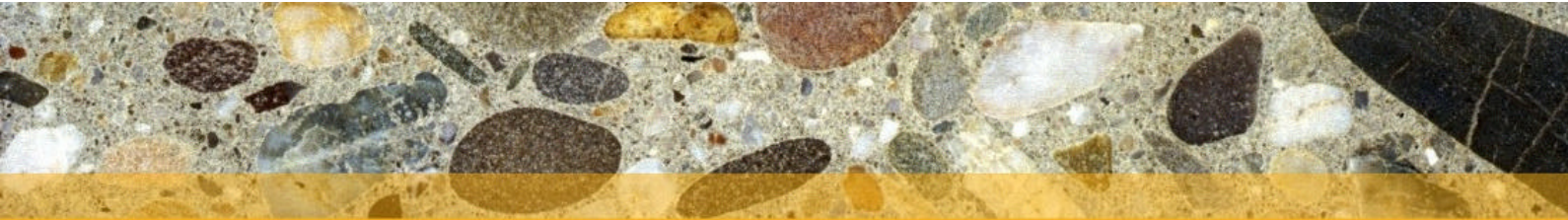




**ecra**

european cement research academy



## Newsletter 2/2003

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### Next seminars and workshops to come:

- Interactions between Cement and Concrete Admixtures  
May 27, 2003
- Trace Elements in Cement Production and Products  
June 12, 2003
- Training of Plant Operation with the SIMULEX Cement Plant Simulator  
June 23-26, 2003
- Limitation of Sulphur and Chloride Cycles Using Bypass Systems  
September, 30, 2003
- Concrete in the Construction of Traffic Routes and Tunnels  
October 2, 2003

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# Interactions between Cement and Concrete Admixtures

One of the most significant evolutions in the technology of mortar and concrete has been the use of admixtures. Very important in this field is the interaction between cement and admixture. Investigations of the Research Institute of the Cement Industry were undertaken to find out the cement properties influencing the behaviour of admixtures and those of admixtures influencing cement hydration.

For controlling the concrete properties in Europe currently more than 500 technically approved concrete admixtures are available. The properties of both the fresh concrete, such as setting behaviour and workability, and the hardened concrete, such as compressive strength and durability, can be deliberately influenced depending on the type of concrete admixture used. 80 to 90 % of the concretes manufactured contain admixtures, with the focus being on the application of plasticizers and superplasticizers.

## Superplasticizers

The Research Institute has investigated the effects of concrete plasticizing admixtures and the adjusting of the consistency of concrete using superplasticizers over the last few years.

The work is continued with the investigations of superplasticizers of the "new generation" based on polycarboxylate ethers. Powder-rich pastes and mortars are in the foreground of these investigations since they are necessary for selfcompacting concrete.

The advantage in using these new superplasticizers is the fact that to the electrostatic repulsion by the transfer of positively charged surfaces (due to the sorption of the dissociated main chains of the polymers) a sterical repulsion is added because of the additional side chains. By adding a stabilizer, a further increase in the flowability can be achieved, since glide surfaces are being created at the interfaces between the individual solid particles which will further decrease the inner friction of the suspension (tribological effect).

Fig. 1 illustrates this effect in a schematic presentation. First hydration products can grow in the space

between two sterically divided cement grains, without substantially influencing the movement of the suspension. A strong initial plasticizing and/or prolonged workability period of fresh concrete can be adjusted by varying the length ratio of the main chains to the side chains.

The effectiveness of these superplasticizers and the influence of reactivity, grain size distribution and volume proportion of the solid particles in the suspension, as well as the surrounding temperatures, are being investigated by extensive research work in the Research Institute of the Cement Industry.

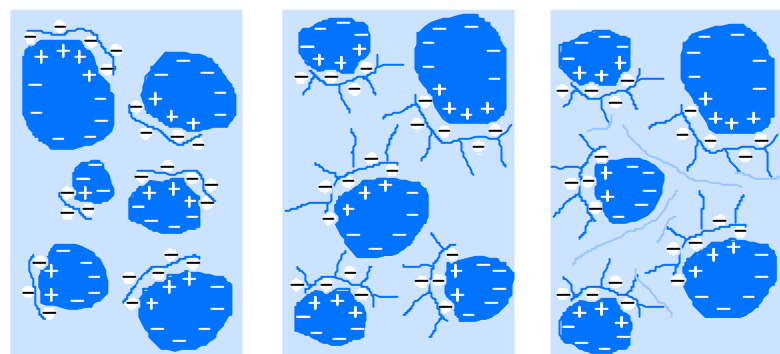
## Retarders

A relatively new functional group consists of recycling aids, which use primarily phosphonic acids as a reagent. Recycling aids for washing water are long-term retarders that facilitate the cleaning of concrete mixer trucks and concrete mixers and allow the re-use of washing water in plants that have only small or no recycled water basins. Recycling aids for residual concrete are to al-

low the re-use of residual concrete up to rest periods of 72 hours. After the scheduled rest period, the strongly retarded residual concrete is activated by adding at least the fourfold quantity of fresh concrete (concrete premixture).

