Success with siloxane

Dr. Dmitry Davydov, James D. Greene and Dr. Wei Cai, WACKER, **explain how cementitious materials can be protected and improved using oligomeric siloxane based technology.**

Global warming and climate change are largely driven by greenhouse gas (GHG) emissions. GHGs can be broken down into carbon dioxide, methane, nitrous oxide, and fluorinated gases, and therefore the reduction of any of these GHG emissions can contribute to slowing down climate change. The production of cement is a major contributor to CO_2 emissions, consequently, the cement and concrete industry, including members of the Global Cement and Concrete Association (GCCA), have an array of initiatives aiming to achieve net-zero emissions by 2050. The CO_2 reduction goals are 20% CO_2 reduction per ton of cement (from 0.77 to 0.6 million t per ton of cement) produced and 25% reduction per m^3

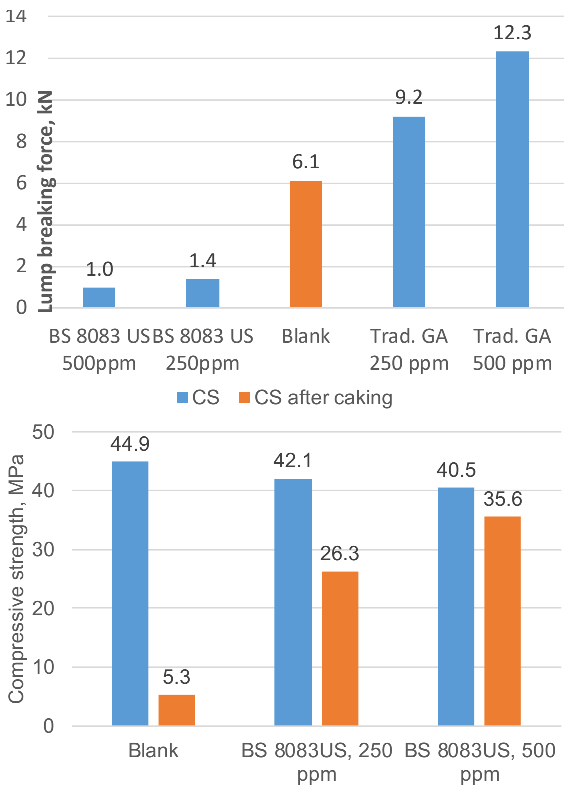

Figure 1a (Top). Lump breaking force.
Figure 1b (bottom). Breakage in mortar.

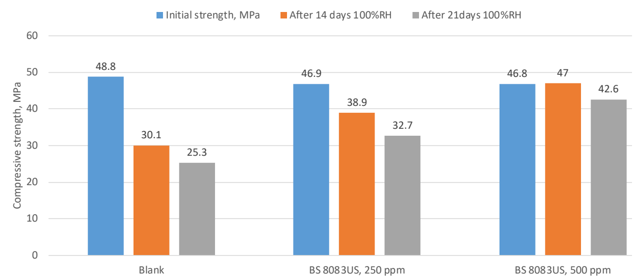

Figure 2. Laboratory tests. Strength of cement after exposure to 100% relative humidity, 23˚C. Cements were ground with the addition of SILRES BS 8083US.

Figure 3. Industrial trial (left) non-treated cement (right) treated cement.

of concrete (from 0.373 to 280 million t/m^3) produced by 2030. One of the methods of achieving this is by reducing the overall clinker content in cement and consequently also concrete. For example, over the past three years, the US cement industry has quickly shifted from Ordinary Portland Cement (OPC) to Portland limestone cement (PLC). According to the Portland Cement Association, lower-carbon cements like PLC which contain 10% or more of limestone are helping to reduce CO_2 emissions. Last year, the use of PLC in the US surpassed OPC use, a change that reduced CO_2 emissions by more than 4 million t, more than twice the CO_2 savings over the previous year.

The other method for reducing CO_2 emissions is by increasing the concrete life cycle as pointed out in the recent publication by Olsson et al. The addition of some supplementary cementitious materials (SCM) such as fly ash, or slag and specialty siloxane chemicals can extend the life time by mitigating Alkali Silica Reaction (ASR), as well as increasing freeze thaw resistance. This article will illustrate methods being used by industry to increase cement shelf life, increase freeze thaw resistance, and mitigate ASR which will increase the life cycle of cement/concrete reducing significantly GHGs.

Increasing shelf-life and improving grinding efficiency of clinker

The current cement production process is to grind the clinker, gypsum and limestone using either a horizontal ball mill or a vertical mill, which is then transferred to silos and subsequently packaged into bags or bulk. Many cement plants are located in hot, humid areas, and therefore, in a short period of time, the cement begins to form hardened clumps (hydrated cement particles) in silos and in bags. The shelf life of these cements can be reduced to less than 3 months, which decreases confidence in the quality and causes an overconsumption of the cement as well as an increase in waste. However, the use of new oligomeric siloxane grinding enhancers reduces the amount of hydration occurring in the stored cement as well as increasing the free flow properties of the cement. The industry has found that the incorporation of 500 ppm or less of new oligomers (such as SILRES® BS 8083 US or BS 8010) provides enough hydrophobic properties which mitigates the unwanted early hydration and increases the shelf life by more than 1 year. In addition, the increase in grinding efficiency and transportation out of the mills and silos increases production output.

