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Volume 1

Keynote speaker session

Hydration of Portland cement

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Abstract - The latest thinking on the mechanisms of hydration is outlined.

Keywords: Hydration, induction period, main hydration peak, C-S-H.

1. Introduction

The resources of the earth mean that almost all cement will continue to be based on Portland cement clinker. The most realistic way to continue to reduce environmental impact is to replace part of this clinker by supplementary cementitious materials. Nevertheless, the early properties are dominated by the hydration of the Portland clinker component.

- The hydrations reactions can be broken down into three stages:
- Up to the end of the induction period;
- The main hydration peak;
- Later hydration after the main peak.

2. Up to the end of the induction period

Initially cement reacts rapidly and then after only a few minutes the reaction slows to a low rate: the so called “induction period”, lasting a few hours. This pattern of reaction is very important from a practical standpoint as it gives time from concrete to be mixed and transported to site. For many years the most widely believed hypothesis for this initial slow down and the induction period was the formation of a layer of hydrates around the cement grains which inhibited further reaction. Work over the past few years has shown that this is certainly incorrect.

Instead the induction period can be simply attributed to the build up of ions in solution which lower the undersaturation. It is well known from studies in geochemistry that minerals show a similar behaviour. When they first come into contact with water the undersaturation is very high and this provides the energy to increase the surface area with dissolution at many sites and formation of a rough surface. As dissolution proceeds the undersaturation decreases and so the energy to form new surfaces, progressively dissolution becomes localised at defects. Then there is a dramatic fall in dissolution rate which corresponds to a switch to dissolution only at steps. This fall in dissolution rate may occur when the solution is still many orders of magnitude more dilute than saturation. Experiments with alite immersed in water and then in saturated lime solution [1] demonstrate that this transition also occurs for alite and can explain the rapid fall in reaction rate and the onset of the induction period. The hypothesis has been well validated by theory [1], experiment [2] and modelling [3]. Furthermore, unlike the inhibiting membrane hypothesis, it can explain all experimental observations.

Calcium silicate hydrate precipitates very soon after the addition of water. This C-S-H has a much lower Ca/Si ratio than alite and so the Ca/Si ratio of the solution increases during the induction period

During the induction period reaction continues at a slow rate. Eventually the precipitation of calcium hydroxide occurs. This leads to an increase in the undersaturation and so to an increase in the rate of dissolution. Changes may also occur in the C-S-H precipitates which lead to the onset of rapid growth of both C-S-H and CH.

3. Main hydration peak

The main hydration peak is characterised by the rapid growth of C-S-H and CH. Most C-S-H grows from the surface of the cement grains, but will also take place on other surfaces, such as SCMs. CH growth is concentrated in the pore space. During this period there is first an acceleration in the rate of reaction and then a deceleration, such that the reaction has again dropped to a low rate by the end of the first day (at 20°C). The two main mechanisms proposed to explain this pattern of reaction have been impingement of hydration products or onset of diffusion control through a layer of hydrates. Careful quantitative study of the reaction kinetics through experiment and modelling have clearly shown both these hypotheses are wrong. At the maximum of the peak, the amount of hydrates formed is much less than that needed for impingement to be the factor slowing down hydration. There are also many arguments against diffusion through a hydrate layer being the mechanism:

- It does not fit quantitative models;
- there is no “layer” – in places the alite surface is still visible
- there is a gap between the grain and hydrate shell
- there is no change in activation energy.

Study of a large number of parameters (particle size, water to cement ratio and ion doping) clearly indicates that the kinetics in this period are controlled by the growth of C-S-H needles. This “needle” hypothesis has been demonstrated to well match the experimental data, with no fitting – taking its parameters only from experimental observations.

4. After the main hydration peak

Unfortunately, this period has received far less attention than the previous two periods. Despite the fact that at one day the degree of reaction is around 50% and the mechanical strength around 25% of its final value. Another month is needed to reach around 80% hydration and 80% of mechanical strength. Careful study of the cumulative heat of hydration [4] clearly indicates that the amount of space available plays a critical role. After a few days it is observed by ¹H NMR relaxation and by MIP that the water filled pores decrease to a certain critical size and then do not decrease further. This suggests that after this point the pores are too small to allow classical crystal growth. At the point when this limiting pore size is reached not only does the rate of the clinker reaction slow dramatically, but also the reaction rate of SCMs such as slag and calcined clay. In systems with additions of calcined clay and limestone it is also seen that the carboaluminate phases no longer form and alumina from the continuing reaction of the calcined clay goes into the C-S-H phase instead.

