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Identification of refractory material failures in cement kilns

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IDENTIFICATION OF REFRACTORY MATERIAL FAILURES IN CEMENT KILNS CORRECTIONS

Peter Lugisani

CORRECTIONS EXAMINER 1

1. The heading “Identification of failure of refractory materials in cement materials” appearing on top of each page (page 1 to page 6) should be in same font throughout the text such as the one appearing on page 7 and for the rest of the next.

The headings have been corrected

2. p.iii. The sentence starting with …the calculated values…should be re-written in order to clarify the meaning of …no oxidation of oxides.

p.iii. The partial pressure of oxygen is low (1.333×10^{-4} atm), it indicates the stability of Fe_3O_4 and Mn_3O_4 and therefore does not favour the oxidation of Fe_3O_4 to formation of Fe_2O_3 and Mn_3O_4 to formation of Mn_2O_3.

3. p.3. Peray and Waddell (1972) also reported that that…second should be removed

p.3. Peray and Waddell (1972) also reported that refractory-lining failure occurs due to repeated kiln shutdown and start-up, or severe operating upset which usually create large temperature changes in the kiln and subject the lining to thermal shock.

4. p.16. Figures titles should appear below the actual figures: Fig 2-3 and Fig 2-4 in Fig 2-3 (c) should be lower case letter.

Figure 2-1, 2-2, 2-3, 2-4 and 2-5 were all removed, they were not referenced in the text.

5. p.34. … temperature defference … should read… temperature difference…

p.32. *R* defines the minimum temperature difference to produce fracture and *R'''* expresses the degree of thermal shock damage in materials with similar crack propagation properties, that is, similar values of work of fracture (γ_{wof}).

6. Reference for ΔG^o (J) = -282,400 + 86.81T

p.45.

This gives:

$$PO_2 = \left(\frac{PCO_2}{PCO}\right)^2 \frac{1}{e^{-2\Delta G^\circ/RT}} \qquad \text{E.q 2-8}$$

where $\Delta G^\circ\ (J)$ according to Azad (2006) is expressed as follows:

$$\Delta G^\circ\ (J) = -282{,}400\ + 86.81T \qquad \text{E.q 2-9}$$

7. Reference for T = 11.4 L / NDS

The residence time of the charge in the kiln is approximately 1 hr and can be calculated according to Alsop (1998) as follows: (p.52)

$$\mathrm{T} = 11.2\ \mathrm{L} / \mathrm{NDS} \qquad \text{E.q 3-1}$$

8. p.71 and 72. Figures 4-4a, 4-5a and 4-6a are not referenced in the text

p.71. The SEM micrographs of unused and damaged magnesia bricks are respectively shown in figures 4-4a, 4-4b, 4-5a, 4-5b, 4-6a and 4-6b. All of the SEM micrographs show similar morphology and therefore no clinker diffusion took place into the damaged magnesia bricks.

9. p.96. refarctory should read refractory

p.98. The mechanisms for failure of the magnesia refractory lining were discussed based on chemical analysis, post-mortem microstructural examinations and interaction predictions by ternary phase diagrams.

10. p.100. pictures of Figure 5-1. Should be located in the same page (p.100)

p.102. Figure 5-1 is now located in a same page. See the figure below.

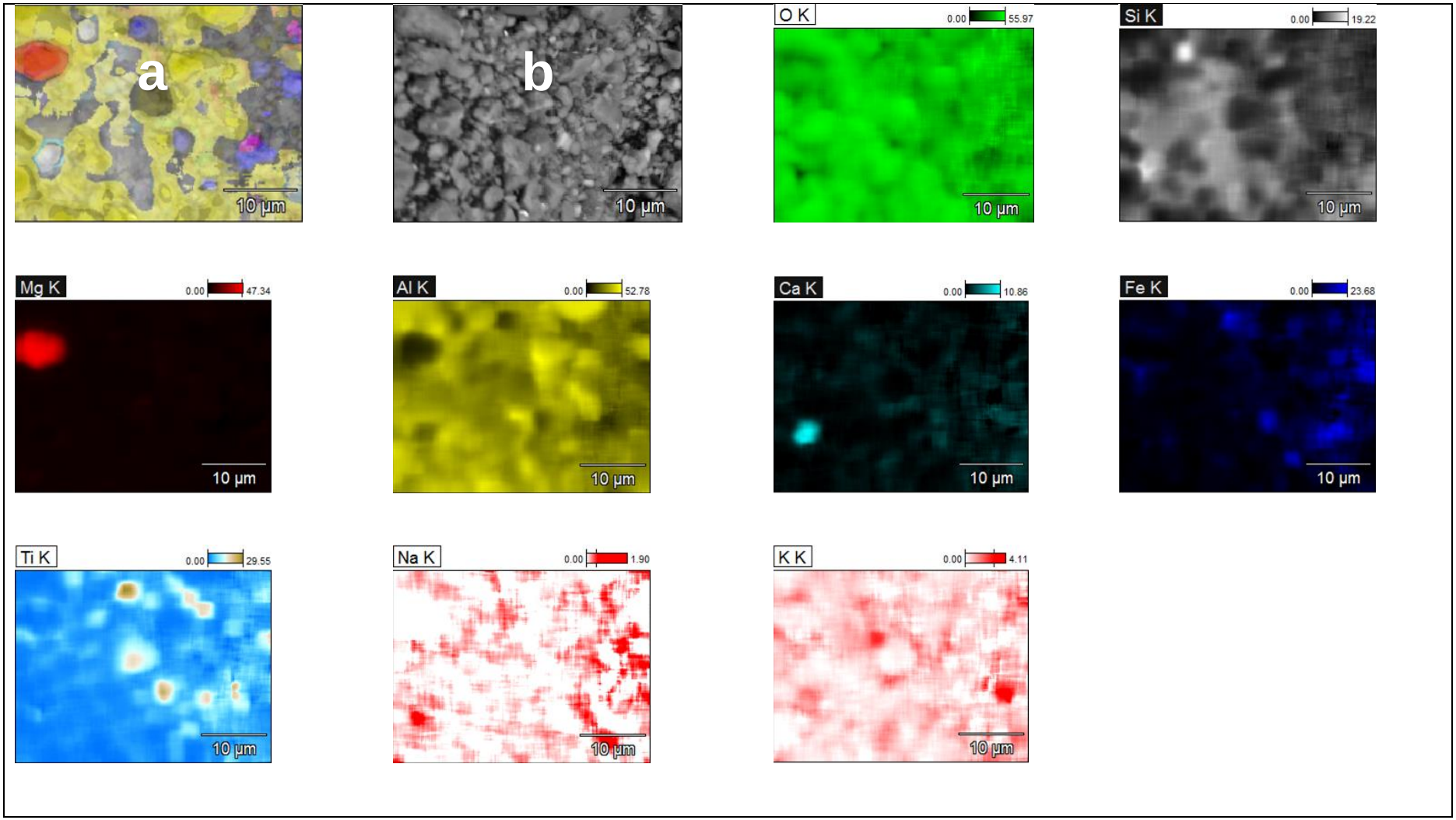

Figure **Error! No text of specified style in document.**-1. SEM-EDS mapping of the damaged high-alumina powder sample

11. p.114. It is evidence that chemical… it is evident that chemical…

p.119. It is evident that chemical attack can be one of the causes of the high-alumina brick failure.

12. p.117. Eq. 6-1 given in page 117 should be same as Eq. 2-8 given in page 46. -2ΔGº should replace -ΔGº for which the equation is given as:

ΔGº = -282,400 + 86.81T (j/mol)

p.122. Equation corrected as below:

$$PO_2 = \left(\frac{PCO_2}{PCO}\right)^2 \frac{1}{e^{-2\Delta G^\circ/RT}} \qquad \text{E.q 6-1}$$

13. References should be rearranged according to the alphabetical order.

Aksel, C., Riley, F.L… should be placed before Aksel, C., Warren, P.D. …

Ghosh, A. … before Gilchrist, J.D. …

Maharajan, Y.R. … before Mazzoni, A.D. …

Pena, P. …before Peray, K.E. … before Petkov, V. …

P.134-137: reference

Aksel, C., Rand, B., Riley, F.L., Warren, P.D. (2004a). Thermal shock behaviour of magnesia–spinel composites. *Journal of the European Ceramic Society*, no. 24, pp. 2839-2845.

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Aksel, C., Warren, P.D., Riley, F.L. (2004b). Fracture behavior of magnesia and magnesia-spinel composites before and after thermal shock. *Journal of the European Ceramic Society*, no. 24, pp. 2407-2416.

Alsop, P. A., (1998). *The cement plant operations*. 2nd Edition, Tradeship Publications Ltd., Houston.

Azad, A. (2006). Fine-tuning of ceramic-based chemical sensors via novel microstructural modification. Part II: Low level CO sensing by molybdenum oxide, MoO_3. *Sensors and Actuators B 120*, pp. 25-34.

Bartha, P., Sodje, J. (2001). *Degradation of refractories in cement rotary kilns fired with waste fuels*. Report no.61, Vol.5, pp. 64-72, Refratechnik, Gottingen.

Caballero, A., Serena, S., Sainz, M.A. (2009). The system Clinker-MgO-$CaZrO_3$ and its application to the corrosion behavior of $CaZrO_3$/MgO refractory matrix by clinker. *Journal of the European Ceramic Society*, no. 29, pp. 2199-2209.

Ghosh, A., Sarkar, R., Mukherjee, B., Das, S.K. (2004). Effect of spinel content on the properties of magnesia–spinel composite refractory. *Journal of the European Ceramic Society*, no. 24, pp. 2079–2085.

Gilchrist, J.D. (1977). *Fuels, Furnace and Refractories*. Pergamon press, Newcastle.

Hayes, P.C. (2003). *Process principles in minerals and materials production.* Third edition, Hayes publishing co., Queensland.

Kunnecke, M. (1998). *Wear phenomena of refractory linings in the burning zone of rotary cement kilns*. Report no.5, Refratechnik, Gottingen.

Obregon, A., Rodriquez-Galicia, J.L., Lopez-Cuevas, J., Pena, P., Baudin, C. (2011). MgO-CaZrO3-based refractories for cement kilns. *Journal of the European Ceramic Society*, no. 31, pp. 61-74.

Pena, P., Rodriguez-Galicia, J.L., De Aza, A.H., Rendon-Angeles, J.C. (2007). The Mechanism of corrosion of MgO-$CaZrO_3$-calcium silicate materials by cement clinker. *Journal of the European Ceramic Society*, no. 27, pp. 79–89.

Peray, K.E., Waddell, J.J. (1972). *The rotary cement kiln*. Chemical publishing Co., New York., pp. 1 – 23.

Potgieter, J.H., Godoi, R.H.M., Van Grieken, R. (2004). A case study of high-temperature corrosion in rotary cement kilns. *Journal of the South African Institute of Mining and Metallurgy*, pp. 603–606.

Riley, F.L., Aksel, C., Rand, B., Warren, P.D. (2002). Mechanical properties of magnesia-spinel composites. *Journal of the European Ceramic Society*, no. 22, pp. 745-754.

Serena, S., Sainz, R.M., Caballero, A. (2004). Corrosion behavior of MgO/$CaZrO_3$ refractory matrix by clinker. Journal of the European Ceramic Society, no. 24, pp. 2399–2406.

Szczerba, J. (2010). Chemical corrosion of basic refractories by cement kiln materials. Ceramic International, no. 36, pp. 1877-1885.

Taylor, H.F., 1997. *Cement chemistry*. 2nd Edition, Thomas Telford Services Ltd, Aberdeen.

CORRECTIONS EXAMINER 2

Editorial comments

Dissertation title

The document has a confusing title, which does not give a good first impression. I propose the following change:

Current: “Identification of Refractory Materials Failure(s) in Cement Kilns”

Proposed: “Identification of Refractory Material Failures in Cement Kilns”

The title changed to the suggested title: “Identification of Refractory Material Failures in Cement Kilns”

Declaration

The second sentence of the declaration page i is incorrectly constructed. I propose the following change:

Current: “It is being submitted to the degree …”

Proposed: “It is being submitted for the degree…”

p.i.

I declare that this dissertation is my own unaided work. It is being submitted for the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

Table of Contents

The following problems were identified in the table of contents:

1. Inconsistent capitalisation. Second level headings are sometimes written in title case (sections 1.1 and 1.2), but mostly in sentence case.

p.5.

1.1. Research objectives

1.2. Research questions

2. Long section titles

In many cases very long section titles are used, which makes the table of contents difficult to read and interpret. Many of the titles can be made shorter.

For example, in chapter two the phrase "of refractory materials" is repeated in titles while this is the focus of the document. It therefore does not need be repeated.

Titles shortened through-out the text.

3. Missing appendix titles

In the case of appendix B, C, and D, no titles are provided.

p. 139-152. Appendix corrected as follows:

Appendix A: XRD results

Appendix B: Calculations for conversion from mass% to mole%

Appendix C: ASR data

Appendix D: Kiln feed composition

Appendix E: Residence time in Kiln

List of figures

The list contains long captions, instead of short captions. Long captions should only be used in the text where the figures appear, while clear short captions should be used in the list of figures. Long captions in the list of figures makes the list difficult to read, and therefore less useful. Figure 2-1 is used as an example:

Current: "Figure 2-1. Equilibrium diagram of the quaternary system MgO-CaO-ZrO_2-SiO_2: (a) solid state compatibility relationships ..."

Proposed: "Figure 2-1. Equilibrium diagram of the quaternary system MgO-CaO-ZrO_2-SiO_2."

Figure 2-1, 2-2, 2-3, 2-4 and 2-5 are all removed from the text.

In the case of Figure 5-2 and 5-3 the captions are vague. Captions need to be clear enough to be interpreted away from the graphic in the list of figures.

In the case of Figures 5-4 to 5-8 the captions are not specific enough. As an example, the Figure 5-4 should be changed as follows:

Current: "Figure 5-4. System Al_2O_3-CaO-SO_3 at 1200ºC and 1 atmosphere

Proposed: "Figure 5-4. System Al_2O_3-CaO-SO_3 ternary phase diagram at 1200ºC and 1 atmosphere"

Figures are corrected as follows:

Figure 4-1: SEM-EDS mapping of magnesia-spinel brick type A (p.62)

Figure 4-2: SEM-EDS mapping of magnesia-spinel brick type B (p.63)

Figure 4-3: SEM-EDS mapping of magnesia-fused spinel (p.64)

Figure 4-4: The SEM micrograph polished brick section of magnesia-spinel brick type A, a) the unused, and b) the damaged (p.73)

Figure 4-5: The SEM micrograph polished brick section of magnesia-spinel brick type B, a) the unused, and b) the damaged (p.74)

Figure 4-6: The SEM micrograph polished brick section of magnesia-fused spinel, a) the unused, and b) the damaged (p.75)

Figure 4-7: The SEM micrograph fracture of magnesia-spinel brick type A, a) the unused, and b) the damaged (p.76)

Figure 4-8: The SEM micrograph fracture of magnesia-spinel brick type B, a) the unused, and b) the damaged (p.77)

Figure 4-9: The SEM micrograph fracture of magnesia-fused spinel, a) the unused, and b) the damaged (p.78)

Figure 4-10: System $MgO-Al_2O_3$-KCl ternary phase diagram at 1500ºC and 1 atmosphere (p.82)

Figure 4-11: System $MgO-Al_2O_3$-KCl ternary phase diagram at 1500ºC and 1 atmosphere (p.83)

Figure 4-12: System $MgO-CaO-SO_3$ ternary phase diagram at 1500ºC and 1 atmosphere (p.85)

Figure 4-13: System $MgO-CaO-SO_3$ ternary phase diagram at 1500ºC and 1 atmosphere (p.86)

Figure 4-14: System $MgO-CaO-SO_3$ ternary phase diagram at 1500ºC and 1 atmosphere (p.87)

Figure 4-15: System $MgO-Al_2O_3-Na_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.89)

Figure 4-16: System $MgO-Al_2O_3-Na_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.90)

Figure 4-17: System $MgO-Al_2O_3-Na_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.91)

Figure 4-18: System $MgO-Al_2O_3-Na_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.92)

Figure 4-19: System $MgO-Al_2O_3-K_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.94)

Figure 4-20: System $MgO-Al_2O_3-K_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.95)

Figure 4-21: System $MgO-Al_2O_3-K_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.96)

Figure 4-22: System $MgO-Al_2O_3-K_2O$ ternary phase diagram at 1500ºC and 1 atmosphere (p.97)

Figure 5-1. The SEM-EDS mapping of the damaged high-alumina powder sample (p.102)

Figure 5-2. The SEM micrograph of high-alumina polished brick section, a) the unused, and b) the damaged (p.107)

Figure 5-3. The SEM micrograph of fracture high-alumina brick, a) the unused, and b) the damaged (p.109)

Figure 5-4: System $Al_2O_3-CaO-SO_3$ ternary phase diagram at 1200ºC and 1 atmosphere (p.112)

Figure 5-5: System $Al_2O_3-SiO_2-Na_2O$ ternary phase diagram at 1200ºC and 1 atmosphere (p.114)

Figure 5-6: System $Al_2O_3-SiO_2-Na_2O$ ternary phase diagram at 1200ºC and 1 atmosphere (p.115)

Figure 5-7: System $Al_2O_3-SiO_2-K_2O$ ternary phase diagram at 1200ºC and 1 atmosphere (p.117)

Figure 5-8: System Al_2O_3-SiO_2-K_2O ternary phase diagram at 1200ºC and 1 atmosphere (p.118)

List of Tables

The following problems were identified:

The Table 3-1 and Table 6-1 captions are vague and insufficient

The captions for Table 4-5 and Table 5-5 are unclear. As an example, the Table 4-5 caption should be modified as follows:

Current: “Percentage mole fraction from analysis by XRF of the damaged magnesia lining”

Proposed: “Molar composition of the damaged magnesia lining, based on XRF assay.”

