

Hydraulic Binder

The invention relates to a hydraulic binder containing CaSO_4 , blast furnace slag and heat-treated clays and marls.

The composition and production of supersulfated slag cement is based on the addition of calcium sulfate to cement. According to the International Standards Organization (ISO), supersulfated cement is defined as a mixture comprising at least 75% by weight of disintegrated, granulated blast-furnace slag, large additions of calcium sulfate ($>5\%$ by weight SO_3) and a maximum of 5% by weight of slaked lime, Portland cement clinker or Portland cement.

For the production of supersulfated cement, the granulated slag, according to German standards, must contain at least 13% by weight of Al_2O_3 and correspond to the formula $(\text{CaO} + \text{MgO} + \text{Al}_2\text{O}_3)/\text{SiO}_2 > 1.6$. According to Keil, an amount of 15 to 20% of aluminum oxide slag having a minimum modulus of $(\text{CaO} + \text{CaS} + 0.5 \text{MgO} + \text{Al}_2\text{O}_3)/(\text{SiO}_2 + \text{MnO}) > 1.8$ is preferred. According to Blondiau, the CaO/SiO_2 ratio must be between 1.45 and 1.54 and the $\text{Al}_2\text{O}_3)/\text{SiO}_2$ ratio must be between 1.8 and 1.9.

In that case, lime, clinker or cement is added to increase the pH in the cement paste and enhance the solubility of alumina in the liquid phase during the hydration of the cement. Hardening of supersulfated slag cement can be effected without chemical additives or a special forming treatment.

In conventional Portland cements and slag cements in which hydration occurs in the liquid phase free of dissolved alumina, the content of calcium sulfate is limited to a low percentage in order to avoid potential internal disintegration due to the formation of calcium sulfoaluminate (Candlot bacilli) as a

consequence of the alumina that has not dissolved. In those cements, the main impact of calcium sulfate resides in its deceleration effect exerted on the setting time. The basicity of hydrated calcium aluminates and the insolubility of the alumina contained in the aluminates are functions of the concentration of lime in the liquid phase of the cement during hydration, irrespectively of whether the hydrated calcium aluminates are present in crystalline form or in amorphous form in the hardened cement. The concentration of lime in the liquid phase determines the type of impact of calcium sulfate on the setting time of the cement and the maximum amount of calcium sulfate the cement may contain without causing internal disintegration by the time-displaced formation of ettringite.

In supersulfated slag cement, the concentration of lime in the liquid phase is below the insolubility limit of alumina. Larger additions of calcium sulfate for the purpose of activating the reactions of blast furnace slag determine the formation of tricalcium sulfoaluminate having a high hydraulic activity based on the dissolved lime and the dissolved alumina, without leading to potential disintegration. The addition of calcium sulfate to granulated blast furnace slag will not produce expansion cement, but act as an accelerator in the formation of hydrated components. In supersulfated cement, larger portions of calcium sulfate are not to be regarded as disturbing. The resulting tricalcium sulfoaluminates would, in fact, contribute to increasing the hydraulic activity rather than cause disintegration, as would happen with Portland cement and conventional slag cement.

The initial setting and hardening of supersulfated cement is accompanied by the formation of the high-sulfate form of calcium sulfoaluminate from the slag components and the added calcium sulfate. The addition of Portland cement to cement is in this

case required to adjust the correct alkalinity so as to enable the formation of ettringite. The most important hydration products are mono- and trisulfoaluminate tobermorite-similar phases and alumina.

During hydration, supersulfated cement binds with more water than does Portland cement. It meets all standard regulations of cement in terms of grinding fineness. It is regarded as a cement having a low calorific value. Like any other Portland or slag cement, it can be used in the form of concrete, plastering mortar or grout. The requirements to be considered when using supersulfated cement are identical to those which are decisive in selecting, mixing and applying other cements.

In order to enhance aluminosilicate binders, it has already been proposed to activate the same by an alkali and, in particular, soda lye or caustic lye.

Alkali-activated aluminosilicate (AAAS) binders are cement-like materials which are formed by the reaction of fine silica and alumina solids with an alkali or alkali-salt solution to produce gels and crystalline compounds. The alkali-activation technique was originally developed between 1930 and 1940 by Purdon, who discovered that the addition of alkali to slag yielded a fast-setting binder.

Unlike supersulfated cement, a great variety of materials (natural or fired clay, slag, fly ash, belite slurries, ground rock etc.) can be used as sources of aluminosilicate materials. Various alkali solutions can be used to generate hardening reactions (alkali hydroxide, silicate, sulfate and carbonate etc.). This means that the sources of AAAS binders are almost unlimited.

During alkali activation, a high concentration of OH ions in the mixture acts on the aluminosilicates. While in Portland or supersulfated cement paste, a pH > 12 is produced because of the solubility of calcium hydroxide, the pH in the AAAS system is above 13.5. The amount of alkali, which in general ranges from 2 to 25% by weight of alkali (>3% Na₂O), is a function of the alkalinities of the aluminosilicates.

The reactivity of an AAAS binder depends on its chemical and mineral composition, the degree of glassification and the grinding fineness. In general, AAAS binders are able to start setting within 15 minutes, offering rapid hardening and a strong increase in strength in the long run. The setting reaction and the hardening process are still not very clear. They proceed under the initial leaching of alkali and the formation of slightly crystalline calcium hydrosilicates of the tobermorite group. Calcium aluminosilicates start to crystallize in order to form zeolite-like products and, subsequently, alkali zeolites.