After this limiting critical pore size is reached, the rate of reaction, again slows dramatically, but does continue. The mechanisms controlling reaction at this stage are far from clear, but probably involve densification of the C-S-H phase.

4.1 Why do we get a gap between the hydrating cement grain and the hydrate shell

It has long been a mystery as to why a gap opens up between the shell of hydrates (mainly C-S-H) formed during the main hydration peak. From our present understanding of the hydration mechanisms it now

appears that this is a consequence of the growth rates of outer and inner C-S-H. During the main hydration peak, the growth rate of the C-S-H needles is rapid and it is favourable for growth to occur on the outer surface of the hydrate shell. As the rate of growth of the outer C-S-H slows down it becomes similar to the rate of growth of inner C-S-H so it becomes equally favourable for growth to occur on the grain surface and at the ends of the needles. Gradually the gap fills in of about a week. Thereafter the growth of the outer and inner product is closely linked a growth of outer product is needed to allow more dissolution of the anhydrous grain and so more space for inner product.

5. Outstanding Questions

Despite the considerable progress in understanding hydration mechanisms in recent year, many questions remain. Most of these concern growth of C-S-H:

- Why is it slow during the induction period and is the increase in rate at the end of the induction period only linked to the precipitation of calcium hydroxide or is there also some structural change which facilitates growth?
- Why to the needles grow rapidly to a certain length and then their growth rate slows dramatically?
- What are the changes occurring after the limiting pore size is reached?

More knowledge about C-S-H growth is important to increase the efficiency of the hydration of Portland cement which would facilitate greater levels of clinker substitution and further reduction of its environmental footprint.

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Application of new concrete processes and materials

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Abstract

In this talk, the application of new process and materials to produce high modulus concrete and high bending resistance cement-based composites will be introduced. Along this line, the ultrasonic technique has been adopted in concrete mixing to improve the interface density for high modulus concrete development. The high modulus concrete developed through the ultrasonic vibration and addition of nano particles will be introduced on its optimization in materials formulation, dimension stability behavior and structural performance. Moreover, 3D printing process has been applied to produce sophisticated cement-based architectural and decoration products. The application of both selective reaction and direct deposition techniques will be introduced.

Recently, it becomes popular to achieve enhanced mechanical properties of cement-based materials through incorporation of nano particles. In this presentation, advanced cement-based materials through application of nanotechnology will be introduced. One example is to use cement to generate 5 nm nanoparticles which is utilized to enhance the mechanical properties of hydrogel. By adding 5-nm inorganic particles in organic matrix, hydrogels with the best all-round performance in the world has been successfully developed in aspects of strength, elastic recovery and ultimate stretch ratio. In addition, by adding organic or inorganic nano particles into cement based materials, the flexural strength of the cement-based materials increased significantly. For cement paste, bending strength is increased by three times without lowering the compressive strength. Finally, newly developed inorganic-organic integrated nano particles for lowering hydration heat will be explained on their mechanism and effect.

Performance of SCMs – Chemical and Physical Principles

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Abstract

The influence of supplementary cementing materials (SCMs) on the hydration and durability of blended cement has been evaluated using chemical and physical principles. Similarities and differences between various SCMs have been considered grouping them into latent hydraulic or pozzolanic with sub-division into siliceous, aluminous, carbonaceous etc. Synergy between SCMs producing calcium aluminate hydrate and calcium carbonate maximize water binding leading to reduced porosity and increased strength by forming calcium monocarboaluminate hydrate. Any magnesium content in the carbonate leads to hydrotalcite formation in the presence of aluminates.

The interaction of SCMs with plasticizers and use of hydration accelerators are also treated.

The influence of SCMs on durability issues like chloride ingress, carbonation, alkali aggregate reactions, sulphate resistance and freeze-thaw resistance is discussed as well. Generally speaking SCMs improve the resistance of blended cements to most degradation mechanisms at equal w/c, except for carbonation resistance that can be improved by reducing w/c.

Keywords: Supplementary cementing material, hydration, durability, microstructure, porosity.

The unabridged version of this article can be found in Volume 2 - New cementitious binder, page 2.