Tables corrected as follows:

Table 3-1: Industrial kiln feed chemical composition (p.50)

Table 4-1: Chemical compositions of virgin and damaged magnesia brick, based on XRF assay (p.60)

Table 4-2: Elemental composition of virgin and damaged magnesia powder sample, based on SEM-EDS analysis (p.61)

Table 4-3: Phase composition of the virgin and damaged magnesia bricks, based on XRD analysis (p.65)

Table 4-4: Elemental composition of the damaged magnesia polished brick section, based on SEM-EDS chemical analysis. (p.70)

Table 4-5: Molar composition of the damaged magnesia lining, based on XRF assay (p.80)

Table 5-1: Chemical compositions of virgin and damaged high-alumina brick, based on XRF assay (p.100)

Table 5-2: Elemental composition of virgin and damaged high-alumina powder sample, based on SEM-EDS analysis (p.101)

Table 5-3: Phase composition of the virgin and damaged high-alumina lining, based on XRD analysis (p.103)

Table 5-4: Elemental composition of the damaged high-alumina polished brick section, based on SEM-EDS chemical analysis. (p.105)

Table 5-5: Molar composition of the damaged high-alumina lining, based on XRF assay (p.110)

Table 6-1: Volume percent of CO_2 and CO, measured from industrial kiln (p.122)

List of Symbols

Some of the entries in the list are problematic:

XRF: Incorrect definition.

Current: “X-ray fluorescence spectrometry”

Proposed: “X-ray fluorescence”

XRD: Incorrect definition

Current: “X-ray diffractometry”

Proposed: “X-ray powder diffraction”

Tq: Subscript formatting missing.

Tqc: Subscript formatting missing.

μm: unnecessary

MgO: Incorrect, it must be either magnesia or magnesium oxide. It is also unnecessary.

Abbreviated phase formulae: These abbreviated formulae, such as C_3A, C_7A_3Z should be included in the list.

(p.vii-viii.)The list of symbols corrected as follows:

XRF:	X-ray fluorescence
XRD:	X-ray powder diffraction
SEM:	Scanning electron microscopy
EDS:	Energy dispersive spectrometry
ASR:	Alkali sulphate ratio
E:	Young’s modulus
MOR:	Modulus of rupture
RUL:	Refractoriness under load
T_{qc}:	Critical quench temperature
T_q:	Quenching temperature

wt%:	Weight percentage
$\gamma_{wof.}$:	Work of fracture
$MgAl_2O_4$:	Spinel
L:	Liquid
MS_pI:	MgO, β-Ca_2SiO_4, $C_{12}A_7$, C3A_3, $CaSO_4$, C_3A, C_4AF
MS_pII:	MgO, β-Ca_2SiO_4, $CaZrO_3$, $MgAl_2O_4$, $Ca_{20}A_{13}M_3S_3$, $C_{12}A_7$, C_3A_3.$CaSO_4$, C_4AF
C_7A_3Z:	$Ca_7Al_6ZrO_{18}$
EDX:	Energy dispersive x-ray spectrometry
R:	Thermal shock resistance parameter
(C_6A_4 (M, F) S):	Ca_6Al_8 (Mg, Fe) SiO_{23}
C_2 (A, F):	Calcium alumina-ferrite
C_3A:	$Ca_3Al_2O_6$
C_3A_3Z:	$Ca_7Al_6ZrO_{18}$
C_2S:	Ca_2 [SiO_4]
C_3S:	Ca_3 [SiO_4] O
C_3MS_2:	Ca_3Mg [SiO_4]$_2$
M_2S:	Mg_2 [SiO_4]
CMS:	CaMg [SiO_4]
MZ:	Magnesia-zirconia
MSp:	Magnesia-spinel
C_4AF:	Ca_2AlFeO_5
$C_{12}A_7$:	$Ca_{12}Al_{14}O_{21}$
C_3A_3.$CaSO_4$:	$Ca_4Al_6O_{12}$ (SO_4)

Poor Sentence Construction

The text is plagued by incidents of poor sentence construction. It is infeasible to list them all, but here are a few examples:

p.iii “The alkali sulphate ratio of which values indicated that the kiln operating conditions were favourable for the chemical attack to occur.”

The values of alkali sulphate ratio indicated that the kiln operating conditions were favourable for chemical attack to occur. (p.iii).

p.3 “It was found that an addition of …thermal expansion. Greatly improvement of refractoriness.”

Failure of basic refractories might occur from excessive thermal expansion owing to lower spinel content. It was found that addition of 20 wt% spinel content will result in a gradual decrease in thermal expansion and will greatly improve refractoriness under load and increase retained strength after thermal shock (Ghosh et al. 2004) (p.3-4).

p.12 “Any chemical reaction between the refractory …chemical reaction to proceed.”

The chemical reaction between the refractory and clinker results in a mass product transport that allows corrosion to take place. (p.12-13).

p.13 “It was also shown that the reaction interface of … (Pena et al., 2007).”

Pena et al. (2007) found that the clinker/MgO reaction is slightly faster than that of clinker/MgO-$CaZrO_3$-calcium silicate materials. (p.15).

p.20 “Serena et al., 2004 concluded that corrosion process …”

Serena et al., 2004 concluded that the corrosion process is slowed by formation of a MgO sintered layer on the refractory substrates. The formation of MgO sintered layer stops the progress of corrosion attack. (p.18).

p.23 “Szczerba et al. (2010) reported … and kiln feed materials.”

Szczerba (2010) reported XRD results of the reaction product between refractory materials and kiln feed materials. (p.21).

p.43 “The pure MgO without spinel was … in spinel content.”

The fracture analysis of pure MgO was found to be mostly transgranular while a large proportion of intergranular fracture was observed on the MgO materials with spinel content. The intergranular fracture of the MgO materials increased with an increase in spinel content. (p.42).

p.46 “Oxidising conditions are referred to …”

This statement has been removed (p.46).

Spelling

p. ii – clinkerization: South African English does not use a “z”, but rather an “s”. This word is spelled correctly elsewhere in the document. I propose that it be changed to “clinkerisation”.

The presence of low melting phases of KCl, (Na, K) Cl, K_2SO_4 and $CaSO_4$ compromised the refractoriness of the magnesia bricks because they are liquid at temperatures below clinkerisation temperature (1450 °C). (pii).

p.22 – compents

Portland clinker volatile components were K_2O 1.1%, Na_2O 0.1% and SO_3 2.5%. (p.20)

p.34 – defference

R defines the minimum temperature difference to produce fracture and *R'''* expresses the degree of thermal shock damage in materials with similar crack propagation properties, that is, similar values of work of fracture (γ_{wof}). (p.32).

p.96 – refarctory

The mechanisms for failure of the magnesia refractory lining were discussed based on chemical analysis, post-mortem microstructural examinations and interaction predictions by ternary phase diagrams. (p.98).

Problem with Terminology

The following problems were identified with terms used, and should be corrected:

Percentage mole fraction: This must be replaced by either "mole fraction", "mole percent", or even molar composition.

Table 4-5. Molar composition of the damaged magnesia lining, based on XRF assay (p.79)

Table 5-5. Molar composition of the damaged high-alumina lining, based on XRF assay (p.108)

APPENDIX B: Calculations for conversion from mass% to molar% (p146)

Burning zone, lower transition zone: These terms are used early on in the text, but only defined in Figure 3-2. No references provided to this figure to inform the reader of the meaning of the terms.

The kiln has a burning zone (see figure 3-2) where clinkerisation takes place between 1450°C and 1500°C. After clinkerisation the clinker flows through a lower transition zone (see figure 3-2) where the temperature drops off in order to contain the clinker phases. The

bricks used in the burning zone are basic magnesia-spinel and magnesia-fused spinel and those for the lower transition zone are high-alumina. (p.2).

The schematic diagram of the kiln, in Figure 3-2, shows different kiln zones clearly marked. See notes in the diagram. The lower transition and burning zones are well defined in Chapter 1, introduction. (p.53).

Magnesia chrome-free refractory bricks: I suggest that this term be changed to "chrome-free magnesia refractory bricks" if this is the intended meaning. Otherwise it should be corrected to be clear.

The good corrosion resistance of the derived MgO-$CaZrO_3$-calcium silicate materials makes them an attractive material to produce binder fine filler for chrome-free magnesia refractory bricks, which are used at the burning zone of rotary cement kilns. (p.18)

The good corrosion behaviour of the studied material justifies their use as a matrix in chrome-free magnesia bricks for the burning zone of rotary cement kilns. (p.19)

Refractory mixers. I encountered this on page 22. I suspect that the author means "refractory mixtures".

The refractory mixtures of magnesia spinel identified as MSpI (MgO 92.1%, Al_2O_3 5.5% and SiO_2 0.3%), MSpII (MgO 82.7%, Al_2O_3 12% and SiO_2 0.4%) and MZII (MgO 82%, ZrO_2 11%, CaO 5.5% and SiO_2 0.3%), were mixed with kiln feed materials or Portland clinker in a mass ratio of 3:1 (Refractory: kiln feed or Portland clinker). (p.20)

The refractory sample disks for test work were made from refractory brick mixtures. (p.20)

Kiln meal: This term is never defined or explained.

These disks were then polished before being pressed with the hot kiln feed or with the Portland clinker. (p.20).

The $CaZrO_3$ is the result of the chemical reaction between the zirconia from the MSpII brick and the CaO from the hot kiln feed. (p.22).

The high-refractory calcium zirconate and the calcium zirconium aluminate $Ca_7Al_6ZrO_{18}$ (C_7A_3Z) could be formed in the magnesia-spinel bricks as the reaction products with the hot kiln feed and Portland clinker. (p.23).

Alkali/sulphate ratio: This ratio is used but not explained in the text on page 29. A definition is included in Appendix C, but the reader is never informed of this, leading to poor readability.

It was also reported that this wear problem could be resolved by reducing the alkali salt content and balancing alkali / sulphate ratio (refer to appendix C) in the recommended range of 0.8 – 1.2 (Kunnecke, 1998). (p.27).

Alkali/chlorine/sulphur ratio: This ratio is not defined or explained.

The infiltration by alkali and alkali-earth salts and trace elements in the refractory lining were found to be influenced by prevailing temperatures, oxygen partial pressure, and especially alkali sulphate ratio in the various zones in the kiln. The alkali salts are in a balanced ratio when the ASR value = 1 (recommended 0.8-1.2), ASR value > 1 when there is excess of alkali and ASR value < 1 when there is excess of SO_2/SO_3 (Bartha and Sodje, 2001). (p.28)

Brick horizons: The term is used without definition or explanation.

Under the influence of continued SO_2/SO_3 attack, the formation of forsterite (M_2S) can additionally occur. As a result, sulphate salt $CaSO_4$ is formed, densifying the brick structure in deeper brick horizons (brick phase). (p.29)

The formation of $CaSO_4$ is accompanied by an increase in volume, leading to weakening of the physical properties of the affected brick horizons (brick phase), and which results in the destruction of the brick texture. (p.66-67)

These reactions are accompanied with an increase in volume, leading to weakening of the physical properties of the affected brick horizons (brick phase), and finally to a destruction of the brick texture. (p.28)

Grounding/ground: These terms are used when "polishing/polish" should be used.

The mixed materials samples were ground (polished) and pressed. The samples were then heated between 1200ºC - 1400ºC. Identification of phases was done through XRD analysis. (p.20).

Representative brick samples were cut to a predefined size by a diamond blade in order to produce brick sections. The brick sections were then cold mounted and ground (polished) in three steps: 80, 220 and 1200 grit using the diamond discs. (p.54)

The Joel JSM 6510 SEM, equipped with NSS software, was used for microstructural and qualitative chemical analysis. The refractory brick section samples were cold mounted and ground (polished) in three steps; 80, 220 and 1200 grit using the diamond discs. (p.55)

Phase diagrams interactions: This is used on page 58. and in other locations in the document. What does this mean? Simply referring to "phase diagrams" is adequate.

The magnesia-spinel brick type A, magnesia-spinel brick type B and magnesia-fused spinel were all applied at the burning zone of the rotary cement kiln. Analytical methods such as XRF, XRD, SEM-EDS and computational thermochemistry (phase diagrams) were used to establish the failure mechanism of the refractory lining. (p.59).

4.6 Thermodynamics (phase diagram) (p.80)

The high-alumina brick was applied at the lower transition zone of the rotary cement kiln. The failure mechanism of the high alumina lining was studied by using XRF, XRD, SEM-EDS and computational thermochemistry (phase diagrams). (p.100)

5.5 Thermodynamics (phase diagrams) (p.110)

Refractory lining failure of damaged magnesia bricks and used alumina bricks was investigated by XRF, XRD, SEM-EDS analysis and computational thermochemistry (phase diagram). (pii).

Data Presentation

The following problems were identified in the document:

Presenting composition data in paragraph: From page 79 several material compositions are presented in paragraphs instead of in tables. This makes it very difficult for the reader to read and interpret the data. It is a bad practise.

The composition data corrected as follows:

Table 4-6. Normalise composition of the damaged magnesia lining, for Cl_2 effect (p.81)

Chemical species	Mole %. Damaged		
	Magnesia-spinel brick type A	Magnesia-spinel brick type B	Magnesia-fused spinel
Al_2O_3	7.00	0	7.72
MgO	90.53	0	91.65
KCl	2.47	0	0.64
Total	100.00	0	100.00

Table 4-7. Normalise composition of the damaged magnesia lining, for SO_3 effect (p.84)

Chemical species	Mole %. Damaged		
	Magnesia-spinel brick type A	Magnesia-spinel brick type B	Magnesia-fused spinel
CaO	5.75	1.03	1.08
MgO	93.70	98.43	98.70
SO_3	0.55	0.54	0.22
Total	100.00	100.00	100.00

Table 4-8. Normalise composition of the damaged magnesia lining, for Na_2O effect (p.88)

Chemical species	Mole %. Damaged		
	Magnesia-spinel brick type A	Magnesia-spinel brick type B	Magnesia-fused spinel
Al_2O_3	7.08	7.43	7.75
MgO	92.48	92.31	92.00
Na_2O	0.43	0.26	0.43
Total	100.00	100.00	100.00

Table 4-9. Normalise composition of the damaged magnesia lining, for K_2O effect (p.93)

Mole %.			
Chemical species	Damaged		
	Magnesia-spinel brick type A	Magnesia-spinel brick type B	Magnesia-fused spinel
Al_2O_3	7.03	7.38	7.73
MgO	91.65	91.46	91.73
K_2O	1.32	0.98	0.54
Total	100.00	100.00	100.00

Table 5-6. Normalise composition of the damaged high-alumina brick, for SO_3 effect (p.111)

Mole %.	
Chemical species	Damaged
	High-alumina brick
Al_2O_3	98.14
CaO	1.54
SO_3	0.32
Total	100.00

Table 5-7. Normalise composition of the damaged high-alumina brick, for Na_2O effect (p.113)

Mole %.	
Chemical species	Damaged
	High-alumina brick
Al_2O_3	75.84
SiO_2	23.76
Na_2O	0.40
Total	100.00

Table 5-8. Normalise composition of the damaged high-alumina brick, for K2O effect (p.116)

Mole %.	
Chemical species	Damaged
	High-alumina brick
Al_2O_3	75.92
SiO_2	23.79
K_2O	0.29
Total	100.00

Figures

The following problems were detected related to figures:

Figure 2-1

- There is no reference to this figure in the text. This makes it difficult to determine its relevance and integrate it with interpretation of the text.
- The text of sub-figure (b) is too small, making it difficult to read and interpret.
- No citation

Figure 2-2

- There is no reference to this figure in the text. This makes it difficult to determine its relevance and integrate it with interpretation of the text.
- No citation

Figure 2-3, 2-4, 2-5

- There is no reference to this figure in the text. This makes it difficult to determine its relevance and integrate it with interpretation of the text.
- No citation
- Captions poorly formatted
- Poor graphic quality
- Poor typesetting. Part of the figures appears on a different page from the caption.

Figure 2-1, 2-2, 2-3, 2-4, 2-5 are all removed from the text.

Figure 2-6 and 2-7

- These figures are referred to on page 26, but only presented on page 28. They should be placed closer to the point where they are referred to.
- These figures should be in colour, not in black and white.

Figure 2-6 and 2-7 has been corrected as follows (p.24-25.):

Potgieter et al. (2004) studied high-temperature chemical corrosion in the short and long kilns. The XRF analysis showed higher concentration of sulphur in the short kiln. This indicates that the corrosion that took place was sulphur dominant. The long dry kiln analysis showed a higher concentration of chloride and potassium which points to a chlorine type of attack of the kiln shell. The EDX spectra of each corrosion scale (Figure 2-1 and 2-2) confirmed the analysis from XRF. The X-ray map images of the individual elements indicated high levels of K and Cl with respect to other elements.

