

Mineralogical and Thermodynamic Investigation of CLU Converter Lining Failures in Commercial Production of Medium Carbon Ferromanganese

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1. ABSTRACT

The results of investigations into the causes of three magnesia-chrome refractory lining failures on a 25 t CLU (Creusot-Loire Uddeholm) converter in medium carbon ferromanganese (MC FeMn) production are reported. Operational conditions leading up to the failure are scrutinised and key processing conditions relevant to the failure are discussed. Results of application of a variety of mineralogical examination techniques to further diagnose the causes of failure are presented.

In an attempt to find explanations for the refractory failures, some of the fundamental thermodynamics of heterogeneous refractory lining interactions in the CLU converter are reviewed. The role of manganese metal and manganese vapour in reduction of the magnesia-chrome refractories is confirmed, permitting many of the characteristics of refractory lining attack during commercial medium carbon ferromanganese production to be explained rationally. Ultimately, tighter specifications of refractory requirements are presented, that were fixed with refractory suppliers to address identified shortcomings of the magnesia-chrome refractories typically used in CLU converter linings for MC FeMn production.

2. INTRODUCTION

Between the latter half of 1994 to early 1995 the CLU converter of the IC3 (Intermediate Carbon Charge Chrome) business unit of Samancor Chrome was switched to MC FeMn

production. Two variants of commercial MC FeMn production were practiced (Figure 1), but adoption of a practice involving recovery of MnO_x by FeSi reduction in an initial reduction period soon lowered slag Mn contents, to realise maximum Mn yields (Figure 2).

Although numerous similarities with IC3 production¹ existed, significantly poorer refractory performance was associated with MC FeMn production. Compared with an average 78.7 heat lining life (later improved to an average 139.0 heats) on IC3¹, initial bricked refractory converter lining life on MC FeMn production with magnesia, tar-bonded magnesia or pitch-impregnated magnesia was a paltry 36.1 heats per lining (Figure 3). This poor refractory performance was attributed to the more naturally fluxing nature of the MnO_x slags compared to CrO_x slags, resulting in accelerated attack of the binder phase between the magnesia grains, exposing the refractory to excessive erosion and wear.

To counter this problem use was made of magnesia-chrome refractories varying from high-fired, to 25% fused grain and 100% reconstituted fused grain types. This resulted in an improvement to an average 70.1 heats per lining (best of 180 heats per lining — Figure 3), yet was still well short of the average IC3 refractory performance. To elucidate the reasons for the increased refractory attack with MC FeMn production both mineralogical and thermodynamic investigations of refractory failures were conducted.

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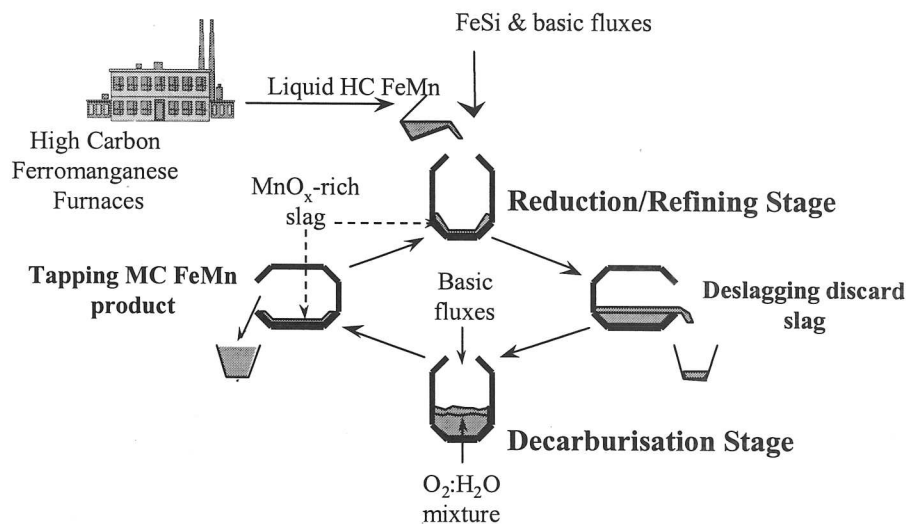


Figure 1: Schematic of overall MC FeMn production process in a CLU converter

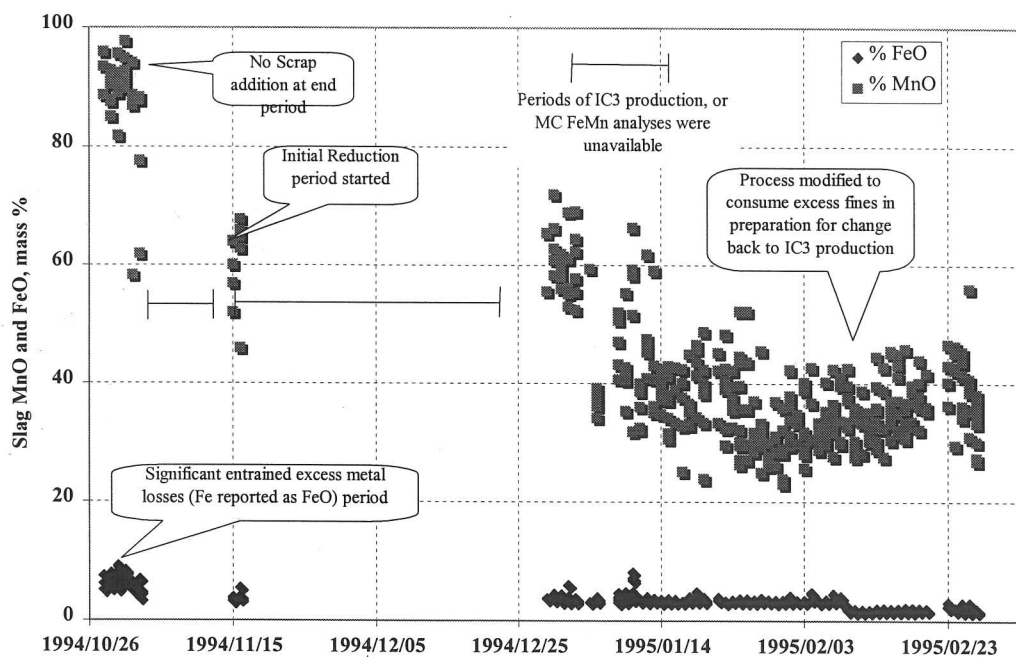


Figure 2: Converter refractory performance over the MC FeMn production campaign

3. CAMPAIGN OPERATIONAL DESCRIPTIONS

Investigation of three specific MC FeMn campaigns is reported:

1. M24 (60% MgO, 100% reconstituted fused grain) lasted 99 heats before a tuyere failure. Following tuyere repair an additional 67 heats were achieved before ultimate failure. The maximum lining temperature recorded was 1720°C.

