

PORTLAND CEMENT MODIFICATIONS AND THEIR IMPACTS ON THE FIBRE CEMENT INDUSTRY

MR. CHRISTOPH HAERING

*CemTec Beratung GmbH, Feldstrasse 10, CH-6330 Cham, Switzerland,
Phone +41 41 781 41 36, Fax +41 41 781 41 37, E-mail: cemtec@mails.ch*

ABSTRACT

Due to regulations, e.g. to reduce the CO₂ output and chromium VI, and because of the increasing pressure to reduce energy and costs, cement producers intensified their efforts in recent decades to constantly reduce the percentage of clinker in the Portland cement.

As simultaneously some fibre cement plants add additionally fine inert materials, latent hydraulics or pozzolanic material to their Portland cement the clinker percentage of the cement is even more reduced. There are air cured cases where the clinker percentage in the final binder system is only 50% or even lower therefore. Fibre cement manufacturers are not always aware of this and may have to grapple with undesired consequences without realizing the real cause.

So, if the fibre cement manufacturer is not 100% aware of the composition of its Portland cement he quite certainly will face some undesired consequences in his production process and end product.

In the following we will go more into cement types, quality and the negative aspects and their impacts on the fibre cement production process and products if the composition is excessively changed and will present approaches to avoid them.

The following excerpt may illustrate the diversity of problems that may occur as a result of above:

- loss in loads and strength
- cracks in stacks, at roof or facade.
- freeze-thaw damage may increase in countries with active frost cycles
- sticking on templates may increase by lower temperature level
- corrosion of templates
- brown discolouring and staining at the products due chromium reduction Fe (II) sulphate

KEYWORDS:

Cement modifications, fibre cement process, curing, chromium VI reduction, cracks.

INTRODUCTION

Due to regulations, e.g. to reduce the CO₂ output and chromium VI, and because of the increasing pressure to reduce energy and costs cement producers intensified their efforts in recent decades to constantly reduce the percentage of clinker in the Portland cement.

As simultaneously some fibre cement plants add additionally fine inert materials, latent hydraulics or pozzolanic material to their Portland cement the clinker percentage of the cement is even more reduced. There are air cured cases where the clinker percentage in the final binder system is only 50% or even lower. Fibre cement manufacturers are not always aware of this and may have to grapple with undesired consequences without realizing the real cause.

So, if the fibre cement manufacturer is not 100% aware of the composition of its Portland cement he quite certainly will face some undesired consequences in his production process and end product.

NEGATIVE IMPACTS ON THE FIBRE CEMENT PRODUCTION DUE TO THE CLINKER REDUCTION IN PORTLAND CEMENT

In the early stage of hydration the Portland cement clinker (and its grinding fineness) is the main way to increase the temperature and hydration speed during the curing process.

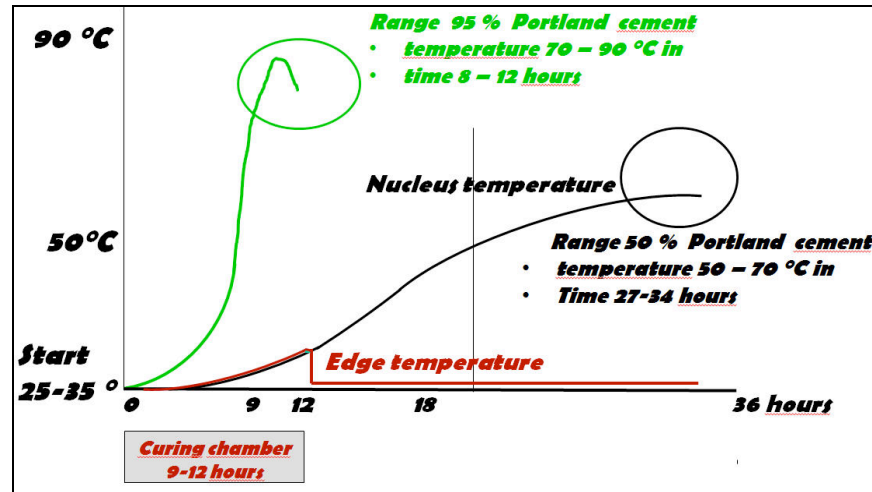


Figure 3 - Curing temperatures influenced by clinker content

Reduction of curing temperature and retard of temperature peak

Temperature measurements in the last years with loggers in the stacks illustrate that a huge thermodynamic change took place due to the clinker reduction in Portland cement to about 50%. So, not only did the time to the temperature peak increase noticeably by about 15-20 hours on average but also the peak temperature itself decreased by approximately 15-30°C at the same time.

