Review paper

WHITE CEMENT - PROPERTIES, MANUFACTURE, PROSPECTS

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INTRODUCTION

Special cements differ from conventional Portland cements in their chemical and phase composition as well as in their properties. Their properties can be achieved by using a modified raw material mix, a grinding admixture or by adjusting the grinding fineness of the cement. Special cements include a number of cements whose production volumes are considerably lower compared to those of conventional cements (max. 5 to 10 %). However, they constitute a significant part of the assortment supplementing the conventional cement. These materials include cements with high early strengths, sulphate-resistant Portland cements, road cements, white cement and coloured cements, expanding cements, Portland cement with a low heat of hydration, Portland cement with a higher MgO content, insulating Portland cement, plasticized Portland cement, strontium and fungistatic cements.

The present review has the aim to summarize the aspects concerning white cement as no article devoted to this subject has as yet appeared in the professional literature, not even in the form of review papers read at international congresses on the chemistry of cement [1 - 4]. Exceptions are represented by some publications in which a separate chapter has been devoted to the subject of white cement, as for example in the book by Rojak and Rojak [5] or that by Butt, Sychev and Timashev [6]. Most extensive information can be gained from the patent literature dealing particularly with the issue of cooling white cement clinker.

The properties of white cement

The whiteness is understandably one of the most important properties of white cement. This must be taken into account already in the selection of the raw materials proper. White cement is made from raw materials with a low content of colouring elements such as Fe, Mn, Cr and Ti. Use is made of high-grade limestone or chalk containing less than 0.15 wt.% Fe_2O_3 and less than 0.015 wt.% MnO, and of white clay, kaolin or by-products of its processing, and other materials which should not contain more than 1 wt.% FeO and 0.8 wt.% TiO_2 [5, 7, 8]. Gypsum, active and inert mineral additives are introduced in grounding stage and must also exhibit whiteness corresponding to cement of the given class. The raw materials, the intermediate product and the final product must also be protected from contamination at all stages of the technology. The initial composition of the raw materials or their properties are dealt with e.g. by [9 - 16].

White cement may be manufactured with standardized surface-active plasticizers or hydrophobic additives (in amounts of up to 0.5 wt.%) not impairing the whiteness of the product. According to the whiteness degree, white cement is divided into three groups of the reflection coefficient: I. min. 80 %, II. min. 75 % and III. min. 68 %. The whiteness degree is determined according to the reflection coefficient in percent of the absolute scale. White cement is manufactured in strength classes of 325, 400 and 475.

The typical silicate module of a white cement clinker is 4 to 6 (in contrast to 2.3 - 3 of grey Portland cement), and its aluminate module is 15-20 (that of grey Portland cement being 1.5 - 2.5).

$M_S = SiO_2/(Al_2O_3 + Fe_2O_3)$
$M_A = Al_2O_3/Fe_2O_3$

In view of its low iron content the raw material melts at higher temperatures, at 1420 - 1450 °C (conventional Portland cement at about 1250^{o}C) with consequently high temperatures in the sintering zone (up to 1600 °C) [8,17].

The problems involved in the manufacture of white cement

The content of Fe_2O_3 in white cement may vary over the range of 0.35 to 0.5 wt.%. If the limit is exceeded, the iron oxides are responsible for a greenish shade of the clinker which would be undesirable for example for architectural applications of white cement.

The following reducing reactions of colouring ions take place during manufacture of white cement clinker in a reducing atmosphere:

$Fe_3O_4 + CO \rightarrow 3FeO + CO_2$
$Fe_2O_3 + CO \rightarrow 2FeO + CO_2$
$MnO_2 + CO \rightarrow MnO + CO_2$
$2CrO_3 + 2CO \rightarrow Cr_2O_3 + 2CO_2 + ″ O_2$ [18].

The colouring effect of Fe, Cr, and Mn cations depends on their valency in the crystalline phases in cement. Oxidized forms of free oxides of Fe^{3+}, Mn^{3+} and Mn^{4+} absorb more light than reduced forms Fe^{2+} and Mn^{2+}. The higher the temperature and/or the concentration of the reducing agent such as CO, the whiter the cement appears to human eye. This is important particularly in the cooling of white cement clinker. If it is cooled slowly from the initial temperature in the kiln (1200 - 1100 °C or lower) in the presence of oxygen, the colouring oxides of higher-valent metals will be reformed. Contrarily, if the cooling is quick, the high-temperature reduced crystalline forms are "frozen-up" and the light absorption will be lower.