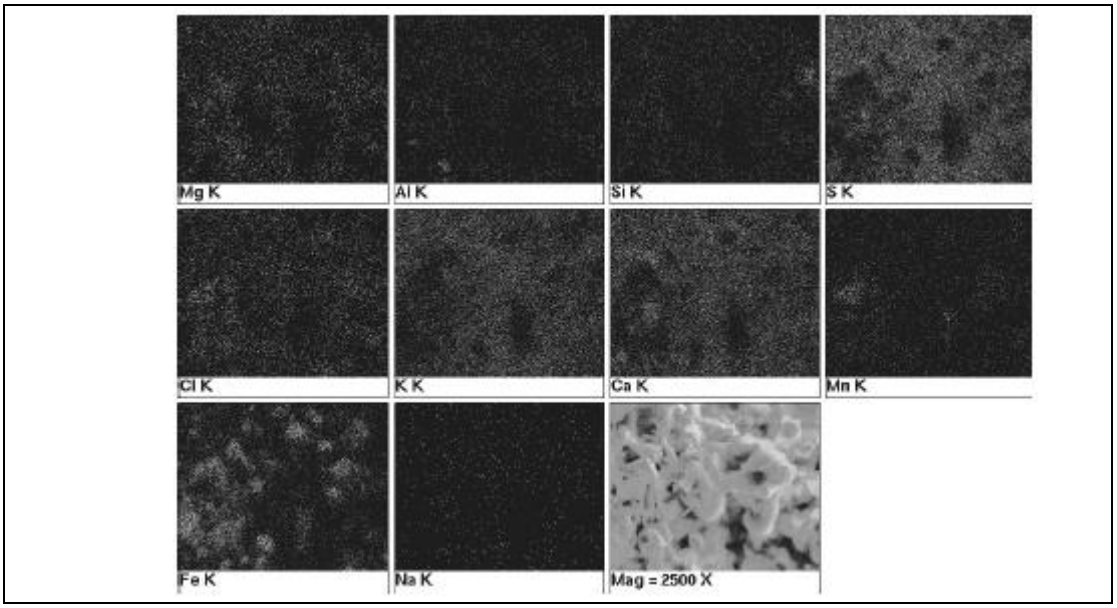

Figure **Error! No text of specified style in document.**-2. X-ray maps of corrosion scale from case 1 kiln

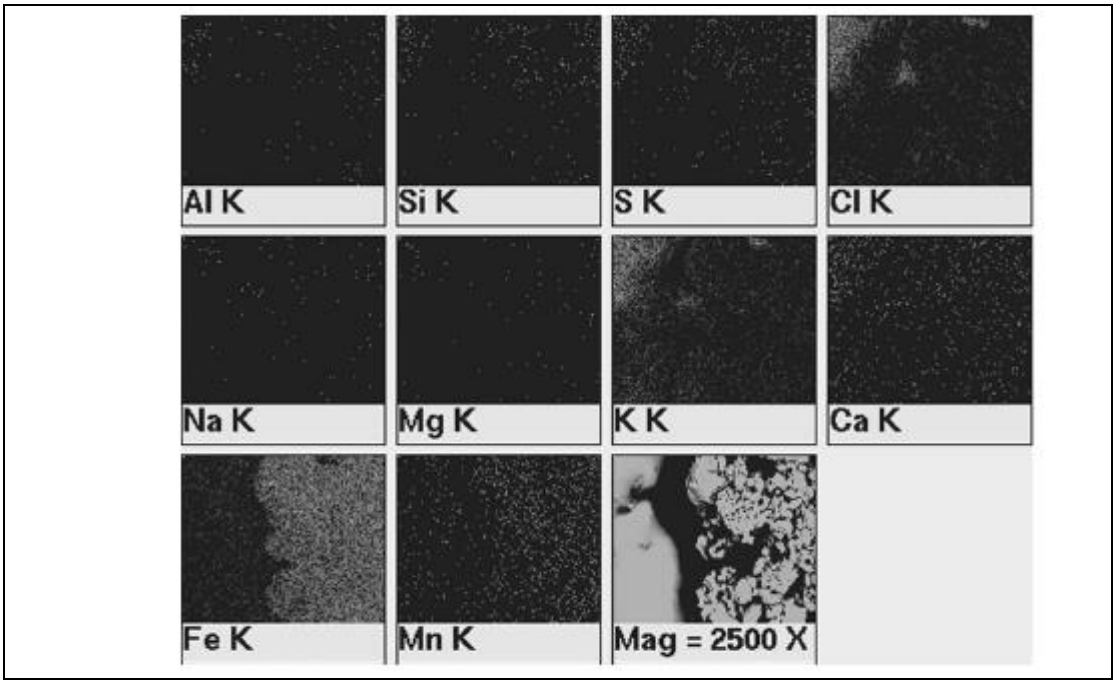

Figure 2-3. X-ray maps of corrosion scale from case 2 kiln

Figure 3-3. The caption is insufficient and it does not agree with the caption in the list of figures.

The caption is corrected and agrees with the caption in the list of figures.

The caption is changed from ASR of the damaged magnesia-spinel lining to ASR of the study kiln (p.57).

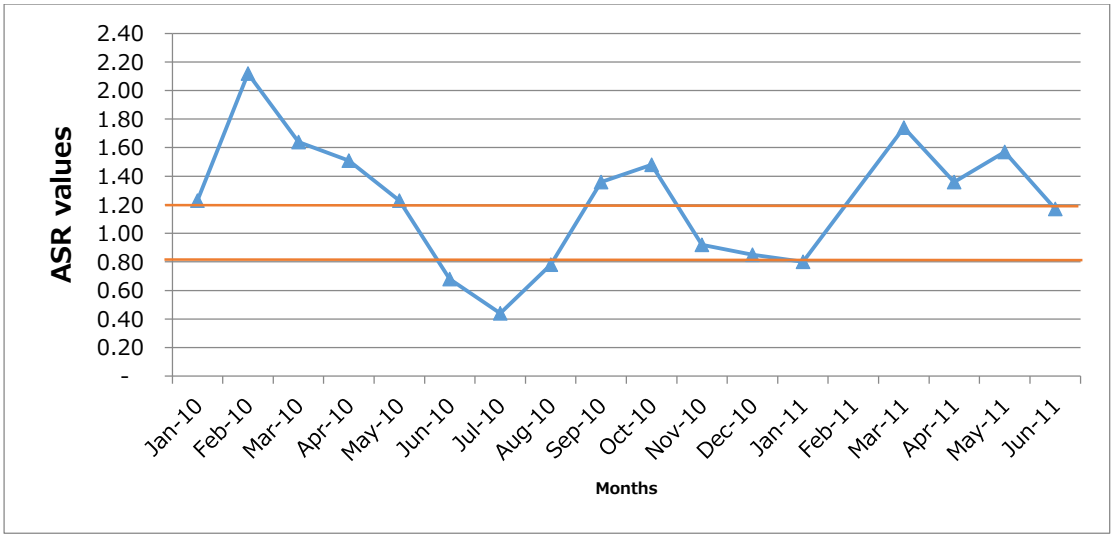

Figure 3-3. ASR of the study kiln

Figure 4-1, 4-2, 5-1. Poor typesetting. Part of the figure appears on a different page from the caption.

The figures have been corrected and now appears in a single page.

Fig 4-1 (p.62), Fig 4-2 (p.63) and Fig 5-1 (p.102).

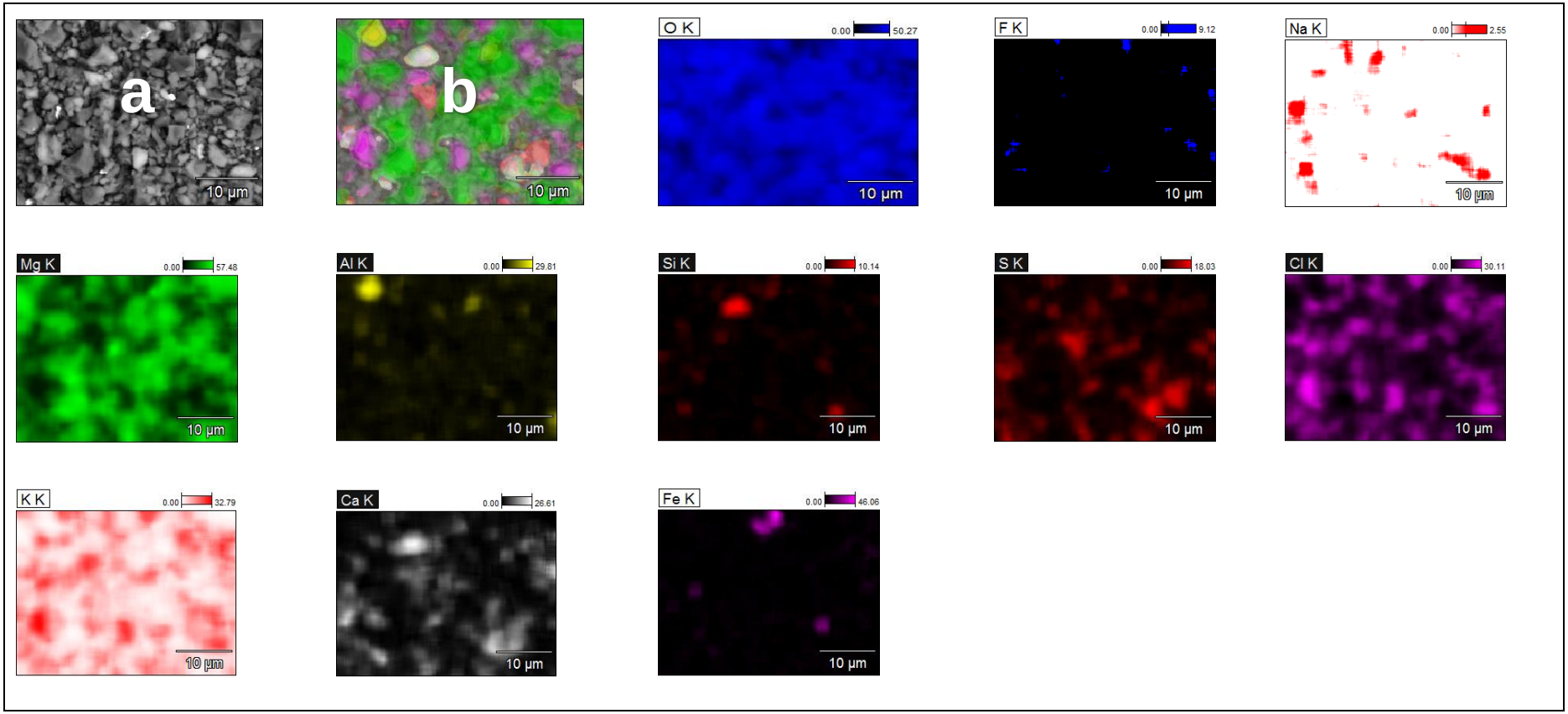

Figure 5-1. SEM-EDS mapping of the damaged high-alumina powder sample

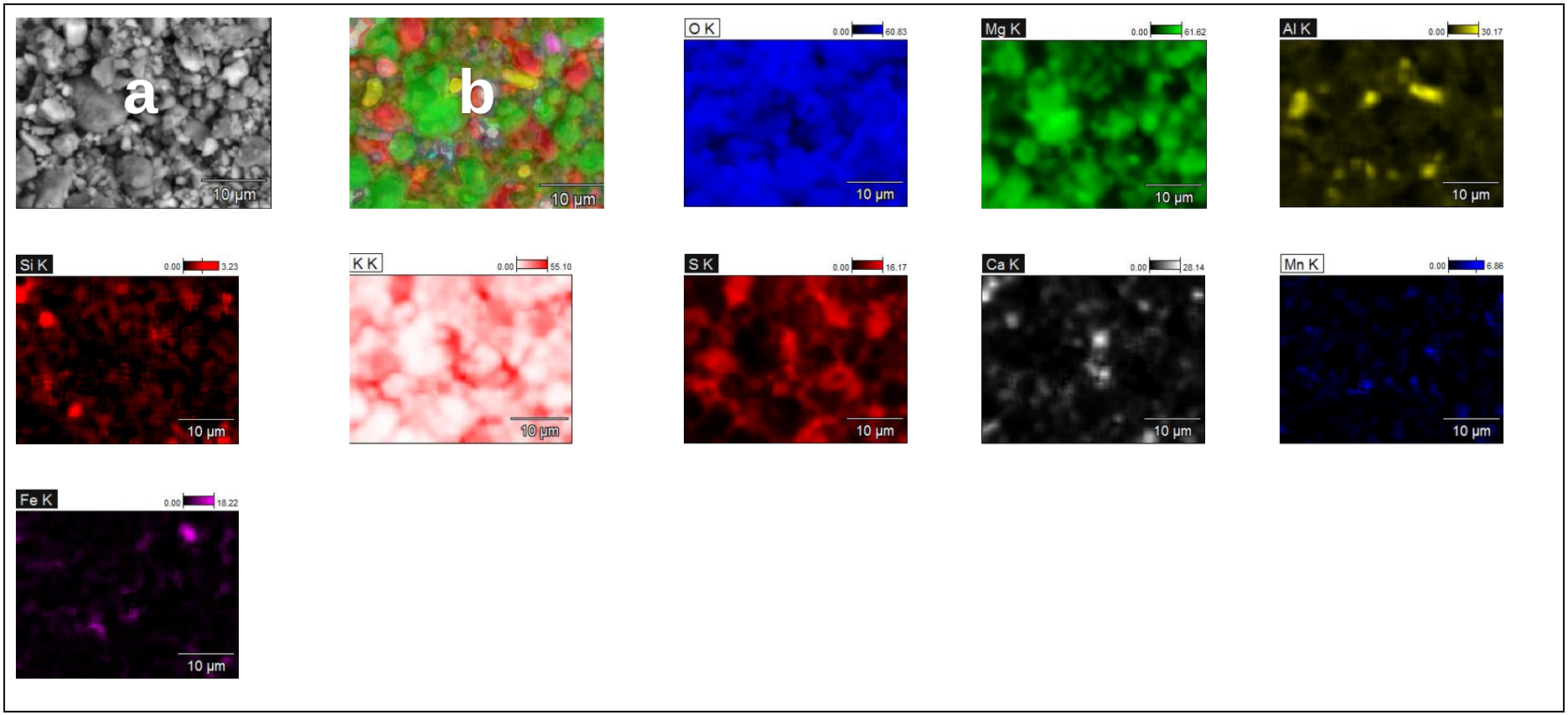

Figure 4-1. SEM-EDS mapping of magnesia-spinel brick type A

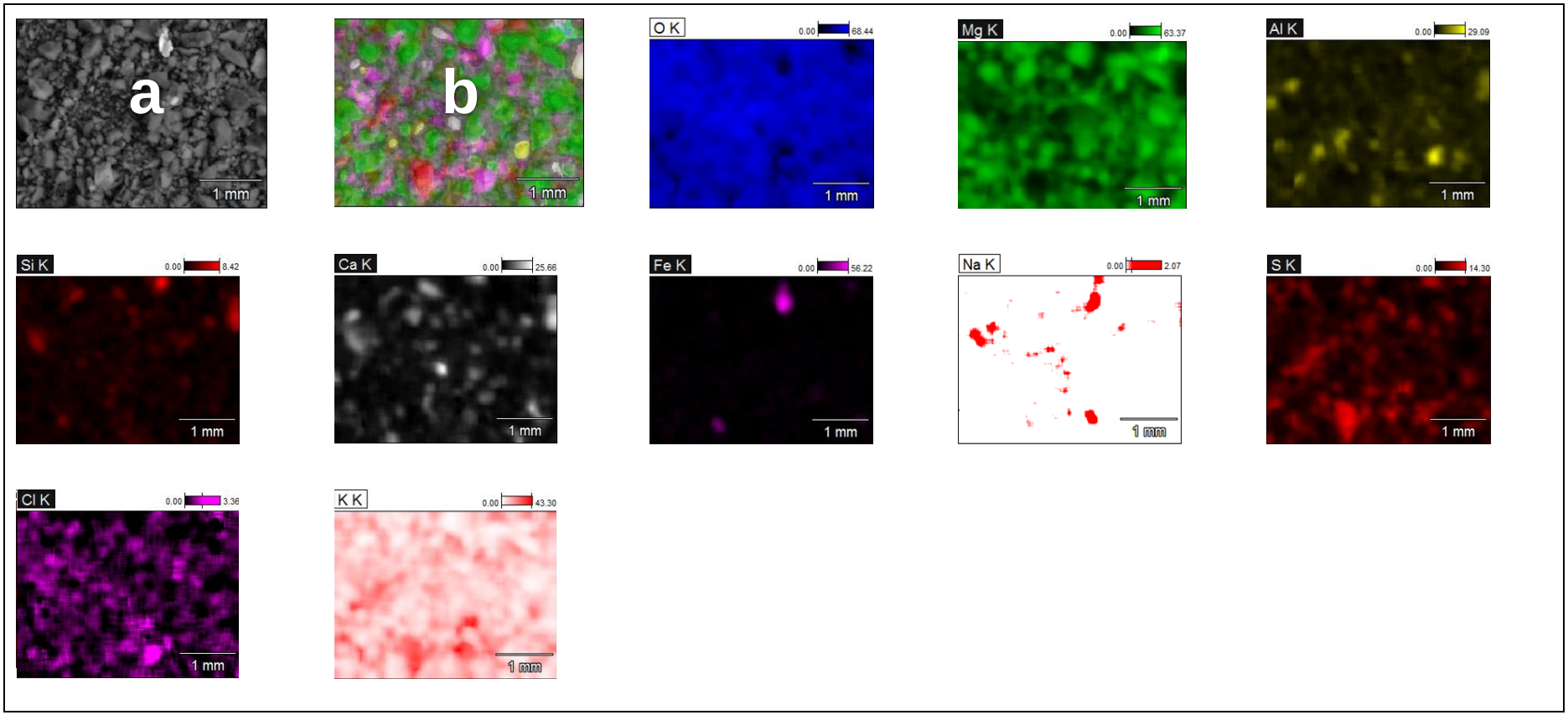

Figure 4-2. SEM-EDS mapping of damaged magnesia-spinel brick type B

FactSage ternary diagrams. The graphics of all figures containing ternary diagrams generated by FactSage contain title information, which is repeated in the caption. Only the caption should be used, and not the title information in the graphic.

