A case study of high-temperature corrosion in rotary cement kilns

by J.H. Potgieter*, R.H.M. Godoi†, and R. van Grieken†

Introduction

Corrosion as far as cement is concerned is usually associated with its application in concrete and specifically the degradation of rebar in the concrete structure. The subject of reinforcement corrosion is well and widely described1-8, but descriptions of corrosion of the structures producing cement seldom appear in literature. Just as there are numerous variables influencing the corrosion of rebar in the concrete composite called concrete, the corrosion occurring in rotary cement kilns is a complex phenomenon that depends on many different processes and environmental conditions.

A rotary cement kiln does not present a homogeneous environment on the inside; rather, it can be seen as a complex chemical reactor with various temperature zones and differing container wall constituents in the different temperature zones9. To complicate matters, the equipment design (the number of pre-heaters, for example), raw materials composition and operating conditions can all influence the corrosion occurring in a rotary cement kiln.

Of all the variables of interest, the chemical composition of the raw meal being used and specifically its chloride, sulphate and alkali contents, and the type of refractory used in the kiln are probably the two most important ones in terms of their contribution to corrosion occurring inside the kiln. Alkalis are normally introduced into the kiln through raw materials, while sulphur and chlorine originate mainly from the fuel10. Chlorides and sulphates of alkalis form low melting eutectics, with melting points between 770ºC and 1080ºC11. Alkali vapours can be deposited on the raw meal being pre-heated and are then recycled back into the furnace, thereby increasing in concentration under circulation. Chlorine combines preferentially with the alkalis, whereas sulphate often combines with CaO in the bricks and infiltrates through the refractory lining; sulphates can even combine with the MgO in the refractory bricks during the infiltration process12. In both cases the increase in molar volume of the products that are formed will lead to a decrease in brick strength and subsequent increased infiltration of the lining. Magnesia spinel bricks are known to be sensitive to alkali attack in the transition zone or further away from the burning zone13. Kiln stoppages and unstable operating conditions, in combination with the oxidizing atmosphere that exists in the kiln, are aggravating factors that can further salt infiltration into the refractory and ultimately hasten corrosion that occurs on the kiln shell11,14.

This paper describes a case study of corrosion of the kiln shell of two different rotary cement kilns and illustrates the different natures of the observed corrosion. One of the kilns was a long dry-process furnace with only one pre-heater fitted to the feed-end; the other was a short kiln fitted with five pre-heater stages.

Synopsis

This paper describes two cases of corrosion that occurred in dry-process, rotary, cement-clinker kilns. In the case of the kiln with five pre-heater stages, the attack occurred primarily from sulphates that probably originated in the raw feed and fuel being used in the plant and that penetrated the refractory lining. The corrosion was similar to ash-deposit corrosion often observed in steam boilers. In the second case the plant consisted of a long dry kiln with a single pre-heater fitted to the feed-end. In this case the corrosion could be ascribed to alkali chloride penetration through the refractory-brick lining and subsequent hot corrosion of the kiln shell.
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**Examination**

**Sites and materials**

The corrosion scales examined in this investigation were removed from the shells of two kilns during maintenance when the refractory bricks in the transition zones were replaced. In both cases dolomite bricks were used. The corrosion scales are brittle and porous, and their colours varied from brown to black; in some areas salt crystals were observed. The scales have a layered appearance. In both kilns corrosion occurred in the transition zone about 30 m from the coated clinkering zone. The length of the first kiln (kiln 1) is 85 m in total. To preheat the raw meal entering the kiln, five pre-heaters are fixed at the feed-end of the kiln. The second furnace (kiln 2) is a rotary kiln about 140 m in length and it has a single pre-heater stage at the feed-end.

**Analysis**

The chemical composition of the corrosion products was analysed by means of X-ray fluorescence (XRF) and their phase compositions by means of X-ray diffractometry (XRD). Microanalysis and mappings were undertaken by means of energy dispersive X-ray spectrometry (EDX); images were recorded by scanning electron microscopy (SEM).

**Results and discussion**

The chemical compositions of the two corrosion scales as determined by XRF analysis are given in Table I. The corrosion products in the two samples differ from each other. In the sample from the short kiln with 5 pre-heaters (sample 1) there is a high sulphate concentration, which seems to indicate a sulphur-dominant type of corrosion attack. In the sample from the long dry kiln with a single pre-heater (sample 2) the concentrations of both chloride and potassium are high, which points to a chloride type of attack of the kiln shell.