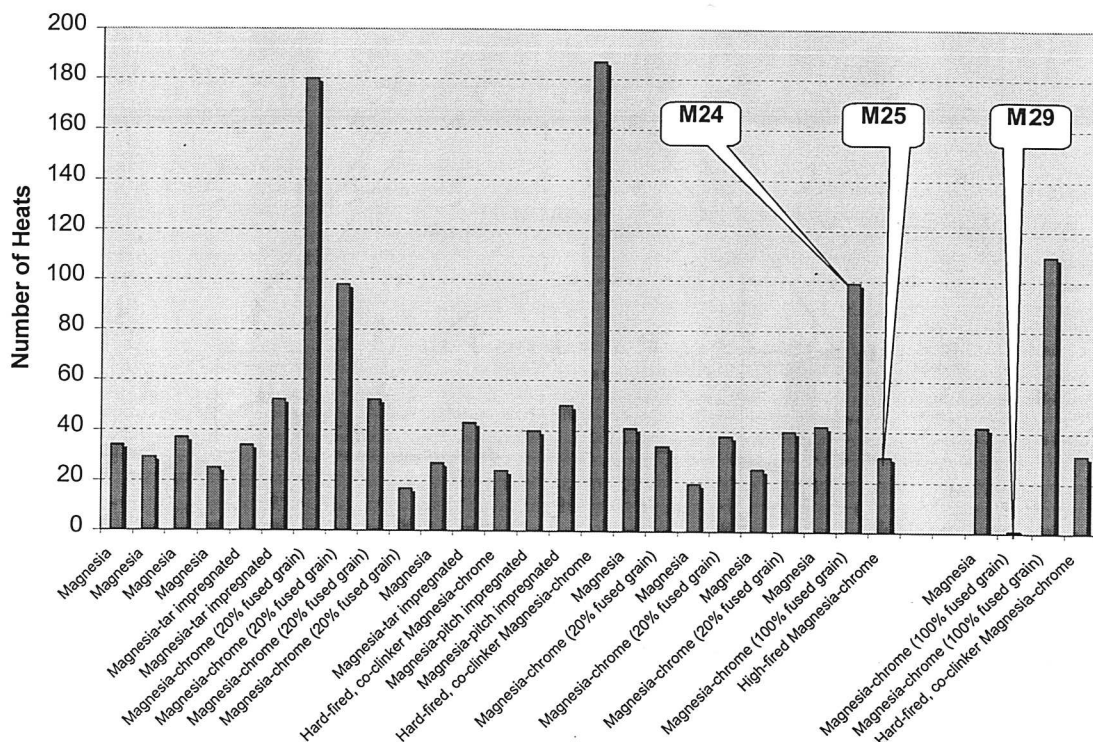


Figure 3: Converter refractory performance over the MC FeMn production campaign

2. M25 (60% MgO, high-fired magnesia-chrome) lasted only 30 heats. This lining failure was a little unusual, in that the failure occurred in the upper barrel section, on the uppermost side, opposite to the direction in which the converter was tilted (Figure 4). Upon examination of the lining inside the converter it immediately became apparent that the lining had been severely attacked around its circumference well above the slag-line.
3. M29 (also 60% MgO, 100% reconstituted fused grain) failed remarkably in the very first heat, during the initial decarburisation stage (in the first heat there is no MnO_x -rich slag to reduce as there is no prior heat to yield such slag). The breakout of metal on the converter was observed on its lower side (in the direction of tilting – Figure 4) between the converter barrel and upper cone sections. The actual physical penetration of metal through the refractory hot-face actually occurred lower in the barrel section in the converter, and there was evidence that metal had accumulated between the working and safety linings (alumino-silicate — 60% Al_2O_3 /40%

SiO_2). This metal had eventually penetrated through the joint between the barrel and cone sections. This catastrophic failure occurred with hot metal containing a typical 0.3% Si content, and before any FeSi reduction period, and so could not be ascribed to attack by an abnormally acidic slag. Also, low Al_2O_3 contents of converter accretions confirmed that excessive carryover of furnace slag with the hot metal could not have occurred. The maximum temperature recorded was low at 1685°C ('thermal inertia' always renders the first heat colder than subsequent heats).

4. VISUAL AND IMAGE ANALYSIS OBSERVATIONS

A generic sketch of the different regions within the bricks (Figure 9) could conveniently describe the used condition of the converter bricks (Figures 5-8). Distinct parabolic concentration gradients appeared to exist in the bricks in cross-sections taken through their widths, suggesting a refractory attack mechanism involving accelerated mass transport along the brick joints.

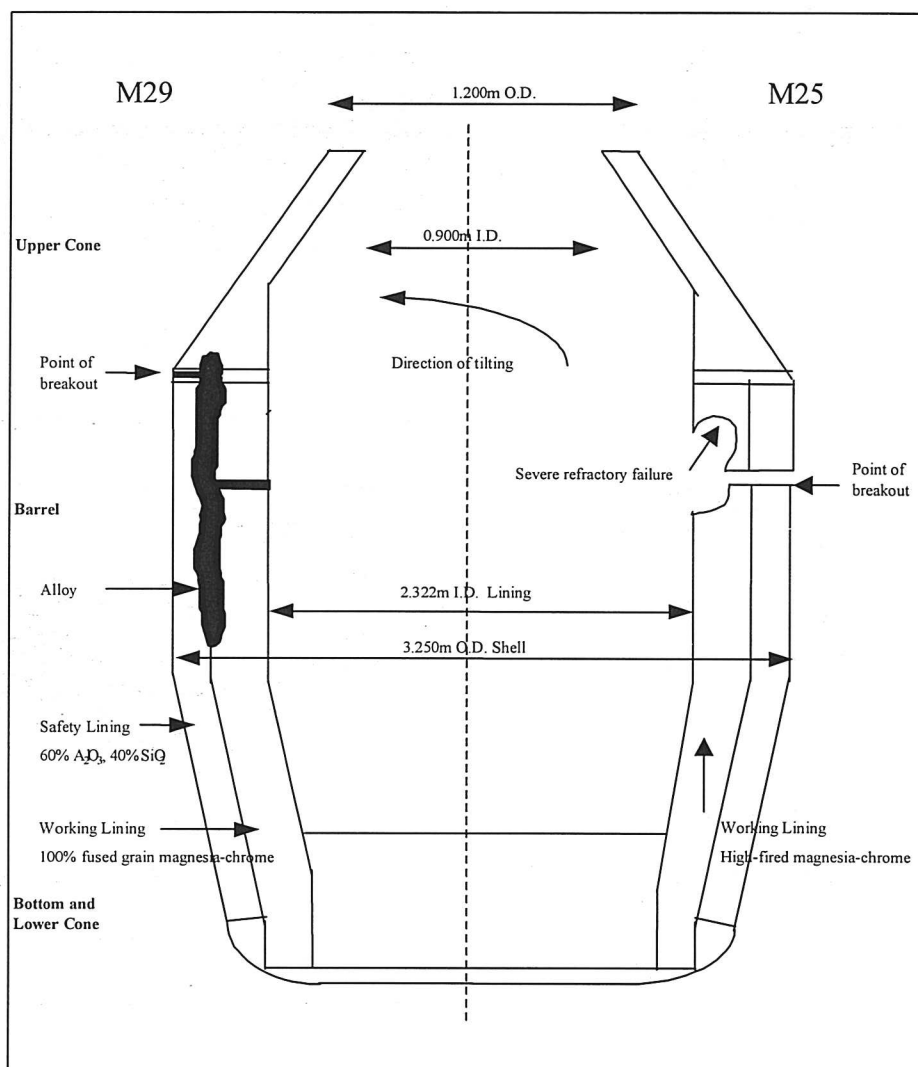


Figure 4: Schematic representation of a cross-section through the converter vessel illustrating the failures observed in campaigns M25 and M29

The regions consistently identified in sequence from the hot-faces of the brick samples included:

- Converter slag (zone S)
- an outer slag accretion layer (zone Ai)
- a densified and plastically deformed altered zone adjacent to the hot-face (zone Aii) containing little, to no chromite, while deeper in the bricks up to 32% chromite by surface area was recorded (by image analysis)
- a porous and metallised zone (zone Bi) with up to 7.3% metal by surface area — located at between 10 to 25 mm into the brick, and up to 30 mm thick
- a lighter coloured altered region (zone Bii) containing some metallisation of about 3.6% by surface area

- a brown coloured altered region (zone Ci) of up to 6.3% porosity by surface area
- 'virgin' unaltered refractory brick (zone Cii) of slightly higher porosity (7.4 to 10.8% by surface area, in some instances) and frequently high gangue content (over 10% by surface area^{*}).

^{*} Quantitative image analysis results for gangue and porosity may be compromised by similarities in the reflectance of the darker forsterite-type gangue phase and mounting resin used in vacuum impregnation of polished sections.

