WHITE CEMENT FOR ARCHITECTURAL CONCRETE, POSSESSING PHOTOCATALYTIC PROPERTIES

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ABSTRACT:
White cement is a key ingredient in architectural and decorative concrete. By using it, in particular, the resulting concrete not only becomes an expressive material that having an infinite range of colour tones, intensifies one of its aesthetic qualities, but could also gain remarkable validity in terms of structural qualities due to its high mechanical strength.
This paper is intended to provide technical information to both designers, architects and contractors, in order to obtain a high performance concrete, similar to the natural materials like marble, possessing relevant properties in terms of durability, performances and added environmental properties. Indeed, a new type of white cement is here proposed, containing TiO_2, possessing photocatalytic properties which allow to maintain the aesthetic characteristics of concrete over time and contribute to eliminate dangerous pollutants from the urban environment.
A remarkable application is also described, concerning the innovative construction of a church in Rome, named "Dives in Misericordia" whose sails were built using white High Performance Concrete, based on this new cement. Main physical and mechanical properties of this HPC are described.

1.0 WHITE CEMENT

Thanks to the continuous laboratory research efforts aimed to obtain outstanding properties besides the excellent degree of whiteness, white cement has been rendered increasingly and noticeably a high performance binder. White clinker is produced by taking care that the content of ferrous composites and other heavy metal composites does not exceed 0.15%, whose presence give common Portland cement its distinctive grey colour. To this purpose, it is first of all necessary to carefully select the raw materials: only mineralogically pure kaolins and white limestones are used.

1.1 Colorimetric properties

Chromatic control (especially in the case of white cement) takes the form of reflected light colorimetry using highly reflective materials such as magnesium oxide or titanium.
Briefly, the "white" quality of the cement is measured using three parameters:
- purity, i.e., the intensity of the shade. Purity is measured by colour percentage;
- dominant wave length, i.e., the tonality of the shade that accompanies and characterises each white (for this reason, not all white bodies are equal). The length of the dominant wave lies between yellow and blue;
- brilliance, i.e., the power to reflect incident light (the most distinctive characteristic of white bodies), expressed as the difference in percentage between the light reflected by a surface of white cement and that reflected by a similar surface of magnesium oxide, traditionally considered as the ideal white body.

In any case, as far as cements are concerned the colorimetric characteristic can only be represented by two parameters: brilliance and purity, as the third parameter (i.e., the basic wave length), which is normally requested for the various powders in the cements, remains roughly the same (for ordinary cements, $\lambda = 577 \pm 2$ nm; for white cements, $\lambda = 567 \pm 2$ nm).
Figure 1 shows the brilliance/purity curve with the colorimetric data for different types of hydraulic binders: ordinary cements, clear binders and white binders [1].
Reading from the left to right, the chromatic component increases: this is between 8 and 17% for grey cements; 5-7% for light cements and 4-5% for white cements: The brilliance also increases from 25 to 40, from 50 to 60 and from 80 to 90 respectively.
This graph allows us to compare the variability in purity with that of the brilliance. It is worth noting that the inaccuracy of visual evaluation of the brilliance (at least in the case of white cements) is about 2 points.

1.2 Photocatalitic properties

Scientific studies on photocatalysis were started about three decades ago [2-9]. Since then research has taken several turns, but it is in the last 10 years only that the most exciting potential of this technology has emerged: the application of photocatalysis to environmental clean-up [10].
This also gave impulse to industrial applications and institutional researcher. A huge increase in worldwide patent applications was observed and in 1999 more than 400 international applications were filed [11].
The strict environmental regulations imposed by the authorities have stimulated academic and industrial research groups to develop new strategies in the abatement of dangerous aqueous and gaseous pollutants. As regards the latter case, much attention has been focused on the removal of NOx, hydrocarbons and organic chlorides, since these pollutants are an issue of high social impact in everyday life.
In particular, it should be noted that reactions in the atmosphere between NO_x and several hydrocarbons, under solar irradiation (Photochemical Smog), increase health hazards especially within heavy traffic urban areas.