On the setting and hardening control of alkali-activated slag cements

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Abstract

Sodium silicate activated slag often gives high early strength but sets too rapid. Commercial retarders for Portland cement and replacement with other cementing components have been proven little effective. This study investigated the approach of controlling setting by alter activator ion composition and silica polymer status. The roles of activators during the alkali-activation process were studied via pore solution chemistry analysis and microstructural analysis of hydration products. The addition of Na_2CO_3 does not, but NaOH does alter the polymerization of silicate ion groups in sodium silicate solution due to the increase in pH and Na_2O concentration. The specific effect of Na_2CO_3 on the setting of alkali-activated slag depends on the relatively contents of NaOH and $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ in alkaline solution. The reaction degree of AAS is dependent on activator composition, which governs the kinetics of formation and intrinsic characteristics of the hydration product calcium aluminosilicate hydrate. The setting and strength development of sodium silicate-activated slag can be controlled by manipulating the composition of Na_2CO_3 - NaOH - $\text{Na}_2\text{O}\cdot n\text{SiO}_2$.

Biobased building materials

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Abstract

Construction industries are expanding worldwide, and so does demand for building materials and resources as a result. With a share of 36% of CO₂ emissions in EU, the construction sector contributes significantly to greenhouse gas emissions. The industry must therefore play a key role in the EU policy targets for a low carbon economy by 2050. Energy saving in the production of building materials and increased thermal insulation of buildings does not suffice for the transition. Therefore shift towards more CO₂ neutral resources will be needed and the options for circular and bioeconomic solutions were explored in the building and construction industry. A focus of R&D and innovations is on the increased use of renewable and recyclable raw materials. Besides the use of traditional timber and wood derived materials, fibre crops such as flax and hemp play a key role in this regard. Polymer and mineral composite materials can be produced with these lignocellulosic fibres. Composites based on bioresins and bioplastics are tested at lab and applied in demonstration building projects. For biobased materials an environmentally safe protection against decay is important for extension of the durability. The use of various other natural biopolymer derived components with anti-microbial properties or uv protection properties are explored in coatings and adhesives. Other innovations in the building and construction sector that are aimed at reducing the ecological impact include the design of light weight constructions, tiny houses and reusable elements. An overview of the current state of the art and new trends for green and circular building will be presented.

Keywords: biobased products, lignocellulose, CO₂ neutral, circular building

Techniques for analyzing microstructures

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Abstract

Microscope examination is classical and the easiest way for understanding and explaining microstructure. Looking back on its history, there was a pioneering work by Scrivener and Platt as a milestone in cement microscopy. Their work using BSE image analysis had introduced a new perspective of quantification into evaluation for microstructure. Then the development of IT and AV utilization has achieved the sophistication of image analysis. Nowadays, image analysis for microstructure is a quite common tool for not only research fields but also practical evaluations of concrete structures. In this presentation, image analysis techniques for microstructure in concrete is briefly reviewed with a focus on what we've been evaluating. Furthermore, a new direction which is aiming at an evaluation of spatial structure, not a simple quantity is also introduced. A quantity of a phase of interest is simply evaluated through a binary segmentation and tallying pixels. Once a threshold value for the segmentation is determined, quantification of a phase is instantaneously done with image analysis software. Thresholding is generally based on grayscale values in images. These days, various types of images are used in image analysis. For example, pseudo-color images of EPMA mapping for an element is used for evaluating supplementary cementitious materials. The background of this process is the fundamental stereology, Delesse's rule ($A_A = V_V$). Combining the evaluated quantity with simple cement chemistry or kinetics model such as the Powers model, capillary pore structure that is the most important in determining properties of concrete is evaluated with regard to volume changes in the hydration of cement. However, it should be noted that whether the presence of finer pores smaller than the resolution is ignored or taken into account affects the interpretation of microstructure and relevant properties in concrete.

Another important approach to the analysis of microstructure is to evaluate spatial distribution, not a quantity. In the early stage of the image analysis from the 80s to 90s, it was difficult to evaluate it in the complicated and inhomogeneous microstructure. Nowadays, spatial statistics functions have been actively introduced into random heterogeneous microstructure like concrete. This trend is greatly attributable to the availability of reliable software. Some are downloadable as free software. For example, densification of concrete microstructure with time is well known as a decrease in porosity. However, using those functions, the evolution of pore structure is understood as changes in spatial structure, which includes not only the porosity but also continuity and connectedness of pores. In particular importance, this evaluation of structure gives characteristic length parameters that are significant in the interpretation of many transport phenomena in concrete. For example, to discuss durability such as permeability or frost resistance of concrete, depth from a surface or spacing between air bubbles are key issues. Some approaches to these issues using the spatial statistics functions are described. They lead to future research of simulation of 3D microstructure in concrete.

