



**ecra**

european cement research academy



**1 / 2009**

# NEWSLETTER

## Contents

- Shrinkage reducing admixtures – their development and how they work **p. 2**  
Numeric simulation of processes in precalciner kilns **p. 3**

## Next ECRA events to come:

- Cement and Admixtures  
8 April 2009
- Impacts of Secondary Fuel Combustion in the Calciner  
24–25 June 2009

# Shrinkage reducing admixtures – their development and how they work

The importance of the relative humidity, a fine pore system and the disjoining pressure

Concrete shrinkage leads to deformations which may cause stress in structural elements in the case of constraint. As a consequence, cracks (superficial cracks or separation cracks) which impair durability may occur. Shrinkage may jeopardise the crack-proofness of large structural elements, such as floor slabs, and of high-strength concrete components at an early age.

Shrinkage is mainly induced by variations in the moisture content of concrete, which change the interior forces in the microstructure of the hardened cement paste matrix as a consequence of the environmentally induced drying or self-desiccation of the concrete. This results in tensile stress, which causes the hardened cement paste matrix to contract.

Shrinkage Reducing Admixtures (SRA) were developed in Japan in the early 1980s to reduce concrete shrinkage. They have been in use in Europe since around 1997. In many cases, shrinkage reducing admixtures have until now primarily been employed in floor screed works and in mortar applications. They have, however, not been used in load-bearing structural elements made from concrete, reinforced concrete and prestressed concrete.

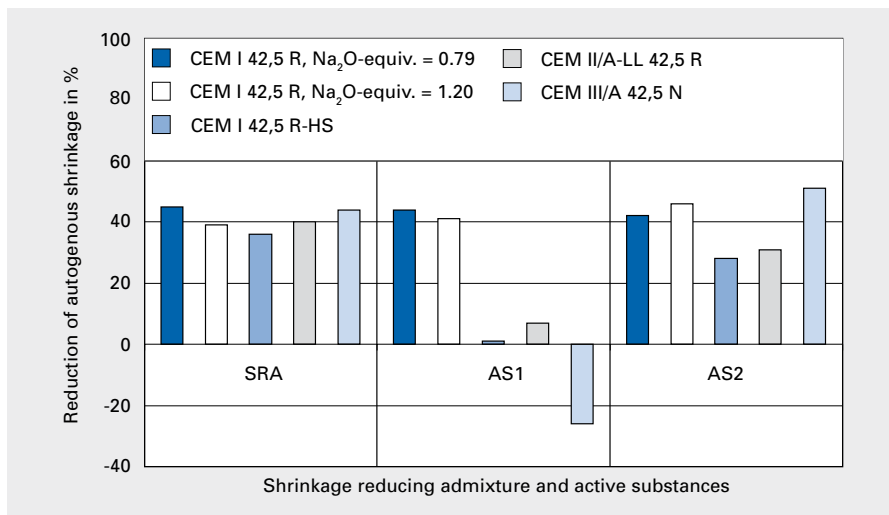
## Reduction of surface tension

SRA are generally organic, hygroscopic substances. The active substances used include propylene glycol ether, alkane diols and polyaliphatic or cycloaliphatic ethers. The active substances lower the surface tension of the pore solution. In the past it has been assumed that this reduces the capillary pore pressure in the microstructure of the hardened cement paste so that the internal tensile stresses, and therefore the shrinkage, are reduced. The SRA investigated lowered the surface tension of the pore solution permanently, by as much as 60 %. The concentration of the SRA-molecules in the pore solution increased with ongoing hydration time. The increase indicates that the molecules of the SRA are only marginally adsorbed on the cement hydration products.

