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METHOD OF PREPARING FIBERS FROM SOLIDIFIED PHOSPHORUS-FURNACE SLAG

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This invention relates to the manufacture of fibers from phosphorus-furnace slag, and particularly to the production of such fibers by a process which provides a high quality, stable product.

Ores rich in phosphates and other useful minerals are found in large quantities in the United States, particularly in the Western United States and Florida. Furnace grade ores typically contain 22 to 26% P_2O_5, 29 to 43% CaO, 10 to 30% SiO_2 and the balance minor constituents such as about 3 to 10% Al_2O_3, 0.5 to 2% Fe_2O_3 and moisture, and are one of the world's main sources of phosphorus.

Phosphorus is produced from these ores most commonly by smelting the ores in an electric furnace together with coke and additional SiO_2, normally introduced as quartz sand which is about 95% SiO_2. The ore, SiO_2 source and coke are used in a weight ratio typically of about 10.5 to 0.7 to 1.3 parts by weight, respectively, with the amount of ore being expressed on the basis of its P_2O_5 content. All percentages expressed herein are weight percentages.

This process has been proved over many years of commercial production. However, it has one vital drawback. While it provides for recovery of the phosphorus from the ore, both as elemental phosphorus and as a mixture of iron and phosphorus known as ferrophos which is useful in manufacturing steel, a large part of the other elements present in the ore and silica feed, which represent the bulk of the raw materials going into the process, are discharged as a slag byproduct having no real utility other than as a bulk ballast material, for example as road ballast and the like. This slag typically has a composition of 40 to 50% SiO_2, 45 to 50% CaO, 0.1 to 3% P_2O_5, 3 to 10% Al_2O_3, 0.1 to 1% Fe_2O_3 and 1 to 3% F, and represents on the order of 75% of the coke-free furnace burden.

It has long been desired to find a practical commercial outlet for such slags, which makes economic use of the minerals in the slag, and one direction in which workers have searched is in the field of mineral fibers. Other slags, notably steel furnace slags with quite different compositions, typically of 35 to 42% SiO_2, 35 to 42% CaO, 12 to 15% MgO, 2 to 5% Al_2O_3, 0.1 to 0.3% Fe_2O_3 and 0.1 to 0.3% F, have been melted and converted to mineral fibers useful in fire resistant products such as building insulation, ceiling tiles and the like.

However, despite the plentiful and low-cost supply of phosphorus furnace slag, attempts to produce fibers composed of these slags have not been encouraging, because often such fibers produced by the commercial method of spinning molten slag from a spinner wheel to form streams of molten slag and blowing these streams to form fibers, exhibit a tendency to be weak and even to degrade physically on aging.

It is an object of our invention to provide a method by which phosphorus furnace slag can be converted to useful and high quality fibers.

We have now found that fibers which are of excellent quality and are resistant to physical degradation on aging can be produced from solidified phosphorus furnace slag by heating the slag to a conditioning temperature at least 100° C. above the temperature at which the slag is melted and has a satisfactory spinning viscosity of about 15 poises, holding the molten slag at its conditioning temperature for a conditioning time of at least 10 minutes to provide a conditioned slag, feeding the conditioned slag to a spinner wheel which throws streams of the molten, conditioned slag outwardly therefrom, the slag being at a conditioning temperature while on the spinner, and intercepting the streams of slag by a high velocity flow of a gaseous fluid to attenuate the stream into fibers.

Quite surprisingly, the fibers produced by our process are of high initial quality and do not degrade physically upon aging, whereas fibers produced by the same slags by the same process but in which the temperature of the slag is not raised to the conditioning temperature for the conditioning time, frequently lose their physical properties on aging. Furthermore, our new process makes a fiber having an unusually low content of shot, or pellets, and one which makes very good insulation boards and the like.

The conditioning temperature at which we heat our slag is at least 100° C. above that which provides a spinning viscosity of 15 poises for the particular slag. This viscosity of 15 poises is a viscosity at which slags, for example phosphorus furnace or steel slags, as well as others, can be spun readily from a spinner wheel to provide streams of molten slag which can be attenuated into fibers by a high velocity flow of gaseous fluid such as steam or air issuing as jets. There is no real limit on the upper temperature which can be used, other than a practical one taking into consideration the temperature at which components will volatilize from the slag, equipment corrosion and the need to cool the slag to a suitable temperature (at or above its minimum conditioning temperature) for spinning in the fiber-forming process. Temperatures, measured while the slag is on the spinner, at which the herein phosphorus-furnace slags may be spun and blown into high quality fibers normally range from about 1240° to 1450° C., temperatures at which the viscosity of the slag is about 0.5 to 7 poises or less. This viscosity of 0.5 to 7 poises is substantially below the about 15 poises at which fibers may be spun and obviously for economic reasons would not be resorted to in the absence of an understanding of the importance of our conditioning temperature.