1.2.1 Cement containing photocatalysts

Within the framework of a strategy aimed at remedying environmental pollution through the use of construction materials containing photocatalysts, a system comprising Titanium dioxide (TiO_2) and white cement was investigated.
A first technology including the photocatalytic degradation of organic pollutants was utilised for maintaining the aesthaetic characteristics of concrete structures [12-15].
The introduction of suitable amounts of TiO_2 into cement mixes allowed to render photocatalitically active the surface of cementitious structures.
In fact, concrete products are expected to maintain their aesthetic characteristics unchanged over time, in particular the colour, even in the presence of aggressive urban environments.
The maintenance of aesthetic appearance of cementitious materials, in particular those based on white cement, is specially desired. Indeed, the main reason that brings about a colour change in cementitious materials is the presence of coloured organic compounds which remain on their surfaces.
The inorganic powders adhere to the surface of the cementitious material in the presence of an organic interface or of macroporosities. The technology of heterogeneous photocatalysis is based on the irradiation of a semiconductor photocatalyst. Semiconductors are characterized by a narrow band gap between their valence and the conduction bands.
The absorption of a quantity of luminous energy being greater than or the same as the band gap (E_{BG}) of the semiconductor results in an abrupt transfer of electrons from the valence to the conduction band and the consequent creation of holes (h^+) in the valence band.

Such charge transfer introduces some unbalanced conditions which in turn lead to the reduction or oxidation of the species adsorbed onto the surface of the semiconductor.

In order to verify the efficacy of the photocatalytic activity on a cement matrix containing TiO_2, many experiments focusing on the oxidation of several kinds of aromatic organic compounds were carried out.
Figure 2 shows the surface restoration by irradiation of cementitious mortar samples containing TiO_2 and phenanthroquinone. TiO_2 can form two different cristallographic forms: rutile and anatase. The photocatalyitic activity is much higher when TiO_2 is mainly in the anatase form.

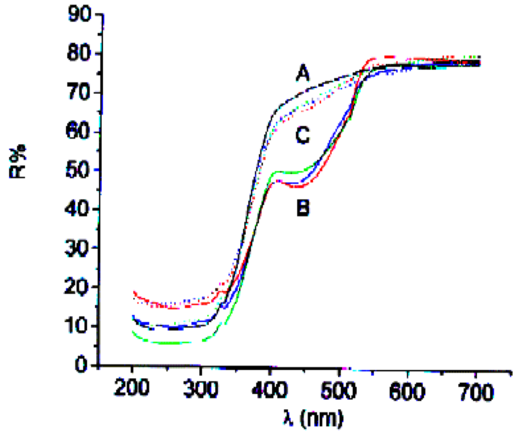

Figure 2. Reflectance spectra versus wavelength for a white cement sample

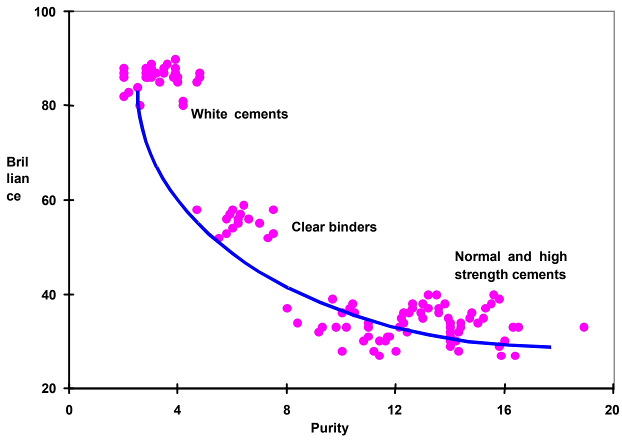

Figure 1. Brilliance/purity for the various types of cement

Samples of white cement having a thickness of 2 mm were placed on supports having a discoid form with a diameter of 3.2 cm and a thickness of 7 mm, containing 5% of TiO_2 (P-25 Degussa type).
In order to obtain reproducible organic substances on the sample, a phenanthroquinone solution in methanol was deposited by means of an aerograph thereby giving to the surface an amount of phenanthroquinone equal to 0.1 mg/cm^2. At the end of the treatment, the sample showed a homogenous surface having a yellow colour.
Both before and after the deposition of phenanthroquinone, reflectance spectrophotometric analyses were carried out with a Perkin Elmer lambda type spectrophotometer. The instrument was fitted with an integrating sphere to eliminate any scattered light responsible for anisotropy and surface irregularities. The samples were irradiated by means of a solar flow simulator, emitting radiation with a wavelength greater than 290 nm. The device used for irradiating purposes