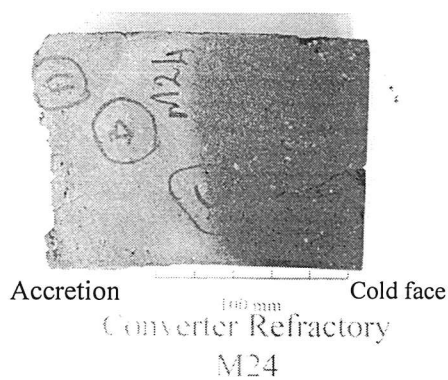


Figure 5: Campaign M24 brick

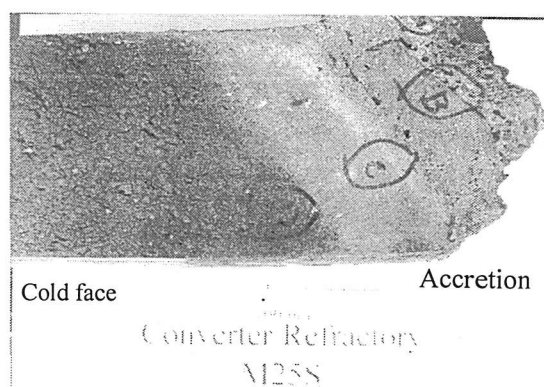


Figure 6: Campaign M25 — sidewall brick

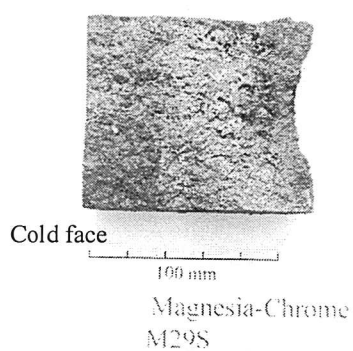


Figure 7: Campaign M29 — sidewall brick

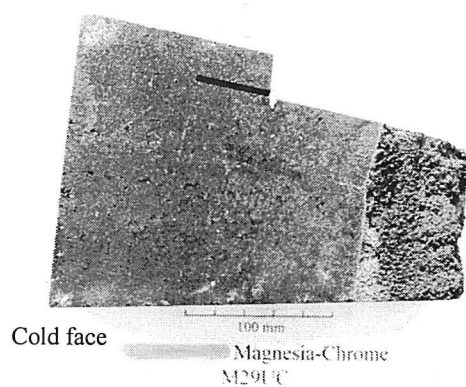


Figure 8: Campaign M29 — upper cone brick

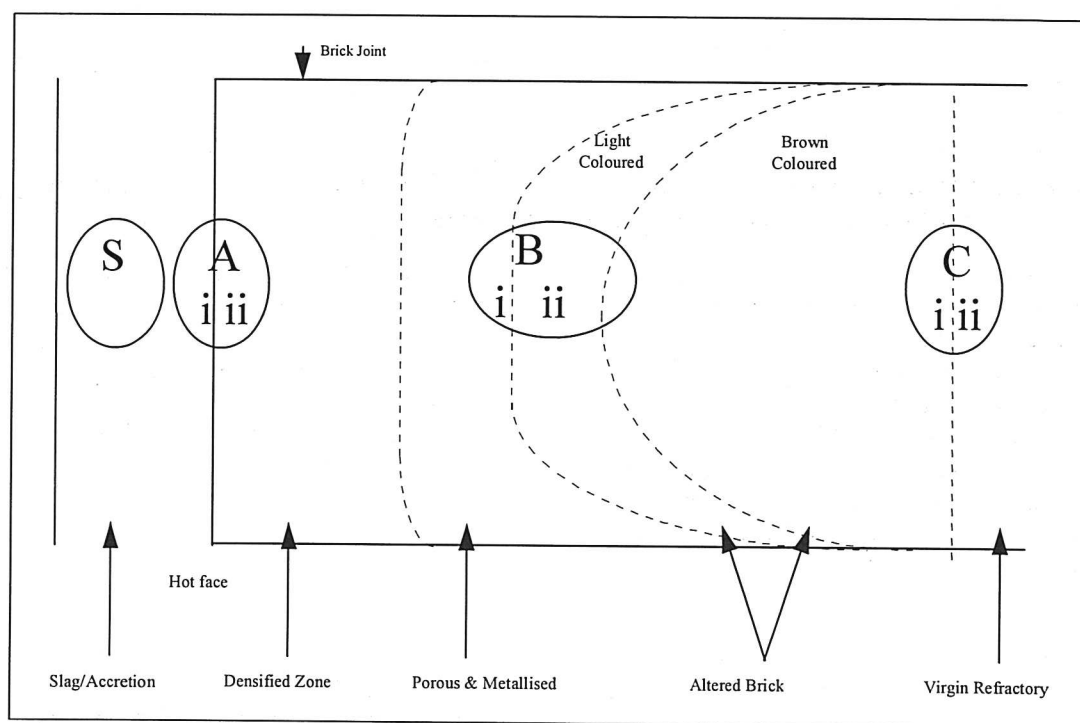


Figure 9: Schematic representation of the different zones observed within the refractories, indicating sites where polished sections were taken from.

5. POLISHED SECTIONS — RLM AND SEM-EDS EXAMINATION

Reflected Light Microscopy (RLM) investigation was used to identify bulk phases, supported by image analysis. Scanning electron microscopy coupled with energy dispersive spectroscopy (SEM-EDS) analyses was used to confirm the identification of major phases and to identify the chemical compositions of any minor phases associated with each of the generic zones identified above.

Key mineralogical phase identifications and refractory brick characteristics pertinent to explanations of specific refractory attack mechanisms can be described as follows (Figures 10-23):

- Magnesia-chrome refractory is characterised by a MgO matrix within which fine 'protected' spinel is ideally dispersed (Figures 10-15).

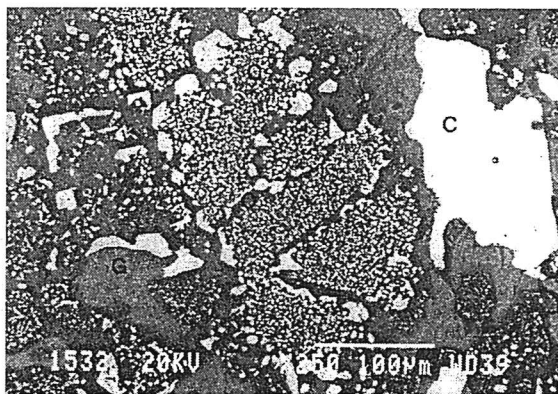


Figure 10: SEM photomicrograph of brick from M24-Cii (virgin refractory). Notice a rare large 'exposed' chromite grain (C) surrounded by gangue. Remnant spinel outlines are also observed where spinel underwent fusion with MgO (dark colour) to yield a MgO matrix containing tiny 'protected' spinels. (x250)

- Undesirable characteristics of the virgin refractory include: large free 'exposed' chromite grains (Figures 10-12); porosity, especially when of interconnected nature (Figures 12-13); and gangue (Figures 10, 11, 14 and 15), typically found as a brighter monticellite-type and a darker forsterite-type (Figure 16).
- Attack by MnO_x slag frequently results in formation of solid solutions with MgO or spinel (Figures 17-19 and 21).
- Reduction of chromite spinels can occur through: Mn alloy, resulting in Mn-containing FeCr alloy and MnO_x products (Figure 20); CO and H_2 gas, resulting in a Mn-free FeCr metal product (Figures 10, 11, 15, 19 and 20); and Mn(v) resulting in FeCr alloy and MnO_x reaction products. Some evidence for Mn(v) attack appeared to exist along interconnected pores (Figure 21).

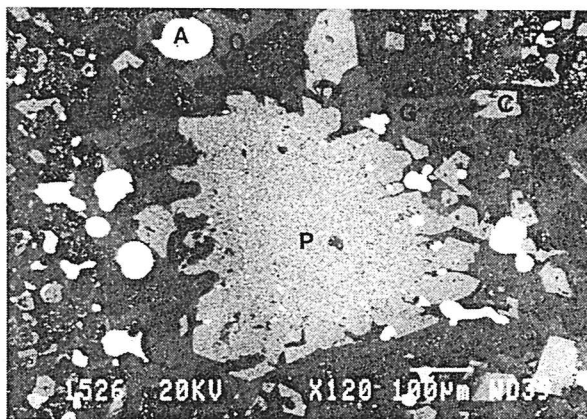


Figure 11: SEM photomicrograph of brick from M25 Sidewall-Bii (porous and metallised zone). Notice metallisation starting within, and around the PAC, assisted by the presence of residual gangue (G). The large metal blebs (A) are Fe-rich. Notice angular fragments breaking off from the large PAC (P). Virgin high-fired brick contained a preponderance of 'exposed' large chromite grains surrounded by gangue (U) — susceptible to reduction. Small spinels contained in the dark MgO matrix are 'protected' and less susceptible to reduction. (x120)

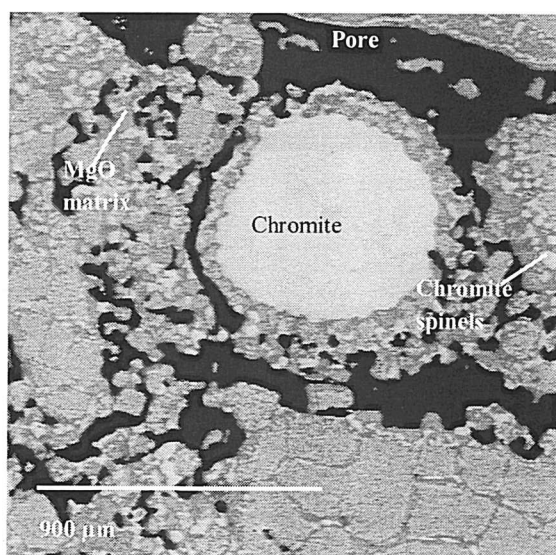


Figure 12: SEM photomicrograph taken of section M29 Upper Cone-C. Interconnected pores and a large 'exposed' chromite grain (675 μm in diameter — 18.87% MgO, 10.87% FeO, 0.54% MnO, 49.64% Cr₂O₃, 17.79% Al₂O₃, 0.78% SiO₂, 0.25% CaO and 0.50% TiO₂) are observed. The lower right hand section shows well-fused brick with small chromite spinels 'protected' by a MgO matrix (88.36% MgO, 5.96% FeO and 5.41% Cr₂O₃). (x50)

