AEROSIL®, AEROXIDE® and SIPERNAT® products for the construction materials industry

Technical Information 1398

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Contents

Introduction

One certainty demonstrated during recent times is that the construction industry lies at the very heart of economic life for the World Economy. When considering the various aspects of the industry: engineering, industrial, infrastructural, public, and domestic construction objects, one can see why the annual business volume of construction industry exceeds a thousand billions of Euros world-wide.

The variety of construction objects necessitates a huge number of materials for today's engineers from the simple and time tested, such as wood, stone and concrete, to those highly designed and of the latest technology, like plastics, alloys, and composites. Another aspect of construction engineering, however, is the reach back to some of the oldest materials in order to extend their properties and expand their capabilities to fabulous new limits. Concrete certainly is the focus of such recent engineering consideration.

Concrete, plaster and mortar are multi-component systems, which contain chemically reactive ingredients. The peculiarities of these chemical reactions determine the physical and chemical structure of these materials and influence their mechanical strength, pore structure, water permeability, durability, etc. and because silica (or silicon dioxide) plays a central role in the chemistry of concrete, plaster, and mortar, its nature has an overwhelming impact on the ultimate properties sought through construction engineering. For example, cured concrete can have different mechanical strength just by variation of the grain size of sand.

With its comprehensive portfolio of AEROSIL® fumed silica and AEROXIDE® fumed metal oxide grades as well as SIPERNAT® specialty silica, Evonik Industries offers new, powerful ingredients for modern construction design.

Areas of impact for AEROSIL®, AEROXIDE®, and SIPERNAT® products include:

- increase of early strength of concrete
- increase of consistency of ultra high-performance concrete
- improvement of mechanical strength for pore (gas) concrete
- reduction of bleeding and segregation in self-compacting concrete
- improvement of flow properties of powder premixes
- improvement of mechanical properties of plasters
- photo catalytic activity of surfaces
- reduction of dirt pick-up on the plaster and concrete surfaces

Properties of AEROSIL® fumed silica, SIPERNAT® specialty silica and AEROXIDE® titanium dioxide

AEROSIL® fumed silica is a highly pure, very fine type of silicon dioxide. The manufacturing process is based on the flame hydrolysis of silicon tetrachloride with overall chemical reaction:

$$SiCl_4 + 2\ H_2 + O_2 \rightarrow SiO_2 + 4\ HCl$$

Synthesis temperatures above 1000 °C and complex particle dynamics, which include processes of nucleation, coagulation, surface growth, sintering and aggregation, lead to fractal-like morphology of silicon dioxide – numerous approximately spherical primary particles are comprised in sub-micrometer sized aggregates. Separated from the gas flow by filtering, these aggregates build micrometer-sized agglomerates. All AEROSIL® fumed silica products are completely amorphous as shown by X-ray diffraction [1].

Besides its high chemical purity and amorphous structure, AEROSIL® fumed silica possesses unique morphology, which leads to numerous advantages in a variety of applications. High surface area without a significant amount of micropores results in: a high chemical reactivity for AEROSIL® fumed silica in the pozzolanic reaction, high rheological activity in wet mixtures, and high efficiency as an anti-caking agent in dry mixtures. All these properties are beneficial for use in concrete, mortar, and plaster.

The AEROSIL® process is also used in the manufacture of AEROXIDE® fumed titanium dioxide, leading again to an aggregated fractal-like particle structure. Unlike AEROSIL® however, AEROXIDE® titanium dioxide is a crystalline material (containing a majority anatase phase and the balance rutile).

Evonik Industries also offers the high function of AEROSIL® and AEROXIDE® powders in convenient dispersed form under the trade name: AERODISP®.