consisted of four 400 Watt lamps placed at the vertices of a square having at its center a carrying sample roundabout rotating on its own axis. By means of that device, simultaneous irradiation of more samples with the same amount of photons per time unit was possible.
The irradiation device SOLAR SIMULATOR SET-UP12/24 allowed accelerated ageing test to be carried out, whereby approximately 100 irradiation hours correspond to 1 year of sunlight. For samples at different times by various percentage reflectance values (R%) as a function of wavelength (nm) were obtained. The percentage of reflectance of the samples was reported in Figure 2 at different times as a function of the wavelength (nm). With particular regard to Figure 2, curve A represents the spectrum before depositing the organic substance, curve B represents the situation after deposition of the substance, curves C represent the situation after 8 hours of irradiation respectively.
As can be seen, already after 8 hours of irradiations the situation is almost the same as before the treatment with the pollutant.

1.2.2 Photocatalysis and the removal of NO_X

Two main practical directions of NO_X elimination can be cited:
i) Reduction by hydrocarbons or ammonia
ii) A two-step adsorption-reduction or thermal destruction process

Photocatalysis has recently gained considerable recognition as a reliable method of NO_X abatement under mild experimental conditions, employing sunlight as a low cost renewable energy source. It is interesting that, in this field too, recent developments suggest the use of mixed catalysts in which a photoactive component such as TiO_2 is mixed with adsorbents, e.g., zeolites [16]. As reported, this improves the overall efficiency of NO_X elimination since the high absorbing capacity of zeolites compensates for or complements the low adsorbing power of TiO_2.
The use of mixed catalysts therefore seems a promising research direction in photocatalysis, too. Realising that a composite system consisting of TiO_2 dispersed into a cementitious matrix is one of such photocatalysts holds important practical implications. Research under way at our laboratories and at other research institution [17] shows that concrete containing TiO_2 has very good potential application as a resolving technology in pollution control.
The mechanism of nitrogen oxide removal by photocatalysis is not simple. It is assumed that NO in the air is oxidised when the catalyst is exposed to light. Through the intermediate step of nitrogen dioxide (NO_2), it is then converted to nitrate. When NO_2 is formed, part of the gas may escape from the photocatalytic surface but, in the presence of the cement matrix, the gas may be effectively entrapped together with the nitrate salt formed.
Laboratory tests of photoconversion of NO_X were carried out on films of:

- TiO_2 mixed with cement (5% by cement weight)
- Cement matrix without photocatalyst

Figure 3 summarises the tests carried out in the dark. NO_X is considered as a residual amount; a percentage is referred to an initial concentration of 100%. In this case, the observed concentration decrease is only due to adsorption. It is probable that such absorption is attributed to the ability of alkaline oxides forming the cement matrix to adsorb NO_X.
Photochemical tests after 7 hours of light of the samples, still considered as a percentage referred to an initial concentration of 100% are reported in Figure 4 below
It can be noted the removal of NO_X by action of the photocatalyst plus the cementitious matrix which is higher than the photocatalyst alone.
The reason is that on the surface NO is oxidised to NO_2 by reaction with OH radicals:

$$NO + OH^{\cdot} \longrightarrow NO_2 + H^+ \quad (1)$$

NO_2 is oxidised and, like nitrate, remains adsorbed :