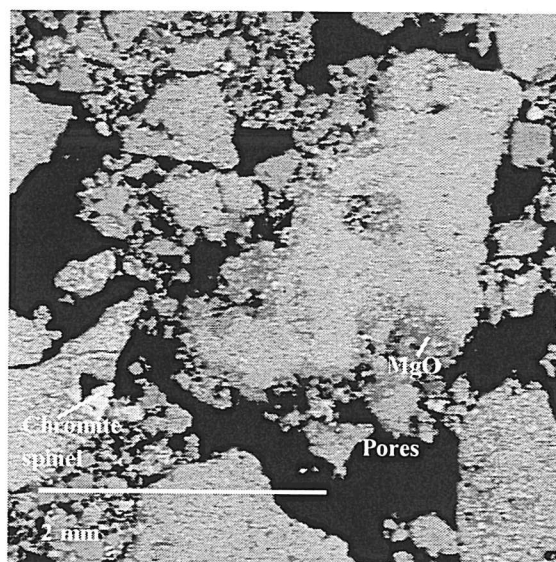


Figure 13: SEM photomicrograph of section M29 Base-C showing the very centre of the brick and the presence of a multitude of large interconnected pores (several mm in length). Well-fused grains are evident, with small chromite spinels (24.54% MgO, 14.36% FeO, 0.44% MnO, 15.88% Al₂O₃, 44.51% Cr₂O₃, 0.29% SiO₂, 0.13% CaO and 0.23% TiO₂) 'protected' by a MgO matrix. (x20)

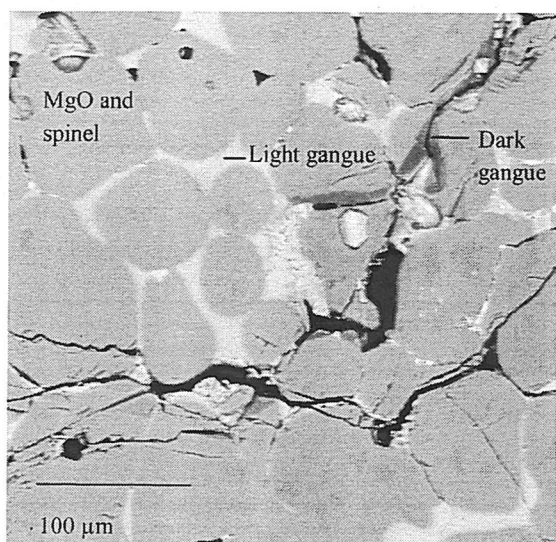


Figure 14: SEM photomicrograph of section M29 Floor-B showing the presence of gangue, pores and microcracks between boundaries of well fused grains. (x300)

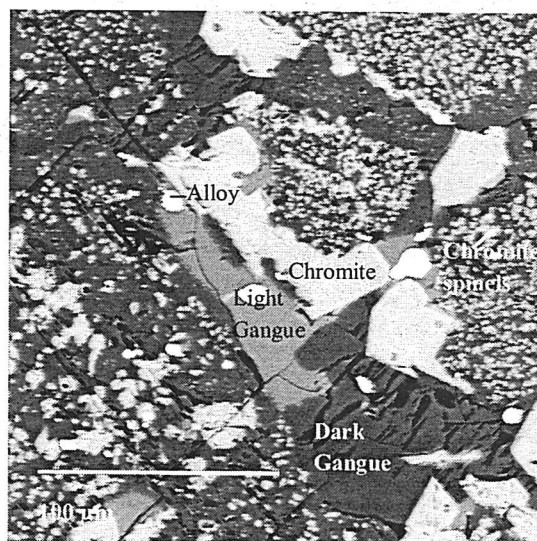


Figure 15: SEM photomicrograph of section M29 Upper Cone-B. Several large chromite grains (± 70 μm in diameter) and pores are observed often surrounded by gangue. (x250)

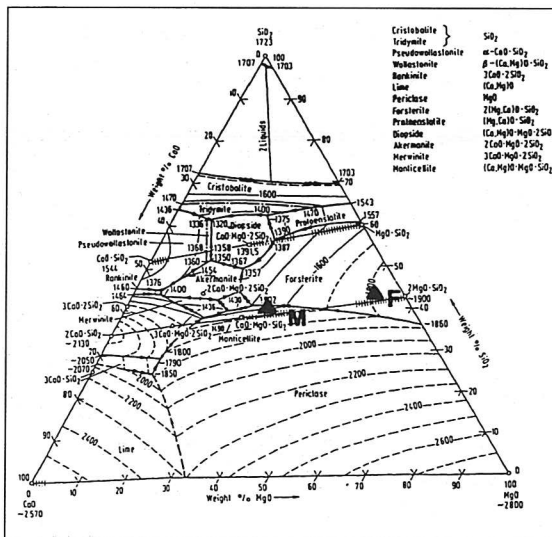


Figure 16: Phase relations in the system CaO-MgO-SiO_2 showing liquidus temperatures². The brighter 'monticellite' gangue phase is marked M (32.95% CaO , 24.25% MgO and 37.98% SiO_2). The darker forsterite gangue phase (48.845% MgO , 41.64% SiO_2 and 5.01% CaO) is marked F.

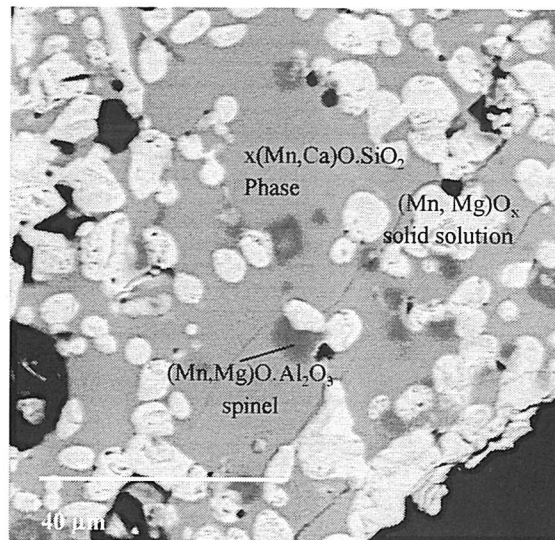


Figure 17: SEM photomicrograph of section M29 Upper Cone-A along the very edge of the brick. Brighter $(\text{Mg,Mn})\text{O}_x$ solid solutions exists in calcium manganese-silicate (12.92% CaO , 48.86% MnO and 28.01% SiO_2). MnO solid solution with spinel (32.27% MnO , 8.36% FeO , 2.89% MgO , 3.21% Cr_2O_3 and 52.78% Al_2O_3) is observed. (x1000)

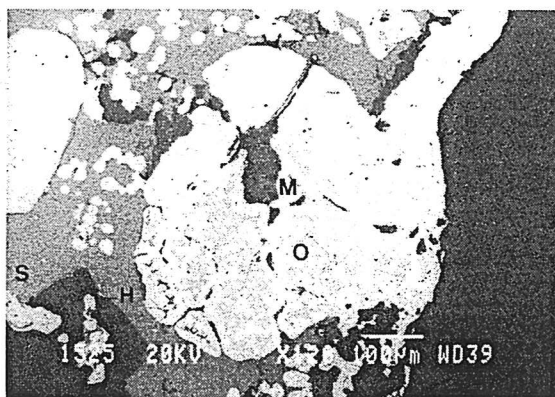


Figure 18: SEM photomicrograph of section M25 Sidewall-S/A — slag accretion (marked S) at the brick hot face. A large MgO grain (darker core, marked O) is undergoing topochemical solid solution with MnO_x (brighter rim, marked M — 66.48% MnO , 32.77% MgO). A typical pore (resin impregnated polished sections) is marked H. (x120)

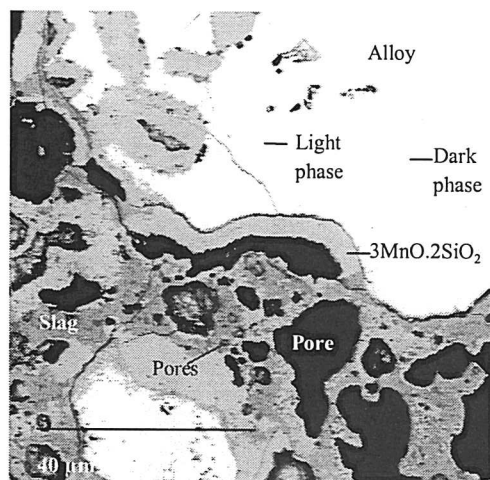


Figure 19: SEM photomicrograph of section M29 Floor-B showing Mn and/or MnO_x attack of MgO resulting in two Mn-Mg phases, a bright phase and a darker core. The metallic blebs also contained two phases (not clear on the photomicrograph — one (Cr,Mn,Fe) carbide (43.42% Cr , 28.96% Mn and 16.00% Fe), the other Mn-rich (42.61% Mn , 49.85% Fe , 6.94% Cr). (x150)