The time for which the slag is held at its conditioning temperature, the so-called conditioning time, is dependent on the conditioning temperature employed; the higher the conditioning temperature, the lower the conditioning time, and vice versa. However, as a practical matter the conditioning time should not be lower than about 10 minutes, although it may be higher, as much as 120 minutes, or even more if a temperature near the minimum conditioning temperature is employed. There is no maximum conditioning time, it being necessary only to heat the slag at the proper temperature for the minimum time required. Obviously these conditions apply only to formation of fibers by a process commencing with a spinner wheel from which streams of slag are thrown outwardly, and proceeding through attenuation of these streams of slag with a high velocity flow of air or steam. Other manners of forming fibers do not operate under the same conditions as apply in the case of spinner wheel techniques.

The reason for the improved characteristics of fibers produced from our conditioned phosphorus furnace slags as compared with fibers produced from the same slags which have not been conditioned by our process is not entirely clear, although it is very real. It is possible to theorize, however, that the particular chemical makeup of the phosphorus furnace slags is such as to cause them to have a unique characteristic of forming crystal nuclei upon being solidified. Likely these nuclei or possibly other solids harmful to fiber-forming are not destroyed when solid slag is melted to a temperature at which it has a viscosity of about 15 poises at which it can be spun and blown into fibers.

This would explain our discovery that heating the slag to a temperature substantially, at least about 100° C., above the temperature at which the spinning viscosity of about 15 poises is reached, removes the tendency of the fibers produced from the slag to have poor physical properties and/or to degrade physically on aging. That is, if crystal nuclei or other solids are present in the molten slag and are not destroyed (as they are by our heating of the fibers to a proper conditioning temperature for a proper conditioning time) these nuclei may well tend to cause the property-destroying crystallization or other nonuniformity within the fibers.

This theory is advanced only as a possible explanation of why our conditioning process is effective, and its correctness is not necessary to the validity of our findings of fact or to our appended claims which derive therefrom.

The phosphate ore used normally is mined in the Western United States and in Florida. It normally contains 22 to 26% P_2O_5, 29 to 43% CaO, 10 to 30% SiO_2 and the balance minor constituents such as about 3 to 10% Al_2O_3, 0.5 to 2% Fe_2O_3 and moisture and are one of the world's main sources of phosphorus. This ore is best fed to an electric furnace as pellets having an average size of about ¼ to 3 inches in diameter. Such pellets are normally calcined at 2250 to 2500° F. in a rotary kiln, a grate calciner or the like before being used in the phosphorus-making step.

The SiO_2 ordinarily is obtained as quartz sand, and is used to provide a weight ratio of SiO_2 to CaO in the feed of 0.75 to 1.05 parts of SiO_2:1 part of CaO. This ingredient is best fed in the form of pebbles, on the order of at least ¼ inch in diameter.

The coke also normally is fed as pieces having a size of at least 80% greater than ¼ inch in diameter. It is not essential that coke itself be used, it being possible to employ other reducing carbonaceous fuels such as coal and the like, and when coke is referred to herein, it is intended that these equivalent materials be included. The coke is used in the amount of 100 to 110% based on the weight of the P_2O_5 and the transition metals calculated as oxides. It serves both as an electrical conductor between the electrodes of the furnace which typically operates at about 1350° to 1600° C., and as a reductant for the P_2O_5. The overall reaction yields elemental phosphorus and carbon monoxide which are removed as gases.

The reaction in the furnace leaves behind both a molten composition known as ferrophos, composed of 55 to 60% Fe, 20 to 28% P, 4 to 5% V and 4% Cr, and a slag which is largely $CaSiO_3$. The slag typically is composed of 40 to 50% SiO_2, 45 to 50% CaO, 0.1 to 3% P_2O_5, 3 to 10% Al_2O_3, 0.1 to 1% Fe_2O_3 and 1 to 3% F. This slag is tapped from an intermediate level of the phosphorus furnace, and is passed into containers where it is cooled to a solid and broken into pieces of a size which permits handling.