$$NO_2 + OH^{\cdot} \longrightarrow (NO_3)^-_{ads} + H^+ \quad (2)$$

NO_x treatment in the dark

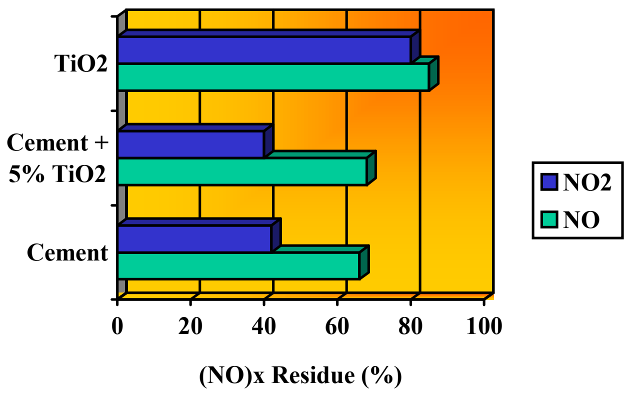

Figure 3.

Furthermore, the examination of the data of Figure 4 shows that also the cementitious matrix without TiO_2 holds a certain catalytic effect, as often observed in the case of organic substrates, probably due to the presence of photocatalytic oxides in the matrix itself.

NO_x treatment under UV light

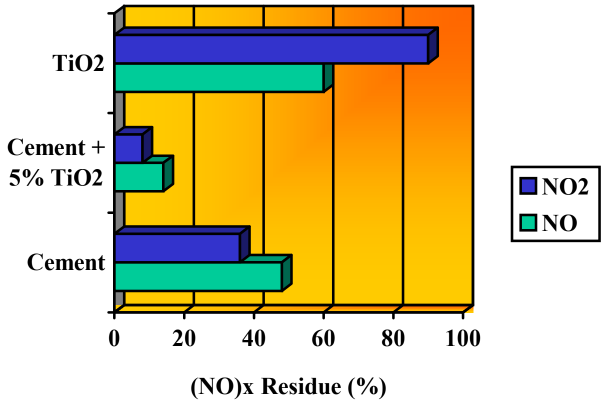

Figure 4.

A white cement containing TiO_2 (TX Millennium) has already been used for the construction of the Church for the Jubilee "Dives in Misericordia" in Rome [18], for the construction of the "City of Music" in Chambérie (France) and for the construction of a school in Mortara (Italy). Cementitious paints containing photocatalysts were developed, too [19].

2.0 WHITE CEMENT CONCRETE: MIX DESIGN

The mix design for a concrete made with white cement needs to be developed taking into consideration two fundamental aspects:

- the aesthetics or surface finish (including photocatalytic properties, eventually);
- the strength or structural suitability

In other words, the right materials need to be chosen to create a delicate balance between the mix components and to guarantee the rheological behaviour of the resulting mix.
In the particular case of High Performance Concrete (HPC), the raw materials are: water, cement and aggregates (the same as in the ordinary cement mix), to which mineral and superplasticizer admixtures may be added as required. As a result, HPC has a microstructure significantly differing from the one of ordinary concrete: high compacity, low porosity and improved interfacial binding between cement paste and aggregates thus leading to different macroproperties in terms of strength and durability [20].

2.1 Aggregates

In the case of white cement concrete, an adequate choice of aggregates is absolutely necessary, in order to achieve the white colour in the concrete.
All aggregates must be clean, free from clay, mineral dusts and impurities. Contamination with other materials must be avoided.

Coarse aggregates. Their colour is of utmost importance for the surfaces to be treated to reveal the aggregate (e.g., bush-hammered, sand-blasted and washed). They should be reasonably uniform in colour.
Fine sands. Their use is decisive for the colouring of the open surfaces without further treatment after the removal of the formworks (extremely light sand is needed if we specifically want a perfectly white surface, while a coloured sand can be sufficient if a more particular tone is required).
In both cases, the use of white cement in the "open" concrete allows to obtain a far more brilliant mortar in contrast to the colour of the aggregate, thus enhancing this if the surfaces are "worked" and making casts brighter if the surfaces are left "as they are". The surface of a so-obtained mortar with white cement:

- acquires more brilliance, the less brilliant the sand
- assumes an increasingly less pinkish and more bluish tone than that of the sands. In fact, the wavelength of the loose materials is longer than that of the hardened surfaces.
- loses colour percentage (the colour is weaker) and thus the use of coloured sands is not enough on its own to get a concrete with distinctly coloured surfaces.