Development of the methods of bleaching white cement

To increase the whiteness, the clinker is fired under the conditions mentioned above and the bleaching is affected by rapid quenching with water. The clinker at 1250 - 1350 °C is withdrawn from the kiln through a special outlet into a water bath and hence passes into a drying chamber where it is dried at temperatures not exceeding 300 °C. According to Grachyan, Gayzhotov, Zubyechin and others [5] the bleaching by quenching proceeds in order to fix the phase composition of the clinker formed at high temperatures and exhibiting a high reflection degree. On slow cooling, the iron oxides are bound to calcium aluminoferrites C_6A_2F, whereas on fast quenching they are fixed to a smaller number of particles of type C_6A_2F aluminoferrites while separating white calcium aluminates. The whiteness of cement increases with increasing content of tricalcium silicate (C_3S) and aluminate, and decreases with increasing content of dicalcium silicate (C_2S).

In 1937, Cherepovskii and Aleshinova [9] submitted a method of bleaching in oxygen-free atmosphere at 1100 - 1200 °C, where at a low concentration of CO_2, dissociation to Fe_3O_4 takes place as a result of different partial pressures of the oxides. The clinker obtained in this way acquires a higher whiteness degree because Fe_3O_4 suppresses the colouring ability of iron oxides. Implementation of the method requires introduction of special bleaching coolers inhibiting penetration of oxygen from the ambient atmosphere. The gas employed for bleaching (containing $O_2 < 0.2$ vol.%, $CO_2 > 5$ vol.%), prepared by heating producer gas in special kilns, is then passed to the hermetically sealed bleaching cooler. Clinker from the kiln passes into this bleaching cooler and is cooled down to 200 °C while not coming into contact with the ambient atmosphere, i.e. with oxygen.

As demonstrated by Zubyechin´s experiment [5], positive results were obtained by firing the clinker in an oxygen-free atmosphere and subsequently bleaching it in a water bath. Grachyan [5] has devised an efficient two-stage bleaching method. The clinker discharged from the sintering zone is cooled for 1-2 minutes in a converted gas and then enters a water bath. The converted gas is obtained by reacting natural gas with water vapour at 900 - 1000°C according to the equation $CH_4 + H_2O \rightarrow CO + 3H_2$. In statu nascendi, carbon monoxide and hydrogen exhibit high reactivity and have strong reducing effects on iron and manganese oxides. The scientists also succeeded in achieving a higher whiteness degree by bleaching in water with an addition of magnesium, as well as in solutions of dilute acids – hydrochloric, sulphuric and others. It is assumed that in a gaseous environment or during rapid bleaching in a water bath of low-ferric clinker the whiteness is promoted by reducing the valency of iron oxides, by changing the coordination of colouring oxides and as a result of adjusting the proportions of the aluminate and silicate phases.

In 1990 a Chinese study dealt with the effects of additions of chlorides - NaCl, $CaCl_2$, NH_4Cl to the raw-material mix at temperatures above 650 °C [20]. The chloride reacts with iron oxides in the raw material and forms volatile $FeCl_3$ which is withdrawn with the flue gases. However, the method is only suitable for the wet clinker-making technology and for raw materials with a higher Fe content. In the case of the dry technology the chlorides vaporize in dependence on the degree of reacting with the iron oxides.

The effect of intensifiers on clinker firing

Mineralizers and/or plasticizers (of course not those containing colouring admixtures) are often added to the raw material in order to accelerate the reactions of the sintering process and to facilitate the firing with obvious economic and technological advantages.

The suitable intensifiers include fluorides - CaF_2 [21], sodium fluorosilicate, calcium sulphite, mixed silicate fluoride sulphate. For example, an addition of sodium fluorosilicate to the raw material speeds up the interphase reactions and reduces the melt forming temperature to the level usual for sinter of conventional Portland cement. During the nineties, several laboratories [22, 23, 24] dealt with the effects of fluorides on the firing of white cement clinker, particularly with those of CaF_2 and $CaSO_4$. CaF_2 alone reduces the temperature of thermal decomposition of $CaCO_3$, changes phases in thermodynamic equilibrium, modifies the properties and temperature of melt formation, etc. The alite forming reactions take place at lower temperatures and at a much higher rate. On the other hand, $CaSO_4$ reduces the melt viscosity and consequently promotes the mobility of ions. A reduced rate of alite formation was observed at a higher content of $CaSO_4$ in the raw material. This reduction may lead to a decrease of the controlling force of this reaction as well as to affecting the stability range of C_2S. The firing may thus be partially improved by an addition of the plasticizing/mineralising combination of fluoride (e.g. CaF_2) with gypsum, thus allowing white cement clinker with a C_3A content of less than 5 wt.% to be produced, which means a sulphate-resistant white cement or a white cement resistant to seawater. In this type of material the main fluorosulphate melt contains molten fluoroellestadite (60 - 75 wt.%) having the composition $3Ca_2SiO_4{\cdot}3CaSO_4{\cdot}CaF_2$, ferrites and aluminates. The rate of alite formation is even higher than the rate established for mixes mineralized with CaF_2 [22]. On the other hand, presence of these compounds allows the raw material to sinter at temperatures between 1350 and 1400 °C. The white cement clinker may thus be produced at temperatures lower by about 200 °C below the usual sintering temperature of traditional raw material mixes for white cement. This of course brings about substantial savings in energy not only in the manufacture of white cement clinker, as the method may also be employed in the manufacture of conventional grey Portland cement.