Keywords: image analysis, stereology, spatial statistics, second-order function

Natural and artificial Pozzolanes - Industrial residues and natural supplementary materials

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Due to the necessary reduction of CO₂ during the production of cement clinkers several possibilities exist to reduce the contents of volatile gases during the different production stages. As the amount of industrial residues is not sufficient for producing all type of composite cements other natural and artificial mineral products may be applied. The different strategies for CO₂-reduction producing cementitious materials can be summarized :

- Replacement of cement clinker by addition of different other raw materials to produce
- composite cements
- Replacement of limestone by CO₂-free natural/industrial raw materials
- Increase of reactivity of clinker minerals leads to a reduced amount of cement materials in
- cement application
- Reductions in process conditions (reduced temperatures, other phases, mineralizers,
- grinding aids, the total efficiency of processes)
- Clinker minerals with reduced CO₂-output-different compositions
- Activation of slowly reacting cements by introducing highly reactive clinker minerals
- Production of clinker minerals with increased specific surface and increased reactivity
- Activation of clinker minerals
- Cement clinkering using mineralizers
- Hydration reaction replaced by the carbonation process

Therefore different materials coming from natural and artificial sources are used in these strategies. Different origins of the materials result in many varying compositions. Many different industrial residues and natural materials can be used under this aspect to produce composite cements. In this context the focus lies on the usage of industrial residues (fly ashes, slags, thermally optimized mineral mixtures, leaching residues, plant ashes) and also natural sources with volcanic or sedimentary origin (pyroclastics, altered and weathered rocks, altered clays, clastic rocks). The use of calcium-poor chemical compositions of pozzolans can lead to a substantial reduction of CO₂, despite combined with excellent qualities of these cementitious materials. Different materials, qualities and measurement methods combined with essential details of the varying compositions of these different materials will be given.

As the supply from industrial residues is not sufficient, also natural products like volcanic ashes and thermally pre-treated clay materials are discussed.

Keywords: pozzolane, industrial residue, CO₂-reduction, supplementary material, cement

Use of Supplementary Cementitious Materials to Manufacture High Performance Concrete

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Abstract - Supplementary cementitious materials (SCMs) are very valuable and indispensable for the manufacture of high performance concrete. Use of SCM is necessary for the recycle of solid waste and to produce green and sustainable concrete. The using situation of CSMs in China is shortly reviewed. Fly ash and ground granule blast furnace slag are the most important mineral admixture in Chinese cement and concrete industry. Silica fume is used only for high strength concrete. New kinds of mineral admixture from metallurgical slag is now explored. 20%-40% of binder is SCM in ready-mix concrete for both normal and high strength classes. Even higher dosage of SCM is used to prepare massive concrete or the concrete with high durability. The properties of complex binder containing different kinds and different dosage of mineral admixture are evaluated. Some examples are given to show the performance of high volume mineral admixture concrete and how to use it in the building construction.

Keywords: Supplementary cementitious material; high performance concrete; high volume mineral admixture concrete; fly ash; ground granule blast furnace slag

Bio-based admixtures

W. Schmidt

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Abstract

Due to the high carbon emissions linked to concrete production and a rapidly increasing demand for cementitious materials, particularly in the global South, it is inevitable to use cement in concrete more efficiently. This can be achieved best by minimising the Portland cement content in the binder and by developing concrete mixtures with low water to cement ratios. For both approaches, chemical admixtures are required to cope with the negative rheological influences of supplementary cementitious materials that are often observed, and the higher solid volume fraction, respectively.

However, particularly in the growing economies of the Southern hemisphere, where a massive part of the future construction activities will take place, the supply chains are often poor with regard to performance enhancing chemical admixtures, and local production facilities are lacking today. This paper presents case studies of polysaccharide based alternative admixtures such as acacia gum, cassava starch and the gum of the bark of *Triumfetta pendrata* A. Rich, which can be used effectively as superplasticizer, robustness enhancer, and thixotropy incorporating agent, respectively. Their modes of operation are discussed based on their zeta potentials and hydrodynamic diameters in the presence of calcium ions. Eventually, local value chains are discussed for bio-based by products on the example of cassava peels wastes.