The results of the sand/mortar colour experiments show that it is not necessary to use particularly white sands, which are often hard to find, to create a white cement concrete: we can quite use normal sands.

The "colour loss" or rather the shades obtained by passing from sand to mortar can have a very pleasing chromatic effect, often preferable to pure white.
However, when the designer wants to achieve a brilliant and definite colour, he changes the colour of the surface by adding a mortar of the relevant colour capable of accentuating the colouring and giving the required dominant wave length.
In this way, it is possible to get a virtually infinite spectrum of colour tones.

2.2 Mineral additions

For the improvement of strength, chemical and physical durability, mineral additions can be included in the mix design.
In the case of white cement concrete, it is clear that fine pozzolanic materials (such as silica fume, blastfurnace slag, fly ash, rice husk ash and metakaolin) must be white and among all the materials currently available only the latter can be considered [21-23]. Indeed, particular types of white silica fume or precipitated silica are too expensive.
Metakaolin is by nature white and is highly reactive, sometimes used as a valid alternative to silica fume. It is an aluminium silicate obtained through calcinations of pure kaolin within a set temperature range. The average size of the particles is 1.5 micron (ten times finer than Portland cement CEM I 52.5 R). Metakaolin works in different ways:

- as a filler, with immediate action
- by accelerating the hydration at greater intensity within the first 24 hours
- by means of a pozzolanic reaction with the C-H between the 7th and 28th days

Besides, other advantages can be obtained:

- reducing water permeability
- limiting efflorescence problems - presence of $(CaOH)_2$
- controlling the hygrometric shrinkage

- improving the paste/aggregate bond
- controlling bleeding.

2.3 Water-reducing admixtures

Since water demand levels in HPC is corresponding to a water/binder ratio of 0.20-0.35, the use of acrylic superplasticizers is preferable, rather than melamine-formaldehyde or naphthalene-formaldehyde solphonate condensates. In the particular case of white concrete, the choice of admixtures is also strictly connected with their colour.
Besides, if there are possibilities of cement-admixture incompatibility, the use of a compatibilizing agent is absolutely needed. Recently, this problem was solved by using a system of admixtures supported by the metakaolin used as pozzolanic addition [24].

3.0 WHITE SAILS FOR THE CHURCH "DIVES IN MISERICORDIA", IN ROME

The Church "Dives in Misericordia", a project of Richard Meier, a master of contemporary architecture, is the first example in which Italcementi participated using photocatalytic innovative materials belongs to. The simple yet severe design which manages to combine the sacredness of the inside of the construction with the liveability of large external spaces, is characterised by three large white concrete sails which swell as though driven by a wind from the East.
In the church there are two distinct architectural bodies: the sacred building, approximately 2,500 sq.m which occupies the southern part; the community centre, approximately 4,300 m^2 situated in the northern part. The churchyard connects the Church to the centre of the residential area. The church roof is a glass skylight which runs along the entire length and impressive glazed windows characterise the lateral facades. Four large shells in reinforced white concrete measuring 16 and 28 metres in height embrace the central body of the nave occupying more than 700 m^2; the main hall, the weekday chapel and the baptistery separate the spaces inside the building. There is a 26 m high pillar-bell-tower near the central body. The impressiveness of the work and the specifications of the project: 20,000 m^3, 22 metres high, the tall bell-tower and the three immense curved shells, required Italcementi's contribution for the bold technical-structural solutions. Italcementi, technical sponsor of the project, is accompanying the construction of the Church which is currently underway, by supplying know-how, technical assistance and structural calculations, in addition to the highly technological and innovative products amongst which is the new white cement "TX Millennium", whose formulation (patented) guarantees unparalleled whiteness which remains constant over time.
The three sails are made of 346 white, reinforced, precast concrete blocks (mean dimensions: 3x2x0.8 m), Figures 5 and 6. They are spherical, curving horizontally and vertically. a single stainless-steel formwork, adjustable on the ends only, was used for every block.
All the rows are post-tensioned vertically and horizontally with steel rods and cables so that the entire shell is in continuous compression.