Due to this drastic development in curing an adaptation of the traditional curing conditions and procedures (e.g. time in templates) actually would have become necessary and vital in order to avoid negative impacts on the end product. Unfortunately hardly any change was noticeably done in the industry. So it is not a coincidence that the temperature and hydration differences between the nucleus and the edges of fibre cement sheets have increased drastically and became very common in the industry as the de-stacking happens too early and long before of the actual temperature peak.

Reduction of soluble potassium and sodium sulphate

Another result of the clinker reduction in Portland cement is that the soluble potassium and sodium sulfates in the process water are also proportionally reduced. As an example, we recently found in the water of a closed water circuit of a manufacturer of un-pressed sheets levels of only around 10g per liter sodium and potassium in the water circuit which while they accelerate the hydration speed, reduce strength.

On the one hand the alkalinity has a negative effect to the strength development, but on the other hand, the following retarding of temperature development leads to more in homogeneity in hydration over the sheet.

Reduced and retarded pH development due to slow temperature development

The pH development in the curing chamber that is normally accelerated by the temperature is therefore also reduced and retarded when the temperature development is reduced by cement with low clinker content. So the passivation of steel templates may be also lost and corrosion may take place.

CONSEQUENCES FOR FIBRE CEMENT SHEETS

The following negative consequences for fibre cement sheets base may be caused by an in homogeneity in curing process due to a slow/retarded temperature development and a retarded temperature peak, sheets may

be de-stacked too early with the result that the moisture content in the stack nucleus is still too high and may lead to the following problems:

Loss in load and strength of sheet

With the de-stacking long before of the temperature peak, the edge temperature of the sheet nearly decreases to the level of room temperature with the result that the pozzolanic hydrations process at this position is interrupted, retarded or even stopped. Only in the nucleus of the sheets the pozzolanic hydration process continues. The result is a huge gradient between the nucleus and the edge of the fibre cement sheet.

Due to the delayed pozzolanic hydration at room temperature, the strength development at the edges of the sheet is still drastically behind the one in the nucleus after 21 days. The situation becomes even worse when the sheets subsequently are stored outside at the sun or wind. Then with a direct insolation the moisture in the edges evaporates even faster, so that, due to lack of water, the hydration in the edges of the sheets cannot continue.

So, for instance, the edge of corrugated sheets in the load test may crack long before the system has even reached the full capacity of load respectively its strength potential (red curve). Corrugated sheets without such a big gradient between edges and center will develop their full potential of load (blue curve)!

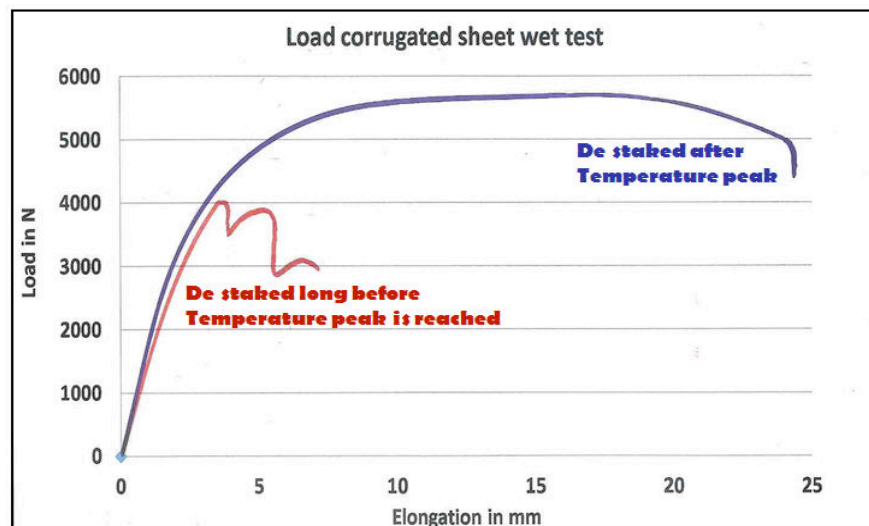


Figure 4 - Load of corrugated sheets

Too high moisture content of the sheets

Often edge cracks are caused due to high moisture gradients, provoked by low temperature during curing. Sheets stored at the outside-with too high water content inside the stack are supposed to crack. The black curve in figure 3 is from 7 sheets, cured “cold”. The sheets in the templates where cured out of the curing chamber with a plastic cover.