Keywords: admixtures, concrete, cassava, acacia gum, *Triumfetta pendrata* A. Rich.

The unabridged version of this article can be found in Volume 5 - Biogenic and functionalized materials, page 2.

Cementitious materials for marine structures

Z. Shui

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Keywords: Please insert a maximum of 5 keywords.

Abstract - With the continuous exploitation of the ocean, the scale of infrastructure construction in the marine environment is experiencing a booming increase. Concrete is the main material for marine infrastructure construction due to its high reliability and low cost. However, in such an environment rich in aggressive components such as chloride, sulfate and magnesium ions, the concrete structures suffer a faster damaging than that in the mainland. Concerning that, it is of great significance to investigate the damage behaviors and relevant mechanisms of concrete structure in the marine environment and provide some effective methods to prolong the service life of the concrete. In recent years, the research group of the reporter devoted to studying the damage of concrete in the marine environment. Some of the research findings are reported here for concrete serving in the marine environment including several aspects:

1. Performance and microstructure degradation

To obtain reliable information on the long-term behaviors of concrete under real marine conditions, this part aims to identify the mechanisms of degradation in Portland cement mortar exposed to simulated seawater attack under drying-wetting cycle conditions. Hardened mortar mixtures with different supplementary cementitious materials (SCMs) are exposed to NaCl, NaCl+MgCl₂, NaCl+Na₂SO₄ and NaCl+Na₂SO₄+MgCl₂ solutions with a fixed chloride concentration. The results show that the degradation process of mortar samples in single and composite solution coupled with drying-wetting includes three stages, 1) performance enhancement stage; 2) stable stage and 3) performance deterioration stage. The samples exposed to the NaCl+Na₂SO₄ solutions show higher mass and dynamic modulus of elasticity changes compared to the single NaCl solution, and the NaCl+Na₂SO₄+MgCl₂ solution reveals severe performance degradation. The phase composition highlights that the presence of SO₄²⁻+Mg²⁺ in chloride environment increases consumption of portlandite at the surface and causes the decalcification of C-S-H, thus aggravates the degradations of mortar. Microstructure analysis shows that the presence of SO₄²⁻ in chloride solution changes the pore structure and results in an increase of porosity. The SO₄²⁻+Mg²⁺ in chloride environment further increases the harmful pore volume, which accelerates the ingress of corrosive ions in the mortar matrix. The ability to resistance aggressive solution attack can be significantly improved with the utilization of SCMs.

2. Chloride binding and hydration product conversion

Chloride binding is considered to be a process that can restrain the free chloride diffusion and therefore benefit the chloride corrosion resistance of the concrete structure. This part is aimed to identify the key factors affecting the chloride binding capacity of cement-based materials. Several cementing systems including, mineral admixture (MA)-Portland cement, MA-C₃S and MA-lime system are employed here.

The MA used here are pozzolanic materials (FA, MK, SG) and aluminum compounds (Al_2O_3 , $\text{Al}(\text{OH})_3$, AOOH). Sodium chloride is added in either exposure solution or mixing water. Results show alumina-rich pozzolans (ARP) can improve the chloride binding capacity of cement-based materials and MK performs the best. For a give ARP, chloride binding capacity is depended on the incorporation level, and the optimal chloride binding capacity is achieved at $\text{CaO}/\text{Al}_2\text{O}_3$ ratio between 3 and 6. For a given $\text{CaO}/\text{Al}_2\text{O}_3$ of the system, the chloride binding capacity decreases with the increase of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. That means the potential of ARP to improve the chloride binding capacity of cementitious materials can be limited by the high amount of amorphous silica in ARP. The silicate in cementitious materials restrains chloride binding due to two negative effects: 1) dilute the total mass of $\text{CaO}+\text{Al}_2\text{O}_3$; 2) its hydration reduces the portlandite available for chloroaluminate formation. As for aluminum compounds, very higher potential to improve chloride binding capacity of cement-based materials is observed due to no silica contained in aluminum compound, therefore more portlandite can be involve in the formation of chloroaluminate.

