USE OF PHOSPHATES TO REDUCE SLAG PENETRATION IN CR2O3-BASED REFRACTORIES

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

The US Government has rights in this invention due to the employer/employee relationship between the Government and the inventors.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to high-chromium refractories and in particular high-chromium refractories for use in slagging gasifiers and coal combustion power plants. More particularly, this invention relates to high-chromium refractories having improved resistance to penetration by molten coal slag for the extension of refractory service life.

2. Description of Related Art

Integrated Gasification Combined Cycle (IGCC) power production is one of the cleanest and most efficient means of producing chemicals compounds and electricity from coal, petroleum residues, and other low- or negative-value feedstocks. Gasification of the carbon-containing feed results in the formation of synthesis gas, typically called syngas (primarily a combination of carbon monoxide and hydrogen), and which can be used to generate electricity using a combination of gas and steam turbine technology. In addition to producing power with thermal efficiencies that are significantly higher than those obtained in conventional coal power plants, IGCC systems are also more environmentally friendly, with air emissions that exceed U.S. Clean Air Act standards.

The gasifier at the heart of the IGCC system acts as a containment vessel for the reaction of carbon-containing materials with oxygen and water to form a syngas. Gasifiers may be either dry ash or slagging systems, with the most severe environments occur in the slagging gasifiers, where operating temperatures can range from 1300° to 1600° C., depending upon the melting point and viscosity of the residual ash. In addition to high temperature, the refractory lining inside a slagging gasifier must also be able to withstand a number of other challenges, including: large and sometimes sudden variations in temperature; alternating oxidizing and reducing environments; corrosive slags and gases; erosion by residual particulate; and high pressures. Compounding these challenges is the current push within the industry for fuel flexibility, which results in slag chemistries and operating conditions that can vary widely as the feedstock for the gasifier is supplemented with alternative sources of carbon, such as petroleum coke and biomass. Several studies have indicated that because of the severity of these challenges, high-chrome bricks are the only commercial materials that are viable for this application.

Refractory liner materials high in Cr_2O_3 are used in slagging coal gasifiers to protect the steel shell from attack by heat, ash, and sulfur-containing compounds that are the principal by-products of the reaction. The gasifier operates at a temperature up to about 1600° C. (2900° F.) and pressures of 400 PSI or greater. The melting point of coal slag is variable, depending upon the composition of the starting feedstock, but is typically about 1200° C. (2200° F.). Slag chemistry shows that under such operational conditions, coal slags are under saturated with respect to many oxide components. As a result, coal slags will aggressively attack and dissolve virtually all refractory materials. Cr_2O_3-based refractories are used by the industry since they exhibit the best available slag resistance. Currently, the best chromium-based refractories provide less than two years service life in a gasifier. This is a shorter service life than necessary for economic operation of the IGCC. Every day of downtime that occurs as a result of refractory failure will cost a gasifier company millions of dollars in lost revenue. In order to provide high-chromium refractories with increased service life, it is desirable to provide a high-chromium refractory with improved resistance to coal slag penetration.

BRIEF SUMMARY OF THE INVENTION

An object of this invention is to provide a high chromium refractory that resists the penetration of coal slag into the cured refractory during use. The service life of the refractory can be extended by reducing the depth of slag penetration.

Another object of this invention is to provide a high chromium refractory that slows the penetration of coal slag into the cured refractory.

These and other objectives of the invention, which will become apparent from the following description, have been achieved by a novel refractory material for the reduction of coal slag penetration comprising an aggregate and a matrix (binder) comprising a mixture of chromium oxide and phosphates. Typically, aluminum oxides are added to the matrix to improve the mechanical properties of the matrix. In addition, the matrix may comprise a mixture of phosphorous compounds as provided by phosphates, phosphoric acid, phosphorous oxides and other inorganic oxides, such as zirconium oxide, as well as inorganic and organic binders. The organic binders are used during the "green" or pre-fired stage to improve the adhesive strength of the matrix. This invention is applicable to high-chromium refractory materials with at least sixty weight percent of chromium oxide and preferably at least seventy weight percent chromium oxide. Preferably the phosphates for use with this invention are inorganic oxides. The phosphates may be formed by the reaction of phosphoric acid and/or P_2O_5 with inorganic oxides. The possible inorganic oxides include, but are not limited to, Al_2O_3, Cr_2O_3, ZrO_2 and combinations thereof. Ideally, the matrix mixture should contain from about one weight percent to about ten weight percent phosphates. The refractory material may be made from "green" (unfired) chromium oxide or chromium oxide that has been sintered or fused. Preferably, the binder should contain less than about 0.1 weight percent of a halogen and more preferably the phosphorous compounds, such as phosphoric acid, should contain less that 0.1 weight percent of a halogen, such as fluorine, chlorine, bromine, and iodine.

The invention also relates to a process for manufacturing a refractory material for reduction of coal slag penetration comprising providing an aggregate; blending the aggregate with a matrix (binder) comprising a mixture of chromium oxide and phosphates, to form a green refractory; forming the green refractory into a shape, and curing and firing the refractory. Typically, aluminum oxides are added to the matrix to improve the mechanical properties of the matrix. The phosphates may be formed by the reaction of phosphoric acid or P_2O_5 with inorganic oxides and hydroxides. The matrix may also include ZrO_2 and Al_2O_3 as well as inorganic and organic binders. This invention is applicable to high-chromium refractory material with at least sixty weight percent of chromium oxide and preferably at least seventy weight percent chromium oxide. Preferably the phosphates, phosphoric acids and other phosphorous compounds for use