Corrected to the following:

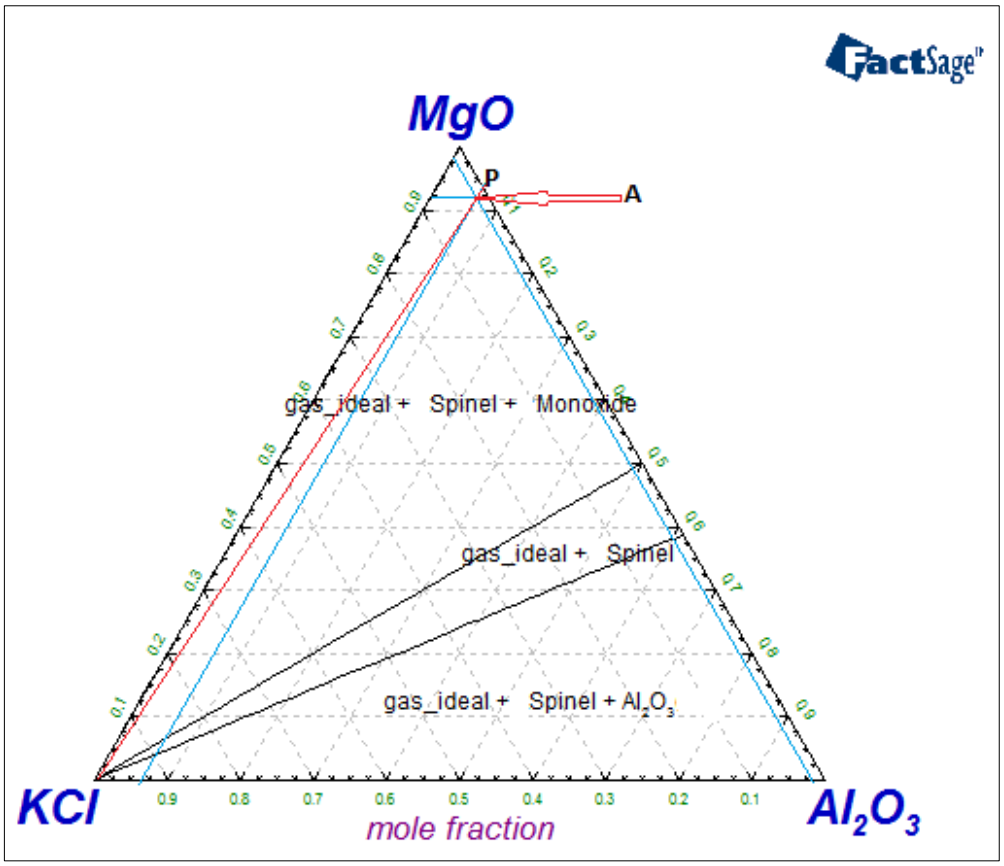

Figure 4-10. System MgO-Al_2O_3-KCl ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type A

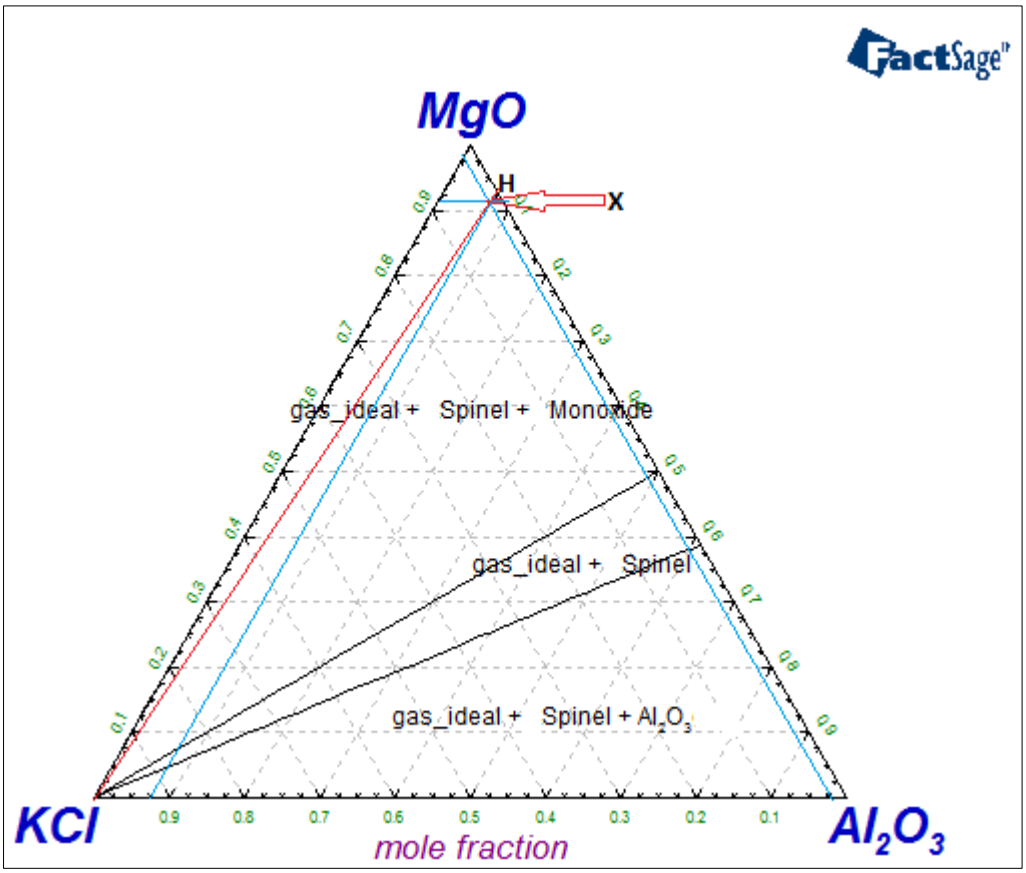

Figure 4-11. System MgO-Al_2O_3-KCl ternary phase diagram at 1500 ˚C and 1 atmosphere for magnesia-fused spinel

p.83

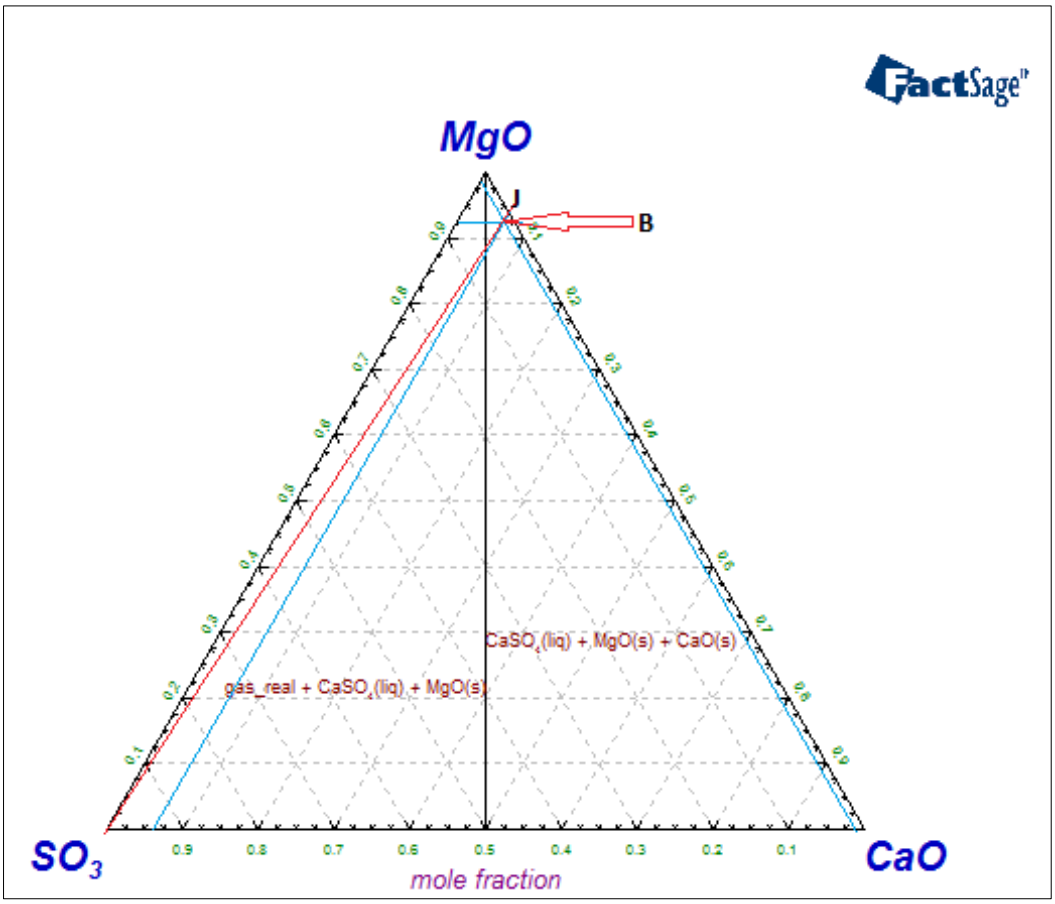

Figure 4-12. System MgO-CaO-SO_3 ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type A

p.85

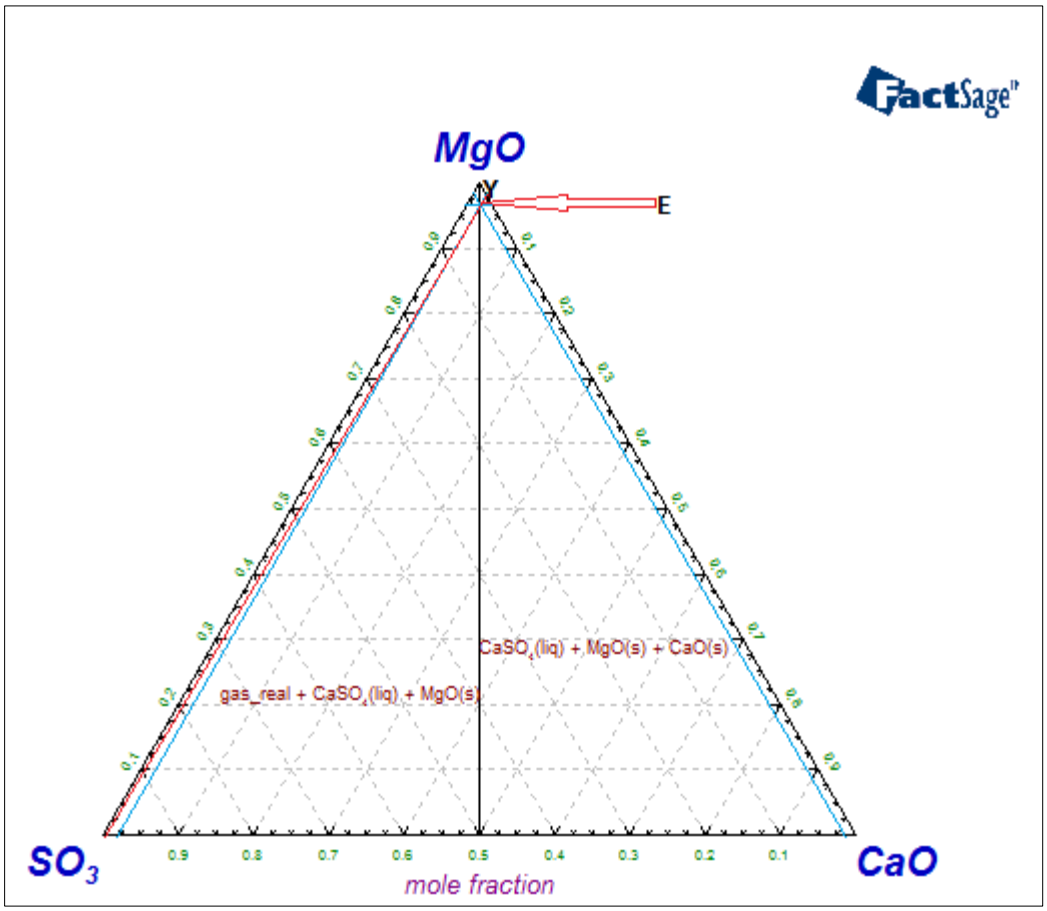

Figure 4-13. System MgO-CaO-SO_3 ternary phase diagram at 1500 ˚C and 1 atmosphere for magnesia-spinel brick type B

p.86

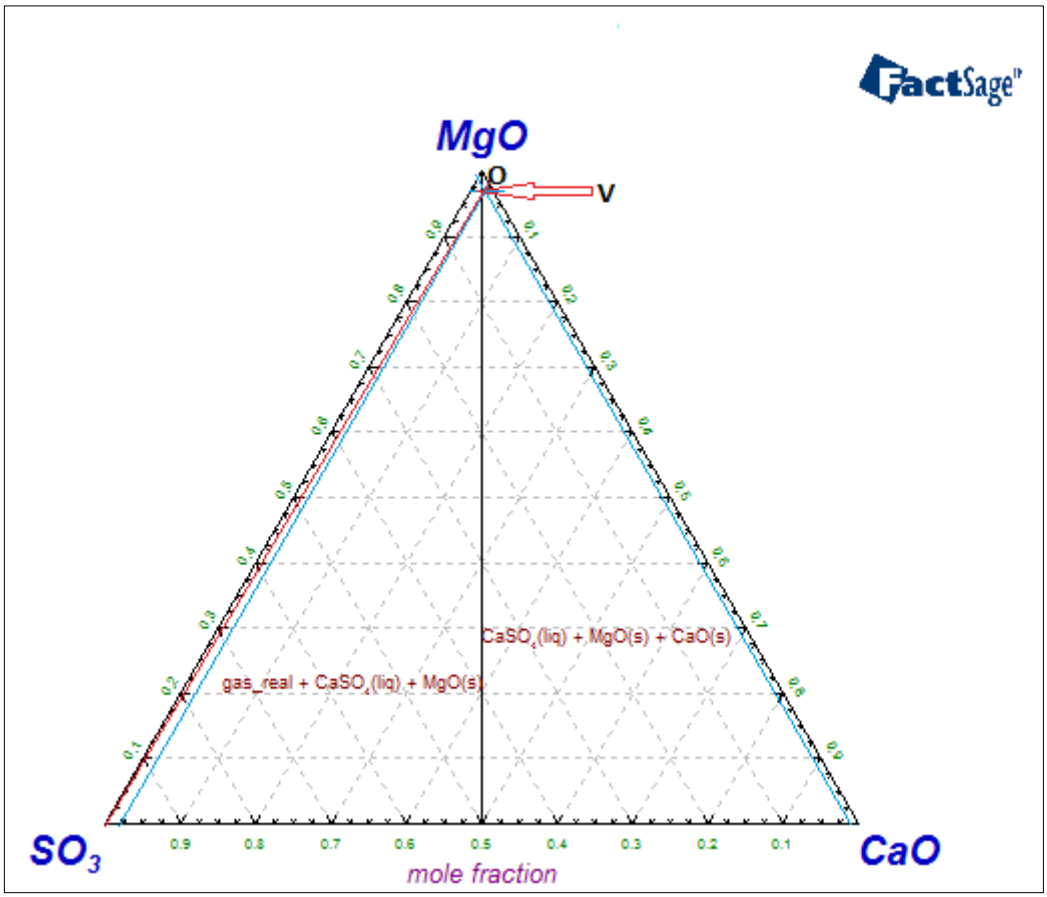

Figure 4-14. System MgO-CaO-SO_3 ternary phase diagram at 1500 ˚C and 1 atmosphere for magnesia-fused spinel

p.87

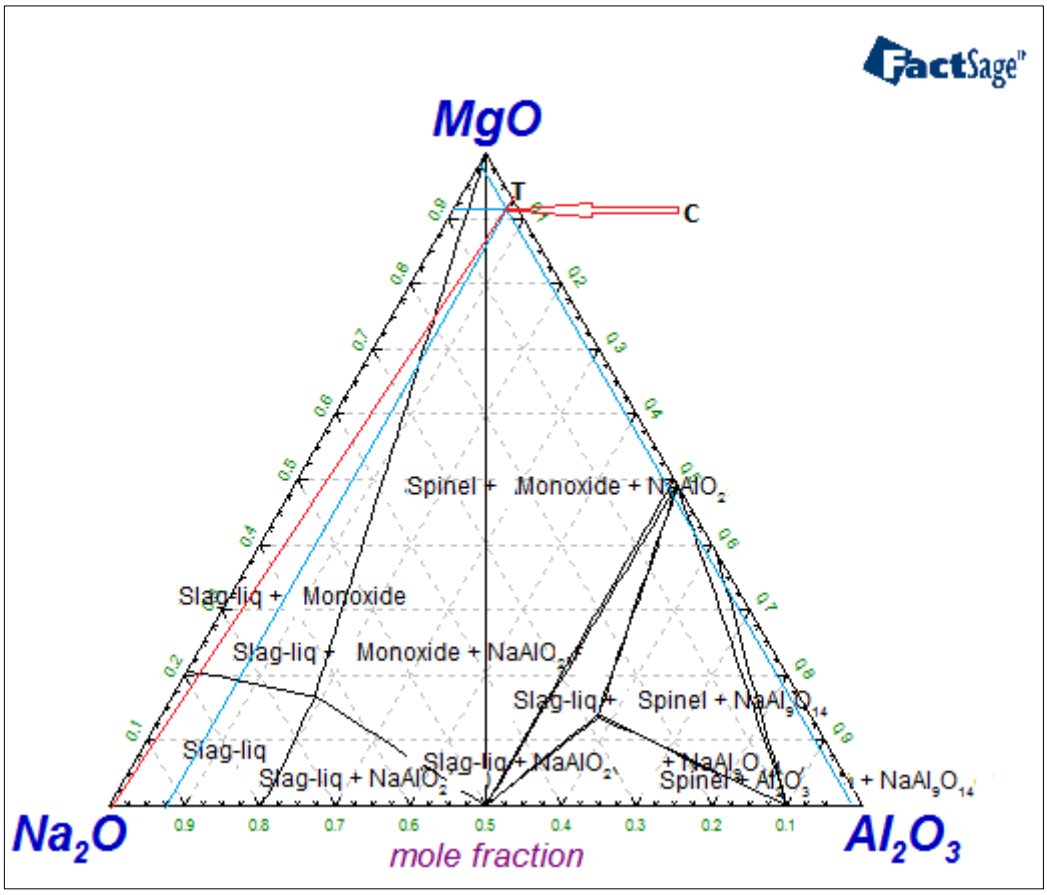

Figure 4-15. System MgO-Al_2O_3-Na_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type A