Chloroaluminate in hardened samples exposed to sodium chloride is mainly formed from other AFm phases such as carboaluminate, stratlingite and monosulfoaluminate and OH-AFm. The transformation of these phases to chloroaluminate can improve the alkali in pore solution, reduce portlandite and increase chemically bound water in matrix. Besides, chloride exposure also promotes delayed ettringite formation in hardened cement, because the sulfates in monosulfoaluminate are replaced by chlorides and the released sulfates react with monosulfoaluminate to form delayed ettringite in return. In the presence of admixed chloride, the reaction of calcite is restrained. When sulfates are coupled with chlorides in mixing water, the chloride binding capacity is reduced because sulfates can compete with chloride to insert into the interlayer of AFm. During carbonation, the chloride previously bound in chloroaluminate can reverse to free chloride. This indicates that, for the concrete contaminated with chloride, the carbonation of matrix results in the neutralization of pore solution as well as improvement of free chloride solution, which can be expected to significantly accelerate steel corrosion.

3. Chloride diffusion behavior

The chloride diffusion induced reinforcement corrosion seriously threatens the durability of concrete construction in the marine environment. This part investigates the effects of sulfate and magnesium ion in simulated seawater on the chloride diffusion behavior of Portland cement mortar with continuous full immersion and drying-wetting cycle. Results indicate that the samples exposed to $\text{NaCl} + \text{MgCl}_2$ solutions show the highest chloride content at the outmost layer (0–5 mm). The presence of SO_4^{2-} in the composite solution decreases the chloride ingress and reduces the apparent chloride diffusion coefficient at 60 days of exposure, while the opposition is observed at later exposure period. The $\text{SO}_4^{2-}+\text{Mg}^{2+}$ in chloride salt accelerates chloride ingress and increase apparent chloride diffusion coefficient. The drying-wetting cycle further accelerates chloride ingress. Nevertheless, the addition of SCMs significantly improves the resistance to chloride ingress into mortar specimens.

The above findings help a better understanding of the damaging behaviors and mechanisms of cementitious materials used in marine environment, and provide some guidance for the design of cementitious materials suitable for marine environment and concrete with chloride-containing ingredients. In the upcoming researches, the group of the reporter will also focus on the use of marine sand in concrete structure modified with design cementitious materials, aiming to improve the stability of marine sand concrete structure.

Specification of building materials for in service durability

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Abstract

To assess whether a structural element made of a given building material can withstand the expected mechanical load and environmental exposure in service, designers need information on the material resistances and loads as well as the local conditions. The durability of a building material in the structure can only be assessed if these factors are taken into account. Usually, the material resistances are obtained from laboratory tests. However, the performance of materials under standardized laboratory conditions differs from those occurring in the field. This paper considers this assessment problem and develops a solution strategy based on carbonation-induced corrosion as an example.

Keywords: durability design, concrete, reinforcement, material resistances, modeling.

The unabridged version of this article can be found in Volume 2- New cementitious binders, page 25.

Portland cement – SCM blends: insights from solid-state NMR spectroscopy

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Abstract

Society's increasing demands for new construction materials with low embodied CO₂ emission promote research in new binders and cement blends where a significant part of traditional cement is replaced by a supplementary cementitious material (SCM). These materials comprise generally industrial waste products, natural pozzolans and activated minerals that exhibit either hydraulic or pozzolanic properties. As separate materials and in contact with water, most SCMs will not show any significant hydraulic reactions of cementitious value. However, as fine powders and under alkaline aqueous conditions or in contact with calcium hydroxide they will react chemically, *i.e.* 'the pozzolanic reaction', and form hydration products similar to those of cementitious systems. Typical SCMs used by the cement industry are limestone and by-products such as fly ashes, blast furnace slags, silica fume, and rice husk ashes. However, the availability of some of these materials varies regionally and they will not be able to cover the global needs for SCMs in the future. In particular, the amounts of fly ashes are decreasing since coal-fired power plants are being phased out for environmental protection purposes in several countries. Thus, there is an urgent need for developments of new SCMs that are comparable or superior to fly ashes and slags. In this context, limestone and clays represent important types of material available in large deposits all over the world.

