

Chapter 1: INTRODUCTION

Reheating slabs in an oxidising furnace atmosphere at high temperature is a common step before hot rolling. Since the steel is treated for an extended duration, surface oxidation is inevitable. The resulting oxide scale is hydraulically removed by water sprays at high pressure before hot rolling to ensure good surface quality of the hot-rolled strip.

The product surface quality is strongly linked to the upstream operations such as continuous casting, reheating and descaling before hot rolling (Kizu *et al.*, 2002).

The occurrence of rolled-in-scale defects strongly depends on the adhesion of scales formed on steel surface during reheating, and the residual thin scale after descaling seriously deteriorates surface quality defect in the final product (Kizu *et al.*, 2002).

Riquier and Dumortier (1997) reported that the steels (316L, 316LN and 347) that oxidise the most are easily descaled and the steels that oxidised less (304, 304 LN and 321) develop sticky scales with nodules deeply encrusted in the underlying alloy. These nodules cannot be removed by water descaling and generate sliver defects during hot rolling (Riquier & Dumortier, 1997).

Hence for efficient removal of the scale, the effects of the slab surface contaminants on the scale-metal adhesion have to be well understood.

1.1 Background and Motivation

The oxidation of slabs in the reheating furnace is the first and determining process of the scaling of hot rolled flat products. The structure of the scale formed during reheating and the width of the internal oxidation zone are not only influenced by the heating parameters, but also by the chemical composition of the steel (Dénes *et al.*, 2003). The primary scale formed on the slab has to be efficiently removed by hydraulic descaling.

Previous studies showed that, under mechanical descaling conditions, the entanglement that arose at the steel-scale interface was in fact effective to maintain steel-scale adhesion. In the case of type 304, descaling proceeds by fracture along chromite layers, which formed on the austenite grain boundaries; for this steel, the extent of descaling depended most strongly on austenite grain structure and the presence of unoxidized metal tendrils at the interface and not primarily on the conditions in the reheating furnace (Pistorius *et al.*, 2003).

1.2 Problem Statement

Steel-scale adhesion is expected to be dependent not only on the thickness of the scale but also on the nature of the different phases present in the scale and interfacial morphology of the scale.

The work carried out in this study attempted to:

- Identify and understand possible effects of residual mould flux contamination on the scale-steel adhesion,

1.3. Aims of Investigation

The main aim of this project is to improve the descaling effectiveness of the stainless steel. The study focused on the issue of descaling of reheated slabs, and specifically the possible effects of residual mould flux contaminant on the scale-metal adhesion, because it was found that oxide dispersions on the steel surface may affect phase formation at the interface, mechanical properties of the scale and the interfacial morphology, all of which influence the adhesion between scale and steel (Nagai, 1989).

The approach was hence to contaminate steel surface with mould flux, then grow scale under simulated reheating furnace conditions where temperature, gas atmosphere and mass transfer to the sample surface are controlled; determining the effects of steel composition (alloying elements, impurities on and in the steel) and the effect of reheating conditions on the scale-steel adhesion.

1.4. Approach

The basic hypothesis is that the microstructure of different phases present in the scale, the segregation of specific elements at the interface and the degree of interfacial roughening affect the adhesion between steel and scale and so influence the descaling effectiveness.

The main parameters considered in this study were:

- Reheating conditions (time, temperature and gas atmosphere)
- Descaling parameters (water flow rate, system pressure, nozzle height, water spray angle, stock velocity)

Chapter 2: LITERATURE SURVEY

2.1 THERMODYNAMIC CONSIDERATIONS

2.1.1 Introduction

Reheating before hot rolling is performed in an oxidising atmosphere which forms by reacting fuel with an excess of oxygen, necessary to ensure complete combustion of fuel. Under these conditions surface damage due to oxidation or scaling is inevitable. The oxide layer must be removed before hot rolling.

In order to minimise or prevent surface deterioration and to avoid surface reactions (carburising or nitriding), one possible option is to control the gas composition (Birks & Meier, 1983).