In contrast to AEROSIL® fumed silica, SIPERNAT® specialty silica grades are manufactured in a liquid-phase precipitation process [2]. Here a solution of sodium silicate (also called "water glass") is neutralized by sulfuric acid and as a result of the following chemical reaction, small particles of silicon dioxide are formed:

$$Na_2O \cdot 3.3\ SiO_2 + H_2SO_4 \rightarrow 3.3\ SiO_2 + Na_2SO_4 + H_2O$$

After washing, filtering, and drying steps, one obtains micrometer-sized aggregates of sponge-like structure, which are composed of tiny primary particles. Like AEROSIL® fumed silica, SIPERNAT® specialty silica has amorphous structure and high surface area.

The main chemical and physical properties of AEROSIL® fumed silica, AEROXIDE® fumed titanium dioxide and SIPERNAT® specialty silica grades that are commonly used in construction materials are listed in **Table 1**.

AEROSIL® and SIPERNAT® in concrete

The addition of even a small amount of AEROSIL® or SIPERNAT® products increases early strength of concrete. This effect can be explained by the high pozzolanic reactivity of these finely dispersed silicas. The pozzolanic reaction takes place in concrete between calcium hydroxide and silica or silicic acid in presence of water. This reaction leads to formation of calcium silicate hydrate:

$$\mathbf{Ca(OH)_2 + SiO_2 + 2H_2O \rightarrow Ca^{2+} + H_2SiO_4^{2-} + 2\,H_2O}$$
$$\mathbf{\rightarrow CaH_2SiO_4 \cdot 2\,H_2O}$$

The main reaction product – calcium silicate hydrate $CaH_2SiO_4 \cdot 2\,H_2O$ is usually abbreviated as C-S-H – has phases with a fibrous structure that mechanically bind together concrete components. Therefore, formation and concentration of C-S-H phases are decisive parameters for concrete strength. Since AEROSIL® or SIPERNAT® products offer much more surface than commonly used SiO_2 source such as sand, even small amounts of these materials can accelerate pozzolanic reaction significantly.

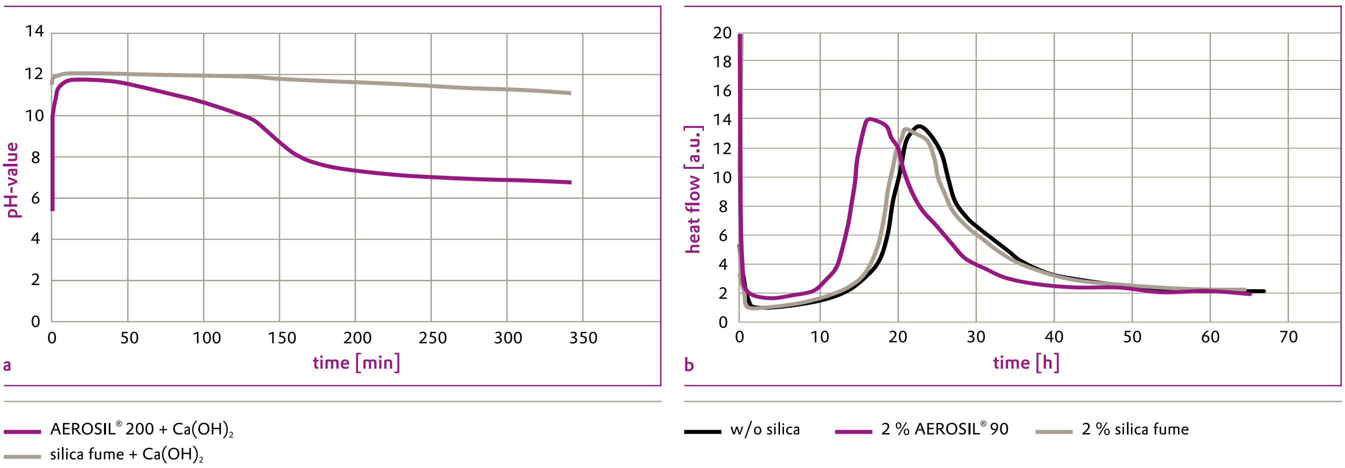
AEROSIL® fumed silica and SIPERNAT® specialty silica are not comparable with widely used silica fume, also known as microsilica. Silica fume consists of spherical non-aggregated particles with much lower specific surface areas of just several square meters per gram. Typically silica fume is added in high concentrations to cement to increase density and strength of cured concrete. In contrast to silica fume, AEROSIL® fumed silica has specific surface area of hundred square meters per gram and more. Due to the difference of specific surface area, pozzolanic reactivity of AEROSIL® fumed silica is much higher than of silica fume. This higher reactivity leads to higher early strength, but has no significant effect on the strength and density of cured concrete.