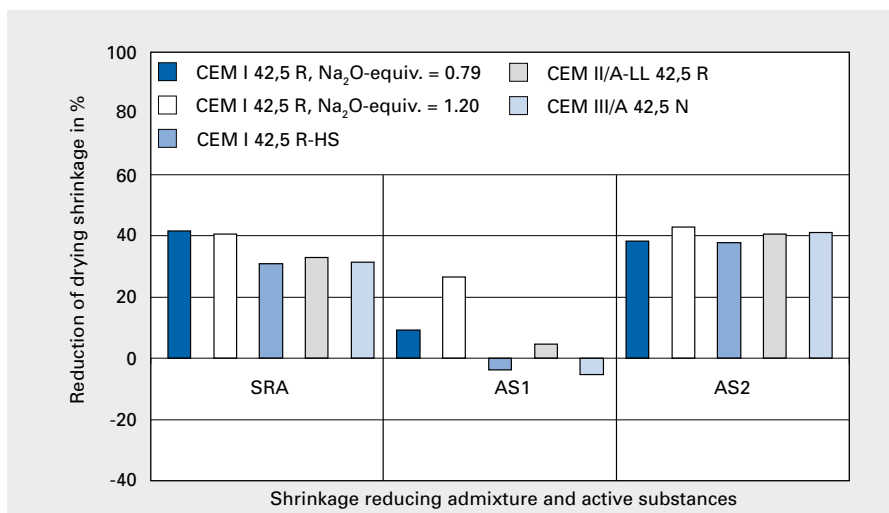
## Reduction of shrinkage deformation

Nearly all SRA lowered the autogenous shrinkage and the drying shrinkage of hardened cement paste. **Fig. 1** and **fig. 2** illustrate exemplarily the impact of one SRA containing the active substances AS1 (propylene glycol) and AS2 (propylene glycol ether) on the autogenous and drying shrinkage of hardened cement paste with five different cements in relation to reference samples not containing shrinkage reducing admixtures. **Fig. 1** shows that the SRA reduced the autogenous shrinkage extensively with a w/c-ratio of 0.42 at the age of half a year independently of the cement by as much as 45 %. With the application of the active substances AS1 and AS2 a partly clear influence of the cement was determined. In one case the autogenous shrinkage even increased compared to the sample without SRA.

The drying shrinkage at 20 °C und 65 % relative humidity at the age of



**Fig. 1: Reduction of the autogenous shrinkage of hardened cement paste at 182 days by shrinkage reducer (SRA) and active substances AS1 and AS2 relative to reference samples without shrinkage reducer; w/c = 0.42, dosage = 4.5 mass % w.r.t. water**



**Fig. 2: Reduction of the drying shrinkage of hardened cement paste at 364 days by shrinkage reducer (SRA) and active substances AS1 and AS2 relative to reference samples without shrinkage reducer; w/c = 0.42, dosage = 4.5 mass % w.r.t. water**

one year was reduced by the SRA as well as the active substance AS2 relatively independently of the cement by as much as approx. 40 % (fig. 2). The active substance AS1 showed only a minor impact and partly caused even a greater shrinkage than was the case without the use of a shrinkage reducer.

#### Hydration, porosity, relative humidity

At the dosages of the shrinkage reducers normally used in practice the hydration of the cement was retarded only to a slight extent. At constant total porosity the use of the shrinkage reducers always led to a greater gel porosity (pore radius < 0.01  $\mu\text{m}$ ) and lower capillary porosity (pore radius 0.01  $\mu\text{m}$  to 10  $\mu\text{m}$ ) of the hardened cement pastes. This reduced the capillary water absorption of the hardened cement pastes to a significant extent. Hardened cement pastes made with shrinkage reducers have an internal relative humidity that is up to about 13 % higher than that of

the respective reference samples without shrinkage reducers.

#### Operating Principles

Contrary to former assumptions, the reduction in surface tension of the pore solution by shrinkage reducers is not the sole cause of their shrinkage-reducing effect. The reduced surface tension of the pore solution combined with the formation of a finer pore system probably leads to higher relative humidity in the hardened cement paste. This presumably leads to a higher disjoining pressure in the microstructure of the hardened cement paste caused by self-desiccation. Thus the autogenous shrinkage, especially in hardened cement pastes with very low water/cement ratios, is reduced. The concomitant refinement of the porous system can neutralise the effect of the SRA, especially under drying conditions, and in some cases can cause a greater drying shrinkage deformation. The drying shrinkage of hardened cement paste is significantly reduced by those

shrinkage reducers that cause only a slight increase in the gel porosity (AS2).

In spite of the reduced capillary porosity, with some shrinkage reducing admixtures the compressive strengths of the hardened cement paste at 28 and 91 days was reduced up to 20 % and 10 % respectively in comparison to reference samples without shrinkage reducers. Tribological effects caused by the shrinkage reducers in the pore solution and the increased relative internal moisture content are being discussed as possible reasons. First research results on the impact of SRA on concrete confirm extensively the results which are determined on hardened cement paste. Thus the drying shrinkage of concrete is reduced by SRA by about 20 % and 35 % after one year storage in a climate of 20 °C and 65 % RH.