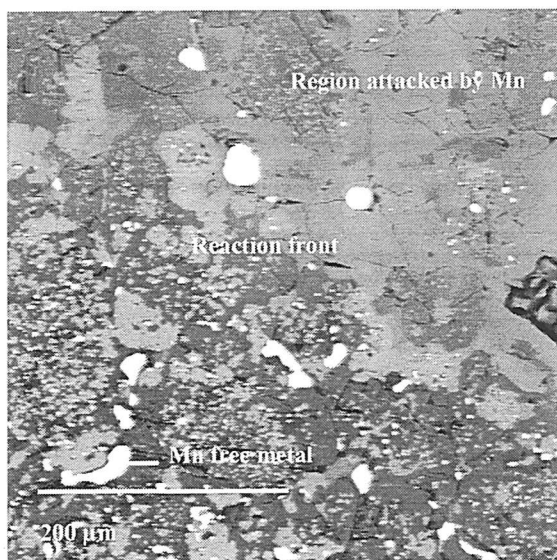


Figure 20: SEM photomicrograph of section M29 Floor-B. The upper region of the brick experienced Mn alloy attack, but the lower section contains no Mn containing alloy, although some spinel reduction had also occurred there (probably by reducing gases). (x200)

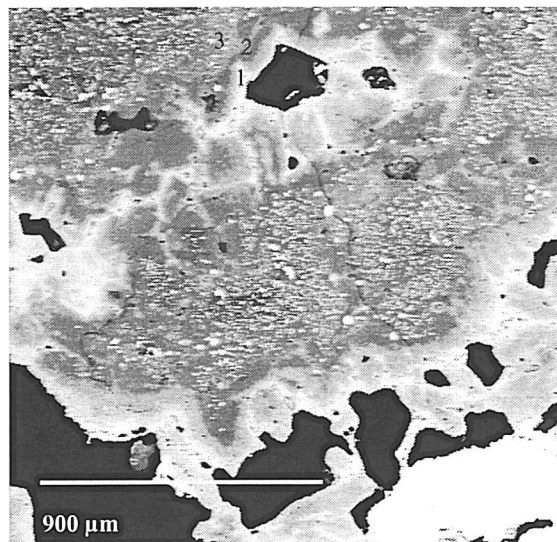


Figure 21: SEM photomicrograph of section M29 Upper Cone-A. A general view taken near the hot-face edge of the sample, indicating infiltration of a Mn source (either Mn (v) and/or MnO slag) along interconnected pores 'at-temperature'. 1, 2 and 3 indicate points analysed by SEM-EDS (Figure 22). (x50)

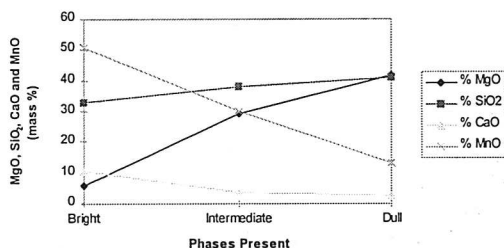


Figure 22: Concentration profiles (SEM-EDS analyses) derived from points marked 1, 2 and 3 on Figure 21 (1 = 'bright'; 2 = 'intermediate' and 3 = 'dull'). The composition (and reflectance) varies as Mn substitution progresses and the proportions of Mg and Ca change in the structure of basic composition $x(\text{Mg}, \text{Mn}, \text{Ca})\text{O} \cdot \text{SiO}_2$

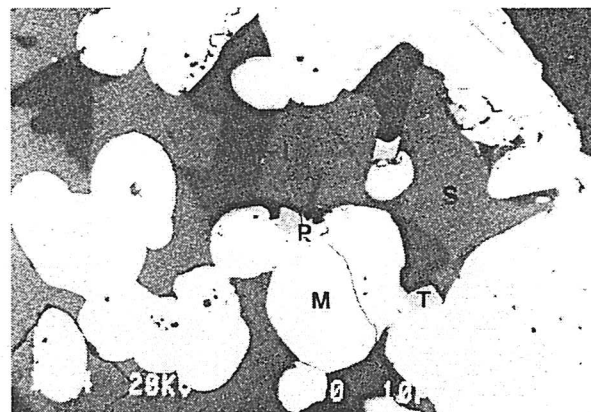
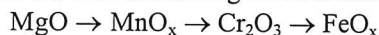


Figure 23: SEM Photomicrograph of M25 Sidewall-S. A dark Al-rich interstitial phase (I) exists in the slag (S). Ti-rich solid solution phase with MnO_x existed on the MnO_x grains ($T = 52.16\% \text{ MnO}, 4.91\% \text{ MgO}, 6.66\% \text{ Al}_2\text{O}_3$ and $31.07\% \text{ TiO}_2$). The MnO_x is undergoing topochemical reduction to produce Mn metal (brighter rims, almost pure Mn at P). (x600)

6. THERMODYNAMIC EVALUATION OF REFRACTORY INTERACTIONS

6.1 Metal-Refractory Interface

At converter temperatures of interest the general order of decreasing oxide stability is:



Specifically, for reduction of these oxides to their constituent metals at 1700°C according to their ideal standard reactions, conditions must be sufficiently reducing that $p_{\text{O}_2} < 10^{-22}$, 10^{-12} , 10^{-11} and 10^{-7} atm, respectively ($p_{\text{CO}}/p_{\text{CO}_2} > 10^8$, 5×10^3 , 5×10^2 and 10, respectively; and $p_{\text{H}_2}/p_{\text{H}_2\text{O}} > 10^5$, 5×10^2 , 50 and 1, respectively). However, in the real system in the converter, less reducing conditions may still be sufficient to cause refractory attack, provided that reduction kinetics remain favourable (Appendix A).

The key observation is that the relatively lower stabilities of oxides of chromium imply that IC3 alloy is unlikely to be too aggressive to chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$), or magnesia (MgO) in the refractories. MC FeMn alloy, however, is likely to be reducing towards chromite and, under extreme conditions possibly MgO , according to the reactions [1], [2] and [3] (Appendix A).

It can be shown thermodynamically that Mn alloy at converter operating temperatures of 1700°C will substantially reduce all FeO in chromite, and continue to reduce Cr_2O_3 at least until the activity of Cr_2O_3 ($a_{\text{Cr}_2\text{O}_3}$) drops to 0.02 (i.e., almost no Cr_2O_3 left). Mn alloy attack of exposed 'free' chromite spinels (depicted in Figure 20) is therefore likely to be a very real possibility.

Furthermore, it can be shown that the equilibrium partial pressure of magnesium (p_{Mg}) in reaction [3] at a temperature of 1700°C is of the order of 0.0025 atm (Appendix A). This implies that as long as p_{Mg} does not equal, or exceed this value, alloy attack of MgO refractories will proceed to some extent (provided reaction kinetics are concurrently favourable). Such a condition can possibly be envisaged when alloy first

contacts the refractory, and when the refractory is continually 'washed' by 'fresh' MC FeMn. Notice that the equivalent equilibrium p_{Mg} of 0.0004 atm for Cr alloy attack of MgO (reaction [4]) is almost two orders of magnitude lower. Clearly, there exists a greater risk of chromite and magnesia refractory attack in MC FeMn production than in IC3 production, consistent with plant observations of comparative refractory lining performance.

6.2 Slag-Refractory Interface

Both IC3 and MC FeMn slags may be fluid at elevated temperatures and capable of significant refractory dissolution, especially of the protective MgO surrounding chromite spinels. Basic slags of sufficiently low SiO_2 contents, and slags doubly saturated in terms of MgO , and additionally Cr_2O_3 , (for the IC3 system) will help to minimise slag dissolution of the refractory.

In IC3 production, magnesia-chrome refractories are naturally resistant to a slag doubly saturated in MgO and Cr_2O_3 - neither magnesia or chromite spinel will be attacked to any significant degree. Moreover, such slags will likely precipitate a solid picrochromite spinel phase ($\text{MgO} \cdot \text{Cr}_2\text{O}_3$) at operating temperatures below 1700°C which, if anything, should protect the refractory from further slag attack. Although more aggressive to the refractories, MC FeMn slags saturated in MgO should also limit refractory dissolution. They should merely undergo solid solution with the constituent magnesia and chromite spinels in the refractory, to form protective coatings of $(\text{Mg}, \text{Mn})\text{O}$ (Figures 17, 18 and 19) and $(\text{Mn}, \text{Fe}, \text{Mg})\text{O} \cdot (\text{Al}, \text{Cr})_2\text{O}_3$ (Figure 17), respectively, of higher solidus temperature.