Prevention or control of scale layer formation would then be a question of controlling the oxygen partial pressure to value low enough to avoid the oxidation reactions:



where MO is the lowest oxide of M. The oxygen partial pressure must be controlled so as not to exceed a value:

$$(P_{O_2})_{M/MO} = \exp(2\Delta G^\circ / RT) \quad (2)$$

For stainless steel containing iron, chromium and nickel as a major elements, the followings reactions may be envisaged:



If we assume that stainless steel type 304 has the composition 18% Cr, 8% Ni and Fe balance (mass basis), the mole fractions of these three elements are $X_{Fe} = 0.733$, $X_{Cr} = 0.192$ and $X_{Ni} = 0.075$.

Taking as a first approximation the activities of Fe, Cr and Ni in the steel to be ideal, and the oxide products to have unit activities, the oxygen pressure at equilibrium can be estimated; the package FactSage was used to perform these calculations, and the results are given in Figure 2.1.

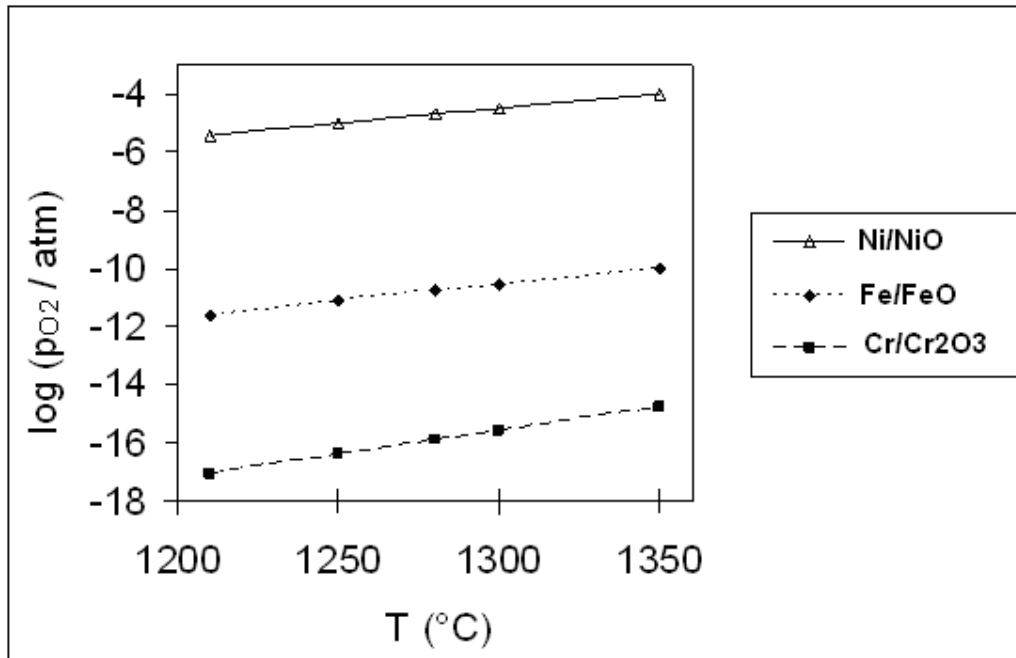
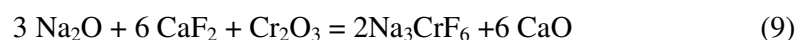
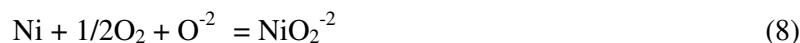


FIGURE 2.1: Variation of the equilibrium oxygen partial pressure with temperature, for the dissociation of iron oxide, chromium oxide and nickel oxide respectively.

It is obvious that the oxygen partial pressures are very low, especially in the case of chromium. To avoid steel surface oxidation, partial oxygen pressure in the furnace atmosphere must be less than 10^{-16} atm which is not realisable for industrial reheating. From the Ellingham diagram for oxides, it is seen that mould flux oxides such as CaO, MgO, Al₂O₃ and SiO₂ are more stable than are the oxides of iron, nickel and chromium since their equilibrium oxygen potentials are much lower than those of oxide scales under reheating conditions.

However, at reheating temperature, basic mould flux oxides and fluorides (CaF₂, Na₂O and K₂O) may release oxygen and fluorine anions (O²⁻ and F⁻) which can influence the oxidation of steel alloying elements (Lee *et al.*, 2002).