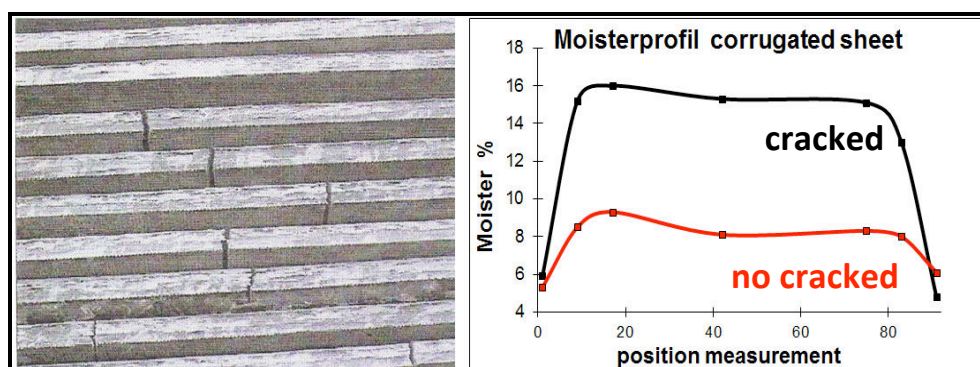


Figure 5 - Typical edge cracks and moisture curve of a cracked and a non-cracked sheet stack

No optimal porosity and coarseness of the sheets

Wet dry cracks are typical for regions with dry periods followed by abrupt rain as certain areas in South America, Africa and Asia or for example in countries where industrial buildings are covered with corrugated sheets to protect industrial ovens.



Figure 6 - Typical wet dry crack happen to 90% at the fixing point

A high porosity with a high amount of pores coarser than 1 micron permits a tension free water exchange as shown in Figure 5 in red. Therefore a sheet with an unsatisfactory porosity (Figure 5 in blue) permits no tension free water exchange with the consequence that the sheet surface expands until it cracks lengthwise, typically at the fixing points.

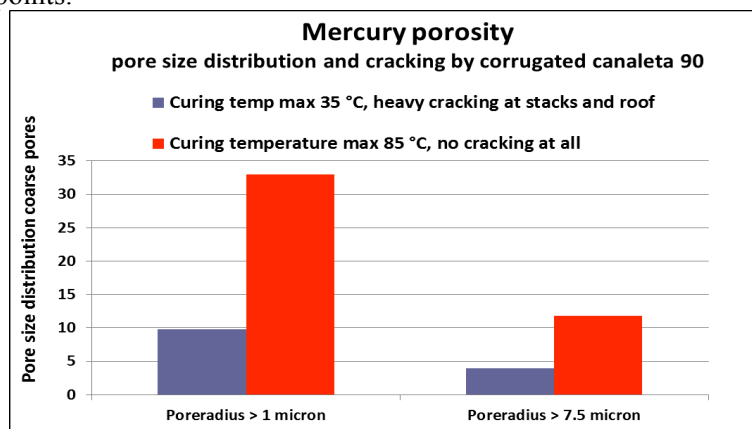


Figure 7 - Pore size distribution by mercury of different cured Canaletta sheets

Sticking of steel moulds

Sticking and corrosion problems in context with steel moulds have steadily increased in the last decade. Up to date the reason for these phenomena was mainly searched in the steel quality. This may be eligible to a certain point, however, there are cement related causes, which have a much bigger influence on the sticking and corrosion problem as commonly expected.

Sticking depends also on the water/cement respectively on the water/clinker ratio. So, the less clinker in the mix is the more it will stick on the steel mould whereas mixes with pure Portland cement with 95% clinker, e.g. EN Cem. I., stick much less. This is also the reason why manufacturers with autoclave mixes with only 25 – 50% clinker suffer much more of sticking.