This presentation focusses on the development of binary and ternary Portland cement – SCMs incorporating calcined clays, glasses and limestone as SCM's and targeting cement replacement levels of 30 – 50 wt%. The glasses exhibit pozzolanic properties similar to fly ashes and slags and they may be synthesized from minerals and clays with a low CO₂ footprint compared to Portland cement. Moreover, thermal activation of clay minerals results in dehydroxylation of the aluminate and silicate species of the layered structure and the formation of disordered structural sites with high pozzolanic activity. Solid-state NMR spectroscopy represents a strong tool for characterization, quantitation, and structural analysis at the nanoscale of a wide range of diamagnetic, inorganic materials. Main advantages of the method are the nuclear-spin selectivity where one nuclear spin-isotope (*e.g.* ¹H, ¹¹B, ¹³C, ¹⁹F, ²³Na, ²⁷Al, ²⁹Si ...) is detected at a time and the equal observation of crystalline and amorphous phases. Thus, rather simple NMR spectra can often be achieved for complex materials, for example reflecting minor constituent phases or guest-ion incorporation. These features will be illustrated in the presentation by quantification of glasses and calcined clays in Portland cement blends, providing kinetic information about their pozzolanic reactivity. Moreover, focus will be paid to the impact of SCM's on the structure and composition of the C-A-S-H phase, the principal binding component, in blended cements.

Keywords: Supplementary cementitious materials, calcined clays, glasses, C-A-S-H phase, NMR spectroscopy

Functional coatings for building materials

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Abstract

New developments in coatings for buildings often rely on nanotechnology developments. Properties like hiding power, colour and even total solar reflectance (for cool coatings) depend on the level of dispersion and spacing of the pigment particles. Dispersants play a key role in this; a relatively unexplored option is to coat the pigment particles with polymer to force a minimum spacing of the particles. Surface properties like dirt pick-up of the coatings film depend on surface tension and surface roughness. Both superhydrophilic and superhydrophobic coatings have been explored. Creating hydrophobic surfaces by utilization of fluorinated polymers seems like an expensive option, again through utilization of nanotechnology the amount of expensive fluorinated polymer can be minimized still obtaining desired effects.

Other developments in the area of coatings for building materials are low VOC coatings to even completely plasticizer free coatings and the use of reactive plasticizers. A*Star is conducting a program called NoSOC (no small organic compounds) that is targeting to reduce and eliminate small organic molecules leaking out of coatings for example. For the purpose of measuring the emission of small organic molecules from coatings and new device has been developed which can detect very small amounts, the so-called “sniffer”.

In the keynote presentation several approaches to create nanostructured particles will be presented and examples of potential applications in coatings and construction materials will be shown.

Keywords: Coatings, anti-fouling, solar reflectance, nanotechnology, emulsion polymerization

Utilization of waste and residues in building materials

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Abstract

Millions of tons of inorganic waste materials and residues are produced annually in Europe. Metal production, energy industry, mining activities and construction and demolition are the main sources of high-volume secondary materials. Some of these secondary materials are utilized but still large amounts of material end up to landfills. Based on the principles of circular economy, materials and their value should remain in the society as long as possible, and virgin raw materials should be used only if there are no recycled materials available. Industrial residues typically consist chiefly of oxides of the most abundant elements of the planet: Si, Al, Fe and Ca. These are also the main elements forming the base of different inorganic binders, such as alkali-activated cements. From the chemical composition point of view, industrial residues are thus interesting raw materials for building materials. Most of the industrial residues have gone through several processing steps such as mechanical and thermal treatments, which improves their properties and therefore their utilization potential. High-potential waste materials that currently are not utilized include e.g. mineral wool waste, crystalline slags from metallurgical industry as well as fly ash from biomass combustion. Some challenges remain in waste and industrial residues' utilization due to high variation in waste material quality, need for local production and utilization, as well as competition against cheap and robust cement-based materials. Despite the challenges, there is a growing interest towards the more sustainable production and use of waste materials in new construction products.

Keywords: inorganic waste, industrial residue, alkali-activated material, building material