p.89

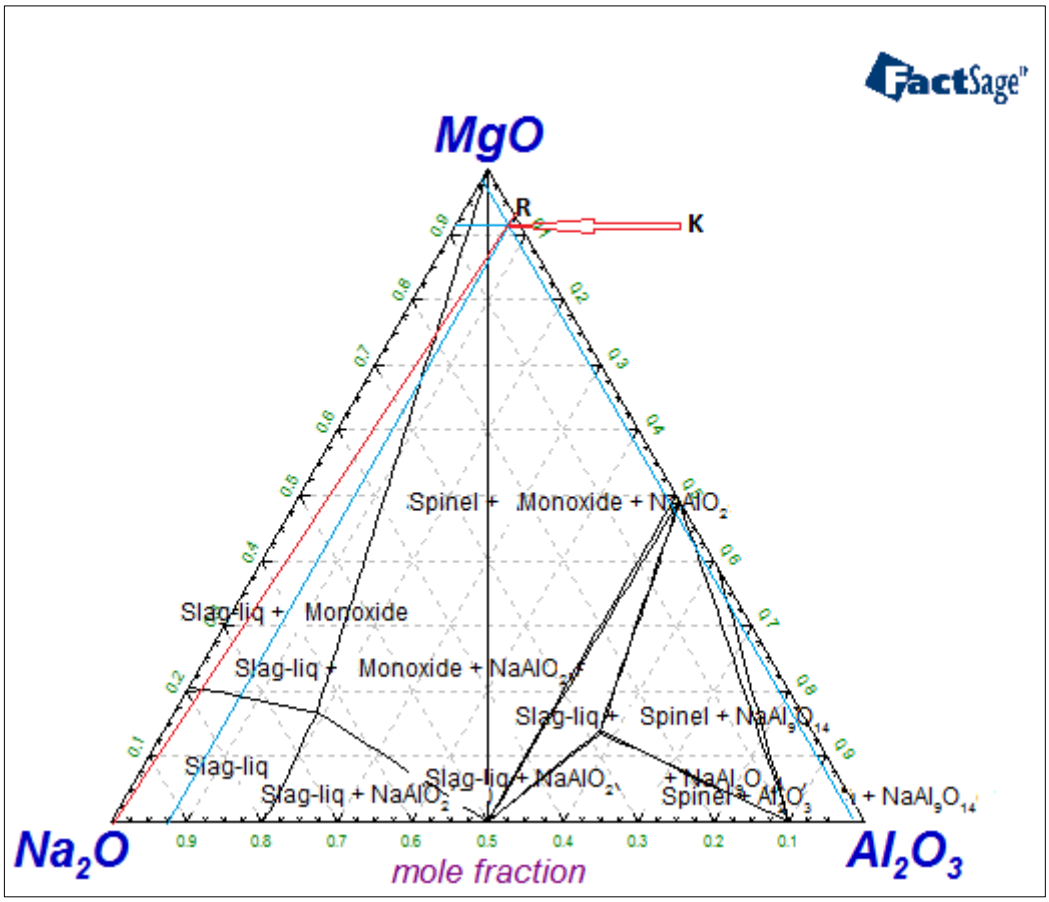

Figure 4-16. System MgO-Al_2O_3-Na_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type B

p.90

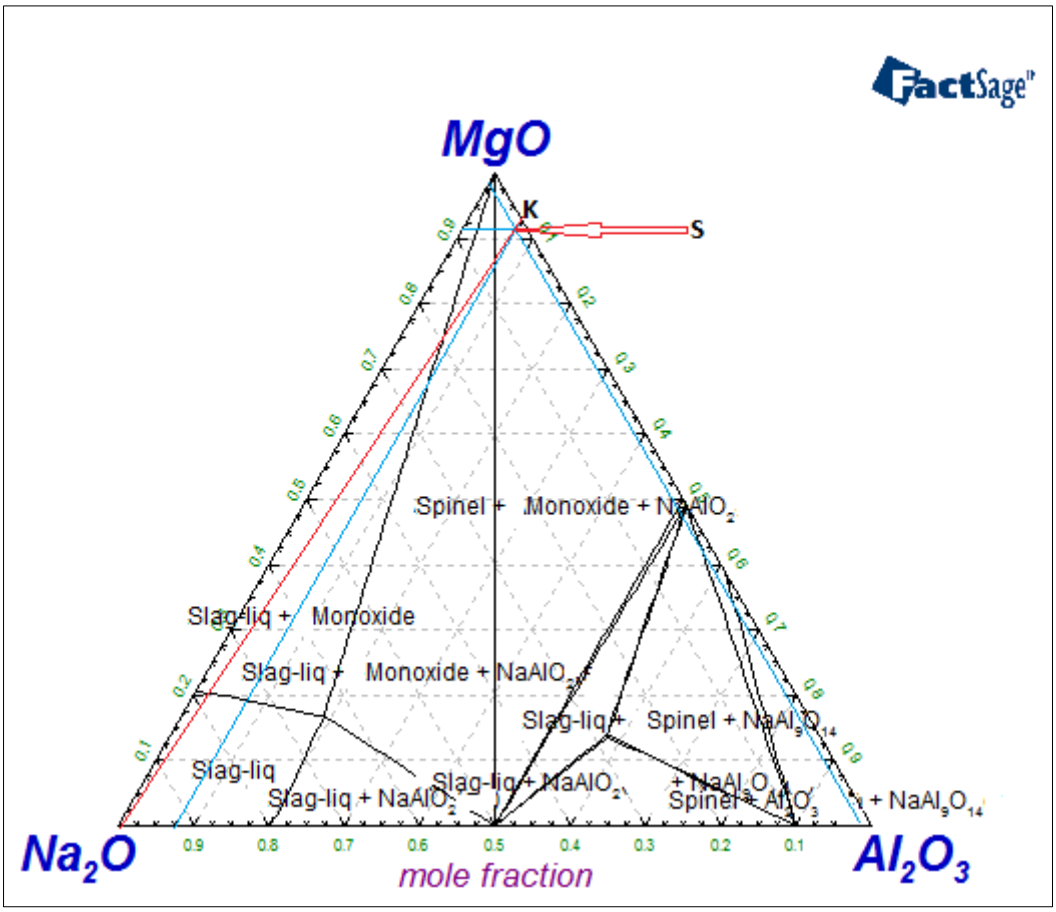

Figure 4-17. System MgO-Al_2O_3-Na_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-fused spinel

p.91

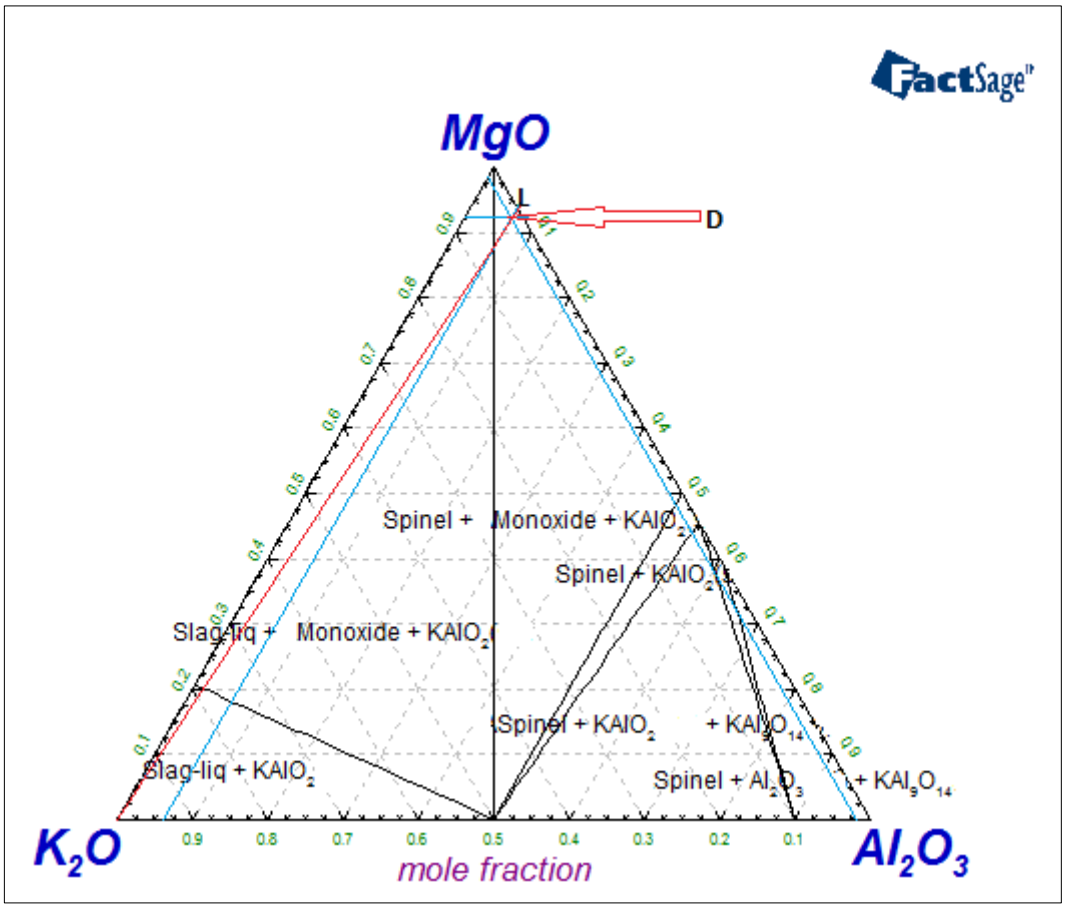

Figure 4-19. System MgO-Al_2O_3-K_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type A

p.94

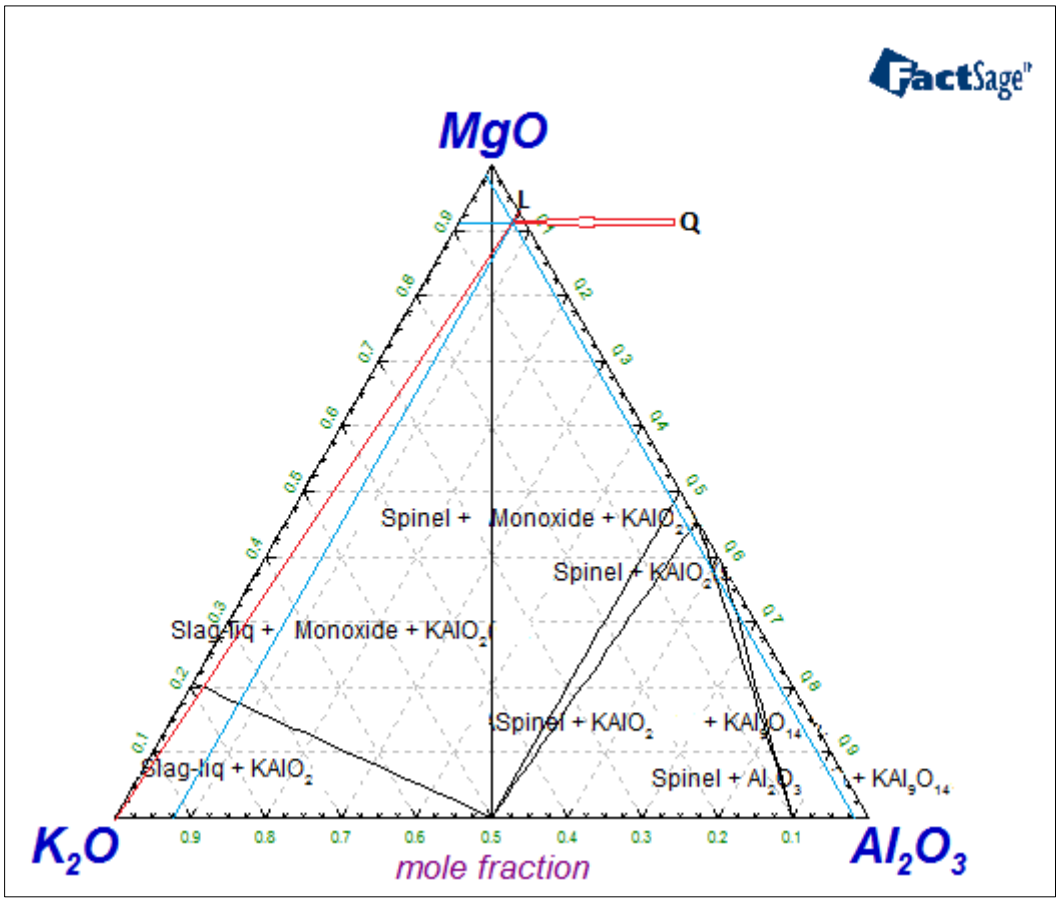

Figure 4-20. System MgO-Al_2O_3-K_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-spinel brick type B

p.95

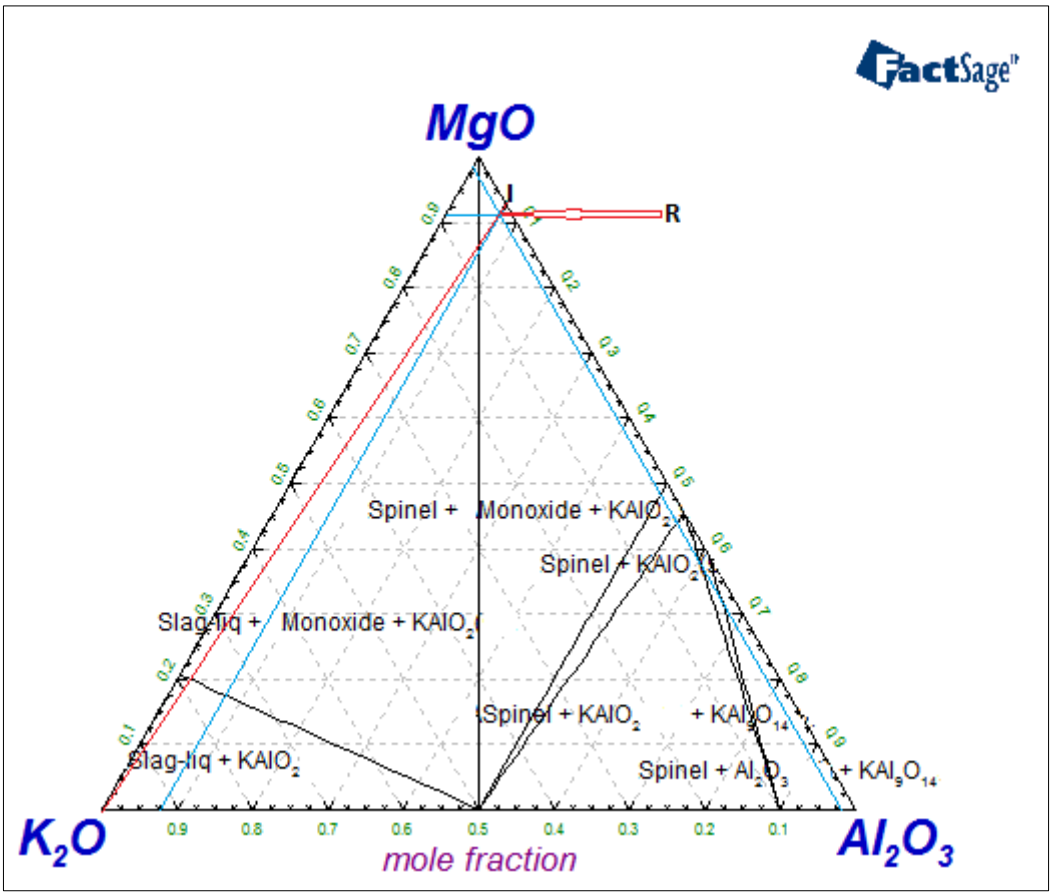

Figure 4-21. System MgO-Al_2O_3-K_2O ternary phase diagram at 1500 °C and 1 atmosphere for magnesia-fused spinel

p.96

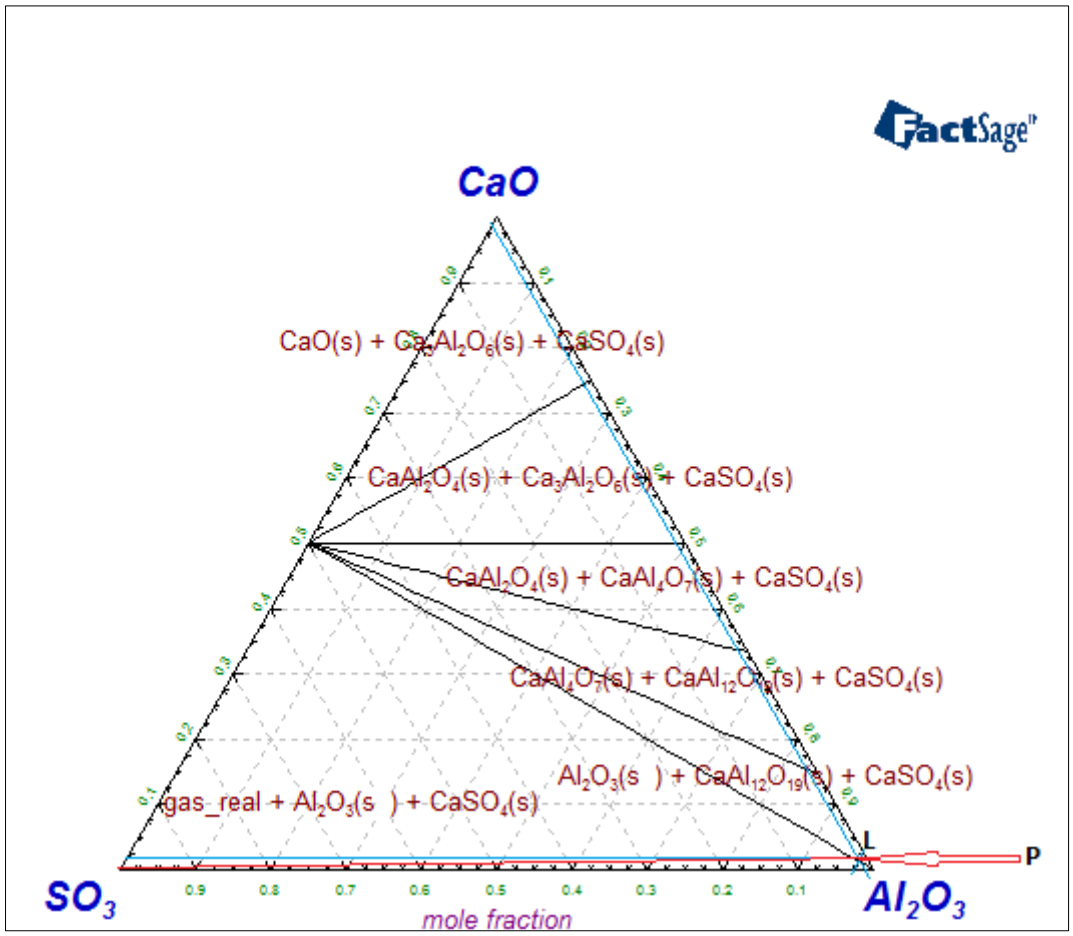

Figure 5-4. System Al_2O_3-CaO-SO_3 ternary phase diagram at 1200°C and 1 atmosphere