The effects of fluorite additions to the raw material mix for white cement manufacture were studied by Shah and Iqbale [24]. These authors found that an addition of fluorite (even in small amounts of 0.2 wt.%) to white cement raw material mix brings about a reduction of C_3S formation sintering temperatures down to 1200 °C (and in the presence of SO_3 even down to 1000 °C) and speeds up formation of silicates, so that the sinter can be produced at lower temperatures and the final product eventually exhibits superior properties, such as strength. The authors also dealt with the properties of clinker containing additions of minority oxides and found that an addition of SO_3 lowers the required amount of gypsum for controlling the setting time.

Muntean et al. [25] studied the possibility of producing clinker fired at low temperature from currently available raw materials in the presence of a mixture of sulphates, without impairing the physico-chemical properties of the resulting cement while attaining a high whiteness degree. They based their experiments on the fact that small amounts (5%) of $MeSO_4$ ($Me = Ca^{2+}$, Mg^{2+}, Ba^{2+}) may be responsible for certain positive changes in the firing and in the bonding properties of the resulting cements. The changes included improved whiteness, especially when combined with quenching in water or in aqueous solutions of triethanolamine (TEA). They monitored the free lime content and the mineralogical composition of belitic clinker with and without the addition, in terms of the character of the cooling medium. X-ray analyses showed that the distribution of ferric ions in the clinker varied in dependence on the cooling medium and on the presence of sulphates, in particular $MgSO_4$. The presence of $MgSO_4$ was thus responsible for reducing the amount of ferric ions in clinker. Also other mixtures of sulphates such as $CaSO_4$ and $BaSO_4$ were found to behave in this way. A superior whiteness was found with all samples containing sulphate additions, especially with samples quenched in the aqueous solution of TEA. Very satisfactory compressive strengths were determined on samples with a 5% addition of $BaSO_4$. It should be noted that the compressive strengths of water-quenched samples were lower by 2.5 MPa than the strengths of samples quenched in TEA.

Methods of firing the white cement clinker

On firing the white cement clinker and its subsequent cooling one should take into account its different properties (cf. the paragraph Properties of white cement, Development of bleaching the white cement clinker) as well as the requirements for the subsequent application of the raw material produced. Since the seventies, the manufacturing processes of white cement clinker have been dealt with by many establishments all over the world. Many methods and items of equipment have been patented, concerned with both the manufacture proper [26-44] and with the cooling methods [e.g. 45, 46]. The survey below deals with the findings associated with the development of technologies and in particular with the cooling process, which had the following special aims:

a) a wide distribution of clinker particles
b) oxidation phenomena
c) high water content in clinker.

Ad a): Rotary kilns are generally used in white cement clinker manufacture. The clinker discharged from the rotary kiln is immediately immersed in water where it is abruptly quenched and prevented from coming into contact with air. The first problem encountered is the fact that that clinker fired in a rotary kiln has a wide particle size distribution so that the cooling rate is not uniform. When the clinker particles are coarse, they should be kept in the water for a longer time than the smaller particles. In addition, larger amounts of water are necessary and the consumption of energy is higher. The solutions look for sinter firing yielding a narrower particle size distribution, but this cannot be achieved with a rotary kiln. Gradual cooling of sinter according to particle size would be advantageous. The kiln can for instance be fitted with ring-shaped outlet openings which would release only fine clinker particles while retaining and classifying the coarser ones by a barrier and allowing them to fall deeper onto a conveyer belt immersed in water, under an angle different from that of the finer particles. In this way the finer clinker particles would dwell in water for a shorter period of time than the coarse ones, and the clinker would be cooled more uniformly. Patents US 4461645 [47], DE 3521586 [48] and DE 3521587 [49] describe methods for cooling white cement clinker in which the clinker is divided into at least two particle size fractions which are then cooled with water. The time of cooling increases with increasing particle size.