6.3 Gas-Refractory Interface

6.3.1 CO and H₂ Attack

The CLU is an oxygen refining vessel that is in fact highly reducing in character, as a consequence of the huge reservoir of reduced metal in the vessel. Large quantities of CO and H₂ (with only traces of CO₂, H₂O and O₂) continuously leave the bath, representing a highly reducing gas that flushes the converter

freeboard, potentially diluting any gaseous products of refractory attack.

From observation that some reduction of MnO_x to Mn metal occurred (Figure 23), it is conceivable that p_{O_2} as low 10^{-12} atm ($p_{\text{CO}}/p_{\text{CO}_2} > 5 \times 10^3$, or $p_{\text{H}_2}/p_{\text{H}_2\text{O}} > 5 \times 10^2$) can exist in the converter at times. This suggests that converter gas permeating refractories above the slag-line (along brick joints, or through interconnected pores) could be well capable of reducing FeO and Cr_2O_3 from chromite spinels. Furthermore, under extremely reducing conditions ($p_{\text{CO}}/p_{\text{CO}_2} > 1120$, or $p_{\text{H}_2}/p_{\text{H}_2\text{O}} > 187.4$) some potential for MgO reduction by CO and H_2 (reactions [8] and [9]) exists if p_{Mg} does not meet or exceed 0.0025 atm (Appendix A).

6.3.2 Mn(v) Attack

A second type of gas-refractory interaction is through fumed species. In the case of pure chromium, $p_{\text{Cr}} = 0.00758$ atm at 1700°C , and so is of little consequence. In MC FeMn, however, Mn(v) losses are significant (up to 3% by mass of the total Mn input, calculated for a mean converter bath p_{Mn} estimated to be about 0.08 atm at a temperature of 1700°C). Mn(v) is highly mobile in the gaseous form, and it is in fact thermodynamically-speaking more aggressive a reductant than Mn alloy towards FeO and Cr_2O_3 and, under certain conditions, possibly even MgO, according to the reactions [5], [6] and [7] (Appendix A).

Substantially all of the easily reducible FeO in 'exposed' chromites (Figures 10, 11, 12 and 15) will be reduced, while reduction of Cr_2O_3 down to $a_{\text{Cr}_2\text{O}_3}$ as low as 0.016 (i.e., virtually no Cr_2O_3 left) is predicted at a temperature of 1700°C (Appendix A). With the equilibrium partial pressure of magnesium (p_{Mg}) in reaction [7] at a temperature of 1700°C of the order of 0.0027 atm (Appendix A), as long as p_{Mg} does not equal, or exceed this value, Mn(v) attack of MgO refractories will proceed to some extent (provided kinetics are favourable).

6.3.3 Prognosis — Gaseous Refractory Attack

In both IC3 and MC FeMn production, some extent of attack of exposed chromite refractory by reducing converter freeboard gases (CO , H_2 and Mn(v)) should be expected. In the extreme, and because the converter freeboard is continuously 'flushed' with fresh reducing gases (diluting the p_{CO_2} , $p_{\text{H}_2\text{O}}$, and p_{Mg} of the product gases), limited gaseous reduction of MgO refractory can possibly occur, if reaction kinetics are concurrently favourable. Unfortunately, in the absence of a condensed Mg-containing reaction product (Mg(v) is a mobile gaseous product) it is not possible to positively confirm that the reduction of MgO had actually occurred. However, under conditions of extreme refractory attack, it is conceivable that the 'protective' MgO matrix of the magnesia-chrome refractories may even become attacked, exposing finely dispersed chromites to rapid reduction (Figures 10-15).

The formation of significant Mn(v) during MC FeMn production provides a possible mechanism for refractory attack (additional to CO and H_2 reduction) above the slag-line in MC FeMn production. This helps to explain the rather high incidence of refractory lining failure experienced in that location on converters at the IC3 Plant (e.g., Campaign M25 — Figure 4).

7. REFRACTORY ATTACK - IMPLICATIONS TO PRACTICE

7.1 Slag Attack

When high MgO contents in particular exist (some converter slags contain 29.2% MgO), 'The Making, Shaping and Treating of Steel'³, recommends the B-ratio to describe slag basicity*:

$$B = (\% \text{CaO} + 1.4\% \text{MgO}) / \% \text{SiO}_2 \text{ (mass \%)}.$$

* The factor of 1.4 is introduced to account for the fact that slag basicity is best represented on a molecular basis, so the relative effect of MgO (with its low molecular mass) needs to be magnified by a factor of 1.4 to yield an equivalent effect on a mass basis.

Too acidic a hot-face slag is indisputably destructive to any basic magnesia or magnesia-chrome refractory lining, as SiO_2 tends to decrease slag solidus and liquidus temperatures leading to accelerated refractory attack by mass transfer-driven dissolution processes.

7.1.1 Performance of Magnesia Refractories

Magnesia refractory, and variants thereof, were initially selected for MC FeMn production, but were found to fail rapidly due to excessive slag dissolution attack. Two methods can be identified to counter this:

- adoption of thick 'sacrificial' rammable or castable linings (e.g., made of magnesia)
- change to magnesia-chrome refractories, especially of the reconstituted fused grain type.

The latter approach was adopted on the IC3 CLU converter for two primary reasons:

- the converter was designed for IC3 production and so was only being utilised as a swing producer of MC FeMn. Consequently, the radical change in converter design necessary to accommodate a sacrificial lining, while retaining converter volume (25 t) could not be economically justified
- the greater thermal inertia of the sacrificial lining would necessarily reduce decarburisation efficiency (promoted by higher operating temperatures, and desirable despite higher temperatures causing poorer refractory performance).

7.1.2 Slag Conditioning

A MgO-saturated slag cannot chemically dissolve MgO refractory, tends to increase slag solidus and liquidus temperatures, generally increasing 'effective' slag viscosities (i.e., viscosities with solid phases present 'at-temperature').

Preoccupation with continually stressing the dangers of overly acidic slags can also potentially lead to undesirable plant operating conditions. The danger lies in that the plant overcorrects on basicity by adding too much lime (which beneficially lowers the MgO content required to achieve MgO saturation of the slag) and operates with too basic a slag.

The $\text{CaO-SiO}_2\text{-Cr}_2\text{O}_3$ system⁴ has a 'valley' of exceptionally low liquidus temperatures (between 1060 and 1566 °C) stretching right across the SiO_2 -rich to Cr_2O_3 -rich ends of the phase diagram at elevated CaO contents. Thus, operation with too lime-rich a slag could potentially lead to lime attack of the spinel content of magnesia-chrome refractories, a possibility that is well recognised in the refractories industry⁵.

In both Campaigns M24 and M25 acid slag attack of the magnesia-chrome linings will have contributed to some extent to their failure. However, in the case of M29, the converter had yet to be subjected to a FeSi reduction stage (primary SiO_2 source), so alternative refractory attack mechanisms must be sought to explain the lining failure within the first heat.

7.1.3 MnO_x Slag Attack

Both the magnesia and chromite constituents of magnesia-chrome refractory appear to have some capacity to withstand attack from MnO_x , as demonstrated by their abilities to undergo solid solution with MnO_x . The former readily forms $(\text{Mg,Mn})\text{O}$ solid solution, as demonstrated by topochemical reaction of original MgO grains with MnO_x (Figures 17, 18 and 20). Although less common, there was some SEM-EDS evidence for some spinel solid solution as $(\text{Mg,Mn})\text{O} \cdot (\text{Al,Cr})_2\text{O}_3$ (Figure 17). In the latter case, Mn^{2+} had acted to fill up vacant Fe^{2+} (and Cr^{2+}) sites in the partly altered and reduced spinel lattice.

This ability of the refractory to 'soak up' some MnO_x to produce high solidus temperature solid solution products (1850°C for $(\text{Mg,Mn})\text{O}$, and between 1720-1850°C for spinel solid solution) lends the refractories considerable protection from slag attack. The fairly low incidence of MnO_x penetration much beyond region Aii in the bulk brick (gangue MnO contents typically as low as 0.2% MnO, as determined by SEM-EDS analysis) demonstrates this inherent ability of the magnesia-chrome refractory to stem ingress of, and attack by, MnO_x .

Possible evidence exists for MnO_x slag attack along interconnected pores in the refractories in the upper cone region of M29 (Figure 21).

The concentration gradients (Figure 22) determined for the MnO and CaO (decreasing away from the pore) compared to MgO (increasing towards the refractory) seem to indicate slag attack, especially as the brighter, outer 'slag' analysis was rather similar to that previously determined in MC FeMn decarburisation slags (about 50% MnO, 15% CaO, 30% SiO₂ and 5% MgO). Specific fundamental knowledge regarding the interfacial tension of such slags and the refractory, would be required to confirm that such slags are indeed capable of 'spreading' and 'wetting' the refractories with such thin layers of slag, and to the extents observed.