In a research project the action mechanism of long-term retarders is currently being investigated. The results showed that recycling aids strongly interfere with the hydration of the cements with the mixing water. The adding of a long-term retarder on the basis of phosphonic acid leads to the fresh concrete becoming heavily plasticized. Even after three days the concrete could still be processed after short mixing. Similar to the admixtures having plasticizing effects, the change in the electrical charge on the grain surface leads to a dispersion of the cement particles, which explains the marked plasticizing of the fresh concrete.

Scanning electron microscope investigations that were performed at the same time clearly demonstrate the strong retardation of the hydration reactions by the long-term re-



Electrostatic effect  
melamine- and naphthaline-  
sulfonates (SP)

Electrostatic and  
steric effect  
polycarboxylate ether (SP)

Electrostatic,  
steric and  
tribologic effect  
polycarboxylate ether (SP)  
in combination with  
stabilizers (VEA)

**Fig. 1: Schematic representation of the action mechanisms of concrete plasticizing admixtures**

tarder. While in the non-retarded system long-fibered calcium silicate hydrates initiate the hardening process after approx. 24 hours as expected, the long-term retarded cement paste can still be processed. Except for ettringite crystals formed immediately after adding the water, further hydration reactions are blocked for up to 90 hours. The radicals of the phosphonic acid latch on to the positively charged spots of cement particles very fast and retard further hydration. The cement continues hydrating after the reservoir of the shielding reagent has been exhausted. Changes of the developing hydrate phases were not observed.

### Air-entraining agents

Concrete with resistance to freeze-thaw with de-icing salt must have, besides an adequate dense hardened cement paste and aggregate with high freeze-thaw resistance, an air-entraining agent which generates a sufficient quantity of small air

voids in the concrete.

The quantity and size distribution of the air voids introduced in the concrete are dependent on the type and quantity of the admixture used. Resin soaps as well as non-ionic and ionic synthetic tensides have proved successful for producing air-entraining agents. Resin soaps are essentially obtained from tall resins, balsam resins, wood resins and derivatives of these resins. These are converted into the water-soluble resin soaps with potassium or sodium hydroxide solutions or soda. Other raw materials used are compounds from the alkylpolyglycol ether, alkyl sulfate and alkyl sulfonate tenside groups.

The type of the active ingredient of the air-entraining agent influences the formation of air voids. Synthetic tensides lead to smaller pores than natural resins, but they need a longer mixing time until they are activated.

Also the type of cement influences the air content. Two main aspects

are the alkali content and the fineness of the cement. The air content increases with increasing alkali content. With increasing specific surface of the cement, the air content decreases.

If Portland fly ash cement is used, the air content decreases with increasing content of fly ash. The amount is influenced by the carbon content of the fly ash. The carbon absorbs the air-entraining agent thus preventing it from stabilizing air bubbles in fresh concrete. The carbon content can be estimated by the loss of ignition.

Regarding Portland slag and blast furnace cements, the quantity of the air-entraining-agent is a function of the fineness and the content of blast furnace slag used. The air content decreases with increased fineness and content of blast furnace slag in the cement.

The use of Portland limestone cement has practically no effect on the air content.

## Trace Elements in Clinker Production and Cement

### Clinker production and release from concrete without negative impact to the environment

**Investigations performed in many laboratories throughout the world have concentrated on the emissions of environmentally relevant constituents from the clinker production process. The emissions of heavy metals are low due to their low input into the kilns, also the elements are largely bound to the clinker. The release of trace elements from concrete under different environmental conditions has also been intensively examined. It could be shown that the trace elements in fresh concrete are to a high degree present in insoluble form. The release of trace elements from hardened concrete is low because the elements are retained by chemical-mineralogical interaction in the concrete and are effectively trapped in the hardened cement paste matrix by physical effects.**

Utilising alternative materials in cement plants improves the cost-effectiveness of the production process. Simultaneously, the cement industry contributes to the environmentally compatible recovery of a variety of waste materials, a reduction in CO<sub>2</sub> emissions and preservations of natural resources. However, the increasing substitution of primary fuels by secondary fuels in the European Union leads to a growing interest of manufacturers, authorities and the public in the impact of trace elements on clinker production and product quality.

Trace elements are introduced into the clinker burning process through the raw materials and fuels. The heavy metal contents in natural raw materials are dependent on their geochemical distribution in the quarry and can fluctuate in relatively wide margins even within one deposit. The fossil fuels used contain trace elements within a wide range of fluctuations. When secondary materials are used, an equivalent amount of natural material is replaced. Depending on the particular situation secondary fuels can contain higher or lower levels of trace elements than fossil fuels.

### Emissions

The relevance of the various heavy metals to the emissions is governed by their reaction under the thermal conditions in the rotary kiln/pre-heater system. The elements or compounds introduced into the burning process with the raw materials and fuels can be entirely or partially vaporized in the hot zones of the preheater and/or the rotary kiln, react with the compounds present in the gas phase and condense again on the kiln feed in the colder regions of the kiln system.