Figure 1a and **b** demonstrate the effect of increased pozzolanic reactivity of AEROSIL® fumed silica for two different AEROSIL® products – AEROSIL® 200 and AEROSIL® 90 (specific surface area of 200 m²/g and 90 m²/g, respectively). In these diagrams, the reactivity of AEROSIL® 200 and AEROSIL® 90 has been compared with the reactivity of silica fume. The pH-value in a mixture containing AEROSIL® 200 and calcium hydroxide changes much more rapidly than in mixture, containing the same amount of silica fume. The decay of pH-value is characteristic for reduction of concentration of calcium hydroxide, and is proportional to the building of C-S-H phases. The development of heat flow of different mortar mixtures is compared in **Figure 1b**. It is obviously, that addition of 2 % of AEROSIL® 90 accelerates heat release much more than addition of 2 % of silica fume.

The acceleration of C-S-H phase formation leads to the increase of early strength, as can be demonstrated in **Figure 2a**. The compressive strength of a CEM I 52.5 R based mortar is analyzed in dependency on time. As demonstrated in this figure, addition of 0.7 % of AEROSIL® 200 (of cement content) increases the compressive strength of concrete by approximately 5 MPa throughout the entire time interval studied. This effect can for instance be used for the acceleration of construction process in pre-cast plants.

Influence of AEROSIL® fumed silica on mechanical properties of concrete depends on concrete composition and, of course, on AEROSIL® fumed silica content, as demonstrated in **Figure 2b** on example of self-compacting concrete that was prepared with a cement compound, which included very fine cement. Both, compressive and flexural strength of self-compacting concrete increase by adding of AEROSIL® 200 into formulation, this increase has, however, a non-linear character.
A continuous increase of compressive and flexural strength is observed for concentration up to 2 %–2.5 % of AEROSIL® 200 (of cement content), further addition of AEROSIL® 200 leads to decrease of compressive and flexural strength. This non-linearity must be taken into account during formulation of concrete mixtures.

Figure 1 High pozzolanic activity of AEROSIL® fumed silica. Development of pH-value in SiO_2-$Ca(OH)_2$ mixtures with and without AEROSIL® fumed silica (a). Heat flow in mortar mixture in dependency on SiO_2 – with and without AEROSIL® fumed silica (b)