7.1.4 Manganese Silicate Phase

An unusual feature of the M29 failure was discovery of some tan coloured crystals at the refractory hot-face. The crystals were determined to be approximately 3MnO.2SiO₂ in composition (57.01% MnO, 31.86% SiO₂ – Figure 19). This is a particularly disturbing finding, because manganese silicates possess exceptionally low liquidus temperatures (1200 to 1300°C), and so may be particularly aggressive to refractories. The source of these manganese silicates remains uncertain.

7.2 High Gangue Content

It would appear that a primary cause of M25 refractory failure was an unacceptably high gangue content in the bricks. Results of qualitative image analysis suggested that gangue contents (10-15.5 area %) were possibly as much as two times higher than the SiO₂ and CaO brick specifications should permit (assuming a CaO.SiO₂-type gangue, total gangue contents of about 3% by mass would be expected). Moreover, SEM-EDS analysis confirmed that gangue contained in virgin refractory was sometimes of lower basicity than converter slags, thus providing a potential source of 'mobile' liquid phase 'at-temperature' (brighter 'monticellite' gangue phase composition possesses a liquidus temperatures as low as 1600°C, point P - Figures 14, 15 and 16). Obviously, the higher the gangue content, the more deleterious the potential effects.

The presence of a liquid phase can lead to densification and gross physical deformation of the bricks. The evidence of some brick

'plasticity' (Figures 5-10) is proof that excessive temperatures existed at times in the converter (excursions in temperatures up to 1750°C were apparently recorded during campaign M25), and these may have contributed towards refractory failure.

In addition, by dissolving the FeO_x and 'CrO' contents of the spinel, the gangue can become more readily 'fluxed' by these species, promoting mass transfer (in a liquid phase) and accelerating reduction of chromites. Gangue contents of up to 2.48% FeO and 0.48% Cr₂O₃ possibly provide some evidence for such a fluxing mechanism, which would have contributed towards reduced hot strength of the refractories and accelerated refractory attack.

7.3 Influence of Physical Wear

The development of the porous and metallised zone (Zone Bi — Figures 5-9) deep in the high-fired bricks (as deep as 40 mm) is cause for concern. Should sufficient stress prevail, cracks may develop (e.g., microcracks — Figure 14) rendering the refractory unusually susceptible to spalling, wear and physical failure. In the extreme such a brick may repeatedly spall 'at-temperature', losing large sections of lining, cyclically exposing fresh refractory to further damage. The evidence of uniform converter lining attack well above the slag-line in the M25 failure, suggests that gross physical failure had been occurring in a ring around the converter lining (Figure 4).

The primary cause of catastrophic refractory failure is apparently not normally slag dissolution and chemical attack, but rather gross physical spalling, or wear. The loss of between 20-35 mm of refractory (Figures 7 and 8) in just a single decarburisation period in M29 before failure is unlikely to be due to slag chemical dissolution attack of the refractories alone, but is more likely an indication of an accelerated coupled chemical and physical attack mechanism, such as discussed above.

7.4 Quality of Bricking

Due to the catastrophic nature of the M29 converter lining failure within one heat, faulty bricking cannot be discounted as a cause of refractory failure. However, the fact that Mn infiltration had in all cases been limited to 160 mm or less penetration along the brick joints,

and not the whole length of the brick surface, suggests that there had been no problem with the bricklaying operation *per se*, in the other two refractory failures investigated.

7.5 Chromite Grade

Reduced hot strength is also frequently associated with a change in raw material source or grade. The supplier had apparently not changed chromite sources between campaigns M24 (99 heats) and M29 (< 1 heat). However, a few random SEM-EDS analyses did suggest that the Cr/Fe ratio may have changed from 8.1 (M24-C remnant spinel) to between 4.02 to 2.73 (M29UC-C large chromite grain, to M29UC-C small remnant chromite grain). It remains a remote possibility that the M29 refractory bricks could have been more susceptible to reduction of any solid solution spinel diffusion bonds, and so possessed a lower hot strength than the M24 bricks, which lasted 99 heats.

7.6 Influence of Chromite Size and Distribution

The fused grain structure of the bricks in the M24 and M29 failure had been excellent, with uniform dispersion of fine 'remnant' chromite spinels (2-3 μm) within a protective MgO matrix (Figures 10-15). Some exceptions to this were observed, of larger chromite spinels (up to 700 μm in diameter - Figure 10 and 12) especially at fused grain boundaries. The relative incidence of such chromites is such that it is not believed that they had had any major affect on refractory performance in the case of either the M24 or M29 converter lining failures.

By stark contrast, in the high-fired magnesia-chrome M25 brick large chromite spinels (sometimes over 1 mm in size) were frequently observed (Figure 11). Such spinels were 'unprotected' by an MgO matrix, and so were especially susceptible to enhanced reduction rates. In the highly reducing MC FeMn production environment (compared to the slightly less reducing IC3 system), the potential was high for severe refractory attack through reduction of 'unprotected' large chromite spinels.

7.7 Binders and Bonding Mechanisms

It is a little surprising that chromites were observed at grain boundaries (Figure 12), as the vendor claims not to add chromite 'binders' to achieve a spinel-fused grain bond. They instead add only green binders to the graded fused grain before compression and firing, relying on solid state diffusion during firing to bind adjacent fused grains. They do not use spinel, or magnesium silicate, binders to give spinel-fused grain, or magnesium silicate-fused grain bonds, respectively.

Reliance on some bonds of gangue (both brighter monticellite-type, and darker forsterite-type) between adjacent fused grains for cold strength was admitted. Sometimes the gangue was observed to make interconnected 'bonds' between fused grains (Figure 14). On other occasions there was insufficient gangue to bind adjacent fused grains (Figures 12 and 13). A cause for concern is the potential for any gangue present to provide a mass transfer pathway 'at-temperature' for enhanced refractory attack and reduced hot-strength.

Failure to add any binders is likely to make the refractory more susceptible to development of the undesirable, weak and extensive network of interconnected pores of bricks observed in M29 if:

- firing temperatures and firing times are insufficient to permit sufficient solid-state diffusion bonding and sintering of adjacent fused grains;
- incorrectly graded fused grain additions are made, which would again compromise the kinetics of the diffusion bonding/sintering process during firing.

7.8 Porosity and Interconnected Pores

Instead of a typical area porosity* calculated by image analysis of 25% (for M24 brick), the porosity of the polished sections of the M29 bricks examined was higher (26.8 to 43.3%). More serious, was evidence that it was frequently of an interconnected nature (Figures 12, 13 and 21), sometimes extending 15 mm. Alteration and chemical attack along

* By contrast, supplier refractory brick porosities ranged between 'typical' values of 16-18%.

interconnected pores is clear evidence that the interconnected pores existed 'at-temperature' and were not an artifact of sample preparation. The deleterious consequences of this would be provision of regions of virgin refractory of:

- compromised physical strength (poor bonding)
- susceptible to ingress by Mn alloy, Mn(v) and MnO_x slags — evidence existed for all three of these mechanisms of Mn-species penetration and subsequent deleterious refractory attack.

The coupling of these two effects would certainly have led to accelerated spalling by a combined mechanical/chemical mechanism which may help to explain the inordinately high rate of uniform refractory wear of the vessel lining in Campaign M29.

7.8.1 Metal Infiltration and Refractory Attack

The polished sections made of the floor brick (Figure 20) clearly indicated that Mn alloy had infiltrated into the refractory and reduced species such as chromite. This resulted in Fe and Cr in the metal phase (lowering the Mn/Fe ratio of the metal relative to its original composition in the converter) and MnO reduction product. The latter was found both in (Mg,Mn)O and spinel (Mg,Mn)O.(Al,Cr)₂O₃ solid solutions (Figure 17). Evidence of Mn-free alloy in lower regions delineated the extent of the Mn alloy reaction front.

7.8.2 Gaseous Reduction — Refractory Attack Above The Slag-Line

The greater susceptibility of the converter refractory lining to failure above the slag-line in MC FeMn (compared to IC3) production suggested a gaseous attack mechanism. A prime example was the failure in Campaign M25 (Figure 4).

The fact that metallised product resulting from gaseous reduction frequently occurred as a metallic rim surrounding MgO grains suggested two primary sources of reducible oxides; namely:

- chromite spinels were being reduced by a mechanism involving diffusion of FeO (and Cr oxide species) to the 'protective'

MgO exterior, where they underwent gaseous reduction to metal

- direct topochemical reduction of the FeO content of the MgO (as high as 10.14% FeO in M25S-Ci) to yield a metallic rim around the MgO grains.

Two plausible gaseous reductant sources have been identified to explain this.