Formation of fibers from such phosphorus slag is carried out by conventional spinner wheel processes, for example by the methods taught in U.S. Patents 2,328,714, 2,646,593, 2,793,395 and the like. In a typical fiber production process, the molten slag is fed either onto the face or onto the periphery of a dish-shaped, cupped or grooved wheel which spins at a speed of on the order of 700 to 2500 r.p.m. Wheels used normally have a diameter of about 5 to 20 inches, although wheels of other diameters may be used. The molten slag is spun off the wheel and the streams, or possibly films, all referred to herein as streams, of molten slag thus discharged are blown into fibers by a high velocity gaseous fluid, such as steam or air in the form of jets, to attenuate the slag into fibers. The fibers are collected by any of a variety of means,

for example on a moving belt, in a hopper in an aqueous or other liquid dispersion.

The following examples are presented by way of illustration of this invention only, and are not to be considered limiting thereof in any way. Temperatures given in these examples and throughout the application and appended claims are those determined with an optical pyrometer. They are about 60° C. lower than the internal temperature of the molten slag when measured with expendable thermocouples inserted into the slag.

Example 1.—Production of phosphorus furnace slag

Thirty-five tons per hour of western phosphate ore composed of 24% P_2O_5, 35% CaO, 26% SiO_2, 1% Fe_2O_3, 4% Al_2O_3 and 10% moisture, 2.7 tons per hour of coke and 1.4 tons per hour of quartz sand were fed into a three-phase, three electrode submerged ore furnace operated at 50 megawatts.

Elemental phosphorus vapor, and carbon monoxide by-product, were removed overhead from the furnace, and molten ferrophos, heavier than the slag, was removed from the very bottom of the furnace.

A slag product composed of 40.5% SiO_2, 47.7% CaO, 6.7% Al_2O_3, 0.3% Fe_2O_3, 2.4% P_2O_5 and 2.4% F was tapped from the furnace as a melt, and collected in a pit where it was permitted to solidify and broken into pieces approximately ½ to 2½ inches in diameter.

Example 2.—Production of fibers by the process of our invention

The slag produced as described in Example 1, was heated to a temperature of 1350° C. (210° C. above the temperature at which it had a spinning viscosity of 15 poises) and held at that temperature for 30 minutes. It was then fed onto the side face of a cup-shaped spinning wheel 14 inches in diameter and spinning about a horizontal axis at 1400 r.p.m. and held at a temperature of at least 1300° C. while on the wheel. The slag was thrown peripherally as streams of the slag melt into the path of a series of steam jets blown perpendicular to the slag streams and in the direction of the face of the wheel. This blowing with steam caused the slag streams to change their direction and be blown into a collection chamber as fibers formed by the blowing steam. The fibers were collected as a loose mat on a moving belt and removed from the collection chamber.

The fibers so produced were granulated, that is converted to small clumps of fibers, screened to remove loose shot and bagged. The fibers demonstrated excellent properties. Thus they had a slurry stability of 298 cc. After aging for three months the fibers were again tested and found to have essentially the same slurry stability, namely 295 cc., as when they were produced. Slurry stability is determined by agitating a 25 gram sample of wool in 500 ml. of water (70° F.±5°) for 20 seconds in a 15,000 r.p.m. Waring Blendor equipped with case hardened blades. The slurry is quickly transferred to a 1000 ml. graduated cylinder and the height in ml. of the settling wool column is recorded after 5 minutes. A wool column 250 ml. or greater is indicative of a material that should run well in wet-processing, e.g., board manufacture. Fibers having a slurry stability of about 225 ml. or more are adequate for insulation and other dry fiber uses.

Example A.—Comparative example

In this example, the process of Example 2 was followed with the exception that the solid slag employed in Example 2 was on the wheel at about 1200° C., a normal spinning temperature at which its viscosity was below 15 poises, but not heated above our conditioning temperature of 1240° C. on the wheel prior to spinning. In this case the fibers produced had a slurry stability of only 205 cc.

Pursuant to the requirements of the patent statutes, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that within the scope of the appended claims the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A method of producing fibers resistant to crystallization and physical degradation on aging from a solidified furnace slag, comprising heating said slag to a conditioning temperature at least 100° C. above the temperature at which the slag is melted and has a spinning viscosity of 15 poises, holding said molten slag at said conditioning temperature for a conditioning time of at least 10 minutes to produce a conditioned slag, feeding said conditioned slag to a spinner wheel which throws streams of said molten, conditioned slag outwardly, said slag being at a conditioning temperature on said spinner wheel, and intercepting said streams by a high velocity flow of a gaseous fluid to attenuate the streams into fibers.

2. Method of claim **1** in which the molten conditioned slag on the spinner wheel has a viscosity of no more than 7 poises.

References Cited

UNITED STATES PATENTS

2,793,395	5/1957	Richardson	65—14
3,097,085	7/1963	Wallsten	264—8

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