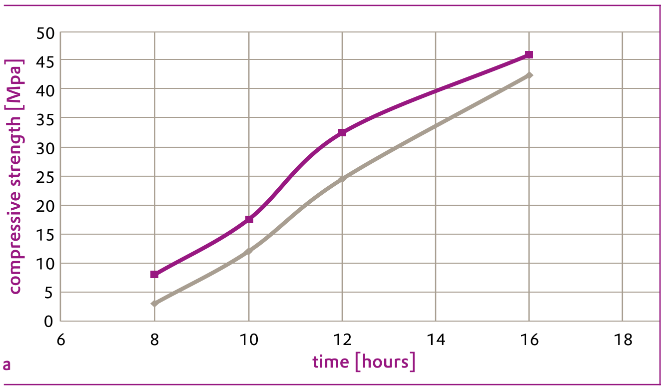


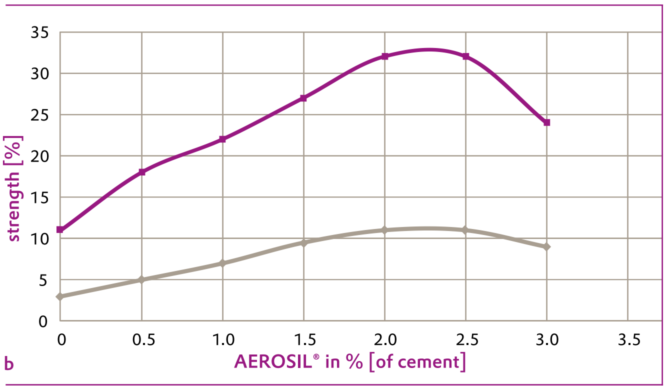
Reactivity and morphology of AEROSIL® fumed silica and SIPERNAT® specialty silica are beneficial for consistency of ultra-high performance concrete (UHPC). As demonstrated in [3], a consistant compressive strength of 150 MPa could be achieved after 28 days. UHPC is a high-density concrete, which has outstanding mechanical properties.

Gas (porous) concrete is just the opposite kind of concrete with respect to its density. The volume of artificial pores inside this kind of concrete is extremely high which leads to light weight and outstanding heat insulating properties. The insulating properties can further be improved by increasing porosity and adding AEROSIL® fumed silica to compensate for the loss of mechanical strength. Usually, 2 %–3 % of AEROSIL® 200 is sufficient to increase the compressive strength of cured gas concrete by factor of 2.

Although **Figigure 1** and **2** show results for different grades of AEROSIL® fumed silica, similar tendencies can be noticed for SIPERNAT® products like SIPERNAT® 22 S, SIPERNAT® 320 DS. The increased chemical reactivity does not just depend only on accessible reaction surface, but also on homogeneity of silica distribution in the mixture. Due to smaller aggregate size AEROSIL® products can be distributed in principle more homogeneously in the concrete mixture and consequently lead to higher early strength than SIPERNAT® specialty silica. However, AEROSIL® products require mixing equipment with higher shear energy what may make SIPERNAT® specialty silica the preferred choice if only low shear equipment is available.

Figure 2 Influence of AEROSIL® fumed silica on concrete strength. Development of the compressive strength of CEM I 52.5 R based mortar with the time (a). Influence of AEROSIL® fumed silica content on strength of self-compacting concrete (b)



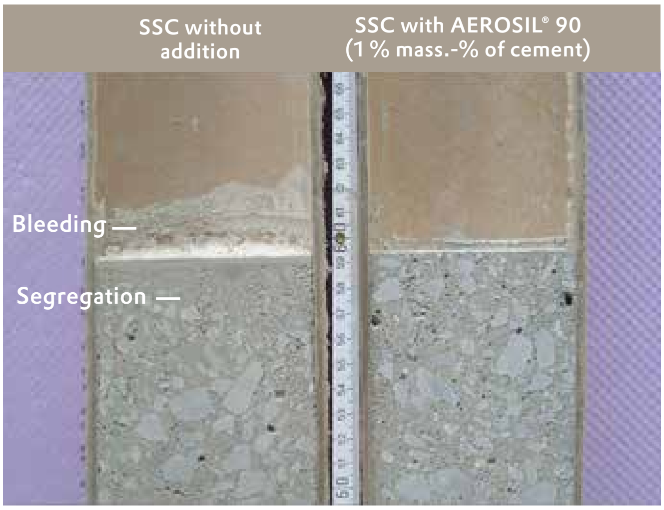


reference
with 0.7 % AEROSIL® 200 (by cement)

1 day flexural strength
1 day compressive strength

Addition of AEROSIL® fumed silica in concrete influences rheology of wet concrete strongly. It has a positive effect on homogeneity of component distribution within highly flowable concrete, such as self-compacting concrete (SCC). AEROSIL® fumed silica stabilizes SCC against sedimentation of coarse components during initial curing stages, it can reduce negative effects like "bleeding" (see **Figure 3**), etc.

Figure 3 Influence of AEROSIL® on concrete homogeneity



However, one should take into account, that use of AEROSIL® fumed silica grades with high specific area (AEROSIL® 200, AEROSIL® 300) increases the viscosity of wet concrete. If viscosity increase has to be limited, AEROSIL® grades with surface area about 100 m^2/g, for example, AEROSIL® 90 should be used.