Natural fibers in building materials

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Abstract

Construction remains a significant consumer of raw materials, specifically non-renewable resources derived from the extractive industries. In addition, construction is a significant contributor to the emission of global warming gases, both through its dependence on the extractive industries, and its consumption of energy during and after construction. Natural fibres have gained interest as reinforcing materials in the composite industry for low-cost housings. Their advantages have been increasingly recognised as a major motivation to be more environmental friendly, cost-efficiency, renewable, and good thermal conductivity and acoustic. The building industry has thus been called to account for its role in the massive use of mineral raw materials and environmental pollution. One solution comes from the bio-building sector which draws on unlimited sources of natural materials such as natural fibres, which is a recyclable carbon sequestrator. The natural fibres can be sourced from plants or animals. From part of the plant where the fibres are sourced, the fibres can be classified into bast fibres (okra, flax, hemp, roselle, jute, kudzu, ramie), leaf fibres (agave, banana, palm, sisal, and pineapple), seed fibres (cotton, coir and kapok), core fibres (hemp, kenaf, jute), grass and reed (wheat, corn and rice), and other types of fibres. Fibbers from animals are for example wool (Sheep) and feathers have been used. Traditionally, natural fibres have been cultivated and used extensively for non-structural applications in rural developing countries for multipurpose such as rope, bag, broom, fish net and filters. The fibres have also been used for applications in housing as roof material and wall insulation. Natural fibre used for insulation can often be used as replacements for mineral- or petrochemical-based insulation. When used appropriately, natural fibre insulation materials can deliver thermal and acoustic insulation comparable to other insulation materials, but with a lower or potentially negative carbon footprint and fewer health issues during the installation of these materials. They can create more energy-efficient buildings. They can also assist in regulating relative humidity, and can provide a vapour permeable system and improve indoor quality. This multi-functionality should be borne in mind when specifying natural fibre insulations in order to ensure maximum value and benefits. A large variation is found in the properties of natural fibres. The properties are affected by several factors such as type of fibres, moisture content and form of fibres. Moreover, the properties are also affected by the place where the fibres are grown, cultivation condition, the part of the plant they are harvested from which region/country, growing period (year) and retting or extracting process. The mechanical performance, conductivity, weathering and carbonation of bio-based building materials made with hemp and rapeseed are discussed.

Keywords: Carbonation, conductivity, fibres, mechanical performance, weathering.

Energy efficiency of building materials

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Abstract

The energy efficiency of building materials divides into two distinct areas; the inherent ‘passive’ savings in energy and embodied CO₂ of modern building materials and ‘active’ materials whose function is to conserve or moderate energy transfer in the built environment or harvest energy such as solar radiation.

Examples of the first group are widespread as the search for ever-lower energy materials continues. The efficiency of Portland cement production has increased markedly over the last 30 years, such that a modern cement kiln operates at only a little above the thermodynamic (theoretical) minimum of ~2.8 GJ/ tonne of cement. Globally, the energy efficiency has continued to increase as dry-process kilns (including staged preheaters and precalciners) replace wet-process kilns, and as more efficient grinding equipment is deployed. Overall, the thermal energy intensity of clinker was estimated at 3.4 GJ/t on average in 2017. This is a remarkable manufacturing success and greatly exceeds the efficiency of other materials (i.e. steel, glass, pharmaceuticals, or plastics) and generates no solid or liquid waste. It does however, liberate carbon dioxide both from fossil fuel use and decarbonating limestone in the kiln. Cement is made of a vast scale (4.1 Gt in 2018) so its production contributes over 5% of anthropogenic CO₂. Indirect emissions from burning fossil fuels to heat the kiln can be reduced by burning alternative fuels, including natural gas, biomass and waste-derived fuels such as tyres, sewage sludge and municipal solid wastes. These less carbon-intensive fuels might reduce overall cement emissions by 18-24 percent from 2006 levels by 2050 but efficiency gains in cement production are incremental and yield diminishing returns.

Practically, the greatest saving is to be made through reducing the amount of cement clinker used in concrete production. Numerous supplementary cementitious materials (SCMs) exist and some have been in use for many years, whilst new materials are developed regularly. Through the use of blended cements we have a range of Portland-SCM binders, some of which offer strength or durability advantages over Portland cement concrete. Focus in recent years has turned to non-Portland cement binders, such as Magnesia Cements, Celitement, Alinite Cement, Calcium sulphoaluminate systems, and Alkali Activated Systems / Geopolymers and each has a role to play in the future of construction. The practicality of such alternatives must be assessed at many levels; the fiscal and environmental impact must be balanced against the long-term security of supply and performance of the materials in service. One thing is certain however, the enormity of the existing Portland cement industry will not change rapidly but evolve to accommodate new ideas and new opportunities.

Finally, it is important to consider ‘active’ materials in the built environment. A modern office block, for example, may be clad with a decorative façade. Recent trends in energy harvesting have seen both solar heat collection and photovoltaic panels incorporated in building cladding, whilst energy generation by thermoelectric glass is an attractive technology allowing electricity to be generated from near-transparent

glass. The incorporation of hydrogels in porous ceramics allows the inner layer of a building façade to offer evaporative cooling, much like sweat cooling mammalian skin. The water in this case is replenished at night, when the air cools to below the dew point. To conclude, it is important to consider the use of phase change materials in regulating heating and cooling needs.