Some possible reactions between mould flux and alloying elements under reheating conditions are as follows:



Reactions (6), (7) are solid-gas reactions (Ma & Garbers-Craig, 2005) and reaction (8) is a solid-gas-liquid reaction (Lee *et al.*, 2002).

These reactions may enhance the chromium and nickel oxidation at the interface and in the scale. The chromium oxidation state in the reheating furnace atmosphere can be (+3), (+6) or (0). For stainless steels chromium (+6) is not desired because hexavalent chromium is soluble in water and is hazardous (Ma & Garbers-Craig, 2005). Sano *et al.* (1997) reported that the equilibrium ratio Cr⁶⁺/Cr³⁺ increases when the slag basicity increases.

Reactions (9) and (10) seem to be not likely due to the very small amount of mould flux contaminant on the steel surface, and expected fluoride volatilization at high reheating temperature.

At reheating temperatures mould flux components (Na₂O, CaF₂ and Al₂O₃) can melt and form cryolite-alumina according to reaction (11). Jentoftsen *et al.* (2002) noticed that this reaction is likely to happen at high temperature and the melting cryolite-alumina formed may dissolve some transition metal oxides (NiO, FeO) at 1020°C. They also found that the concentration of Fe and Ni in cryolite-alumina melts in equilibrium with solid FeO and NiO decrease when the Al₂O₃ wt% increases. The solubility of iron (1.70wt% for 5.9 wt% Al₂O₃) was higher than that of nickel (0.021wt% for 6.26wt% Al₂O₃).

2.1.2 Mechanisms of Metal-Scale Interfacial Roughening

2.1.2.1 Oxidation of Pure Metals

Pure metals generally oxidize by cationic diffusion mechanism (Kofstad, 1988). Since iron is the major element of steel, the classical scale growth mechanism of iron is briefly reviewed as follows: due to oxidising atmosphere in the furnace iron is oxidized to (Fe^{2+}) at the scale-metal interface, releasing two electrons. The iron ions and electrons migrate outwards through the scale. At the scale-gas interface, the electrons react with oxygen to produce O^{2-} ions, which in turn react with the Fe^{2+} ions to form new FeO.

During high temperature oxidation of iron in air, a multi-layered scale is formed in parallel. This scale consists of wustite, magnetite and haematite (Abuluwefa *et al.*, 1997). For oxidation in high temperature range 700-1250°C, the average FeO/ Fe_3O_4 / Fe_2O_3 thickness ratios are 95:4:1 [(Sheasby *et al.*, 1984), (Ajersch, 1992)]. At lower temperatures (below 570°C), wustite is not stable and magnetite grows at the expense of the wustite (Sheasby *et al.*, 1984).

2.1.2.2 Kinetics of Oxidation

During initial industrial reheating condition of steel, oxygen mass transfer to the outer scale surface controls the rate of scale growth (for small scale thicknesses) since Fe^{2+} ion transfer is relatively efficient. The rate of scale growth is then linear- the thickness of the scale formed is directly proportional to time. The maximum thickness of FeO where this holds varies between 0.4 and 0.5 mm; beyond this thickness the scale growth rate changes from linear to parabolic and the rate- controlling step becomes the arrival of Fe^{2+} at the interface (Sachs & Tuck, 1968). The parabolic rate law can simply be represented by the following equation: $x^2 = k_{\text{pt}}$ (Garber, 1959).

During simulated industrial reheating conditions of the stainless steel type 304, the scale thickness was about 2mm after 6h of reheating. The scale consisted of two layers with similar thicknesses. The inner layer was mainly an iron-chromium spinel layer and the outer layer was mainly an iron oxide layer (Pistorius *et al.*, 2003).

The classic Wagner theory predicts parabolic kinetics for oxidation rate controlled by cationic diffusion mechanism through the scale and good agreement between the calculated and experimental parabolic rate constants is found, for temperatures greater than approximately 0.75 times the absolute melting point of the scale (Rapp, 1984). The parabolic oxidation mechanism should favour the formation of a scale with smooth interfaces and uniform thickness, since the scale grows more rapidly at points where it is locally thinner.