p.112

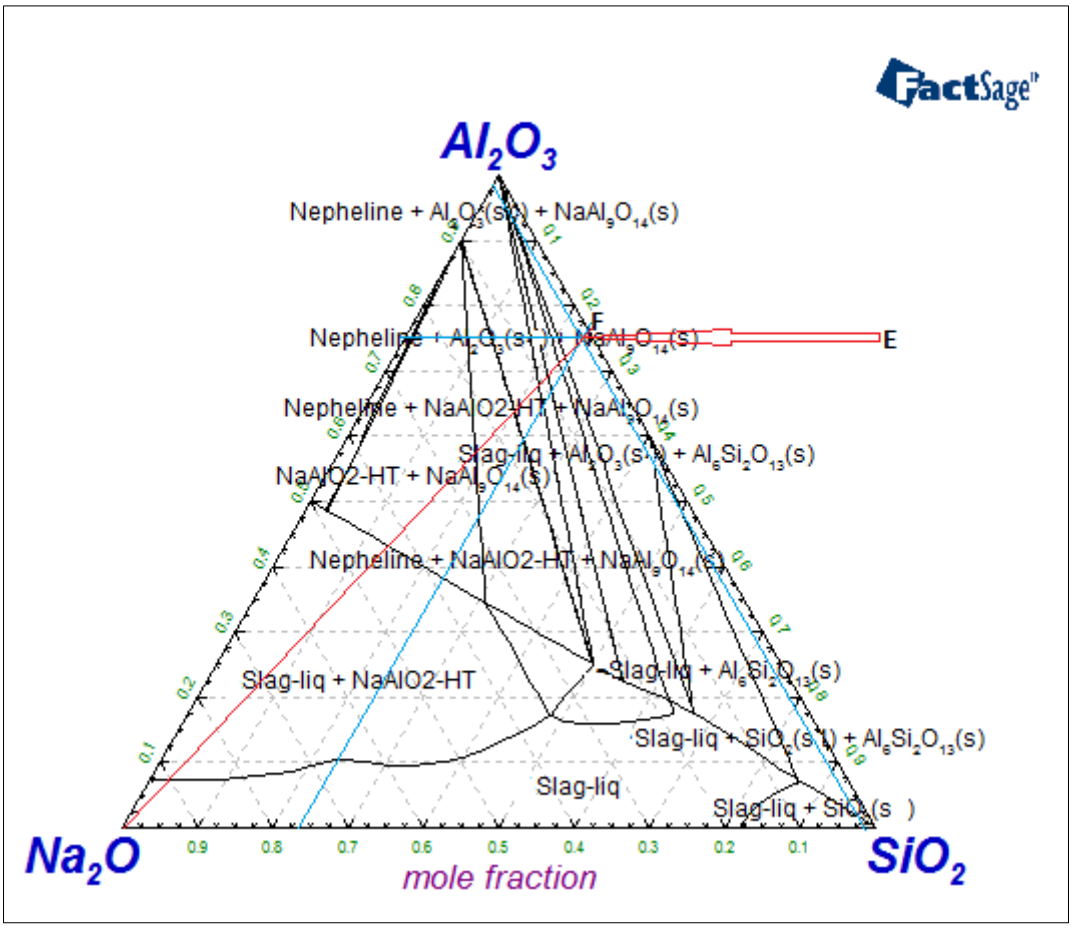

Figure 5-5. System Al_2O_3-SiO_2-Na_2O ternary phase diagram at 1200 °C and 1 atmosphere

p.114

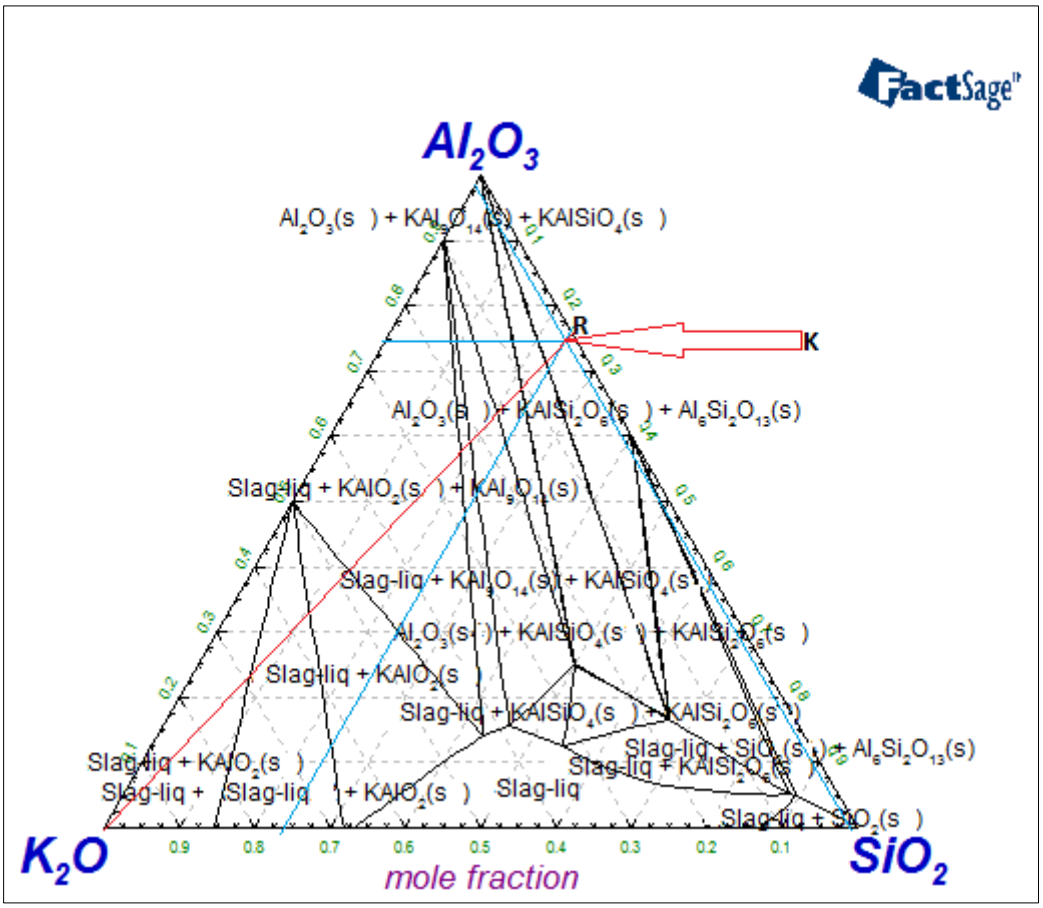

Figure 5-7. System Al_2O_3-SiO_2-K_2O ternary phase diagram at 1200ºC and 1 atmosphere

Tables

The following problems were identified with tables:

Table 3-1: No details are provided about the data in this table. How many assays were used to calculate it? What is the standard deviation?

The information is provided on page 52.in the text as follows:

The chemical compositions of the kiln feed, in Table 3-1, consist of data collected over 18 months from January 2010 to June 2011 (see appendix D). The feed was analysed hourly as it enters the kiln for clinker production. Therefore this information consist of data of 18 months period and 24 hrs per day of the operational period.

Table 4-4. What is the difference between the results in this table, and those in Table 4-2? It seems like the same material and properties, but the values are different. It is not clear what distinguishes the data in these two tables.

The data in table 4-4 is results from polished brick section and the results from table 4-2 is from powder sample. Both results are elemental composition, based on SEM-EDS chemical analysis. The same applies to Table 5-2 and 5-4 results.

Table 6-1. The units provided for gas composition is incomplete. It should clearly specify whether it is volume percent or mass percent.

The results are volume percent (p.120)

Table 6-1: Volume percent of CO_2 and CO, measured from industrial kiln

Gas	% volume
CO_2	7.06
CO	0.1
CO_2/CO	70.6

References and Citations

The following reference and citation problems were identified:

Szczerba et al., 2010: No such item in the list of references

Szczerba corrected as follows:

Szczerba (2010) found that the main cause of refractory-lining failure is the chemical attack of the spinel phase in basic refractories by sulphur and chlorine contained in the kiln feed. (p.3).

The chemical corrosion by volatile cement kiln feed materials were studied by Szczerba (2010) Bartha and Sodje (2001), Kunnecke (1998) and Potgieter et al. (2004). (p.19)

Szczerba (2010) studied the chemical corrosion between volatile cement kiln feed materials by using a laboratory electric furnace. (p.19)

Szczerba (2010) reported XRD results of the reaction product between refractory materials and kiln feed materials. (p.21)

Szczerba (2010) summarised that the new phases in the tested bricks are calcium sulphate aluminate, binary, ternary and quaternary phases of calcium aluminates and calcium alumina-ferrites and silicates phases. (p.23)

Szczerba (2010) concluded that the application of alternative, rich in sulphur fuels in the cement kilns intensifies the chemical corrosion of the spinel phase in basic refractories. (p.29)

Unreferenced items: There are several items in the list of references that are not cited in the text. These should be removed.

The following unreferenced items removed: (p.134-137)

Diaz, L.A., Torrecillas, R., De Aza, A.H., Pena, P. (2007). Effect of spinel content on slag attack resistance of high alumina refractory castables. *Journal of the European Ceramic Society,* no. 27, pp. 4623-4631.

De Aza, A.H., Dominguez, I.R., Gomez-Millan, J., Alvarez, M., De Aza, S., Contreras, L. (2010). Build-up formation and corrosion of monolithic refractories in cement kiln preheaters. *Journal of the European Ceramic Society*, no. 30, pp.1879-1885.

Mahajan, Y.R., Ganesh, I., Bhattacharjee, S., Saha, B.P., Johnson, R., Rajeshwari, K., Sengupta, R., Ramana Rao, M.V. (2002). An efficient $MgAl_2O_4$ spinel additive for improved slag erosion and penetration resistance of high-Al_2O_3 and MgO-C refractories. *Ceramic International*, no. 28, pp. 245-253.

Lee, W.E., Moore, R.E. (1998). Evolution of in-situ refractories in the 20th century. *Journal of the American Ceramic Society*, no. 81, pp. 1385-1410.

Mazzoni, A.D., Sainz, M.A., Aglietti, E.F., Caballero, A. (2007). Carbon coating and reaction on magnesia-alumina spinel. *Materials Chemistry and Physics,* no. 101, pp. 211-216.

Petkov, V., Jones, P.T., Boydens, E., Blanpain, B., Wollants, P. (2007). Chemical corrosion mechanisms of magnesia-chromite and chrome-free refractory bricks by copper metal and anode slag. *Journal of the European Ceramic Society*, no.27, pp. 2433-2444.

Szczerba, J., Pedzich, Z., Nikiel, M., Kapuscinska, D. (2007). Influence of raw materials morphology on properties of magnesia-spinel refractories. *Journal of the European Ceramic Society,* no 27, pp. 1683-1689.

Wojsa, J., Padworny, J., Suwak, R. (2013). Thermal shock resistance of magnesia-chrome refractories–Experimental and criterial evaluation. *Ceramic International*, no. 39, pp. 1-12.

Zeman, F. (2009). Oxygen combustion in cement production. *Energy Procedia*, no. 1, pp. 187-194.

Ambiguity: the first two items in the reference list would be cited as (Aksel et al., 2004) and would be impossible to distinguish them. A letter should be placed after the date e.g. 2004a and 2004b to clearly identify these items.

Aksel, C., Rand, B., Riley, F.L., Warren, P.D. (2004a). Thermal shock behaviour of magnesia–spinel composites. *Journal of the European Ceramic Society*, no. 24, pp. 2839-2845 (p.135).

Aksel, C., Warren, P.D., Riley, F.L. (2004b). Fracture behaviour of magnesia and magnesia-spinel composites before and after thermal shock. *Journal of the European Ceramic Society*, no. 24, pp. 2407-2416 (p.135).

Others Aspects

Some other aspects that were identified, are the following:

Presentation of lists: Section 1.1 and 1.2 present bullet lists without introductory text preceding the lists. This is bad practice. The bullet items are also not punctuated correctly.

The main research objectives of this work and research questions that this work will attempt to answer are provided in section 1.1 and 1.2 respectively.

1.1 Research objectives

The research objectives of this work was to determine the causes of the refractory lining failures considering the effect of feed and kiln conditions. This is summarised as follows:

a. To identify the causes of refractory lining failures in an industrial cement kiln
b. To understand the effects of impurities on the refractory lining materials
c. To understand the effects of cement kiln operating conditions on the refractory lining materials
d. To generate data for use in kiln operations

1.2 Research questions

This research was conducted to answer the questions on how the refractory lining was prematurely failing and the questions were summarised as follows:

a. What are the failure mechanisms that resulted in premature refractory lining failure?
b. What are the effects of the alkalis in the refractory lining?
c. What are the effects of the gaseous sulphur trioxide and chlorine in the refractory lining?
d. What is the effect of oxygen partial pressure in the refractory lining?

Appendices: The appendices are never referred to in the text. This is bad practice. The reader must be informed clearly about additional information in the appendices, and its relevance to the text.

The XRD raw data is provided in appendix A. From Table 4-3, XRD results of the damaged refractory bricks (magnesia-spinel brick type A, magnesia-spinel brick type B and magnesia-fused spinel) showed the presence of contaminating phases such as KCl (sylvite), $CaSO_4$ (anhydrite), K_2SO_4 (Arcanite) and (Na, K) Cl (sodium potassium chloride) (p.66).

The high-alumina refractory lining XRD raw data is provided in appendix A. The phase analysis of the virgin and used high-alumina oxide lining is shown in Table 5-3. The main phases are aluminium oxide, mullite (alumina and silica), quartz (silica), cristobalite (silica) and silimanite (alumina and silica). (p.103).

In this section, the interactions between the impurities (Cl_2, SO_3, K_2O and Na_2O) and the damaged magnesia lining are discussed based on the thermodynamic considerations. The chemical compositions of the lining were calculated (conversion of mass % to mole %) in appendix B and expressed in terms of mole percent (Table 4-5) and referred to ternary phase diagrams of impurity component – MgO – Al_2O_3 or CaO (p.80).

XRF analysis of the used high-alumina brick revealed the presence of the contaminating species SO_3, Na_2O and K_2O (Table 5-1). This led to investigate their interactions with the high-alumina refractory lining. The chemical compositions of the lining were calculated (conversion from mass % to mole %) in appendix B and expressed in terms of mole percent (Table 5-5) and referred to ternary phase diagram of impurity component – Al_2O_3 – SiO_2 or CaO (p.110).

It was also reported that this wear problem could be resolved by reducing the alkali salt content and balancing alkali / sulphate ratio (refer to appendix C) in the recommended range of 0.8 – 1.2 (Kunnecke, 1998) (p.27).

The clinker was analysed to determine the alkali sulphate values. The data were collected over a period of 17 months (see appendix C) (p.56).

The chemical compositions of the kiln feed, in Table 3-1, consist of data collected over 18 months from January 2010 to June 2011 (see appendix D). The feed was analysed hourly as it enters the kiln for clinker production (p.52).

Technical Comments

Unclear and Ambiguous Statements

The author does not communicate clearly in many instances, which is a critical flaw in any technical document. This needs to be rectified by careful review. Here are some examples:

p.iii "The calculated values indicated that the partial pressure of oxygen is too low (1.333×10^{-4} atm) and no oxidation of oxides will take place".

It is unclear what the author means by this in the abstract, and it should be replaced by a clear and explicit statement. The author also does not indicate in the abstract what the significance or relevance of this finding is.

The partial pressure of oxygen is low (1.333×10^{-4} atm), it indicate the stability of Fe_3O_4 and Mn_3O_4 and therefore does not favour the oxidation of Fe_3O_4 to formation of Fe_2O_3 and Mn_3O_4 to formation of Mn_2O_3. (p.iii).

p.4 The partial pressure of oxygen was measured to determine stability of the oxides (Mn_3O_4 and Fe_3O_4).

This sentence seems unrelated to the rest of the paragraph. It is also not clear why and how it is relevant to this investigation.

Bartha and Sodje (2001) found that redox burning conditions represent a low proportion of the overall volume of cases of wear, but can occur more frequently where alternative fuels are used. The mechanism of this failure is by formation of sulphate

salts or sulphides resulting in the structural weakening of the affected brick horizons (brick phase). (p4).

p.5 “This research however took a different approach by collecting the used refractory lining materials from the industrial cement kiln which allowed the investigation of interaction of factors that influences refractory lining failures”. This is vague. The author should clearly describe the approach.

The majority of refractory lining failure research has been conducted by reacting prepared refractory sample materials with either kiln feed or clinker in a laboratory furnace or hot stage microscope for the investigation of chemical corrosion through analysis and microstructural studies. In the case of thermal shock studies the prepared refractory materials of different compositions are fired to set temperatures (1200°C, 1400°C and 1500°C) and subjected to different tests and analysis such as thermal expansion, strength and Young’s modulus, refractoriness under load (RUL) and factography. This research however took a different approach by collecting the used refractory lining materials from the industrial cement kiln which allowed the investigation of more than one refractory lining failure. This research investigated lining failure by chemical and thermal attack using the same samples collected in the industrial kiln. The kiln operating condition during the period at which samples were collected was also investigated to determine the influence of oxygen partial pressure on the stability of Mn_3O_4 and Fe_3O_4 phases on the refractory. (p.6-7).

p.10 This refractory is preferred in the burning zone of the rotary cement kiln because of its ability in forming coating (Peray and Waddell, 1972.).

It is not clear what is meant by this statement.

This refractory is preferred in the burning zone of the rotary cement kiln because of its ability in forming coating which protects the refractory (Peray and Waddell, 1972.) (p.11).

p.13 The reaction at the $MgAl_2O_4$/clinker interface indicated that a complete diffusion proceeded at the interface. It was also observed that the liquid must gradually dissolve the spinel substrate (Pena et al., 2007). The dissolution of spinel by this glassy phase continues until it reaches the equilibrium. At this point, 30% of liquid might coexist with $MgAl_2O_4$.

This is poorly presented. What is a "complete diffusion"?