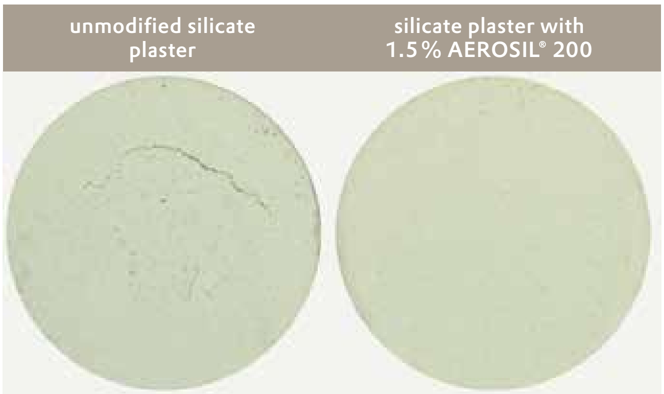
AEROSIL® and SIPERNAT® in plaster and mortar

Mortars and plasters are widely used in construction industry to protect constructions from environmental influence; they are used to "seal" construction joints, for repair of cracks, and for decorative reasons. Among their various technical requirements, durability and layer integrity are the most important. Formulators face the challenge of providing products that are optically attractive, mechanically & chemically stable while also retaining a precise degree of vapor permeability.

Plasters are multi-component system, which include binder, pigment, filler, and functional additives. Curing of such a multi-component systems is often accompanied by migration of filler and pigment particles through the volume of plaster; it is accompanied by volume change, by shrinkage, by transport of water and gases through the pores, etc. All these processes result in gradients of forces, which can cause mechanical deformation, in homogeneities and cracks. If concentration of these defects is large enough, it can lead to failures of plaster after short time, it can necessitate repair and cause unexpected expenses.

Due to aggregate structure and size, AEROSIL® fumed silica can act as stabilizing and reinforcing agent during plaster curing, it can help to achieve a homogeneous pore structure, which is much more stable with respect to shrinkage during plaster curing. **Figure 4** demonstrates this kind of influence of AEROSIL® fumed silica on silicate plaster.

Figure 4 Influence of AEROSIL® on plaster structure

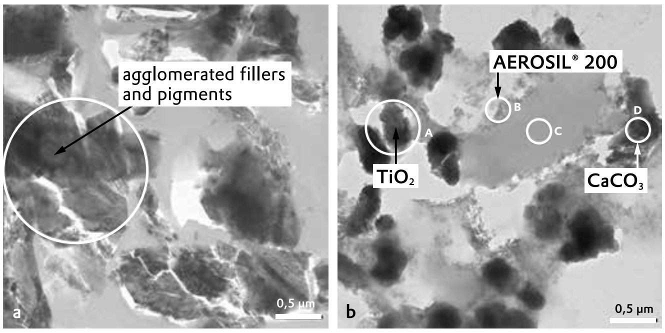


The formulation without AEROSIL® 200 has comparably rough surface with macroscopic cracks. Being exposed to atmospheric humidity, to rain and snow, these cracks will definitely be centers for penetration into volume of cured plaster, they will increase with time and become the reason for material failure and increased dirt pick-up. The same plaster formulation enriched with only 1.5 % of AEROSIL® 200 shows completely different surface structure. It is smoother, no macroscopic cracks can be observed.

Study of these plasters by means of transmission electron microscopy (TEM) shows, that AEROSIL® fumed silica improves distribution of filler ($CaCO_3$) and pigment (TiO_2) particles.

