Alumina-rich Glass Cement from Lignite Coal Ash

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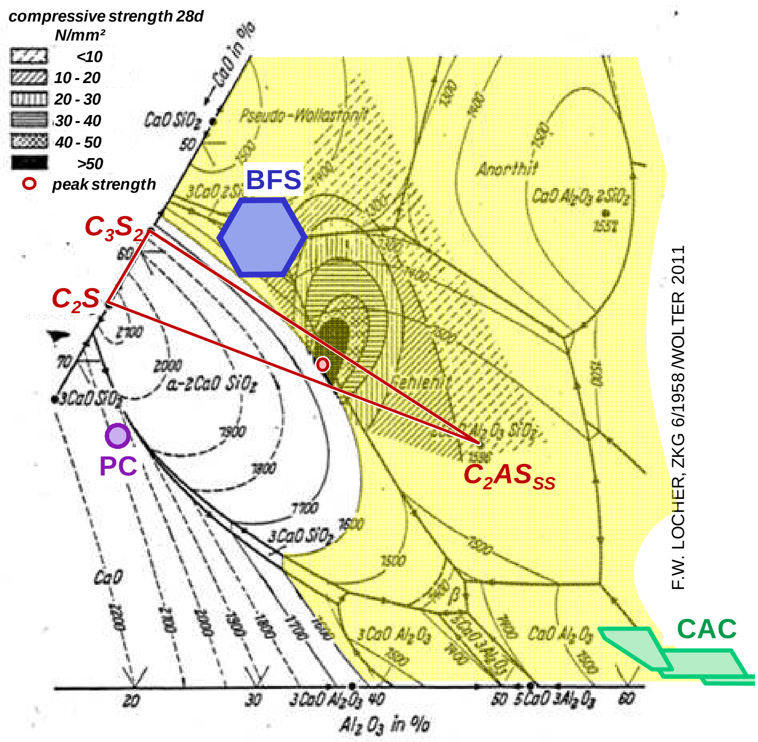
Lime-rich coal ashes can provide a chemical composition which is located between the well known blast furnace slag (BFS), the calcium alumina cement (CAC) and the conventional portland clinker (PC). From the phase diagram CaO-SiO_2-Al_2O_3 it can easily be derived that any composition with a lower CaO content than clinker and a higher alumina content than blast furnace slag, if crystallized, would lead to non-hydraulic phases like gehlenite - except special compositions which are investigated currently as "calcium alumina sulfate / belite cements" (but not shown here).

Fig. 1:
Optimum alumina rich glass composition for sulfate-induced hardening, at 5 % MgO

The acceptable melting temperature area is marked in yellow, i.e. <1600°C in the pure system

The red triangle connects the crystalline lime-rich equilibrium phases at optimum glass composition



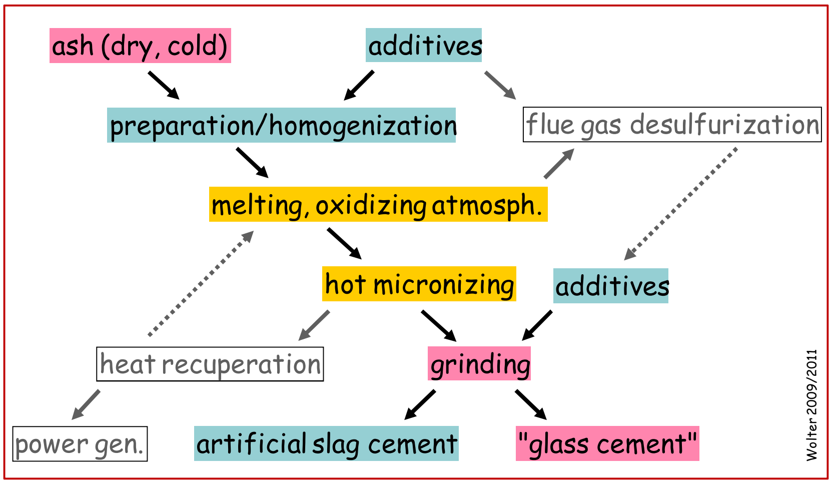
From a technological point of view, however, it seems to be attractive to investigate the melting of such compositions and to save the glassy state by rapid cooling. F.W. LOCHER has investigated a huge number of such glasses regarding their hydraulic behaviour and strength potential. He published his results in 1958, from which the background of figure 1 is derived.

LOCHER did his trials mainly with the scope to identify new and better performing blast furnace slag compositions. Therefore he did not involve SO_3 and iron oxide contents in his raw mix, which are at very low levels in BFS. However, at high amounts they may be present in coal ashes. The alkali content in his glasses was also kept at low levels.

Some European lignite coal ashes are containing high amounts of calcium and aluminium oxides, sulfates and alkalis, in particular if additional calcium oxide was added for the dry SO_2 scrubbing. If such lignite ashes shall be molten and converted into "glass cement", the calcium sulfate decomposition and SO_2 volatilization goes up sharply. Therefore the tentative process diagram, shown in figure 2, must comprise an additional flue gas desulfurization stage.

On the other hand, the triggering of the hardening process by sulfate seems to be promising in alumina-rich glasses, so the recovered calcium sulfate can be utilized as a set regulating and strength accelerating agent in the final product.

Fig. 2:
Principle process sketch of alumina-rich glass cement production by melting and hot micronizing



The melting temperature can be estimated at 150 K above the range of clinker burning because the additional components, i.e. iron oxide, alkalies, MgO and minor constituents, will all tend to lower the actual melting temperature range. After the melting stage, the glassy constitution of the material can only be preserved, if the cooling occurs very fast. Conventional blast furnace slag cooling with excess water (“granulation”) is not favourable for alumina-rich glasses, because its hydraulic reactivity is probably much higher. The remaining water content in the wet sand would complicate the materials handling and reduce or destroy the hydraulic potential.

Therefore the flow of alumina-rich glass will be micronized by nozzle spray. The fine glass spheres which would result from that can be cooled extremely fast by radiation losses.

It is obvious that current state of alumina-rich glass cement development is at a suggestion level. Some process steps must be developed completely new. However, if the CO_2 burden of conventional clinker burning becomes too costly, it will become more and more attractive to substitute clinker by other hydraulic materials, but in composition terms still remaining within the "well known and proven" $CaO-SiO_2-Al_2O_3-Fe_2O_3$ scheme of common cements. The potential of alumina-rich glasses ranges from “artificial slag” composition to new material classes. If the production process can be developed and performed in an economical way, the market potential of alumina-rich glass cement could be very promising.

The tonnage/y of suitable lime-rich coal ashes in Europe is estimated to amount at least at that of BFS. Today they are mostly dumped, because without chemical adjustments and due to lacking of a proven micronizing process at high temperatures such coal ashes do not develop sufficient hydraulic activity. Much research work has still to be done in identifying the optimum compositions, the process steps for melting, quenching and micronizing, as well as the AGC performance in mortar and concrete.