Statement re-written to: (p.14-15)

It was observed that the liquid must gradually dissolve the spinel substrate (Pena et al., 2007). The dissolution of spinel by this glassy phase (liquid clinker) continues until it reaches equilibrium. At this point, 30% of liquid, L_R, might coexist with $MgAl_2O_4$ as indicated by the following equation:

$MgAl_2O_4 + LC_3A$ {Ca, Al, Si, Fe} $\rightarrow 30\%L_R + 70\%MgAl_2O_4$ (Pena et al., 2007)

p.13 The reaction at the MgO/clinker interface indicated that a partial diffusion took place, while the MgO (periclase) substrate showed contrast results in comparison to that observed with spinel (Pena et al., 2007).

What is "a partial diffusion"?

The reaction at the MgO/clinker interface indicated that a small quantity of clinker diffused into the MgO substrate (partial diffusion) which is in contrast to the results observed with the reaction of $MgAl_2O_4$/clinker interface (Pena et al., 2007). (p.15).

p.13 “The liquid phase, at higher temperature, partially dissolved primary MgO grains enhancing their grain growth, and also achieving the substrate densification in the reaction zone by a liquid reaction sintering process”.

This is unclear. How does partial dissolution of a grain enhance its grain growth? A description like this requires a figure to support it. It is difficult to interpret.

Statement re-written to: (p.15).

Pena et al. (2007) found that periclase substrate at temperature higher than 1500ºC revealed an extension of reaction with clinker where small amounts of liquid phases, rich in Ca^{2+}, Al^{3+}, Si^{4+} and $Fe^{2+,3+}$ penetrated through periclase grain boundaries.

p.22 “The surface of the disks was polished before being pressed with the hot kiln meal or with the Portland clinker”.

Perhaps a diagram would have helped, or simply a more clear explanation.

The refractory sample disks for test work were made from refractory brick mixtures. These disks were then polished before being pressed with the hot kiln feed or with the Portland clinker (p.20).

p.22 “In some areas, salt crystals were observed”.

Does this refer to NaCl? Clarify.

In some areas, KCl salt crystals were observed. (P.21).

p.24 “Silicate and aluminate phases found in the samples were compatible with the periclase”.

Compatible in what sense?

Statement removed.

p.24 "The XRD phases formed as a result of reactions between components of the Portland clinker and of basic bricks at 1300ºC were calcium aluminate ($C_{12}A$), calcium sulphate aluminate ($Ca_4Al_6O_{12}(SO_4)$ or $C_3A_3.CaSO_4$) and calcium zirconate ($CaZrO_3$)".

What does this mean? Perhaps "The phases identified with XRD formed…".

The phases identified with XRD from the reactions between components of the Portland clinker and of basic bricks at 1300ºC were calcium aluminate ($C_{12}A$), calcium sulphate aluminate ($Ca_4Al_6O_{12}(SO_4)$ or $C_3A_3.CaSO_4$) and calcium zirconate ($CaZrO_3$). (p.22).

p.26 "…studied high-temperature chemical corrosion in the short and long kilns".

The author refers to "the short and long kilns" as if the reader would be familiar with it. It was never introduced or explained.

Potgieter et al. (2004) investigated the corrosion scales which were collected from the shells of the long (140m) dry-process kiln with one pre-heater and the short (85m) kiln fitted with five pre-heater stages. (p.20 – 21).

p.26 "… a tiny salt crystal …"

Does this refer to NaCl? Clarify.

A further microscopic examination of the piece showed a tiny KCl crystal along the fissure boundaries. (p.25).

p.30 In the case of balanced ASR, alkali sulphate modulus reacts in kiln gas atmosphere to form alkali chloride and alkali sulphate salts, which are bonded in the clinker or infiltrate into the brickwork.

What does this mean?

In the case of balanced ASR, alkali sulphate reacts in kiln gas atmosphere to form alkali chloride and alkali sulphate salts, which are bonded in the clinker or infiltrate into the brickwork. (p.28)

p.30 “Under oxidising conditions, excessive alkali in the kiln atmosphere leads to oxidation of the refractory materials forming alkali sulphates”.

How can refractory materials be oxidised? They should contain stable oxides.

Under oxidising conditions, excessive alkali in the kiln atmosphere leads to reaction of the refractory materials forming alkali sulphates. The formation of these sulphates is accompanied by a significant volume increase (up to 30%) in the refractory which results in structural weakening of the brick hot face. (p.28).

p.34 “This study consisted of measurements of bend strength, modulus and fracture toughness”.

What modulus are you referring to? The same problem occurs in the title of section 2.6.5 and in other locations in the text.

Modulus corrected to Young’s modulus.

p.47 “In this study, the stability of oxides (Fe_2O_3 and Mn_2O_3) will be investigated as they are significantly involved in the reactions between clinker and refractory materials”.

This is vague. Why is this important? How is this involved in reactions?

2.7.1. Introduction

In this study, the stability of oxides (Fe_3O_4 and Mn_3O_4) will be investigated as they are significantly involved in the reactions between clinker and refractory materials. (p.46)

2.7.3. Redox burning conditions (p.47-48).

Bartha and Sodje (2001) found that magnesioferrite ($MgFe^{3+}{}_2O_4$), contained in the alpine magnesia brick, is reduced to magnesiowusite ((Mg, Fe^{2+}) O) and this involves a significant reduction of volume (>20%). If redox burning cycles occur, there are frequent changes between magnesioferrite and magnesiowusite, resulting in the structural weakening of the affected brick horizons. This can lead to a premature wear as a result of spallings of the redox-subjected brick horizons. If additional infiltrated sulphate salts are present in the

structures of the refractory lining, and particularly under the influence of sulphur excess, sulphide compounds can form from these under strongly reducing conditions. The sulphides K_2S, oldhamite (CaS), K_2S_3, $KFeS_2$ were determined in analysed used brick samples. When oxidizing conditions predominate again, an oxidation of the sulphides takes place, accompanied by a significant volume increase. This leads to expansion of the brick structure resulting in the destruction of the brick.

Bartha and Sodje (2001) gave examples of reaction equations in burning conditions of the rotary cement kilns as follows:

Reducing burning conditions:

$$MgO.Fe_2O_3 + CO = MgO + 2FeO + CO_2 \quad \text{E.q 2-12}$$

$$K_2SO_4 + 4CO = K_2S + 4CO_2 \quad \text{E.q 2-13}$$

$$K_2SO_4 + 8CO + 2SO_2 = K_2S_3 + 8CO_2 \quad \text{E.q 2-14}$$

$$MgFe_2O_4 + K_2SO_4 + 13CO + 3SO_2 =$$

$$2KFeS_2 + MgO + 13CO_2 \quad \text{E.q 2-15}$$

Oxidising burning conditions

$$MgO.2FeO + \frac{1}{2}O_2 = MgO.Fe_2O_3 \quad \text{E.q 2-16}$$

$$2KFeS_2 + 8O_2 = K_2SO_4 + Fe_2(SO_4)_3 \quad \text{E.q 2-17}$$

p.47 “Hayes (2003) showed that the carbon monoxide gas generated in the furnace acts as a reducing agent that captures oxygen from metal oxides”.

What furnace is referred to here?

Hayes (2003) showed that the carbon monoxide gas generated in the blast furnace acts as a reducing agent that captures oxygen from metal oxides. (p.46)

p.50 “Each brick sample was collected in each row of the respective zone in order to get representative sample”.

Not clear. A diagram is required.

Samples were collected in the rows of burning zone and lower transition zone (see figure 3-2). (p.51).

p.67 “The formation of KCl could be accompanied by a significant volume increase (up to 30%) in refractory”.

How is this possible if it simply condenses?

KCl migrate into the refractory brick, occupying a space (volume) in the brick thereby expanding the brick in volume up to 30%. Once the brick expand, it doesn’t contract to its original shape/form. (p.67).

p.70 “The results from SEM-EDS analysis showed that there is no clinker element in the brick”.

What is clinker elements?

The results from SEM-EDS analysis showed that there is no major increase of the main clinker elements such as Ca, Si, Al and Fe in the damaged magnesia brick. (p.70 and p.105)

p.71 “In SEM micrograph 4-4b, 4-5b and 4-6b, no clinker diffussion took place into the damaged magnesia bricks. The clinker diffusion is likely to be present as devitrified glassy phase in the refractory materials due to refractory-clinker chemical reaction (Serena et al., 2004).”

An example of a devitrified glassy phase is needed here. How is the reader supposed to interpret the micrographs? The micrographs have no annotation to aid in interpretation.

SEM micrographs shows similar morphology and therefore no clinker diffusion took place into the damaged magnesia bricks. The clinker diffusion is likely to be present as devitrified

glassy phase (see figure 2-1) in the refractory materials due to refractory-clinker chemical reaction (Pena et al., 2007). (p.71).

p.78 “From SEM micrographs, it can be seen that there is an intergranular fracture in all unused and damaged magnesia bricks”

This refers to Figures 4-7, 4-8, and 4-9. I cannot see what the author is referring to. The figures are not annotated, and no examples or clear descriptions are provided.

From SEM micrographs, it can be seen that there is an intergranular fracture (see figure 2-5) in all unused and damaged magnesia bricks. (p.79)

p.102 “Further analysis of SEM micrographs, in Figure 5-2, revealed that no clinker diffusion into the refractory lining took place”.

How would one see this? The SEM micrographs contain no annotations. This interpretation therefore seems to have no basis.

The clinker diffusion is likely to be present as devitrified glassy phase (see figure 2-1) in the refractory materials due to refractory-clinker chemical reaction (Pena et al., 2007). (p106).

Infeasible Chemical Compounds and Equations

The following incorrect or infeasible chemical formulae and reactions are used in the text:

NaKCl: This formula is used in reference to a chloride salt solid solution phase on several pages. I propose that it be changed to (Na, K) Cl.

The presence of low melting phases of KCl, (Na, K) Cl, K_2SO_4 and $CaSO_4$ compromised the refractoriness of the magnesia bricks because they are liquid at temperatures below clinkerisation temperature (1450 °C). (pii).

Sodium oxide and potassium oxide in the kiln feed and chlorine and sulphur in the kiln gas atmosphere migrated into the magnesia brick and react to form KCl, (Na, K) Cl and K_2SO_4. (pii)

From Table 4-3, XRD results of the damaged refractory bricks (magnesia-spinel brick type A, magnesia-spinel brick type B and magnesia-fused spinel) showed the presence of contaminating phases such as KCl (sylvite), $CaSO_4$ (anhydrite), K_2SO_4 (Arcanite) and (Na, K) Cl (sodium potassium chloride). (p.66).

Furthermore, XRD analysis of the damaged bricks revealed the presence of the low-melting phases such as KCl, $CaSO_4$, (Na, K) Cl and K_2SO_4. (p.66).

4.3.3 Formation of (Na, K) Cl (p.68)

Based on the results found by Kunnecke (1998), sodium oxide, potassium oxide and chlorine can migrate into the magnesia lining and react together to form (Na, K) Cl, filling the brick pores (Eq. 4-3).

$2NaO + K_2O + Cl_2 \rightarrow 2(Na, K)\,Cl + \frac{3}{2}O_2$ E.q 4-3 (p.68)

It was reported that the formation of (Na, K) Cl and K_2SO_4 can significantly increase the volume of the refractory brick up to 30%. (p.69)

Low melting phases of KCl, $CaSO_4$, K_2SO_4 and (Na, K) Cl were formed resulting in a decrease in liquidus temperature of the refractory lining. (p.98)

Most damaged magnesia-spinel and magnesia-fused spinel showed the presence of low-melting phases (KCl, (Na, K) Cl, $CaSO_4$ and K_2SO_4), which have adverse effects on the refractoriness of the magnesia bricks. (p.130)

$Ca_{12}Al_{14}O_{21}$: This looks like a $C_{12}A_7$ compound, which should have the formula $Ca_{12}Al_{14}O_{33}$. It is used on page 3.

The sulphur and chlorine can react with the spinel phase to form low melting aluminate phases of $Ca_{12}Al_{14}O_{33}$, $Ca_3Al_2O_6$, $Ca_6Al_8\,(Mg, Fe)\,SiO_{23}$ and $Ca_4Al_6O_{12}\,(SO_4)$ (Szczerba, 2010). (p.3).

Eq. 2-2, p.23: Aluminium and oxygen are not balanced.

$CaSO_4 + 3Ca_3Al_2O_6 + 2SiO_2 + 2CaO + 4ZrO_2 \rightarrow Ca_4Al_6O_{12}\,(SO_4) + 2Ca_2\,[SiO_4] + 4CaZrO_3$

E.q 2-2

(page. 22)

Inconsistencies and Errors

The following inconsistencies and errors were found in the text:

Partial oxygen pressure: the ratio between CO and CO2 is used when discussing partial oxygen pressure. In some cases the ration is referred to as CO/CO2, and in other case as CO2/CO. The latter is correct, and it should be used consistently.

Bartha and Sodje (2001) reported that the common reason for the degeneration of the refractory lining is the complex influence of alkalis, metal compounds and SO_2/SO_3, Cl_2 and CO_2/CO. (p.27)

2.7 The effect of partial pressure of oxygen or CO_2/CO gas mixtures

At a given temperature and standard pressure (ambient; 1 atm), the stability of a pure metal and oxide depends on the partial pressure of oxygen or CO_2/CO ratio in the atmosphere. The oxygen partial pressure in the vicinity of two phases can also be determined by the CO_2/CO ratio in a buffer mixture. At equilibrium, oxygen partial pressure can be related to the ratio of CO_2/CO using the following equations: (p.44)

The oxygen partial pressure and CO_2/CO ratio (at equilibrium) can then be determined by using thermodynamic calculations. (p.45).

Hayes (2003) reported that a large number of oxides can be readily reduced in CO_2/CO gas mixture. The most commonly used iron ore is in the form of hematite, Fe_2O_3. In the presence of CO_2/CO mixtures, this oxide may be reduced to iron in a number of stages. Similarly manganese oxide, Mn_2O_3 can also be reduced in CO_2/CO gas mixture. For each oxide, reaction temperature and a critical CO_2/CO ratio in the gas mixture must be exceeded before the reduction reaction proceeds. Typically the reduction of Fe_2O_3 and Fe_3O_4 occurs between 200 – 250°C, and a minimum CO_2/CO ratio of approximately $\frac{1}{10^4}$ is required. (p.46).

3.6 Carbon monoxide / carbon dioxide (CO_2/CO) measurements (p.56)

Residence time calculation: On page 51, the residence time of charge material in the kiln is quoted as approximately 1h, and a formula is provided to calculate it in Equation 3-1. When this formula is used, a residence time of 15 min is obtained. No units are provided for most of the symbols in Equation 3-1.

3.2 The industrial Kiln (p.52)

The industrial kiln in this study has an effective diameter of 3.8 m and a length of 70 m. The kiln rotates at 3.1 revolutions per minute (rpm) and it is inclined at 3°. The residence time of the charge in the kiln is approximately 25 minutes (refer to appendix E) and can be calculated according to Alsop (1998) as follows:

$$T = 11.2\ L\ /\ NDS \qquad \text{E.q 3-1}$$

Where T= time in minutes, D = diameter in meters, L = Length in meters, N = revolutions per minute and S = kiln slope in degree

Appendix E (p. 152)

Residence time in Kiln "t"= $\frac{11.2 * L}{N * D * S}$

L = Length of kiln in meter

S = Kiln inclination in degree

D = Effective diameter of kiln in meter

N = Rotation per minute (rpm)

Where D= 3.8 m, L= 70 m, S = 5.24 and N = 3.1

Residence time in Kiln "t"= $\frac{11.2 * 70}{3.8 * 3.1 * 3}$

Residence time in Kiln "t"= 22.2 minutes

XRF analysis: On page 54. It is stated that XRF analysis was used for "the identification and characterization of powder samples and crystalline phases". This is inaccurate, since XRD analysis is used for identification and characterisation of crystalline phases.

3.4.1 XRF (p.55).

The identification and characterization of powder samples for elemental and chemical compositions was carried out by PAnalytical Axios X-ray powder fluorescence spectrometry technique (XRF). This technique was used to determine the chemical compositions of the kiln feed and used and unused refractory lining powder samples. In addition analysis of clinker for alkali sulphate ratio (ASR) values was completed through XRF.

Reference to Table 4-2: On page 58: "However, Cl is absent in magnesia-spinel brick type B (Table 4-2 and Figure 4-2)."

This is contrary to the content of Table 4-2.

However, Cl is absent in magnesia-spinel brick type B (Table 4-2 and Figure 4-2). A typing error was made, the composition of sulphur mistakenly inputted under chlorine. This analysis are area scan. The table 4-2 is corrected as follows (p.60):

Table 4-2. Elemental composition of virgin and damaged magnesia powder sample, based on SEM-EDS analysis

Elements	Chemical composition (weight %).					
	Magnesia-spinel brick type A		Magnesia-spinel brick type B		Magnesia-fused spinel	
	virgin	damaged	virgin	damaged	virgin	damaged
O	39.78	39.54	40.60	43.37	44.01	44.89
Mg	55.37	31.95	50.63	26.64	46.89	32.98
Al	1.90	1.39	5.34	4.36	4.06	4.03
Si	0.27	0.53	0.52	0.52	0.88	0.86
Ca	1.87	4.84	2.24	2.86	3.37	4.03
Mn	0.14	-	0.10	0.21	0.79	0.94
Fe	0.67	0.58	0.57	0.80		9.38
K		8.70		15.68		0.47
Cl		8.40				0.06
Na		0.46				2.36
S		3.56		5.56		
F		0.04				
Total	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**	**100.00**

$MgFe_{0.2}Al_{1.8}O_4$ phase constituents: On page 58: "Based on XRD results (Table 4-3), the main phases are periclase (MgO) and spinel ($MgFe_{0.2}Al_{1.8}O_4$). Spinel phase contains MgO, FeO and Al_2O_3."

This is not accurate. The phase formula indicates that iron in the trivalent state. It therefore does not contain FeO, but Fe_2O_3.

Based on XRD results (Table 4-3), the main phases are periclase (MgO) and spinel ($MgFe_{0.2}Al_{1.8}O_4$). Spinel phase contains MgO, Fe_2O_3 and Al_2O_3. (p.59).