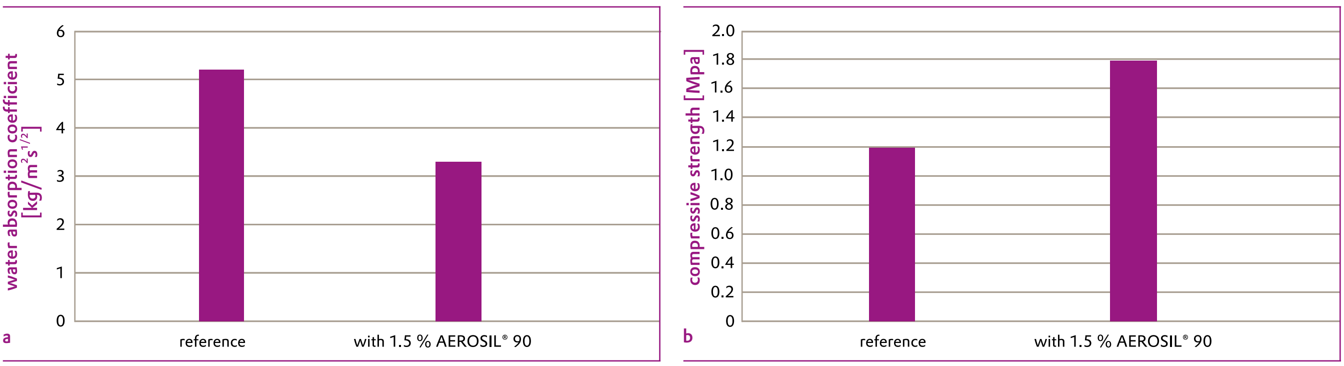
In the reference plaster without fumed silica addition, large agglomerates of filler and pigments can be observed (**Figure 5a**). In contrary to this, in the plaster with AEROSIL® 200 additions (**Figure 5b**), filler particles are finely dispersed, even though pigment and filler are the same in both formulations.

Figure 5 Influence of AEROSIL® on plaster structure (5a: **no addition**, 5b: 1.5 % of AEROSIL® 200). Large area **C** in right micrograph is carbon film from TEM grid



Moreover, influence on pore structure by addition of AEROSIL® fumed silica has positive influence on mechanical properties of lime mortar, as can be seen in **Figure 6b**. Here is shown, that addition of 1.5 % of AEROSIL® 90 to lime mortar improves the compressive strength up to 50 %. The same time, the water absorption coefficient reduces by approximately 50 % (**Figure 6a**). Both, reduction of water absorption and increase of compressive strength are definitely beneficial for long-levity of applied lime mortar.

Figure 6 Influence of AEROSIL® on lime mortar properties. Water absorption coefficient (a); compressive strength (b)



AEROSIL® and SIPERNAT® products can be used not only for improvement of mechanical properties such as early strength, but also for improvement of handling properties of dry mixtures such as dry mortar. For this reason, AEROSIL® and SIPERNAT® products are already widely used as anti-caking agents in different industries. Small particle size and high surface area makes these products act as efficient spacers and humidity adsorbents in powder mixtures. It reduces the overall particle interaction in a powder mixture, which results in better flowability. This ability to reduce particle interaction within such mixtures makes AEROSIL® and SIPERNAT® efficient milling additives. A detailed description of use of AEROSIL® fumed silica and SIPERNAT® specialty silica in powder mixtures can be found in our Technical Information brochures [4], [5].

Use of AEROXIDE® titanium dioxide for photo catalytic applications in the construction industry

With the continuous growth of urban population centers throughout the world, a significant burden on air quality has been widely recognized. It has also been widely recognized that with this environmental pressure the critical technical challenge for the coming decades will be to develop technologies that reduce air-borne pollutants such as nitrogen oxides (NO_x) that are at the heart of smog generation in many of today's cities. One highly attractive technical approach harnesses the energy of the sun to affect the break down of NO_x and is reliant on photo catalytic materials such as AEROXIDE® titanium dioxide. By using photo catalytically active titanium dioxide AEROXIDE® TiO_2 in construction materials, such as concrete, paving stones, and facade coatings a multi-functional surface can be created that mediates the conversion of pollutants to less harmful compounds.