The mechanical strength properties in the AAAS system are attributed to the strong crystallization contact between zeolites and calcium hydrosilicates. The hydraulic activity will be improved by increasing the alkali doses. The relation between the hydraulic activity and the amount of alkali as well as the presence of zeolite in the hydrated products have shown that alkalis do not only act as simple catalysts but participate in reactions in the same manner as lime and gypsum, exhibiting relatively high strengths due to a strong cationic influence.

Many studies relating to the activation of silicoaluminate materials by alkalis and their salts have been reported.

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like soda lye or caustic lye while, at the same time, preserving the strength properties of standard binders. This could be achieved in that aluminosilicates from the group consisting of blast furnace slag, clay, marl and industrial by-products such as fly ash were used with the proviso that the Al_2O_3 content was higher than 5%, wherein blast furnace slag was used in amounts larger than 35% by weight, and clay, marl and/or fly ash were present in amounts larger than 5% by weight, with cement kiln dust having been added as an activator in amounts of 3 to 10% by weight and calcium sulfate having been used in amounts larger than 5% by weight. By using cement kiln dust as an activator, the pH could be accordingly lowered, and it turned out that the activation by cement kiln dust was largely insensitive to the selection of the starting materials. With that hydraulic binder, clay or marl was used after a thermal activation at temperatures between 600° and 850°C , and it was possible to use any granulated blast furnace slag such that the exact composition of the blast furnace slag was largely uncritical.

It is the object of the present invention to provide a hydraulic binder the composition of which can be further simplified with, in particular, the quality of the used furnace slag being merely of minor importance. At the same time, it is to be feasible with the hydraulic binder to ensure accordingly rapid setting times and achieve improved strength properties of the set binder. To solve this object, a hydraulic binder containing CaSO_4 , blast furnace slag and heat-treated clays and marls is further developed to the effect that burnt oil shale is used as heat-treated clays and marls, and that organic and/or inorganic alkali and/or earth alkali compounds are used as strengtheners. By using burnt oil shale as heat-treated clays and marls, supersulfated cement can be formed without using any further activator such as clinker, cement kiln dust or alkalis.

The use of burnt oil shale in the composition according to the invention will improve the late strength and reduce shrinkage, while additionally achieving a reduced oxygen permeability, which in turn will lead to an enhanced durability. For further improving the properties of the set binder, strengtheners in the form of organic and/or inorganic alkali and/or earth alkali compounds are used.

Advantageously, the hydraulic binder according to the present invention is further developed to the effect that CaSO_4 is used in amounts of 5-20% by weight, blast furnace slag is used in amounts of 50-85% by weight, and burnt oil shale is used in amounts of 10-30% by weight, wherein the invention is advantageously further developed to the effect that NaSCN , $\text{KAl}(\text{SO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_2)_2$, $\text{Ca}(\text{HCOO})_2$ and/or triethanolamine are used in amounts of 0.5-5% by weight as strengtheners.

In general, improved early strength properties will be reached if the hydraulic binder has a high grinding capacity. The binder according to the invention can, therefore, advantageously be further developed to the effect that the components of the hydraulic binder are ground to Blaine finesses of ≥ 4500 Blaine.

In the following, the invention will be explained in more detail by way of an exemplary embodiment.

Table 1 compares the composition of a binder according to the invention to a composition of a binder according to the prior art.

Table 1:

Granulated blast furnace slag	84.5	63
Burnt oil shale		20
CaSO ₄	15	15
Activator	0.5	
Strengtheners		2%
1DCS [MPa]	2.4	11.5
7DCS [MPa]	28.0	42.6
28DCS [MPa]	51.6	58.8

The content of granulated blast furnace slag in the binder according to the invention could be reduced to the extent to which burnt oil shale was added, the content of CaSO₄ having been maintained. In this case, the burnt oil shale additionally functions as an activator such that the addition of a separate activator can be omitted for the binder according to the invention. By the addition of strengtheners in amounts of 2%, the mechanical strength properties after 1, 7 and 28 day(s), respectively, could be markedly improved over those of conventional binders.

From Table 2, it is apparent that, in addition to markedly improved late strength properties in concrete, also the oxygen permeability of the binder according to the invention was markedly reduced relative to that of a conventional industrial supersulfated binder.

Table 2:

Type of cement	Industrial supersulfated cement (prior art)	Supersulfated cement with burnt oil shale and strengthener (according to the invention)
Cement content	400 kg/m ³	
Water/cement	0.53	0.52
1DCS [MPa]	7.3	7.8
2DCS [MPa]	16.3	14.4
7DCS [MPa]	32.3	33.5
28DCS [MPa]	40.3	49.5
O ₂ perm. [E-16m ²]	2.44	0.81

Claims:

1. A hydraulic binder containing CaSO_4 , blast furnace slag and heat-treated clays and marls, characterized in that burnt oil shale is used as heat-treated clays and marls, and that organic and/or inorganic alkali and/or earth alkali compounds are used as strengtheners.
2. A hydraulic binder according to claim 1, characterized in that CaSO_4 is used in amounts of 5-20% by weight, blast furnace slag is used in amounts of 50-85% by weight, and burnt oil shale is used in amounts of 10-30% by weight.
3. A hydraulic binder according to claim 1 or 2, characterized in that NaSCN , $\text{KAl}(\text{SO}_4)_2$, $\text{Ca}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_2)_2$, $\text{Ca}(\text{HCOO})_2$ and/or triethanolamine are used in amounts of 0.5-5% by weight as strengtheners.
4. A hydraulic binder according to claim 1, 2 or 3, characterized in that the components of the hydraulic binder are ground to Blaine finesses of ≥ 4500 Blaine.