesis of organic compounds (phosphates, alcoholates 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 % SiO_2) 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.

Table 2: The main technogenic resources of refractory and ceramic raw materials (authors' work).

Types and sources of secondary raw materials	Material composition (base)	Mineral (phase) composition	Stocks (order) [tons]	Possible use
		Magnesian		
Dumping brucite	Brucite, magnesite	$MgO(OH)_2$ $MgCO_3$ $CaMg(CO_3)_2$	n·10^3	Periclase refractories
Substandard magnesite	Magnesite, dolomite	$MgCO_3$ $CaMg(CO_3)_2$	n·10^5	–
Dolomite dumps	Dolomite, calcite, clay	$CaMg(CO_3)_2$ $CaCO_3$	n·10^7	–
Talc–magnesite waste	Magnesite, hematite, chlorite	$MgCO_3$, Fe_2O_3	n·10^4	Filling powders
Magnesian fly dust	Periclase, magnesite	MgO, $MgCO_3$		Magnesia refractories and cements
Chloride and carbonate magnesia wastes	Bischofite, carnallite, hydromagnetic	$MgCl·6H_2O$, $KCl·MgCl_2·6H_2O$	n·10^4	Periclase refractories and concretes
Magnesian secondary refractories	Periclase, mpurities	MgO, $CaMgSiO_4$, Ca_2SiO_4, $MgFe_2O_4$		Basic refractories
		Aluminosilicate and alumina-containing		
Wastes of alumina catalysts for organic synthesis	Alumina, chromium oxide, silica	γ–Al_2O_3, SiO_2, Cr_2O_3	n·10^5	High alumina refractories

Types and sources of secondary raw materials	Material composition (base)	Mineral (phase) composition	Stocks (order) [tons]	Possible use
Alumothermic slags	Calcium aluminates, spinel, corundum	$CaO{\cdot}Al_2O_3$, $CaO{\cdot}2Al_2O_3$, $CaO{\cdot}6Al_2O_3$, $MgAl_2O_4$	$n{\cdot}10^3$	High alumina cement
Sludge wastes of electrocorundum	Corundum, iron	$\alpha{-}Al_2O_3$, $\alpha{-}(Al,Cr)_2O_3$	$n{\cdot}10^3$	High alumina refractories
Aluminosilicate ashes of heat power engineering	Aluminosilicate glass	$Al_2O_3{\cdot}3SiO_2$, Fe_2O_3, Fe_3O_4	$n{\cdot}10^7$	Chamotte lightweight refractories
Pyrophyllite–ontaining rocks	Pyrophyllite, quartz	$Al_2O_3{\cdot}4SiO_2{\cdot}H_2O$, SiO_2, FeS_2	$n{\cdot}10^3$	Chamotte
Aluminosilicate secondary refractories	Mullite, glass	–		–
Dust from fireclay kilns and rotary kilns for alumina production	Kaolinite, metakaolinite, alumina	$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$, $Al_2O_3{\cdot}2SiO_2$, Al_2O_3	$n{\cdot}10^5$	–
Magnesia-silicate				
Tailings of chrome ore enrichment	Serpentine, brucite	$3MgO{\cdot}2SiO_2{\cdot}2H_2O$, $Mg(OH)_2$	$n{\cdot}10^7$	Forsterite refractories and steatite ceramics
Tailings of asbestos enrichment	–	$3MgO{\cdot}2SiO_2{\times}2H_2O$, $Mg(OH)_2$ (Mg,Fe) $(Cr,Fe,Al)_2O_4$	$n{\cdot}10^9$	Steatite ceramics
Substandard chrome ore	Chromite, serpentine	$3MgO{\cdot}2SiO_2{\cdot}2H_2O$	$n{\cdot}10^6$	Chrome–forsterite refractories
Tailings of talc enrichment	Talc, magnesite, chloride	$3MgO{\cdot}4SiO_2{\times}2H_2O{\times}M$	$n{\cdot}10^4$	Forsterite refractories
The olivine concentrates from enrichment	Olivenite, calcite	$(Mg,Fe)_2[SiO_4]$, $CaCO_3$	$n{\cdot}10^4$	–
Slag of carbon ferrochrome	Forsterite, spinel	$Mg_2[SiO_4]$, $Mg(Al,Cr)_2O_4$	$n{\cdot}10^5$	Forsterite–spinel refractories
Zirconium-containing				
Bakor producrs from linings of glass kilns Products scrap of production in continuous casting machine Scrap of corundum–mullite–zirconium products	Baddeleyite Corundum Glass Baddeleyite Corundum mullite	ZrO_2(mon) Al_2O_3 ZrO_2(mon) ZrO_2(cub)	$n{\cdot}10^5$	Bakor Spinel High alumina refractories and special ceramics
Siliceous				
Dusts of silicon alloys	Amorphous silica	SiO_2	$n{\cdot}10^5$	Siliceous masses
Quartz wastes of enrichment of kaolin, clay ores etc.	Quartz, clay	SiO_2, $Al_2O_3{\times}2SiO_2.2H_2O$	$n{\cdot}10^4$	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	SiO_2, $Al_2O_3{\cdot}4SiO_2{\times}H_2O$, FeS_2	n·10^6	–
Quartz–mica wastes	Quartz, muscovite	SiO_2, $K_2(OH)_2(AlSi_3O_{10})$	n·10^6	–
Wastes of molding earths (sands)	Quartz, cristobalite, glass, iron	SiO_2, Fe,Fe_3O_4	n·10^4	–
Lime-containing				
Fly dust from kilns for lime and dolomite firing	Lime, periclase, dolomite	CaO, MgO, $CaMg(CO_3)_2$	n·10^4	Lime–periclase refractories
Dolomite dumps	Dolomite, limestone	$CaMg(CO_3)_2$ $CaCO_3$	n·10^7	–
Самораспадающиеся ферросплавные шлаки	Calcium orthosilicates	γ–$Ca_2(SiO_4)$, $Mg(Al,Cr)_2O_4$	n·10^5	Lime–silicate refractories
Steel–rifining slags	The aluminates of calcium	$Al_2O_3{\cdot}CaO$, $12CaO{\cdot}7Al_2O_3$	n·10^4	–
Electro-thermophosphoric slags	Wollastonite, anortite	$CaSiO_3$, $CaO{\cdot}Al_2O_3{\cdot}2SiO_2$	n·10^4	Slag–forming mixes
Bauxite and nepheline slurries	Calcium silicates, calcite, hematite, aluminates	Ca_2SiO_4, $CaCO_3$,Fe_2O_3,$NaAlO_2$	n·10^6	–
Lime and dolomite slurries	Slaked lime, brucite	$Ca(OH)_2$, MgO, $Mg(OH)_2$	n·10^5	Lime–periclase refractories
Carbonaceous				
Scrap of oxide–carbon refractories	Graphite, periclase, corundum, spinel	C, Mg,Al_2O_3, $MgAl_2O_4$	n·10^3	Oxide–carbon refractories
Graphite spell	Graphite, iron, slag	C, α–Fe	n·10^5	Carbonaceous refractory
Wastes of electrodes graphitizing	Graphite, carborundum	C, SiC, SiO_2	n·10^4	Carbide–silicon refractories
Slurry carborundum	Silicon carbide, iron	SiC, α–Fe	n·10^3	–
Silicon carbide kapseli	Silicon carbide, glass	SiC, SiO_2	n·10^2	Carbonaceous refractory
Electrode cinders of electrolyzers	Graphite, carbon	C_{cr}, C_{amor}	n·10^2	–

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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