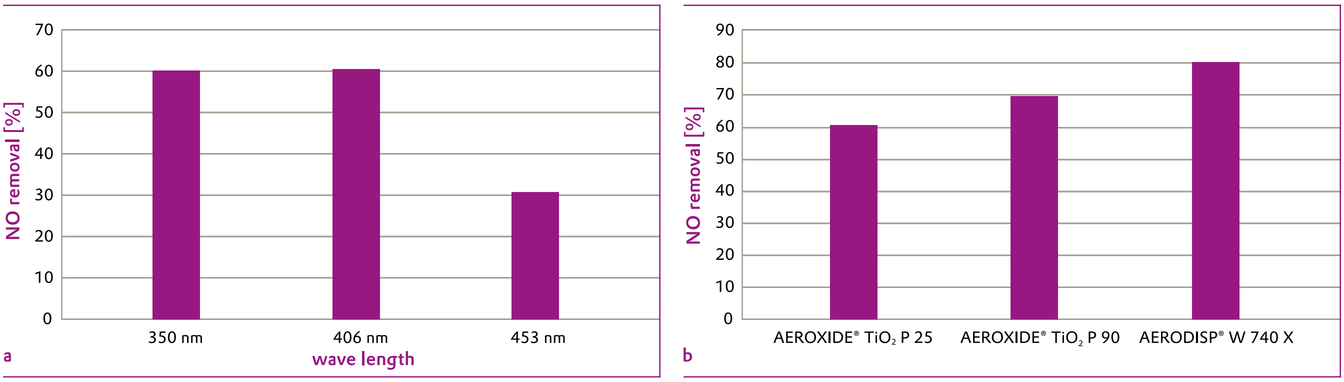
Evonik offers two outstanding titanium dioxide products—AEROXIDE® TiO_2 P 25 and AEROXIDE® TiO_2 P 90 and their water-based dispersions AERODISP® W 740 X and VP Disp. W 2730 X exactly for these applications [6]. Due to high surface area and, consequently, small primary particle size, AEROXIDE® TiO_2 P 25 and AEROXIDE® TiO_2 P 90 have high photo catalytic activity, high chemical reactivity, and nearly no pigment properties—a combination of characteristics that distinguish these titanium dioxides from all others on the market.

To demonstrate the photo catalysis of these materials, three LEDs with different wavelengths and narrow line widths were used to irradiate the surface of AEROXIDE® TiO_2 P 25 under a gas flow with constant NO concentration. As can be seen in **Figure 7a**, the concentration of nitrogen monoxide reduces significantly at all irradiation wave length studied.

The comparison of NO-removal efficiency of AEROXIDE® TiO_2 P 25 and AEROXIDE® TiO_2 P 90 is presented in **Figure 7b**. This comparison, carried out at a visible wavelength of 406 nm, shows the increased activity of AEROXIDE® TiO_2 P 90 versus that for AEROXIDE® TiO_2 P 25. It is likely that the greater activity is due to the higher specific and, consequently, reaction area of AEROXIDE® TiO_2 P 90. Lastly, the substrate treated with AERODISP® W 740 X shows a significantly higher efficiency of NO-removal than AEROXIDE® TiO_2 P 25 and even AEROXIDE® TiO_2 P 90, again most likely due to the ideal particle size, and thereby reactive surface, available from the pre-made dispersion.

These results represent a basis for photo catalytic application of titanium dioxide in construction – as surface treatments for pavement stones, concrete walls, or roofing tiles. When developing such a pollution combating surface, the thickness of the AEROXIDE® TiO_2 layer should be just sufficient to withstand the mechanical influences, erosion, several millimetres will be definitely enough. Generally, a few percent of titanium dioxide in the coating layer is sufficient to achieve significant removal of nitrogen oxides. Particular note should be drawn to AERODISP® W 740 X as it can be easily incorporated into wet concrete mixture without the need for any special dispersing equipment. This is not the case with the powders, AEROXIDE® TiO_2 P 25 or AEROXIDE® TiO_2 P 90, where high-shear mixing and proper dispersion is required in order to achieve maximum performance.