The following results from some laboratory tests outline the effect of the new oligomeric enhancer. The cement was ground in a ball mill with an addition of only 500 ppm of the oligomeric siloxane (SILRES BS 8083 US). The treated and untreated cement powders were then pressed with the same pressure which takes place at the bottom of a typical silo. These pressed cylinders were exposed to 50˚C with 100% relative humidity (RH) for 24 hours. The powdered cylinders were then tested for compressive strength. As expected, the untreated powder had a high degree of hydration which required significantly more force to break. The materials using 250 – 500 ppm of traditional grinding aids required twice (12 kN) the force to break (Figure 1a), whereas the powder treated with the new oligomeric siloxane enhancer was only 1.0 kN which essentially did not have any hydration. The next step was to evaluate the compressive strength of these cements in a mortar (Figure 1b). The cement which was not treated had a compressive strength of 44.9 MPa before exposure to humidity and then after exposure to humidity, heat, and pressure, had a final compressive strength of 5.3 MPa, whereas the cement treated with the 500 ppm SILRES BS 8083 US had 35.6 MPa after exposure to heat, humidity and pressure.

This represents an increase in shelf life for the cement tested both in the laboratory (Figure 2) and on an industrial scale (Figure 3). The industrial trials were performed using a vertical mill and exposed to temperatures of over 30˚C and over 75% RH for 45 days with a significant reduction in hydration and minimal formation of clumps. Moreover, mortars and concrete obtained from treated cement had much lower water uptake in combination with crack prevention. These measures will improve durability of the cement and ultimately reduce CO_2 emissions.

Increasing life cycle of concrete

Concrete should last over 50 years, however with a lack of non-reactive sands/aggregates, as well as an inability to prevent water and chloride ion ingress, premature failure will occur. Concrete produced with these types of raw materials is susceptible to cracking due to ASR and/or failure as a result of freeze thaw resistance. The use of OPC or Type 1L cements with reactive aggregates or sands will fail ASTM C1260 test unless modified with more than 40% additional SCM such as slag or the addition of a small amount of oligomeric siloxane chemistry (SILRES BS 1802 and BS 1803 US) (Figure 4). These new oligomeric materials are added during the mixing of concrete. The new chemistry is similar to quartz in that it maintains a mineral-like structure (Figure 5) which reacts with hydroxyl groups on the sand and/or aggregate. It then makes a silicone resin network in the pores formed during the hydration process (Figure 6). This hydrophobic structure prevents moisture from entering and forming ASR gels, and when tested according to ASTM C 1260, the combination minimal amount of SCM and oligomeric siloxane will extend the test past the target's 14 days and up to 36 days (Figure 7). This is equivalent to extending the durability of the concrete by almost 3 times. In addition, freeze thaw resistance is also improved as can be seen

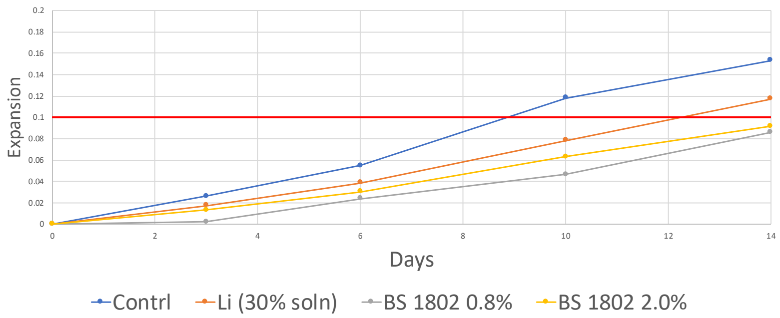

Figure 4. ASR test results: ASTM C 1260.

Figure 5. The 'R' in the silicone resin network realises the hydrophobicity.