Pieraggi *et al.* (1988) suggested that vacancies are created at the interface metal-scale due to the removal of cations from the metal surface during parabolic oxidation (Pieraggi *et al.*, 1988). They also observed that roughening can occur at the scale-metal interface even in the case of pure metals undergoing parabolic oxidation. As oxidation progresses, there is continual removal of the cations (in the case, Fe^{2+}) at the metal-scale interface, which means that vacancies are continually created. Hirth *et al.* (1995) and Taniguchi (1985) suggested that vacancies are generally eliminated by climb of the misfit or miss-orientation dislocations within the metal formed as a result of the epitaxial relationship generally maintained between the scale and the underlying substrate. [(Hirth *et al.*, 1995), (Tanguchi, 1985)].

Void formation at the interface appears inevitable for the conditions during reheating. The extent of void formation is expected to increase as the extent of scaling increases, but it is not clear what the effect on descalability will be. Void formation and location depend, among other things, on oxidation temperature, which means that it is dependent on scaling rate (Taniguchi, 1985).

2.1.2.3 Effects of Alloying Elements

Generally, the oxidation rate of steels is much lower than that of pure iron. The presence of even small additions of alloying elements (impurities) to iron modifies its oxidation behaviour considerably i.e. making it complex (Lee *et al.*, 2005). This complexity may result from the different affinities of alloying elements for oxygen, the different mobility of metal ions in the oxide phase, internal oxidation of one or more elements in the alloy, or solid solubility between oxides, or ternary and higher oxides which can be formed (Abuluwefa *et al.*, 1992).

Interfacial roughening may occur when the alloying element (or impurity) is less likely to be oxidized (is noble) than the iron matrix, or equally when it is more likely to be oxidized (is more reactive) (Pistorius *et al.*, 2003).

2.1.2.4 Internal Oxidation

Internal oxidation is the process by which oxygen diffuses into an alloy and causes sub-surface precipitation of oxides of one or more alloying elements (Birks & Meier, 1983). This results in oxide particles distributed within the metal grains, with often higher concentrations at grain boundaries. These oxides may themselves be deleterious to surface quality, and can also lead to further destabilization of the interface (Whittle & Wood, 1967). The internally oxidized zone extends to the depth at which the concentration of dissolved oxygen becomes too small for formation of oxide (Kofstad, 1966). The depth of the internal oxidation increases with increase in oxidation temperature and time and with decreasing oxygen partial pressure (Kizu *et al.*, 2001).

During oxidation of steels, chromium and aluminium have similar behaviour. In stainless steels where they are present in large quantities, they form protective films of Cr_2O_3 or Al_2O_3 at the metal/scale interface. These films are protective and they inhibit outward diffusion of Fe ions. However, the film often breaks down and a spinel (FeCr_2O_4) forms at the scale/metal interface, which allows some oxidation to occur, although the rate is much lower than with ordinary steels (Fujii & Meussner, 1964).

For stainless steel Type 304, the ability to form Cr_2O_3 scales depends on the chromium concentration available at the alloy surface. This concentration can be lowered below that of the bulk alloy by internal precipitation of chromium-rich compounds (Hänsel *et al.*, 2003).

2.1.2.5 Nickel Enrichment

Nickel and other metallic alloying elements that are nobler, that is, less oxidized than iron, are rejected at the metal/scale interface. At the metal/scale interface, iron and chromium enter the chromite lattice while the nickel is rejected. It therefore follows

that nickel becomes concentrated at that interface and the surface layer of the metallic core becomes enriched in the nickel (Pickens, 1984).

The nickel does not diffuse rapidly back into the core; the Ni-rich filigree (filaments of unoxidised metal) is more resistant to oxidation. The overall increase in scale thickness leads to particles and filaments of Ni-rich metal being entangled in the scale (Sachs & Tuck, 1968).

The presence of this entanglement in the scale increases scale adhesion to the substrate making descaling quite difficult to perform (Morris *et al.*, 1996) - and give sometimes rise to surface defects (Zittermann *et al.*, 1982). This problem is observed in steels with Ni concentrations from 0.05 mass % (Asai *et al.*, 1997).