Table II lists the phases identified in the two samples by XRD and one notes a difference in composition between the two scales. This analysis also points to two different types of corrosion attack in the two kilns. The EDX spectra of each corrosion scale show that sample 1 has high sulphur and calcium contents, while sample 2 has substantial amounts of potassium and chloride present in it. Figure 1 is a mapping of the surface of the corrosion scale of sample 1 as shown in the photomicrograph of Figure 2. The backscattered image of each individual element mapped separately shows high levels of Ca and S (probably SO$_4^{2-}$) species.

### Table I

**Chemical composition (%m/m) of investigated corrosion scales**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample 1 (%m/m)</th>
<th>Sample 2 (%m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>0.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>67.5</td>
<td>78.4</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>0.6</td>
<td>1.3</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>CaO</td>
<td>1.8</td>
<td>0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>2.2</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>16.9</td>
<td>0.1</td>
</tr>
<tr>
<td>C$_6$</td>
<td>2.3</td>
<td>7.5</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>&lt;1.0</td>
<td>1.4</td>
</tr>
<tr>
<td>LOI</td>
<td>7.0</td>
<td>6.7</td>
</tr>
<tr>
<td>Total</td>
<td>100.2</td>
<td>99.4</td>
</tr>
</tbody>
</table>

**Table II**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Sample 1</th>
<th>Sample 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl (sylvite)</td>
<td>—</td>
<td>X</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (hematite)</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ (magnetite)</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>FeS (troilite)</td>
<td>X</td>
<td>—</td>
</tr>
<tr>
<td>FeS$_2$ (pyrite)</td>
<td>X</td>
<td>—</td>
</tr>
<tr>
<td>CaSO$_4$ (anhydrite)</td>
<td>X</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 1—X-ray maps of corrosion scale from case 1 kiln

Figure 2—Photomicrograph (backscattered-electron image) of corrosion scale from the kiln in case 1
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Figure 3 is a mapping of the corrosion scale of sample 2 as shown in the photomicrograph of Figure 4. The X-ray map images of the individual elements plotted separately indicate high levels of K and Cl with respect to the other elements. This, together with the difference in corrosion-scale morphologies shown in Figures 2 and 4, is an indication that the cause of corrosion in the two cases under investigation is different.

Corrosion processes in cement kilns are often similar to those occurring in steam boiler walls that are covered with deposits\textsuperscript{15}. In this respect, the kiln acts as a ‘wall deposit’. In an oxidizing atmosphere, the iron from the steel shell will react with oxygen to form an oxide scale. Generally this scale contains different iron oxides with Fe\textsubscript{2}O\textsubscript{3} (hematite) usually being found at the scale-brick interface\textsuperscript{15}. This is in agreement with results of this current investigation, which observed the presence of different types of iron oxides in the samples of corrosion scale.

The X-ray diffractogram of sample 1 detected the presence of various sulphur compounds. A microscopic examination of the piece showed tiny salt crystals along the fissure boundaries. Although the composition of the fuel and the raw mix used are not given in this investigation, it is well known that they are the most common possible sources of sulphur\textsuperscript{10}. Sulphur from the fuel can react in the oxidizing atmosphere of the kiln to produce acid gases according to the following well-known reactions:

\[ \text{S(g)} + \text{O}_2(g) \rightarrow \text{SO}_2(g) \] \[ \text{2SO}_2(g) + \text{O}_2(g) \rightarrow \text{2SO}_3(g) \]

In the oxygen-restricted environment between the refractory lining and the kiln shell, it is conceivable that SO\textsubscript{2} or SO\textsubscript{3} can act as the oxygen donors and react with iron according to the following reaction\textsuperscript{15}:

\[ 5\text{Fe(s)} + \text{2SO}_2(g) \rightarrow \text{Fe}_3\text{O}_4(s) + 2\text{FeS(s)} \]

If one considers the possibility of an interaction between SO\textsubscript{3} and the dolomite component of the refractory bricks in the lining and the positive identification of CaSO\textsubscript{4} by XRD, the observed corrosion products could be explained by an excess of sulphur oxides present in the kiln atmosphere and their penetration through the refractory lining.

