# CERTAIN ASPECTS IN THE USE OF REFRACTORY MATERIALS AND THEIR WASTE PRODUCTS IN INDUSTRY

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New types of refractory articles and coatings that have been created in recent years and that possess high heat-resistant, physico-chemical, and mechanical properties when in use in corrosive media with high heat demand are presented. Data on the use of refractory scrap as a secondary raw material for the production of refractory materials as well as for the manufacture of runner clay, mortar, and powders for different purposes are presented.

**Keywords:** ecological situation, wastes, refractory materials, use of refractory materials, scrap

In the twenty-first century problems of ecology and environmental protection will be at the forefront on a worldwide scale. Questions related to the ecological cleanliness of technology and and to ensure that production processes of are pollution free will assume considerable importance. Technological requirements and standards are becoming increasingly more stringent every year. Under contemporary conditions, the ecological situation depends on man's economic activity in the creation and development of the technological sphere.

The development of civilization has been accompanied by disturbances in the ecological equilibrium as a result of man's effect on Nature. Pollution of the exosphere by solid, liquid, and gaseous wastes is one of the factors has contributed to this effect. For example, around 7 billion t of all types of wastes are created in Russia every year, only 2 billion t of which are used to any degree. This quantity includes both industrial wastes as well as solid household wastes. According to the 2002 population census, the population of Russia amounted to 145,200,000, thus 48.2 t of waste is generated annually by each person in Russia. By 2003, around 94 billion tons of solid wastes alone (633 tons per person) had accumulated in depositories and dump sites.

Of the total volume of wastes used, around 80% (overburden rock and concentration wastes) are shipped out for stowage of the goaf of mines and quarries, about 2% of the wastes is used as fuel and mineral fertilizer, while only 18%, or 360 million tons, is used as recycled raw material (200 millions tons which in the construction industry) [1 – 3].

Thus, industrial wastes are used as a new type of resource (man-made raw material) together with natural mineral resources, and their incorporation into the production cycle serves to solve two critical problems simultaneously, first the need to locate raw materials and, second, the need to preserve the environment.

An important guiding stimulus to the development of the modern refractory industry has been the need to improve the existing technologies and create new technologies. Increasingly more stringent requirements are being imposed on these technologies as well as on the conditions under which refractory materials are used, for example, temperature, chemical, erosion, mechanical, and other conditions. The demand to increase the service characteristics of refractory materials is indissolubly linked to the need to reduce the production costs of the output and observe ecological standards, possible reuse of production wastes, and recycling of refractory materials. Significant progress has now been achieved in optimization of the physicochemical properties and the chemical composition of refractory materials for specific operating conditions.

The use of new refractory materials and wastes generated by the production of these materials is expanding in metallurgy. For example, refractory substances for the lining of the gutters in the blast furnace industry that use coal-tar pitch, a substance which is classified among substances in the second hazardous class and also contains ecologically harmful substances, has been replaced by ecological clean substances; no components containing ecological harmful materials are used in the preparation of the latter substances. Balls of puddled iron for blast furnaces that use coal tar, a substance that is also classified among second hazardous class of sub-

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stances and that contains up to 1.5% benzpyrene, have been replaced by ecologically clean puddled iron balls in which products of oil refining with benzpyrene content at most 0.02% are used in place of coal tars [4, 5]. Innovative technologies in metallurgy, the chemical industry, and the construction industry are associated to a large degree with the intensification of industrial thermal processes. Of great importance in this connection are materials that function in contact with corrosive melts of metals, slag, and glass. The development and production of corrosion-resistant articles that enable the long-term use of lining in the most challenging parts of furnaces are now under way. Refractory ceramic materials with differing contents of chromium oxide are the most resistant substances under these conditions.

The creation of new refractory and erosion- and corrosion-resistant materials and coatings that are distinguished by high physicochemical, mechanical, and operational characteristics and that remain stable under high temperature conditions and the conditions of corrosive media is one of the most important problems in view of the need to increase the lifetime of the lining of high-temperature plants and the elements of the construction of such plants. New protective and hardening ceramic oxide coatings have shown great promise for practical applications. Such coatings are intended for deposition on the surface of aluminosilicate and thermal insulation materials (brickwork, concrete).

Of particular importance among the refractory materials are fusion-cast refractory materials in view of their exceptionally high corrosion resistance to the action of the mineral melts (glasses, sital, slag, fusing agents, etc.) used in the metallurgical and glass making industries. The range of fusion cast refractory articles from Russian manufacturers is represented by two types of baddeleyite corundum materials, brands Bk and KEL [6].

Refractory materials of corundum and corundum-silicon-carbide compositions are being used increasingly more frequently in recent years in the metallurgical production of ferrous and nonferrous metals. These types of refractory materials are recommended for service that involves contact with melts and slag (for example, in protective inner furnace shells) as well as in the area of the opening of the tap-holes of blast furnace hearths, the slag zones of hot-metal transfer ladles, including mixer-type ladles, and in other metallurgical units [7].