2.1.2.6 Effects of Minor Alloying Elements and Reactive Element Dispersions

a) Reactive Element Impurities at the Metal-Scale Interface

The behaviour and effects of reactive element impurities have been investigated by others researchers. The following is inferred from their studies:

- For Cr_2O_3 -forming alloys, both oxygen-active metal and oxide dispersions at even very small additions can increase or decrease the scale adherence depending on the nature of the interaction of these dispersions with the scale (Nagai, 1989).
- It was suggested that sulphur at normal concentration segregates to the alloy-scale interface where it could promote decohesion of the scale from the alloy (Luthra & Briant, 1989).
- Dispersions of SiO_2 , CaO and Cr_2O_3 in the inner layer may inhibit oxygen diffusion along grain boundaries. It was suggested that CaO so enhances the opportunity for outward chromium migration to establish the protective scale at the surface of the Fe-18Cr (Nagai, 1989).
- Oxides of reactive elements at the surface of Fe-Cr alloys enhance the formation and the development of a continuous layer of protective Cr_2O_3 scale (Moon & Bennett, 1989).

- Reactive element dispersions can change the ionic structure of the scale; the large ionic radii of these metals can cause mechanical stress and cracking of the scale (Nagai, 1989).

b) Formation of Low Melting Point Components at the Metal-Scale Interface

- At reheating temperatures, the presence of alkali oxides (Na_2O , K_2O) at the interface may facilitate the formation of low melting point binary or ternary compounds with some oxides of refractory metals (Cr_2O_3 , SiO_2 , CaO). The presence of the liquid phase at the interface may enhance the oxidation of the metal substrate by internal oxidation (Levin *et al.*, 1964). When a scale consists of both solid oxide and molten phase, besides the electronic conduction in the solid oxides, ionic conduction may occur through the liquid phase and increase the rate of oxidation (Kubaschewski & Hopkins, 1962).
- The addition of P to Si-alloyed steel improves the hydraulic descalability because the P lowers the eutectic temperature of $\text{FeO}/\text{Fe}_2\text{SiO}_4$ during slab soaking. The presence of the liquid compound in the scale/steel interface improves hydraulic descaling (Fukagawa *et al.*, 1997).

2.1.2.7 Stress Development and Relief in Oxide Scale

During high temperature oxidation of steel a protective chromium oxide scale is formed mainly by cationic diffusion. Stresses are produced and build up in the oxide or metal phases due to the difference between the coefficients of linear expansion and molar densities of the oxide and metal (Ajersch, 1992). Stresses are enhanced if several oxides are present at the interface and can cause extensive cracking during cooling (Kubaschewski & Hopkins, 1962). Pieraggi and Rapp (1988) ascribed those stresses to vacancy coalescence at the scale-steel interface and at grain boundaries adjacent to the interface.

Two major effects of the oxide growth stresses are: (a) fracture and subsequently, spallation if large tensile stresses are formed in the scale; and (b) if cracks develop these can enhance oxidation as a result of access of the oxidant to the steel surface.

Relief of growth stresses in oxidizing samples can be through various mechanisms. These are; deformation of the substrate metal, plastic deformation of the oxide, separation at the scale metal interface and fracture of the scale (Pieraggi & Rapp, 1988).

2.1.3 Mould Fluxes

2.1.3.1 Introduction

Mould fluxes are synthetic slags used in continuous casting process of steel. Fluxes are generally added to the surface of the molten steel in a copper mould to provide lubrication between the mould wall and the steel shell (Branion, 1986).

Mould flux reduces the loss of heat from the surface of the steel, and influences the rate of horizontal heat transfer (to the mould) during the solidification of liquid metal in the casting mould. The mould flux also protects the liquid steel surface from re-oxidation with atmospheric oxygen and absorb inclusions (impurities such alumina) from the steel (Persson, 2007).

The mould flux forms a film in the channel between the mould and the steel shell, and after solidification forms a thin solid layer on the solidified steel surface. After continuous casting, steel is covered with a solidified thin layer on the top surface and with a tiny solid layer on the sides. These layers constitute residual mould flux contaminant (Budinski, 1999).