Ad a+b): In JP 60264350 [33], the raw material mixture for white cement clinker production is fired in a fluidized bed kiln and the fired particles are treated by a reducing gas. The reduced particles are first cooled with water down to 600 - 700 °C (the water being sprayed over the clinker) and then with air down to 100 - 150 °C. As a result of the fluidized bed firing the clinker particles are of uniform size with a narrow size distribution. The clinker is cooled rapidly while being separated from ambient atmosphere and thus protected from oxidation. In this way, uniformly cooled white cement clinker with a high whiteness decree is obtained.

Ad b+c): To rule out undesirable oxidation, the clinker being cooled must not be exposed to oxygen. For this purpose the clinker discharged from the rotary kiln is sprayed over with a reducing agent, for example with oil, before immersion in water [50]. The resulting clinker has a high water content (about 15 - 16 wt.%, possibly more in the case of very finely ground material), which may be responsible for lowering the strength of the final cement due to possible hydration. This is why the cooled clinker is exposed to a stream of cooling air that, however, brings about a relatively high consumption of energy. In addition, the processes involve the risk that some of the water vapour released by cooling water penetrates into the rotary kiln and reduces the flame and sintering temperature, with the resulting higher energy consumption of the rotary kiln and higher production costs of the final product, i.e. white cement.

Ad c): US P. 4767462 [51] describes the method and equipment for cooling and further treatment of white cement clinker that is said to eliminate the disadvantages of cooling the clinker in a water bath. The white cement clinker is sprayed with water in an oxygen-free atmosphere and then passes against the stream of warm drying air. The hot clinker discharged from the calcination kiln at about 1400 °C is sprayed with such amounts of water to quench it abruptly down to about 500 - 600 °C, but to acquire only 5 - 8 wt.% water content. On passing out of the subsequent cooling and drying air zone the dry clinker has a temperature of 60 - 100 °C and a residual moisture content of less than 0.5 wt.%. In view of this relatively low moisture content in the clinker and of the short dwell time in the spray zone and in the final drying/cooling zone, the risk of undesirable hydration of the clinker is reduced to a minimum and the same applies to heating costs.

Ad a + b + c): The most recent US patent 5618104 [52] deals with a method of cooling clinker from the rotary kiln, consisting of the following steps: passage of clinker to the first cooling stage where it is simultaneously ground to powder, cooling of the clinker by short periods in an oxygen-poor environment (mean temperature about 650 - 750 °C), transfer of clinker to second cooling stage, transfer of clinker to an oxygen-poor environment for 15 seconds, where the clinker particles are homogenized and cooled own to 550 - 650 °C, transfer of clinker to the third cooling stage using cooling air.

White cements as well as coloured ones have to be kept and transported in appropriate packing (4- or 6-layered). Inert materials (aggregates) of corresponding colours are used in the preparation of renderings, mortars and concrete - white marble, crushed limestone, white silica sand, and the like.

Present situation in the manufacture of white cement clinker

At present there is no national standard specification for the manufacture of white cement, there are only corporation standards. For example, HIROCEM a.s. Rohožník in the Slovak Republic [53] manufactures white cement 52.5 by fine grinding of white silicate clinker with the setting control admixture or auxiliary admixtures. The special admixtures may be added in amounts not exceeding 1 wt.%. The admixtures must not cause corrosion of reinforcement nor impair the properties of cement or the mortars or concrete made from it.

At the RAK White Cement plant at Ras al Khaimah, United Arab Emirates (RAK WCC) [54] a great deal of attention is paid to the raw material mixture. Kaolin must contain less than 0.6 wt.% Fe_2O_3, sand more than 95 wt.% quartz, gypsum must be of 95% purity and high whiteness. The main raw material components are analyzed by a multichannel X-ray spectrometer. The clinker is fired in a rotary kiln connected to a four-stage preheater. A part of the hot gases (700 °C) is passed to the two-stage preheater where it preheats the combustion air to 200 °C. This is said to have a favourable effect on flame stability, improves conditions in the combustion zone and reduces fuel consumption, which is generally high in white cement manufacture. The clinker going out of the kiln enters a cooler where it is quenched with water. The cooler is specially designed to prevent water vapour from entering the kiln and impairing the combustion conditions there, which would have negative effects on the quality of clinker. The cooling is of two-stage type, the second stage comprising a worm conveyer that cools large clinker particles. The steam generated by the cooling process is utilized for drying the clinker in a rotary drier to a moisture content of less than 5 %.