In sample 2 the concentration of KCl in the corrosion scale is high. Whereas chlorine gas can react with the kiln shell, the alkali metal oxides K\textsubscript{2}O and Na\textsubscript{2}O cannot. Alkalies can only penetrate the refractory brick lining as part of a potassium- or sodium-salt melt. The corrosion products contain substantial KCl and in this particular instance therefore the damage was caused by ‘hot corrosion’. In hot corrosion a liquid phase normally takes part in the corrosion reaction. In boilers hot corrosion usually occurs between 800 and 950ºC\textsuperscript{15}, but in rotary cement kilns it is conceivable that it can occur above a critical temperature of between 300 and 340ºC\textsuperscript{11}. Kiln shell temperatures in this plant, as measured by an infrared scanning device, usually fluctuate between 350 and 360ºC. Chlorine build-up in the kiln seems to be the main culprit, which causes the observed kiln corrosion. This build-up is made worse by the prevailing practice at this plant of recirculating kiln dust from the electrostatic precipitators, a dust that is rich in alkalis originating from raw materials of high alkali content.

Conclusions
This investigation describes two different processes responsible for kiln shell corrosion in rotary cement kilns. Current plant practices, the composition of the raw materials and the type of refractory brick could all potentially have contributed to the corrosion that occurred.

Recommendations
A possible solution to the observed corrosion in both cases might be to use a denser brick to resist infiltration by aggressive chemical species. It is known that magnesia-zirconia bricks have good resistance to corrosion by alkali salts, whereas magnesia-enriched dolomite bricks also perform well under such conditions\textsuperscript{13}. Another worthwhile approach might be to abandon the current practice of recycling kiln dust to the raw meal. As a last resort, a chloride or alkali by-pass might be considered.
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Acknowledgements

The authors wish to thank staff at VDZ (Verein Deutsche Zementwerke) in Düsseldorf, Germany and the librarian at the Technical Information and University Library of Hannover (TIB/UB), Germany, for their assistance in this investigation. JHP wishes to thank the FWO-Vlaanderen (Fonds voor Wetenschappelijk Onderzoek) for financial assistance.

References


Outokumpu expands interests to base metal, ferrous and aluminium pyro and hydro fields*

Outokumpu, one of the leading stainless steel, copper fabrication and related technology company in the world, is now extending its metals processing activity in southern Africa.

For many years grinding mills, flotation, thickeners, physical separation and process control systems have been the backbone of the Outokumpu Technology’s process equipment in South Africa. The company is now broadening its products and services to include base metal pyro- and hydrometallurgy, ferrous, sulphuric acid and off-gas, alumina and aluminium processes locally.

Proven know-how in fields such as circulating fluidised bed roasting, vertical smooth flow solvent extraction, electrolytic tankhouses and ferroalloy pelleting and sintering can now be offered locally.

Prior to metals processing becoming an active part of Outokumpu in South Africa about two and a half years ago, sales were conducted from overseas. This resulted in projects that have built up a solid installed base in the metallurgical field.

Some installation examples are at the largest platinum base metal refinery in Southern Africa (which uses an Outokumpu hydrometallurgical process to recover cobalt), gold reclamation acid plants and several large ferrochrome pelletisers.

‘Since these installations, business steps have been created to set up MetPro locally, to introduce ourselves to the market, and to explain how our structure and acquisitions such as Lurgi Metallurgie fit in to our local company,’ says Peter Jerman, Outokumpu’s director of metals processing.

‘Over the past few months we have been tracking down old customers and launching our after-sales service in metals processing.’

‘Prospects look good in ferroalloys, where new plants and capacity are on the drawing board. The Hernic ferrochrome expansion is already under way.’

‘Heavy mineral producers are eyeing the potential benefits of using our roasters for the pre-reduction of ore,’ comments Jerman ‘and the sulphuric acid field is very active, driven by environmental factors such as reducing SO₂ emissions into the atmosphere and shortage of acid to leach ores in places like Zambia and the Democratic Republic of the Congo. We offer proven, state-of-the-art technology. I like to think that we are good social partners; our processes are environmentally friendly owing to reduced emissions and effluents—as well as being efficient in the use of fuel and energy.’

The company’s goals are to increase the local component of projects where possible and practical, as well as increase value for its customers.

‘What is very encouraging is the number of potential projects away from home. Activity in Botswana and Zambia is pleasing and we see opportunities further afield in places like Madagascar and Mozambique,’ concludes Jerman.

Rather than simply selling off-the-shelf hardware, the company’s philosophy is to understand the customer’s perspective. Its metallurgical background is a decided advantage.

‘This approach draws the company into joint ventures, partnerships, test-work, investigations, projects and turnkey proposals.’

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