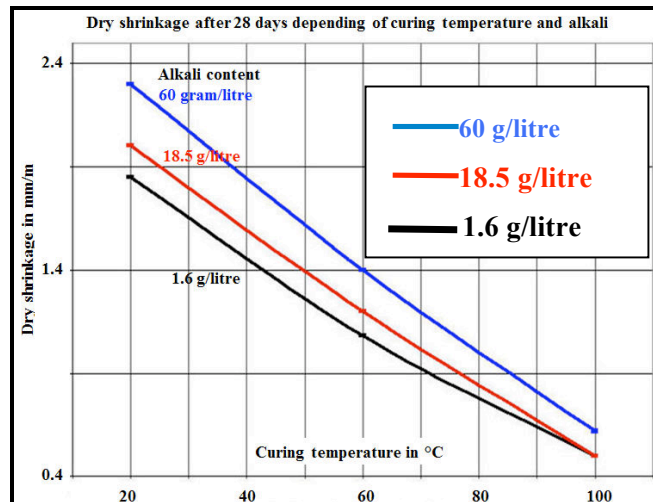


Figure 8 - Shrinking depends on curing temperature in project "closed water circuit", CemTec and Heidelberg Cement 1986

Additionally, if we consider a fiber cement sheet that is produced by cement with 95% clinker content, the temperature increases in a few hours from 35 to 85°C. A 4000 mm steel mould expands by a delta temperature of 50°C about 1.8 mm. At the same time, the fiber cement sheet is losing water and shrinks in the same time, depending of the mix about 1.0-2.0 mm. As a result, we have a relative horizontal movement of a few mm between sheet and the steel mould that separates the sheet from the template. By using a cement with only 50% clinker content the expansion of the steel templates respectively the shrinking of the fibre cement sheet is much less.

This may explain why 30-40 years ago we had less sticking even though the oiling and cleaning efforts were less.

In laboratory tests we verified that sticking is also advantaged by an unsatisfactory oiling or by the use of inadequate oil like Diesel or Diesel/water mixes, independently whether the steel moulds were made of hot-rolled steel or hot-dip galvanized steel.

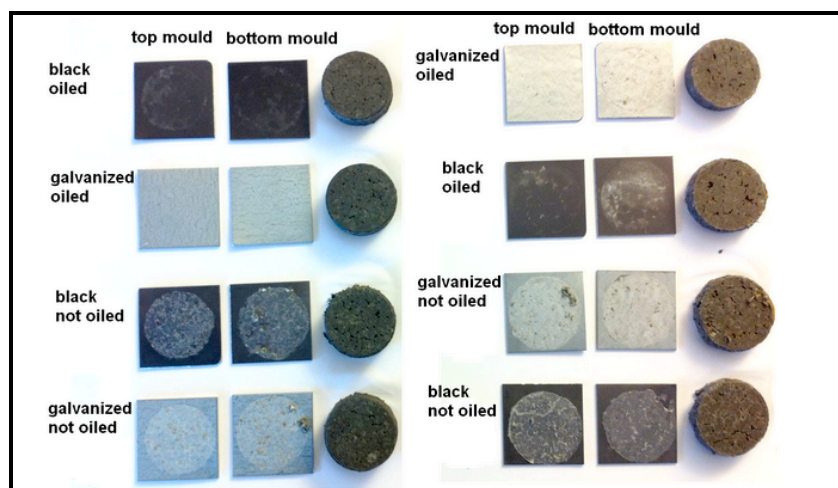


Figure 9 - Example of oiled and unoled steel moulds black and galvanized surface. Left and right different template

Corrosion of steel moulds

There are at least three important facts why steel moulds start to corrode when they are used in the fibre cement production:

1. Passivation

With clinker and alkali reduced cement concepts, the pH value can stay below the passivation limit of 12.5-12.7. In this case the corrosion can start by black/carbon steel. In this field we have very accurate scientific studies and facts from the steel reinforced concrete.

2. Reduction of pH development by lower temperature

The pH increase with temperature, so with lower temperature, the pH development in the steel moulds starts later, i.e. only after de-stacking.

3. Chromium VI reduction in Europe and Switzerland

Chromium VI is a perfect inhibitor against corrosion. So, the Chromium VI reduced cement is in many cases directly responsible for the heavy corrosion on black steel moulds. After the introduction of the chromium VI reduction in Portland cement in January 2005, also the concrete producers have started to claim more and more about heavy corrosion at steel moulds. We had the same observations in Switzerland with our customers in the concrete production when the chromium VI reduction was introduced.

