RESEARCH

UNFIREd LIGHT-WEIGHT FIRECLAY REFRACTORIES PRODUCED BY ACTIVE SYNTHESIS OF HIGH-TEMPERATURE STRUCTURAL ELEMENTS IN A HYDROTHERMAL-FORCE FIELD

V. N. Sokov


The theoretical views underlying the manufacture of unfired light-weight fireclay refractories are set forth. It is hypothesized that fireclay mixes should include a chemically active ingredient to act as a catalyst and an electrolyte and to promote the active synthesis of high-temperature structural elements in the course of molding in a heat-and-force field, short-term drying, and service.

The need today. Now that Russia is radically changing its energy policy—the energy-intensive principle of economic development is giving way to strict accounting for and control of fuel and energy consumption, the problem of energy-saving comes to the fore. With reference to high-temperature thermal insulation, an important task is to develop a technology for the manufacture of refractories that need not be fired. With the market being in a state of flux, the elimination of high-temperature calcining and extended drying will go a long way toward cutting down the fuel and energy costs of refractory manufacture.

The object of study was light-weight fireclay refractories, most universal and widely used in furnace construction and elsewhere. According to an analysis, their manufacture is labor-consuming, energy-intensive, and far from optimal in most cases. To a considerable extent, this is because these products are still predominantly fabricated by the inherently complicated foam process, whereas little has been done to adopt the simpler and more promising burn-out additive method, the reason being the prevailing view that the refractories thus manufactured cannot have a porosity of higher than 65%. The traditional theoretical view on the drying of high-porosity mixes as a process whereby the temper water is removed solely by evaporation has led to the use of extended drying (for 2 - 5 days).

Under the guidance of this author, a different approach has been developed to the problem. Lying at its basis is the hypothesis that, instead of evaporation, the excess moisture should be expelled by applying heat and pressure to a movable system enclosed in a rigid perforated mold [1 - 3]. The rationale of the method is this. An amount of prefoamed polystyrene is charged into a paddle agitator and tempered with water, the other dry ingredients are added, and the charge is agitated. The blend thus obtained, with a moisture content of 40 - 50%, is poured to fill fully a rigid perforated mold, and the latter is covered with a lid and heated. At above 80°C, the polystyrene begins to foam. Due to the pressure thus developed (0.2 - 0.3 MPa), 70 to 80% of the moisture is expelled from the mold, and the system is compacted in the same proportion, leaving ware of the desired shape. At the end of foaming, the mold is opened, the green ware is sent on the mold plate to drying and then firing. Thus, taking advantage of the pressure built up by the polystyrene, a new and extremely simple fabrication technique has been obtained, which combines the advantages of the burn-out additive and mix-foaming processes. In fact, the polystyrene foams, the mix is compacted, and the green ware is dried and acquires porosity in a single operation.

Polystyrene grains are spherical in shape and range widely in size. According to the theory of close packing, polystyrene grains can be packed to a density of 82 - 87% and the subsequent burn-out can produce any desired porosity in the material. By varying the polystyrene grain size, it is possible to control the pore size easily and very accurately and to impart to the material the desired properties. The fact that the grains and, hence, the pores have a regular spherical shape serves to reduce the stress concentration in the inter-
pore partitions when a load is applied to the material, thus improving its mechanical properties.

Polystyrene has a very low water absorption (about 1% in 12 h) and complete freedom from swelling. It does not react chemically with ceramic powders and does not dissolve in water. The ash content of polystyrene is virtually zero. At 400°C and higher, it decomposes to form monomer (styrene) vapor, which reacts with oxygen or flue gases to form carbon dioxide and water. The burning rate of polystyrene is very high, being 40 kg/min on the average. Since the average density of foamed polystyrene grains is very low (30-60 kg/m³), whereas their specific surface is rather high (about 800 cm²/g), it may be expected that burn-out of polystyrene will not pose any particular difficulties. Moistened polystyrene grains readily mix with finely ground ceramic powders to form homogeneous blends.