Phase region boundaries: The author constructed the ternary phase diagram in Figure 4-18. Two of the phase boundaries are incorrect. The first is the between the Slag + Monoxide + $NaAlO_2$ and Slag + $NaAlO_2$ phase regions. It is indicated as curved, while it should be a straight line.

The second boundary is the one between the slag + $NaAlO_2$ and slag regions. It is indicated as a straight line, while it should be curved. (p.92).

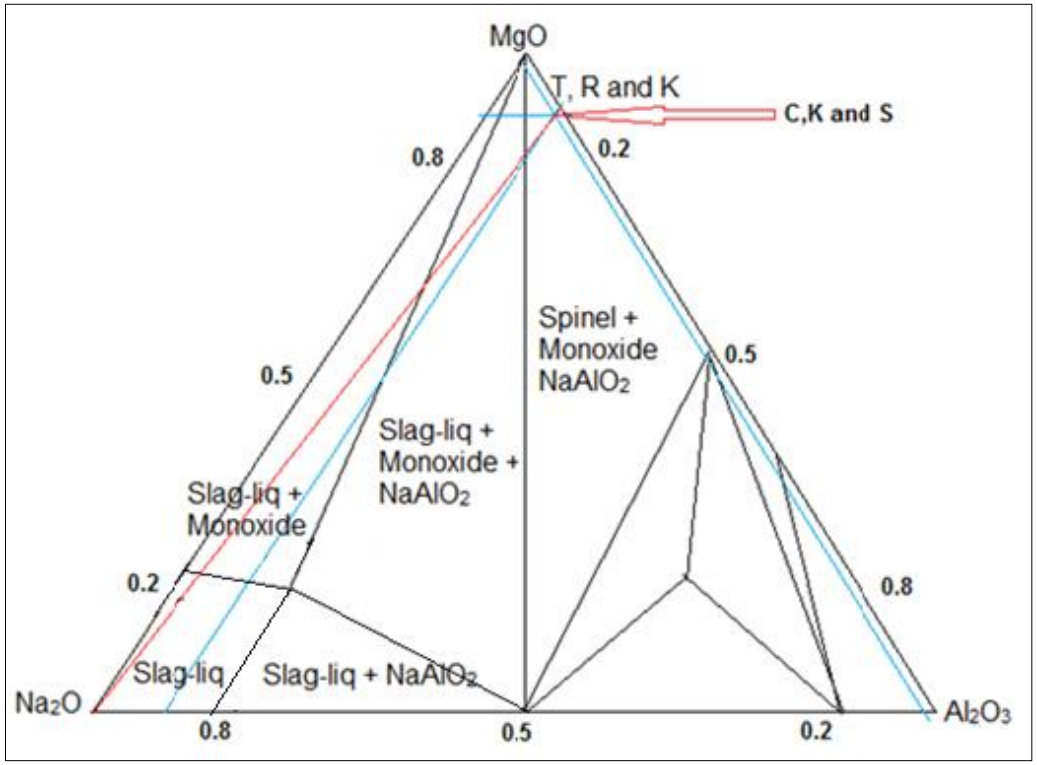

Figure 4-18. System MgO-Al_2O_3-Na_2O ternary phase diagram at 1500 °C and 1 atmosphere

XRD results interpretation: In Table 5-3 on page 101 a nickel-titanium-silicon-oxide phase is identified. Based on the quantity of this phase (14.56%) it indicates that the refractory material contains approximately 8.5% nickel. This is in contrast with the XRF and SEM-EDS results that reported no nickel.

This raises a concern about the candidate's ability to critically assess the data from experiments, measurements and calculations

The XRD results were re-evaluated and the results for both unused and used High-alumina brick reflects the following analysis which are in line with other analysis. Table 5-3 (p.103) Appendix A (p. 146 and 147).

Table 5-3. Phase composition of the virgin and used high-alumina lining, based on XRD analysis

Chemical composition (weight %).		
Phases	**virgin**	**damaged**
Aluminium Oxide (Al_2O_3)	35.84	42.48
Mullite ($Al(Al_{0.69}Si_{1.22})O_{4.85}$)	39.33	-
Mullite ($Al_{2.4}Si_{0.6}O_{4.8}$)	-	22.76
Cristobalite (SiO_2)	5.34	8.02
Quartz (SiO_2)		10.39
Analusite ($Al_2(SiO_4)O$)	-	6.20
Potassium magnesium silicate ($K_2(MgSi_5O_{12})$)	-	10.16
Sillimanite (Al_2SiO_5)	19.49	-
Total	**100**	**100**

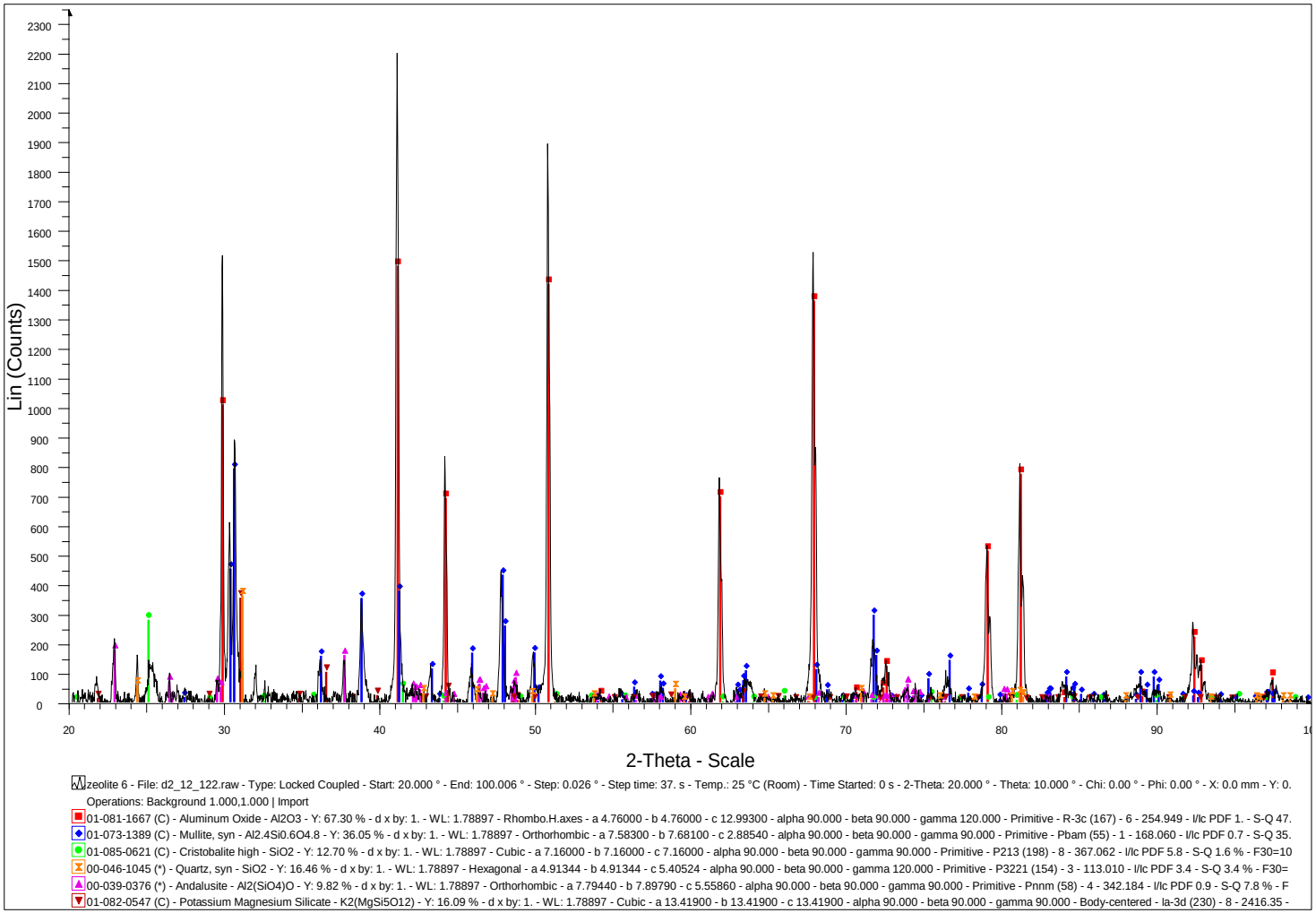

Figure A 1 High-alumina brick: used

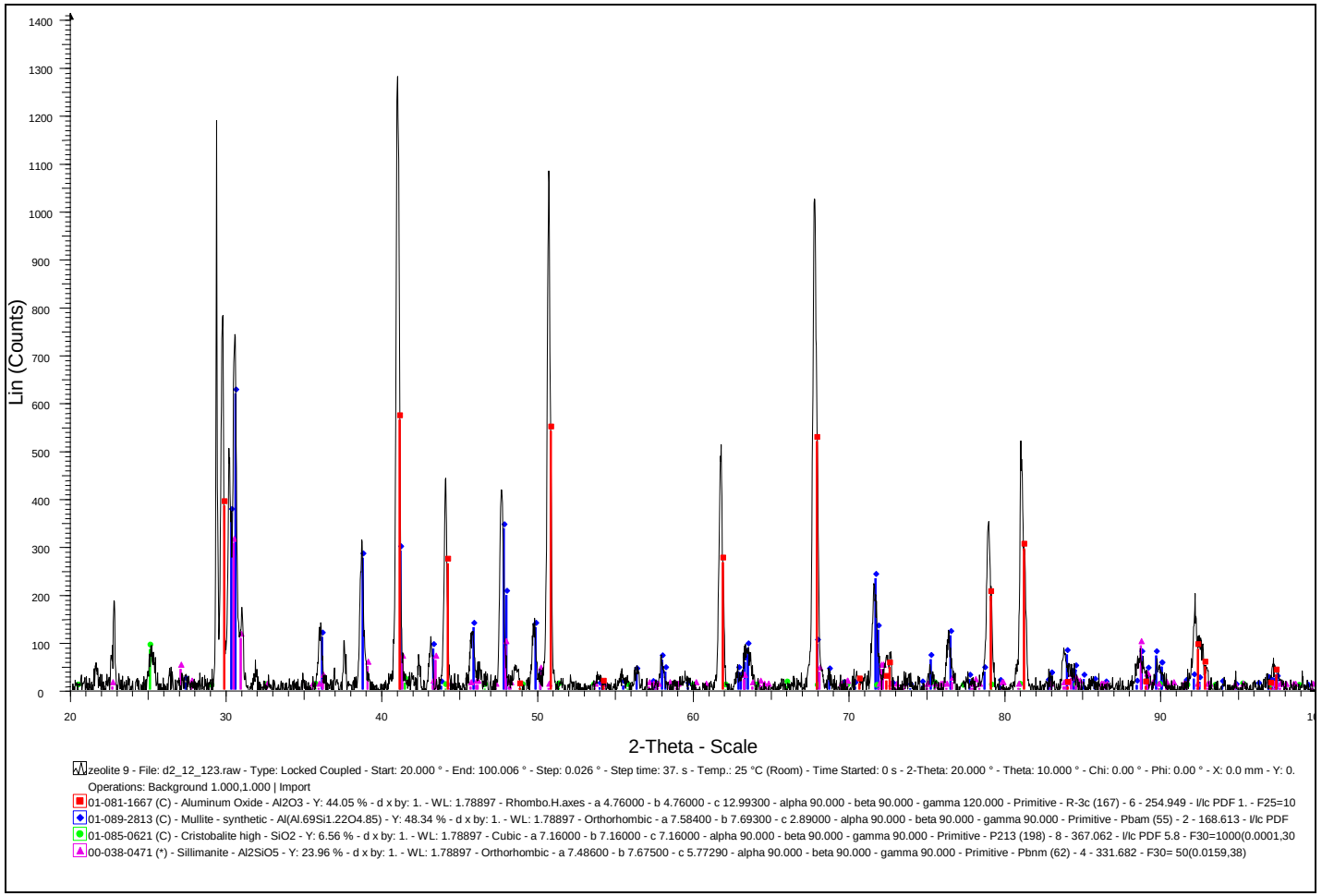

Figure A 2 High-alumina brick unused

Phase transformation in Al_2O_3 refractory material: On page 125: There was no evidence of phase transformation from XRD analysis".

This is not true, based on Table 5-3.

The chemical analysis of the used high-alumina refractory brick which was applied at the lower transition zone showed sodium, potassium and sulphur as impurities. XRD analysis showed the presence of low-melting phase (K_2 ($MgSi_5O_{12}$) which compromises the refractoriness of the high-alumina brick. (p.130).

Relevance

The issue of partial oxygen pressure and reduction and oxidation of oxides in the refractory material was discussed Section2.7, and Chapter 6 and Section 7.5. The author never makes it clear why this is necessary or important. This content can be omitted from the text without losing any valuable information. Including such content creates uncertainty with the reader, and puts the author's credibility in question.

Bartha and Sodje (2001) found that magnesioferrite ($MgFe^{3+}{}_2O_4$), contained in the alpine magnesia brick, is reduced to magnesiowusite ((Mg, Fe^{2+}) O) and this involves a significant reduction of volume (>20%). If redox burning cycles occur, there are frequent changes between magnesioferrite and magnesiowusite, resulting in the structural weakening of the affected brick horizons. This can lead to a premature wear as a result of spallings of the redox-subjected brick horizons. If additional infiltrated sulphate salts are present in the structures of the refractory lining, and particularly under the influence of sulphur excess, sulphide compounds can form from these under strongly reducing conditions. The sulphides K_2S, oldhamite (CaS), K_2S_3, $KFeS_2$ were determined in analysed used brick samples. When oxidizing conditions predominate again, an oxidation of the sulphides takes place, accompanied by a significant volume increase. This leads to expansion of the brick structure resulting in the destruction of the brick. Therefore it was important to establish if the conditions in the kiln had an effect towards the stability of the brick, through calculations of oxygen partial pressure.

Bartha and Sodje (2001) gave examples of reaction equations in burning conditions of the rotary cement kilns.

Reducing burning conditions:

$$MgO.Fe_2O_3 + CO = MgO + 2FeO + CO_2$$ E.q 2-12

$$K_2SO_4 + 4CO = K_2S + 4CO_2$$ E.q 2-13

$$K_2SO_4 + 8CO + 2SO_2 = K_2S_3 + 8CO_2$$ E.q 2-14

$$MgFe_2O_4 + K_2SO_4 + 13CO + 3SO_2 =$$

$$2KFeS_2 + MgO + 13CO_2$$ E.q 2-15

Oxidising burning conditions

$$MgO.2FeO + \frac{1}{2}O_2 = MgO.Fe_2O_3$$ E.q 2-16

$$2KFeS_2 + 8O_2 = K_2SO_4 + Fe_2(SO_4)_3$$ E.q 2-17

Omissions

The following omissions of important aspects were identified:

Limitations of analytical techniques:

In section 3.4, three analytical techniques are introduced as methods used in the project. The accuracy and detection limits of the methods are not stated in the text. This is vital, since it is difficult to interpret analytical results responsibly without knowing what these limitations are.

3.4 Analytical methods (page 54 – 56)

3.4.1 XRF

The identification and characterization of powder samples for elemental and chemical compositions was carried out by PAnalytical Axios X-ray powder fluorescence spectrometry technique (XRF). This technique was used to determine the chemical compositions of the kiln feed and used and unused refractory lining powder samples. In addition analysis of clinker for alkali sulphate ratio (ASR) values was completed through XRF. The limitation of XRF analysis is its inability to distinguish ions of the same element in different valence states and hence XRF was used in conjunction with XRD and SEM-EDS techniques.

3.4.2 XRD

The powder samples were prepared for X-ray diffractometry (XRD) analysis using a zero background sample holder or a universal sample holder for solid metal samples. They were analysed with a PAnalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence and fixed receiving slits with Fe filtered Co-K radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program). The limitation of XRD is its inability to detect a small amount of phase in the sample.

3.4.3 SEM-EDS

The Joel JSM 6510 SEM, equipped with NSS software, was used for microstructural and qualitative chemical analysis. The refractory brick section samples were cold mounted and

ground (polished) in three steps; 80, 220 and 1200 grit using the diamond discs. The samples were then coated with carbon to improve their conductivity under the microscope. The powder samples once received were placed on carbon tape and then coated with carbon before analysis. The carbon coating of the refractory materials limits the accuracy of measuring carbon content on the sample. In addition SEM – EDS technique is unable to measure Li, He and H content.

FactSage details

In section 3.5, it is reported that FactSage was used for thermochemical calculations. Calculations results are reported in subsequent sections. The author does not state the version number, databases and complete list of phases in the text. These are all very important for providing a complete report of the work.

3.5 Computational thermochemistry (FactSage) (page 56)

FactSage (EX Mente) computational thermochemistry software was used to predict interactions through phase diagrams systems. It was developed by Thermfact from Canada and GTT-Technologies from Germany. The developed phase diagrams are used to predict the effect of impurities analysed in this study. The thermodynamic predictions of the chemical reactions were performed using the software package FactSage 6.4 with the oxide and salt solutions databases (FToxid and FTsalt). The results shown by XRF, XRD and SEM-EDS analysis were accurately predicted by FactSage which confirms its suitability for this work.

FactSage suitability

The author used FactSage to analyse a number of material compositions. It is always necessary to consider whether FactSage has the data required to describe the system being considered.

In this case the author did not discuss the database used, the phases selected and whether data available in FactSage is suitable for describing the phases in question.

One always needs to critically assess the equipment, technique and data used for analysis and calculation.

3.5 Computational thermochemistry (FactSage) (page 56)

FactSage (EX Mente) computational thermochemistry software was used to predict interactions through phase diagrams systems. It was developed by Thermfact from Canada and GTT-Technologies from Germany. The developed phase diagrams are used to predict the effect of impurities analysed in this study. The thermodynamic predictions of the chemical reactions were performed using the software package FactSage 6.4 with the oxide and salt solutions databases (FToxid and FTsalt). The results shown by XRF, XRD and SEM-EDS analysis were accurately predicted by FactSage which confirms its suitability for this work.