Figure 7 Efficiency of photo catalytic removal of NO by AEROXIDE® TiO_2 products.
(a) NO removal by AEROXIDE® TiO_2 P 25 at different wave lengths. (b) NO removal by different AEROXIDE® TiO_2 products at 406 nm



Conclusions

This brochure gives a brief overview on effects in construction materials, which can be achieved by use of AEROSIL® fumed silica, SIPERNAT® specialty silica, and AEROXIDE® fumed titanium dioxide. Unique morphology (particle size, phase composition) makes these products to versatile functional additives, which can be used to improve mechanical properties of concrete, plaster and mortar, their handling properties, their long-levity. A range of special environmentally relevant effects can be achieved by use of photo catalytically active AEROXIDE® TiO_2 fumed titanium dioxide. Recommendations on use of silica or titanium dioxide in construction materials according to the desired effect are summarised in **Table 2**.

Table 1 Properties of selected grades of AEROSIL® fumed silica, AEROXIDE® fumed titanium dioxide and SIPERNAT® specialty silica that are commonly used in construction materials

Product name	interaction with water	BET [m^2/g]	Loss on drying [%]	pH-value
AEROSIL® 90	hydrophilic	90	< 1.0	3.7–4.7[1]
AEROSIL® 200	hydrophilic	200	< 1.5	3.7–4.7[1]
AEROSIL® R 972	hydrophobic	110	< 0.5	3.6–5.5[1]
AEROXIDE® TiO_2 P 25	hydrophilic	50	< 1.5	3.5–4.5[1]
AEROXIDE® TiO_2 P 90	hydrophilic	90	< 4.0	3.2–4.5[1]
SIPERNAT® 22 S	hydrophilic	190	< 6.0	6.5[2]
SIPERNAT® 320 DS	hydrophilic	175	< 6.0	6.3[2]

[1] Based on 4 % dispersion
[2] Based on 5 % dispersion

Table 2 Recommendations on use AEROSIL®, SIPERNAT®, and AEROXIDE® products

Application	Recommended products
Concrete: improvement of early strength	AEROSIL® 200, AEROSIL® 90 AERODISP® W 7520 P SIPERNAT® 22 S, SIPERNAT® 320 DS
Concrete: consistency of UHPC	AEROSIL® 90 SIPERNAT® 320 DS
Concrete: improve of SCC homogeneity	AEROSIL® 200 AEROSIL® 90
Concrete: air cleaning	AEROXIDE® TiO_2 P 25, AEROXIDE® TiO_2 P 90 AERODISP® W 740 X
Concrete: self-cleaning /low dirt pick-up	AEROXIDE® TiO_2 P 25 AERODISP® W 740 X
Dry cement-based mixture: anti-caking	AEROSIL® 200, AEROSIL® 90, AEROSIL® R 972 SIPERNAT® 22 S
Silicate plaster: reinforcement, low dirt pick-up	AEROSIL® 200 AERODISP® W 7520 P
Plaster: self-cleaning /low dirt pick-up	AEROSIL® 200 AERODISP® W 7520 P AEROXIDE® TiO_2 P 25 AERODISP® W 740 X
Lime mortar: reinforcement	AEROSIL® 200 SIPERNAT® 22 S, SIPERNAT® 350
Dry mortar: anti-caking	AEROSIL® 200, AEROSIL® R 972 SIPERNAT® 22 S

Literature

[1] TB 11 Fine Particles; AEROSIL® Fumed Silica
[2] Specialty Silica – Overview Brochure
[3] Final report public founded project: Nanotechnologisch optimierter, langlebiger, energieeffizienter und insbesondere anwendungsfreundlicher Hochleistungsbeton, BMBF, 2012
[4] TI 1351: SIPERNAT® specialty silica and AEROSIL® fumed silica as flow aid and anticaking agent
[5] TI 1360: SIPERNAT® and AEROSIL® – an Essential in Industrial Powder Technology
[6] TI 1243: AEROXIDE®, AERODISP® and AEROPERL® Titanium Dioxide as Photocatalyst

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