At present, polystyrene is widely used as a heat-insulating material in civil engineering and transportation. Unfortunately, fine polystyrene beads (less than 0.5 mm across) have a relatively low swelling factor and would increase the average density of polystyrene articles. Therefore, they are discarded, constituting wastes from the manufacture of porous plastics. Since commercial polystyrene carries 12 to 20% grains smaller than 0.5 mm across, there is a large supply of this waste for use in the manufacture of porous refractories.

However, the self-compaction process alone is not enough to produce unfired light-weight fireclay refractories. The fireclay mix must include a chemically active ingredient to act as a catalyst and an electrolyte and to promote the active synthesis of high-temperature structural elements in the course of drying and service. This bonding composition should meet the following basic requirements: it should impart to the green ware sufficient strength before it is subjected to high (working) temperatures, that is, after drying, and should raise still more the strength of the light-weight refractories after the first firing without appreciable shrinkage due to formation of structural elements possessing high refractoriness. It is thus seen that the development of a rational technology for fabrication of unfired light-weight fireclay refractories possessing high thermomechanical properties is an urgent problem of today.

Theoretical foundations for fabrication of unfired light-weight fireclay refractories. In contrast to conventional fired light-weight refractories, unfired polystyrene-based products have to acquire their properties not only at the time of self-compaction and subsequent short-term afterdrying but also during the first and subsequent heating cycles in service. Because of this, the binder plays an important role in imparting to the unfired refractories the necessary structure and properties.

Under existing classifications [4-7], binders may be classed into three broad types according to whether their hardening involves hydration, coagulation, or polycondensation (polymerization). Those of the first are binders on the basis of Portland, alumina, high-alumina, and periclase cements. Those of the second are clay-based binders. Those of the third are based on soluble glass, lump silicates, colloidal silica, and phosphates. Refractories using binders from the first group harden at normal temperatures in a moist environment, when steamed or autoclaved. Those of the second and third do so upon drying or firing.

After manufacture (that is, with the grade strength acquired), light-weight hydraulic-binder refractories have high strength, but they lose a good proportion of their strength after the first heating in the temperature range of 300–500°C; the compressive strength, for example, falls to 40–60% of the original value. In Portland cement-bonded refractories, this is traceable to dehydration of calcium hydroxides and hydroaluminates, sulfate-containing phases, and Ca(OH)₂ and the decarbonization of CaCO₃. In alumina and high-alumina refractories, the cause is dehydration of various calcium hydroaluminates in the temperature range of 350–500°C. For all binders in this group, there is an unfavorable temperature range (600–800°C) where the products tend to segregate into layers and to fail completely.

Refractories based on coagulation-hardening binders can be manufactured using just fibrous materials. Unfortunately, the fibrous ingredient is a scarce raw material, and the ware has to be fired [8]. Products based on polycondensation-hardening binders include mainly two groups: ones using soluble glass or silicate lumps and ones using phosphate bonding compositions. Work on phosphate-bonded refractories has been under way at the Research Institute for Reinforced Concrete (NIIZhB) under Professor K. Nekrasov [9-11], at the Central Ceramics Research Institute (TsNIISK) under Professor V. Kopeikin [12-14], and elsewhere. With phosphate binders, the service temperature for the refractories is as much as 100°C higher than for their counterparts fabricated using other binders.

Characteristically, phosphate-bonded refractories have a high residual strength after the first heating, which is 80–100% of the original [15, 16]. Some authors [6] have reported attempts to produce high-performance refractories using an aluminosilicate aggregate and orthophosphoric acid, but they proved unsuccessful because the binder tended to lose strength—at a temperature higher than 300°C silicophosphates are unstable and convert via a liquid phase to aluminophosphates.

Special promise with regard to the manufacture of high-temperature concretes suitable for lining various high-temperature units is held by binders in the form of fine-grained blends of lump silicate and refractory aggregates. With them, high-temperature compounds are synthesized in the ware itself as the mix is tempered with water, molded, dried at 80–200°C, and heated in a furnace, kiln, or other heating equipment. In this case, polycondensation occurs near the surface of fireclay particles due to dissolution of sodium silicate particles and formation of high-viscosity, high-sodium-alkali soluble glass. An advantage of this process is that polystylicates can be produced when the high-concentration alkali comes in contact with the aggregate particles. When, however, this process is used to make high-temperature concretes,