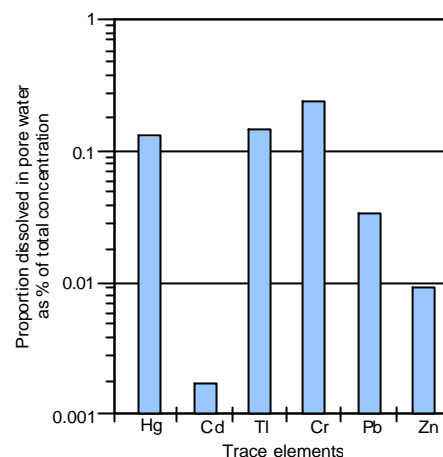
As a consequence, heavy metals practically remain within the kiln system and are ultimately nearly completely bound to the clinker. The mercury input into the kiln system is mainly due to the low concentrations of mercury in the natural raw materials; concentrations of 0.02 to 0.13 mg/kg have been determined. In the kiln system mercury can build up an outer cycle between preheater, raw-mill and the air pollution control device. In some cases it may be necessary to stabilize this outer cycle by removing some of the kiln feed from the system.

Mercury intake and mercury cycles are different for each single kiln. Fig. 1 shows the result of a kiln balance test, which was performed over a 1 week period. The mass flow exhibits a distinct outer cycle. In this case about 50 % of the mercury are emitted and another 50 % are removed from the system via the kiln feed. There is a balance between mercury intake and mercury output, the system is in a stable equilibrium.

### Leaching of concrete

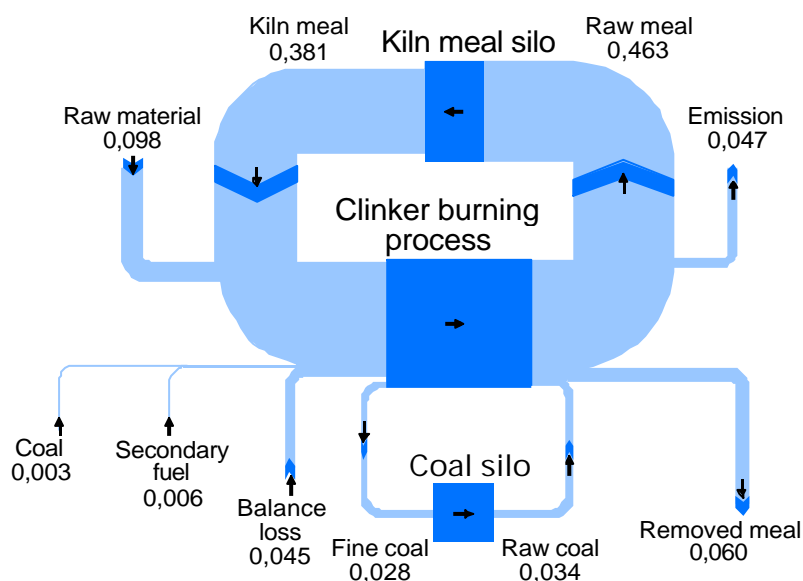
Trace elements enter cement bound building materials via the cement aggregates and possibly the concrete additions. The trace element proportion which is brought in via the mixing water or concrete ad-

mixtures can be ignored. Experience has shown that the trace element contents of mortar and concrete can be compared to those of natural rock, soil and clays. When assessing the environmental compatibility of cement bound building materials it must also be taken into account that it is not the total content of trace elements in the building material that is relevant but only the proportion that is released into the environment during manufacture or use, i. e. in contact with water or soil. The release rates for trace elements in concrete are very low. This fact is attributed to the excellent binding capacity of the hardened cement paste. For 28-day-old hardened cement pastes the proportions of the elements mercury, cadmium, lead and zinc that are dissolved in the pore water are plotted as a percentage of the total concentration of these elements in fig 2. 100 mg/l of each element had been added with the mixing water in the form of readily water-soluble salts. It is clear from the chart that in all cases well over 99 % of the amounts of these trace elements are retained in the hardened cement paste. Equally good retention is found for most elements even when the trace element concentrations has artificially been increased well above today's common cements.



**Fig. 2: Proportions of the trace elements mercury, cadmium, thallium, chromium, lead and zinc dissolved in the pore water, as a percentage of total concentration in the hardened cement paste**

From the pore water only a small amount of trace elements can be released to the environment due to the dense pore structure of the concrete which provides a high resistance against diffusion. Investigations have revealed that for example the elements lead, cadmium, and zinc are present in insoluble form and can therefore not be released. Tests, in which the trace elements had deliberately been added with the mixing water to fresh concrete, have shown that they are integrated into insoluble compounds and fixed in the hardened cement paste. Only chromium is soluble initially. As the hydration progresses, i.e. as the concrete hardens, the dissolved chromate is incorporated in the hydration phases. In hardened concrete all trace elements are practically completely bound and can not be released to the environment.



**Fig. 1: Hg circle with removal of meal (values in g/t clinker)**

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