2.1.3.2. Residual Mould Flux on the Casting Slab

During continuous casting, steel is tapped from the ladle into a tundish before passing through the submerged entry nozzle (SEN) into the casting mould. Level control maintains a nearly constant steel meniscus in the mould and makes it possible to feed powder flux onto the liquid steel in the mould (Ogibayashi *et al.*, 1987). As the casting process progresses, new powder flux is gradually added to ensure that the steel surface is always completely covered with mould powder. Mould oscillation avoids sticking of the steel shell to the mould. The oscillation also facilitates the penetration of mould flux into the tiny gap between mould and steel shell (Mills *et al.*, 2005).

The configuration of the powder flux inside the mould is shown in Figure 2.2. Powders are continuously fed onto the top of the mould and form layers over the steel surface which gradually moves down the mould. The powder bed above the steel meniscus consists of four layers, raw powder layer, sintered layer, mushy layer (mixture of slag globules and carbon particles) and a pool of liquid slag (Mills *et al.*, 2005).

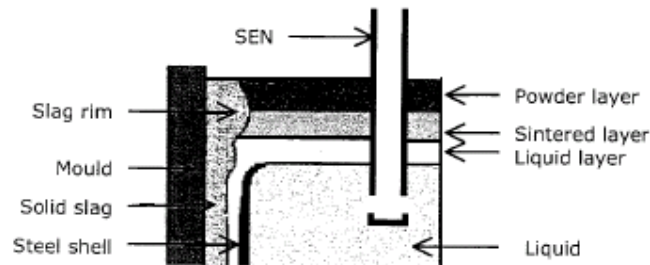


FIGURE 2.2: Continuous casting mould flux layers in copper mould (Mills *et al.*, 2005)

A thin layer of mould flux must preferably remain liquid against the hot steel shell throughout the entire length of the mould in order to act as lubricant (Ludlow *et al.*, 2004). The thickness of the solidified flux against the mould is usually much thicker than that of the liquid flux film and is typically of the order of 2 to 3mm (Schwerdtfeger *et al.*, 2003). The thickness of the liquid flux film is about 0.1mm (Rajil *et al.*, 2004).

2.1.3.3 Constitution of Industrial Mould Fluxes

Synthetic flux powders usually contain:

1. raw material with similar melting points (e.g. lithium feldspar, sodium feldspar, wollastonite) to provide more uniform melting in order to avoid accumulation of material at the meniscus
2. a minimum number of raw materials to achieve the required composition so to keep the recipe simple and simplify quality assurance (D'Haeyer, 1987).

The melting temperature of mould flux depends on its composition and is generally less than slab reheating temperature. The composition and melting temperature of three commercial fluxes are given in the table below.

TABLE 2.1: The constituents and melting temperature of commercial fluxes (Jiang *et al.*, 2004).

	A	B	C
Wollastonite	6.5%	-	6.5%
Cement dust	-	4.0%	3.0%
Magnesium carbonate	2.0%	5.5%	6.0%
Quartz	-	3.0%	-
Fluorite	5.0%	8.5%	6.8%
Soda	7.0%	8.0%	12.0%
NaF	4.5%	-	3.5%
Li ₂ CO ₃	-	2.5%	-
Premelted material	75.0%	68.5%	70.0%
Melting temperature	1168°C	1083°C	1055°C

Mould flux contains a mixture of basic oxides and acidic oxides, with varying chemical composition for different applications and steel types (Turkdogan, 1996). The silicate tetrahedron (SiO_4^{-4}) is the major building block in the molten mould flux. It controls physical properties of fluxes such as viscosity, thermal diffusivity, melting range, crystallization temperature, glass transition temperature, tensile strength of slag film, compressibility, surface and interfacial tensions (Persson, 2007). Basic oxides break up the silicate networks in the molten slag structure. Fluoride containing additives (CaF_2 , Na_3AlF_6) are used as fluidisers; these also decrease the molten slag viscosity by breaking up the silicate network. During casting, the chemical composition of the mould flux is altered by fluoride volatilization and the absorption of impurities (Persson, 2007). Amphoteric oxides like Al_2O_3 contribute to the silicate structure. Alkali oxides regulate the melting behaviour of slag. Carbon is added in different concentrations to control the rate of fusion (D'Haeyer, 1987).