The intensification of processes of glass cooling has led to a significant change in the thermophysical characteristics of glass melts and of the exhaust gases, which has led to a gradual replacement of acidic refractory materials in regenerator brickwork by refractory materials of base composition. New types of products of brands PPLS, PtsSS, and PPLTs have been developed. The introduction of addition and modifier agents has made it possible to manufacture new refractory materials based on high-purity fused periclase (more than 97% MgO) that possess high corrosion resistance, elevated heat conduction, thermal stability, and high-temperature strength. For example, the ultimate compressive strength of the above brands of refractory materials are 79.3, 133.2, and 87.5 MPa and thermal stability (950EC in air) of 15, 15, and 30 thermal cycles, respectively [8].

Rigid constraints are now imposed on power-engineering plants in view of their operating conditions and the strict requirements that are imosed on heat-insulating materials, in particular, to increase their chemical and deformation resistance. New ceramic-vermiculite articles (brand PKL) have been created, characterized by a homogeneous porous structure with number of pores up to 1180 mm3/g and porosity more than 70%, with the pore dimensions from 0.01 to 12 μm.

Around 80% of the refractory materials required by the ferrous metallurgical industry is used in steel smelting production, which is the principal source of the formation of refractory scrap metal. The significant consumption of refractory articles in the steel smelting industry is due to repair of open-hearth furnaces and relining of steel-pouring ladles, which generates the greatest volume of refractory scrap metal. Refractory scrap metal is also formed in plants used for pouring of steel, chiefly in steel-pouring ladles, which are lined principally with aluminosilicate refractory materials. A relatively small quantity of fireclay scrap is formed in the course of repairs of the blast furnaces, pit furnaces, and the furnaces of rolling-mill shops.

The wastes generated by the lining of steel-pouring ladles, which possess an insignificant content of slag inclusions (4% CaO, 2 – 4% Fe, 3.3% FeO) and refractory matter at temperatures of 1600EC and greater are used to manufacture runner clay in blast furnace production. Magnesia scrap is used to manufacture periclase-chromite and chromite-periclase articles and powders at refractory plants. The content of the scrap in the charge of the articles amounts to from 10 to 30% [9].

The scrap of high-alumina (mullite, mullite-silica, mullite-corundum) articles is generated in the repair and dismantling of reheating furnaces and coke ovens and other heating plants in the metallurgical, chemical, and machine-building industries. The scrap is used to produce alumina-rich mortar and runner clay for the solid linings of steel-pouring ladles. The scrap of corundum articles is generated from rubble, defective products, and waste produced by abrasive tools, manufactured from corundum powders. It is widely used following additional preparation in the manufacture of refractory products (ShKKR brand) for tubular recuperative heat exchangers and the production of polishing materials. The scrap from silicon-carbide articles is used as addition agents in charges for the production of silicon-carbide refractory materials and sagger at porcelain factories, and as deoxidizing agents in smelting of pig iron in blast furnaces.

Studies have been performed to determine the possibility of implementing complete or partial replacement of expensive white electro-melted corundum by less expensive types of raw materials (for example, normal corundum, scrap from mullite-corrundum articles, and articles made of corundum concrete following use) in the composition of different types of non-mold refractory materials. Through the application of these materials it becomes possible to expand the raw materials base and reduce the costs associated with the production of non-mold refractory materials while maintaining the indicators of their properties at a sufficiently high level. Fireclay scrap is used to produce powdered fireclay, mortar, the components of concrete mixtures, and their inert additives in the production of refractory articles for mass consumption, such as normal and cupola brick, molded articles for general use, heat-insulating articles, and articles for uphill casting of steel.

Carbonaceous blocks following use in an aluminum electrolyser, fireclay scrap from anode kilns, and the wastes generated by gas cleaning (silica dust in fractions finer than 10 μm with $SiO_2$ content at least 92%) are used to manufacture heat-resistant concrete for use in the lining of aluminum electrolysers.

It should be noted that production technology must observe Public Health Rule No. 1042 (Public Health Regulations for Production Processes, Health Requirements for Production Equipment, SP No. 2527, Public Health Regulations for Ferrous Metallurgy Plants, and DNAOP 1.2.10-1.08, Safety Regulations in Refractories Manufacture).

Fireclay scrap is used in the construction materials industry in the production of porous ceramic (wallboard) and heat-resistant concrete for the lining of the heat-exchange zones of rotating cement kilns and blast cupolas for roasting construction brick.

In the course of use, refractory materials become saturated with impurities from melts and the corrosive gas medium, which places limitations on the use of refractory scrap for the critical elements of linings. The scrap is therefore used by enterprises in the refractories industry as a secondary raw material for the production of refractory materials, as well as by metallurgical enterprises and consuming enterprises in other branches of industry for the production of refractory mortar, powders, and compounds used for different purposes.

A return to the practice in which consuming enterprises together with manufacturers would serve to stimulate studies focused on the analysis of the use of specific types of refractory materials as well as studies of the interdependence of the technical indicators and mechanism underlying the deterioration of refractory materials when in use should be another trend in the modern refractories industry. Establishing what should be the set of standardized indicators for a given standard that are physically critical as regards the operating properties of refractory materials under specific service conditions would be an important step.

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