This fact motivated the HTC, Heidelberg Technology Center, (Bolte 2006), to study the influence of chromium VI to the corrosion of steel and published the results.

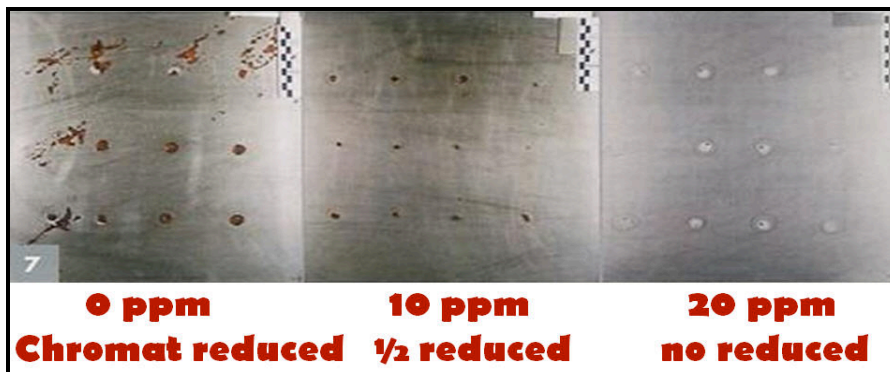


Figure 10 - Strong correlation between corrosion with reduction of chromium VI (Bolte 2006)

Discolouring with chromium reduced cement at the basis of Fe II sulphate

Another phenomena with chromium reduced cement since 2005 appeared there, where the chromium reduction was done with iron II sulfate. The claims of brown yellow discoloring in Portland cement bound products have increased drastically. Below is an example from Norway, where the Chromium reduced Cement was introduced long before the EN regulation took place (Häring 2003).



Figure 11 - Extreme staining at some elements in Norway (Häring 2003)

CONCLUSION

Portland cement was and still is a subject of permanent improvement and adaptations as are many other products. But are you always aware and sure whether there has something changed or not and if yes what? As a matter of fact you actually should! A fibre cement manufacturer may scrutinize the ingredients of Portland Cement, so that it is no black box to him. Too much is at stake that this could be neglected.

With this presentation the author wants to make you aware what negative impacts changes of one of the major raw materials like Portland cement can have for the quality of your fibre cement sheets.

But note that there may is not a general recipe how you overcome these problems. But being aware of the causes of the negative consequences makes it for everybody easier to find a tailor-made solution.

The author offers a range of solution approaches always in context with the changes, which happened to Portland cement in the last decade.

So, when you have problems like loss in load and strength, a too high moisture content or a not optimal porosity of your fibre cement sheets you may not only consider your mix or recipe as the cause, but may also take in account that a possible reason could also be the composition of your Portland cement. When you come to this conclusion then the problems rather are countered by adapting your manufacturing process.

However, the list may is not complete:

- The heat that is generated by the hydration of the cement in the first hours during curing should somehow be preserved by using a more insulated curing chamber for example. This would improve the homogeneity of the water distribution and temperature over the entire sheet.
- You should prolong the curing time by keeping the fibre cement sheets stacked in the steel moulds as long as possible, in the ideal case until the temperature has passed its peak. Due to the resulting higher vapour pressure in the sheet the moisture will be reduced also in the nucleus. So, the moisture gradients may be reduced.
- Protect especially the long side of the sheet stacks after de-stacking from wind and direct insolation.
- The sticking phenomena can be reduced when the fibre cements are de-stacked at higher temperature. The relative movement between the steel mould (temperature expansion) and the fibre cement sheet (drying shrinking) supports the separation procedure of the fibre cement sheet from the steel mould.
- For producers who are using Chromium VI reduced cement the use of hot-dip galvanized steel moulds may be essential to prevent corrosion.
- In the case that cement with very low clinker content is used, hot-dip galvanized steel moulds may be more appropriate to use.

REFERENCES

Bolte G, Dietermann M, Hårdtl R. (2006), Heidelberg Technology Center, Leimen Germany „Betonchemische Erfahrungen mit der Chromreduzierung von Zement“, Beton Werk International BWI 5/2006

Häring C., Cemtec Beratung (2003), GmbH, Cham Switzerland, “Developments in concrete mix design and iron discoloration”, Beton Fertigteil Technik BFT 6/2003