The compressive strength of concrete was lowered by SRA up to 20 % independently of the storage conditions.

## Numeric simulation of processes in precalciner kilns

Combustion and calcination processes in calciners can be considered by CFD methods

The demands which cement manufacturers have to meet nowadays call for development and progress with regard to compliance with emission limits, cutting of operating costs, maximum possible flexibility in production, minimum maintenance and low specific consumption of heat and energy accompanied by maximum kiln availability.

The option of simulating the processes taking place in the calciner simplifies operational optimisation and can thus reduce the number of costly and time-consuming experiments conducted at kiln plants during operation. Moreover, it becomes easier to make substantiated statements on the technical feasibility of installed precalciners in existing plants to reduce harmful

substances by staged combustion. Further areas of application for numerical simulation in this context include damage investigation and concept studies on the design, the thermal optimisation and the versatile utilisation of alternative fuels.

The Research Institute participated in a simulation research project in cooperation with two university departments. The project aims at supporting the operational optimisation of precalciner plants regarding the formation of harmful substances, NOx abatement measures and – possibly in the future – coating formation by means of numerical simulation. Thus, the existing detailed knowledge, which had already been applied in various fields of plant simulation, was compiled, checked with regard to its scope of applicability, and adapted to the special conditions prevailing in calciner firing systems.

Based on coal as the only fuel, the individual processes of fuel burn-out, NOx formation, decarbonation and calcining process, turbulence modulation and influences on radiation were successfully simulated and validated by measurement results which the Research Institute of the Cement Industry had obtained from real cement plants. Considering the complexity of the cement manufacturing process and the difficulty of recording local variables in the calciner by measurement, the conformity of the figures calculated and the experimental values were very good.

#### Turbulence and radiation modelling

The high particle loading, of approx. 1.5 kg solids per kg gas is a distinctive feature of precalciners. This high loading has a direct impact on turbulence and radiation modelling. In the case of fairly fine pulverised coal and lime particles, a transition of the kinetic energy of turbulence from the turbulence whirls in the gas phase to kinetic energy in the particle phase occurs. In this way, turbulence is abstracted from the gas phase, which turns into the particle phase. The influence that particles have on radiant heat exchange at the high particle loading in the calciner consists of sol-