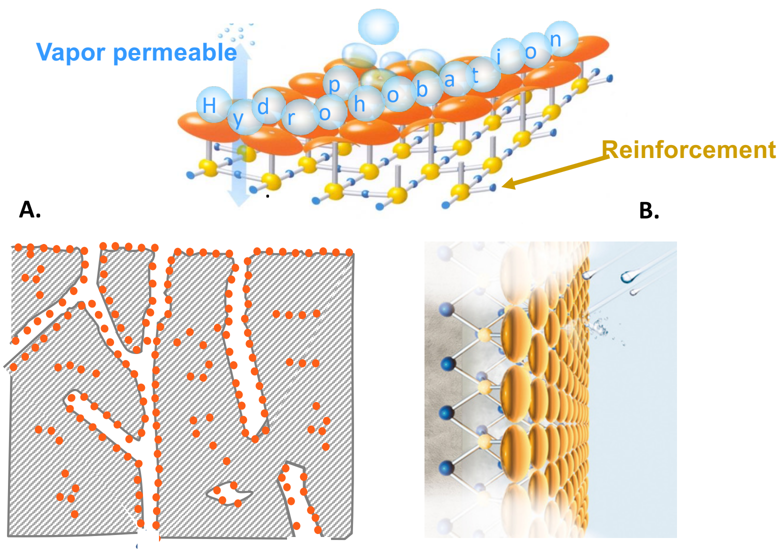

Figure 6. A. The reaction of oligomeric siloxane in the formation of concrete block, B. Formation of silicone resin network throughout the structure and in the pores.

in Figure 8. These mortar cubes were exposed to freezing (-20˚C) and thawing (+20˚C) conditions for up to 300 cycles and then compressive strength was measured. The blank lost 30% of its strength after 100 cycles and after 300 cycles the strength was reduced by 60%, whereas the addition of oligomeric siloxane in polycarboxylate ether (PCE) maintained essentially the same strength.

The addition of these materials to concrete mix design increases freeze/thaw resistance as well as protection from reactive sands, aggregate, and recycled materials to mitigate the damage caused by ASR, in addition to reducing chloride ion ingress. Figure 9 shows pictures of oligomeric siloxane (SILRES BS 1802) added in a ready-mix truck and poured at WACKER's new Ann Arbor Innovation Centre (AIC) which utilised Michigan sand and aggregate, weathering three winters (approximately 3 years). Significant erosion from the surface of the non-treated slabs was observed with a lot of exposed aggregate, and popout, whereas the treated slab appeared to have minimal surface erosion with no surface cracks (appearing as new). The compressive strength of the slabs with and without additives were in the same range. This is additional proof of the need to further modify mix designs with additives to meet the expected greater than 50-year shelf life of concrete.

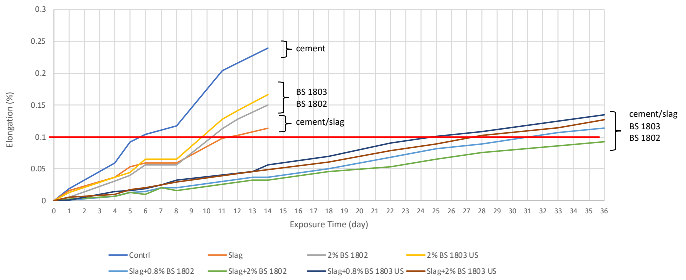

Figure 7. ASR test results: ASTM C 1260.

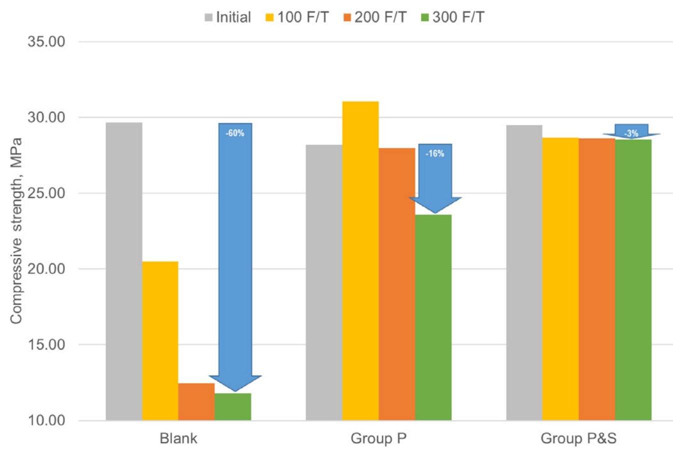

Figure 8. SILRES BS help to effectively increase freeze/thaw resistance.

Figure 9. Poured (ready mix) in driveway at AIC with treated and untreated concrete slab poured in 2021 and then evaluated in 2023 (left) and 2024 (right).

Conclusion

The industry expects to reduce GHG emissions with the goals of being net zero by 2050, however the reduction of clinker as well as the use of recycled materials and poor-quality sand and aggregates will require oligomeric siloxane materials to maintain a high degree of durability. As pointed out earlier the incorporation of these oligomeric siloxanes (SILRES BS 1802 and BS 1803 US) in the making of concrete slabs at WACKER's AIC facility has shown a real increase in durability. In addition, the incorporation of these new materials into grinding of the clinker will increase the shelf life of the cement and increase efficiency in production which will reduce waste and overconsumption. The addition of these materials into the mix design of concrete will increase resistance to degradation due to freeze thaw, chloride ion ingress and mitigate cracking due to ASR. These measures are necessary to increase the life cycle of cement/concrete, and to ultimately help meet the target of reducing GHG set by the GCCA. ■

About the authors

Dr. Dmitry Davydov holds a PhD in Polymer Chemistry and has worked for 10+ years in the cement and concrete industries.

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