One of the largest exporters of white cement, Aalborg Portland A/S in Denmark [55], has an annual capacity of 0.7 million tons of white cement. In the seventies and eighties the works implemented an energy saving programme by converting the manufacture to a semi-wet process. The rotary kiln with pneumatic discharging equipment can be fired with coal or oil by means of a burner connected to primary combustion air supply ducts with different flowrates. A clinker cooler with a variable-speed cooling air fan was installed. All fans have been provided with inlet dampers to reduce the noise level around the cooler.

A new white cement production plant is now under construction at Tudela Veguin in Spain [56]. The know-how and the machine equipment are supplied by Krupp Polysium. The sinter will be fired in a rotary kiln fitted with a cyclone heat exchanger and a specially designed double cooler. The cooling will first be effected in a drum cooler and final cooling on a grate cooler. The plant should have been put into operation in November 1999.

Lehigh Portland Cement Company is one of the largest suppliers of white cement in North America. This manufacturer offers a wide assortment of products: Lehigh White Portland Cement Type I (suitable for structural concrete, construction of swimming pools and spas, reflection surfaces, noise barriers, etc.), Lehigh High Early Strength White Portland Cement Type III (for structures in cold climates, concrete blocks,

Table 1. Technical specifications of products as given by white cement manufacturers.

Manufacturer	To standard	Type	Strength class	Whiteness
Aalborg	EN 197-1	CEM I 52.5	52.5	Not specified
Hirocem	EN 196	CEM I 52.5	52.5	84.5-88 %
Dyckerhoff	EN 196DIN 1164	CEM I 52.5	52.5	85 %
	EN 196DIN 1164	CEM I 42.5	42.5	82.9 %

Table 2. Chemical composition (wt.%) of raw materials as given by the manufacturers.

Manufacturer	Dyckerhoff CEM I 42.5	Dyckerhoff CEM I 52.5	Hirocem
SiO_2	21.82	22.05	21.7 - 22.5
Fe_2O3	0.21	0.22	0.2 - 0.24
Al_2O_3	3.99	3.98	4 - 4.3
CaO	66.58	67.06	65.4 - 67
MgO	0.66	1.62	1.8 - 2.5
SO_3	2.82	2.48	2.2 - 2.7
K_2O	0.57	0.27	Not specified
Na_2O	0.08	0.06	0.12-0.4

sidewalk pavements, roof tiles), Lehigh White Portland Cement Type V (for contact with soils and groundwater with a high content of sulphates), Lehigh White Portland Cement with Water Repellent Added (roof coverings, paintings, stucco), Lehigh White Cement Type N (masonry mortars, stucco mixes, for type N mortars to ASTM C 270), Lehigh White Masonry Cement Type S (for use in high-strength white mortars conforming to ASTM C 270, Type S.

And last but not least, mention should be made of the company Dyckerhoff Weiss which manufactures white cement of types CEM I 42.5 and CEM I 52.5 to DIN 1164. The technical specifications of these and other products are given in table 1, while table 2 summarizes the chemical composition of the raw material as specified by the manufacturers.

CONCLUSION

White cement finds primarily architectonic applications requiring white or coloured concrete, in finishing operations as renderings, mortars and concrete, as surface finishing of large panels and blocks, in repairs and treatment of sculptures and building products, for building decorations [57], in the manufacture of marble and marble-like decorative surfaces [58]; use is made of cement paints based on white cement, and of white cement in the top layers of reflective concrete surfaces [59]. White cement also finds application in repairs of cracks in swimming pools, flood control ducts and other underwater structures [60].

In view of the wide range of applications of white cement the present efforts aimed at increasing the efficiency of its production are highly justified, and corresponding research aimed at energy savings and cost reductions is under way all over the world. The survey shows that white cement clinker can be made from conventional raw materials by means of intensifiers or by adjusting the process, particularly in the stage of clinker cooling. In this way it is possible to produce white cement with the corresponding physico-chemical properties and adequate whiteness without consuming excessive energy.

Within the framework of research now under way at the Department of Glass and Ceramics of the Institute of Chemical Technology in Prague, the possibility is now being considered of utilizing gypsum-free cements based on white cement clinker as refractory materials in view of the low content of Fe_2O_3 in the clinker.

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