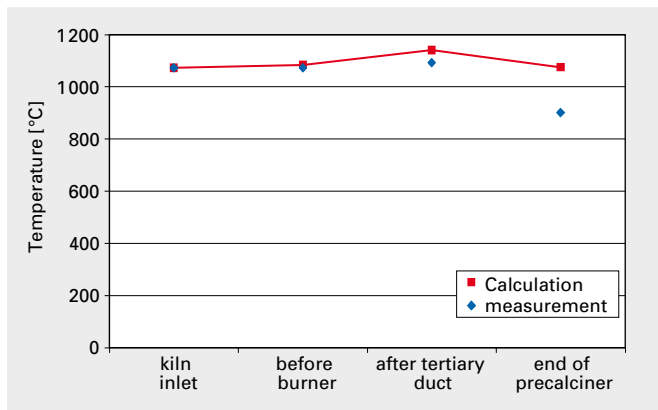


Fig. 1: Comparison of measured and calculated temperatures

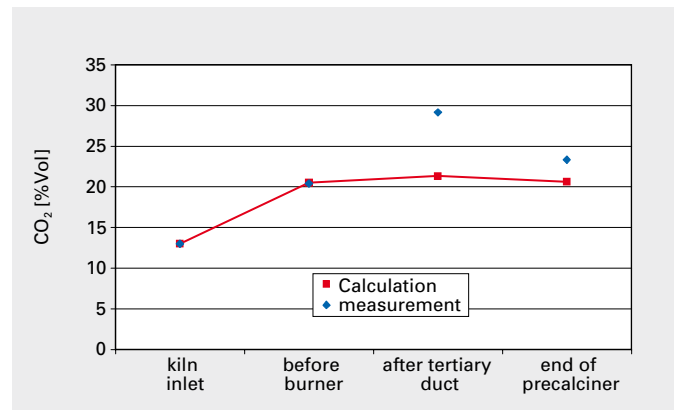


Fig. 2: Comparison of measured and calculated CO<sub>2</sub> concentrations

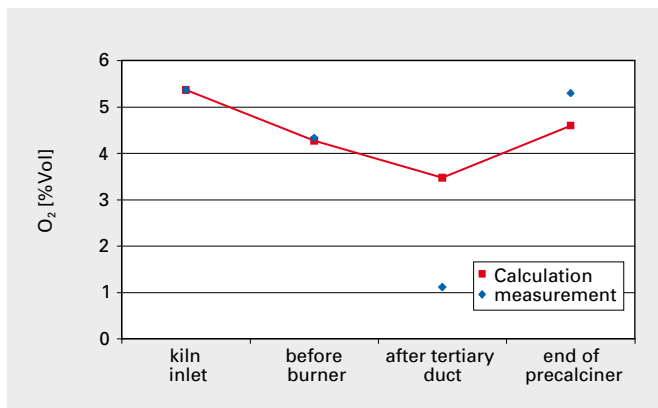


Fig. 3: Comparison of measured and calculated O<sub>2</sub> concentration

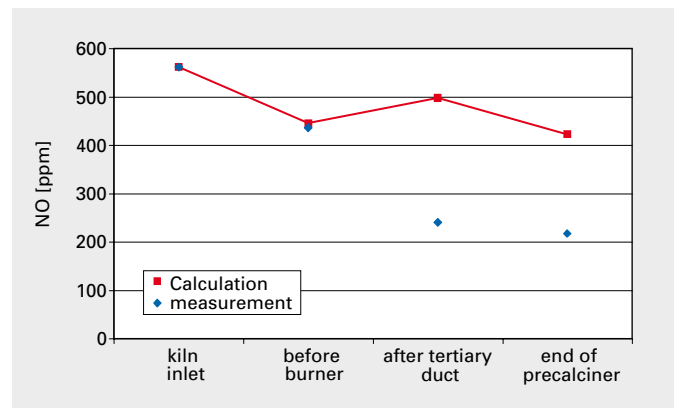


Fig. 4: Comparison of measured and calculated NO concentration

id radiation between particles spaced at close range accounting for a larger share of radiant heat exchange than gas radiation as gas loading increases. When the optical density of the two-phase flow is correspondingly high, solid radiation between particles spaced at close range accounts for a large share of radiant heat exchange in the flow, while gas radiation becomes less relevant. In addition to this, dispersion effects occur whose intensity and directional orientation depends on the size, material, shape and surface of the individual particles. To take these effects into account, a model originally developed for power plant technology was adapted and further developed to the conditions prevailing in the calciner.

### Integration of calcination, sulphatisation and fuel burn-out

Even the models covering the calcination and sulphatisation of meal particles, fuel burn-out and NO<sub>x</sub> formation were implemented in the CFD program and successfully enhanced. The models simulating the calcining and sulphatisation reaction were extended to also include the transient progress of limestone meal porosity and the specific inner surface avail-

able for the reactions now. This allows a more precise simulation of the course of the calcining reaction. Moreover, the formation of a sulphate layer of low porosity due to the sulphatisation reaction is simulated as well. As a result, the model also reproduces the increase in the pore resistance to diffusion and the associated decrease in the velocity of the calcining reaction. Various models for describing NO<sub>x</sub> formation and reduction in the calciner were investigated as well. Finally, a global kinetic model describing both the formation of NO<sub>x</sub> and its reduction under calciner conditions was integrated in the CFD program. All models were validated by taking into consideration the Research Institute's above-mentioned measurement results.

Based on the example of one kiln, **figs. 1 to 4** show the temperatures calculated and the concentrations of CO<sub>2</sub>, O<sub>2</sub> and NO in comparison to the values that the Research Institute measured as part of the industrial trials. The dots represent mean values. The values calculated and the curves of the data measured by the on-site measuring devices at the calciner inlet, upstream of the precalciner burning unit and upstream of the top air supply ("TA") tallied well in terms

of quality and quantity. The deviations (especially regarding NO) in the area of the reducing zone, upstream of the overfire air, were attributable to inaccuracies still affecting the reaction system.

The project thus provided the basis for extending the findings on the CFD simulation of precalciners. It further allowed calciner-specific sub-models (calcination and sulphatisation process, turbulence modulation, radiant heat exchange, coal burn-out, NO<sub>x</sub> formation) to be developed, integrated into the CFD codes, and validated.



European Cement Research Academy

Tannenstr. 2 · 40476 Düsseldorf  
P.O. Box 30 03 32 · 40403 Düsseldorf  
Germany

Phone: +49 (0)211 2 39 83 8-0  
Fax: +49 (0)211 2 39 83 8-500

info@ecra-online.org  
www.ecra-online.org