7.8.2.1 Mn(v) Refractory Attack

Physical evidence for reduction by Mn(v) was provided by the reduction of spinels to FeCr metal, associated with the MnO_x deposition product (when there were no other signs of possible slag penetration), along interconnected pores in the refractory or at brick joints far away from the hot-face (Figures 5-8). Certainly, the mobility of Mn(v) would be sufficient to account for the extensive, yet locally limited, alteration of exposed refractory surfaces. Additionally, volume changes resulting from chromite reduction to metal (density increase, and so volume decrease) and the co-production of MnO_x (density of 5 180 kg/m³) would result in a more mechanically stressed refractory more susceptible to spalling and gross physical failure.

7.8.2.2 Gaseous CO and H₂ Refractory Attack

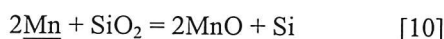
This refractory attack mechanism is characterised by the absence of a MnO_x reaction product. It can be distinguished from FeSi reduction by the simultaneous absence of SiO₂ species. Moreover, in Campaign M29 the converter lining failed before any FeSi reduction period, so gaseous reduction by CO and H₂ cannot be discounted.

Gaseous reduction of exposed chromite in the refractory (i.e., not 'protected' by MgO) is demonstrated by the presence of FeCr metal (Figures 11, 15, 19 and 20). Region Bi (Figures 5-10) is a prime example of the action of such a mechanism, where CO and/or H₂ gas has reduced the chromites, resulting in a porous and metallised zone (reaction products are gas and FeCr metal of considerable higher density than chromite). This is likely to result in a stressed condition in the refractory, which would be unusually susceptible to spalling of

the brick leading to gross physical wear of the lining.

7.9 High Alloy Silicon Contents

Some metal that penetrated between the working and safety linings of the converter in Campaign M29 analysed 4.59% Si (65.5% Mn, 2.39% Cr, 0.98% C and 19.99% Fe). This is a high silicon content when compared to the input hot metal analysis of less than 0.3% Si, but it is almost certain to be evidence of manganese alloy reduction of the silica content of the aluminosilicate safety lining (40% SiO₂) according to the reaction:



Interestingly, in some classical studies of aluminosilicate refractory wear in blast furnace FeMn production, it was proved that the primary cause of refractory failure was not due to slag attack, but instead due to reduction of the SiO₂ content of the refractory by Mn⁶.

8. CONCLUSIONS

1. MC FeMn is a more refractory-aggressive system than the equivalent IC3 system.
2. Magnesite refractories primarily wore by dissolution of the matrix or phase bonding individual MgO grains together. Secondly, they were subject to direct dissolution of the MgO grains by high SiO₂ (and Cr₂O₃, FeO_x and MnO_x) contents from the slag.
3. Potential life-cost benefits to the use of higher quality refractories in the MC FeMn system, such as fused-grain magnesite-chrome refractories rather than high-fired, or co-clinker magnesite-chrome refractories. Such improved performance is afforded through the presence of a far greater proportion of smaller chromite spinels of more uniform size distribution, dispersed through a more continuous MgO matrix, making the refractory less susceptible to attack by gaseous CO and H₂, Mn(v), and Mn alloy reductants. The generally greatly improved performance of the M24 fused-grain brick compared to the M25 high-fired brick tends to support this observation.
4. Converter refractories in MC FeMn production are more susceptible to gaseous attack by Mn(v), and also by CO and H₂,

leading to increased failure above the slag-line (e.g., Campaign M25).

5. Slag-splashing practices⁷ should be considered to help to partially seal the refractory (especially chromite) from attack by reducing gases.
6. The presence of MgO undergoing topochemical reaction with MnO_x to yield (Mg,Mn)O solid solution rims suggests that there were regions of slag accretions on the brick that were locally doubly saturated with respect to MnO_x and MgO. This suggests that operation with slags saturated with respect to MgO may help to limit slag refractory attack. However, SEM-EDS examination of bulk converter slags showed that they were frequently not saturated with respect to MgO (e.g., 8.14% MgO), which suggests that scope exists for improved slag conditioning.
7. 'Typical' vendor refractory specifications were frequently inappropriate to ensuring adequate refractory quality. Specifications unique to the IC3 Plant were sought to guarantee refractory brick quality.
8. Refractory size grading, firing conditions and binder selection required review to prevent recurrence of excessive interconnected refractory porosity.
9. Excessive gangue content was noted in the high-fired refractory (M25).

9. ACKNOWLEDGMENTS

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APPENDIX A: THERMODYNAMICS OF MC FeMn ATTACK OF MAGNESIA-CHROME REFRACTORIES

The basic thermodynamic conditions needed to reduce the magnesia and chromite constituents of magnesia-chrome refractories by IC3, MC FeMn and reducing CO or H₂ gases were estimated (Table A.1) to establish their effects on converter refractory lining.

Table A. 1: Basic thermodynamic data pertaining to magnesia-chrome refractory attack

	Standard Reaction	$\Delta G^{\circ}_{1700^{\circ}C}$ kJ/mol Mn	K	Refractory Attack Condition
1	$Mn + FeO \cdot Cr_2O_3 = MnO + Fe + Cr_2O_3$	- 86.598	$(a_{MnO} \cdot a_{Fe} \cdot a_{Cr_2O_3} / a_{Mn} \cdot a_{FeO \cdot Cr_2O_3})$	Favourable
2	$Mn + \frac{1}{3} Cr_2O_3 = \frac{2}{3} Cr + MnO$	- 28.107	$(a_{MnO} \cdot a_{Cr}^{2/3} / a_{Mn} \cdot a_{Cr_2O_3}^{1/3})$	$a_{Cr_2O_3} > 0.204$
3	$Mn + MgO = Mg(v) + MnO$	+ 91.693	$(a_{MnO} \cdot p_{Mg} / a_{Mn} \cdot a_{MgO})$	$p_{Mg} < 0.0025 \text{ atm}$
4	$\frac{2}{3} Cr + MgO = Mg(v) + \frac{1}{3} Cr_2O_3$	+ 120.347	$(p_{Mg} \cdot a_{Cr_2O_3}^{1/3} / a_{MgO} \cdot a_{Cr}^{2/3})$	$p_{Mg} < 0.0004 \text{ atm}$
5	$Mn(v) + FeO \cdot Cr_2O_3 = MnO + Fe + Cr_2O_3$	- 122.398	$(a_{MnO} \cdot a_{Fe} \cdot a_{Cr_2O_3} / p_{Mn} \cdot a_{FeO \cdot Cr_2O_3})$	Favourable
6	$Mn(v) + \frac{1}{3} Cr_2O_3 = \frac{2}{3} Cr + MnO$	- 63.908	$(a_{MnO} \cdot a_{Cr}^{2/3} / p_{Mn} \cdot a_{Cr_2O_3}^{1/3})$	$a_{Cr_2O_3} > 0.016$
7	$Mn(v) + MgO = Mg(v) + MnO$	+ 55.892	$(a_{MnO} \cdot p_{Mg} / p_{Mn} \cdot a_{MgO})$	$p_{Mg} < 0.0027 \text{ atm}$
8	$CO + MgO = Mg(v) + CO_2$	+ 213.447	$(p_{CO_2} \cdot p_{Mg} / p_{CO} \cdot a_{MgO})$	$(p_{CO} / p_{CO_2}) > 1120$
9	$H_2 + MgO = Mg(v) + H_2O$	+ 187.395	$(p_{H_2O} \cdot p_{Mg} / p_{H_2} \cdot a_{MgO})$	$(p_{H_2} / p_{H_2O}) > 187.4$

Assumptions made if the best case scenarios for refractory protection are investigated include:

- for reduction by Mn, correction for a_{Mn} less than unity must be made. A Raoult's Law activity assumption is made for convenience: $a_{Mn} = X_{Mn} = 0.66$ (HC FeMn charge diluted by 6% C and 14% Fe).
- similarly, for reduction by Mn(v) the mean value of p_{Mn} ($= a_{Mn}$) $\approx 0.08 \text{ atm}$ is used (calculated at the mean converter metallostatic height, and for typical converter operating conditions at Ferrometals of a temperature of 1700°C and a 0.85 atm ambient pressure).
- a_{Cr} unity, despite invariable Cr dilution with existing Fe- and Mn-bearing metal,

except for examination of the case of potential Cr reduction of MgO, where a Raoult's Law assumption leads to $a_{Cr} = X_{Cr} = 0.48$ (initial IC3 alloy of composition 56% Cr, 38% Fe and 6% C)

- a_{MnO} and a_{MgO} are taken to be unity (although in reality they can both undergo solid solution lowering their activities)
- $a_{Cr_2O_3}$ and $a_{FeO \cdot Cr_2O_3}$ both taken to be unity (for simplicity of calculation — in reality solid solution and spinel formation will lower both of these values to below unity)
- $p_{Mg} = 0.0025 \text{ atm}$ at 1700°C assumed, for the case of calculation of the equilibrium gas mixtures required to yield CO and H₂ reduction of MgO.