3.1 Mix design of white HPC for the sails

For this application, Italcementi's R&D Department developed the white HPC for the project, including photocatalytic particles in the mixture which oxidize organic and inorganic atmospheric pollutants, so that the brightness and the colour will not degrade over time [18].

Figure 5. Construction of the Church (sails)

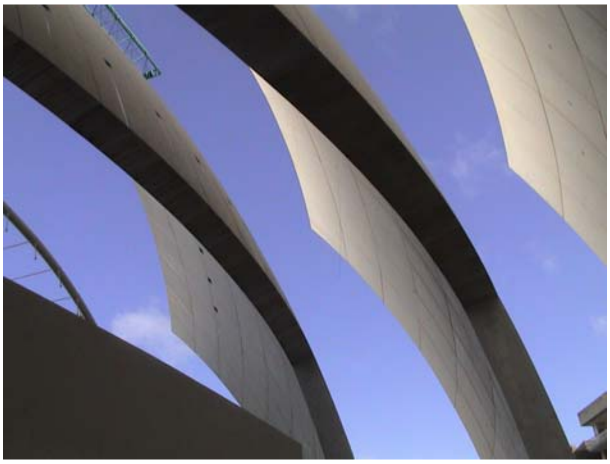

Figure 6. Church in Rome – Internal view

Thanks to the possibility of staying close to a w/b ratio of roughly 0.38 and to the double-admixture technique (compatibility agent + acrylic superplasticizer), the actual amount of white TX Millennium cement needed was quite low (380 kg/m^3) and the workability of the concrete was high. The compatibility agent increases substantially the action of the acrylic superplasticizer in order to maintain the workability of the fresh white concrete till about 60 minutes. As this structure had to be entirely white, a white Apuan marble aggregate was selected (from the Carrara area), consisting of a crushed metamorphic limestone with a fine grain, compact and uniform saccharoid structure. The maximum particle size was limited to 20 mm to ensure that the concrete would flow through the reinforcement and covers (40 mm) and at the same time to contain or at least greatly reduce surface defects (bug holes, gravel clusters, etc.) also linked to the elevated bulk of the aggregate due to the wall effect. A white metakaolin and an acrylic superplasticizer were also used.
Table 1 shows the typical composition of the white HPC utilized [18].

3.2 Physical and mechanical properties
The consistency class was S5, the mean volumic mass weight was 2430 kg/m^3.

Table 1. Mixture proportions

White cement TX Millenium	380 kg/m3;
White metakaolin (with special compatibilizing agent)	38.7 kg/m^3;
Aggregates: Crushed marble d_{max} = 20 mm	1850 kg/m^3;
Acrylic superplasticizer (solution, 30% dry extract)	10.5 kg/m^3;
Water	160 l/m^3

Table 2 below shows the varying compressive strength of the concrete at different stages in the curing process. Other mechanical properties are shown in Table 3.
Further information concerning hygrometric deformation (shrinkage), creep values, freeze-thaw behaviour and thermal behaviour are reported in [18, 25].

Table 2. Compressive strength, MPa

24 hours	35.0
30 hours	41.0
2 days	47.7
3 days	58.2
7 days	69.8
9 days	72.5
28 days	86.2
90 days	89.8

Table 3 – Other mechanical properties

Flexural strength, 7 days	7.0 MPa
Flexural strength, 28 days	10.4 MPa
Indirect tensile strength, 28 days	7.0 MPa
Dynamic elastic modulus, 28 days	44.6 GPa
Static elastic modulus, 28 days	41.0 GPa

4.0 CONCLUSIONS

Cementitious materials containing TiO_2 mainly in the form of anatase, when irradiate with adequate light, enhance the oxidation efficiency on organic substances with which they come into contact.
Building elements containing white cements to which TiO_2 has been added are capable of maintaining their aesthetic appearance unaltered in time.
With respect to the improvement in our living standard, we believe that a massive and continuous use of photocatalysts in construction materials can be a new way of contributing to minimizing the contaminants attacking the urban environment.
Many applications are possible, using white cement: dry pre-mix mortar for aesthetical and structural rehabilitation of deteriorated surfaces, cement-based paints, cladding and flooring, urban settings, art restoration and mortars for plasters and spray coatings.

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