In steelmaking slag basicity is expressed by the equation below:

$$B_s = \frac{\%CaO + 1.4\%MgO}{\%SiO_2 + 1.5\%P_2O_5} \quad (12)$$

Due to the fact that in powders flux CaO and SiO₂ are the main components and because P₂O₅ is absent, the simplified basicity of mould powders can be express as follows:

$$B_f = \frac{\%CaO}{\%SiO_2} \quad (13)$$

Powder flux basicity depends on the application and the plant conditions. It varies between 0.7 and 1.3 (Mills *et al.*, 2005).

The average range of metallic oxides (and fluoride) in the industrial casting powders and their impact on the viscosity, the melting temperature and the solidification are given in the table below:

TABLE 2.2: Chemical composition of mould flux powder and typical effect of increasing flux component on the viscosity and the melting temperature [www.kempro.com/mould.htm]

	Component	%	Viscosity	Melting point
Glass formers	SiO ₂	17- 56%	Increase	Decrease
	Al ₂ O ₃	0 -13%	Increase	Increase
	B ₂ O ₃	0 -19%	Decrease	Decrease
	Fe ₂ O ₃	0 – 6%	Decrease	Decrease
Alkali	Na ₂ O	0 – 25%	Decrease	Decrease
	Li ₂ O	0 – 5%	Decrease	Decrease
	K ₂ O	0 – 2%	Decrease	Decrease
Basic oxides	CaO	22 – 45%	Decrease	Increase
	MgO	0 -10%	Decrease	Decrease
	BaO	0 -10%	Decrease	Decrease
	SrO	0 – 5%	Increase	Decrease
Fluidiser	F	2 -15%	Decrease	Decrease
	MnO	0 – 5%	Decrease	Decrease
Melting rate control	C	2 – 20%	Increase	Decrease
CaO/SiO ₂			Decrease	Increase

2.1.3.4 Estimates of the Expected Mould Flux Concentration on Slabs

Mould flux consumption during casting is an indication of the quality of lubrication. Estimates show that about 90% of the flux consumed is used for the formation of the liquid flux film and the rest is mainly lost to the slag rim and trapped flux in the oscillation marks (Mills *et al.*, 2003).

Mould flux consumption can be calculated using the expression below (Mills, 1998)

$$P_s = \frac{7.6 f P_t}{R_m} \quad (14)$$

where P_s is the powder consumption per unit area of mould [kg/m^2], P_t is the powder consumption per steel mass [kg/tonne of steel], f is the fraction of the powder producing slag. R_m is the ratio of surface area to volume of the cast profile and is expressed by the relation (15) below (Mills, 1998).

$$R_m = 2(e_m + l_m) / e_m l_m \quad (15)$$

where e_m is the width of the mould[m], and l_m is the thickness of the mould [m].

Mould flux consumption increases when the casting speed, the mould oscillation and the flux viscosity decrease. It was noticed that mould flux consumption rate per oscillation cycle depends strongly on positive strip time and also correlates with frequency and negative strip time (Shin *et al.*, 2005).

Neumann *et al.* (1996) pointed out that the dependence of mould flux consumption per unit area (P_s) on the mould dimensions can also be expressed by the relation (16) below (Neumann *et al.*, 1996).

$$P_s = 0.44 \exp(-0.04 R_m) \quad (16)$$

The average thickness (f_l) of the liquid flux film in the mould can be evaluated by means of the equation (17) below (Mills, 1998).

$$f_l(m) = \frac{P_s}{\rho_{flux}} \quad (17)$$

where $\rho_{flux} \approx 2600 \text{ kg}/\text{m}^3$ is the density of the melted liquid flux.

If we assume that, for the case considered in this project, the slab thickness and width are 0.3m and 1.5m respectively, equation (16) and (17) can be used to estimate the amount of mould flux on the slab surfaces. These give the mould flux consumption (P_s) of 0.32kg/m^2 and the average thickness of the liquid film in the mould (f_l) of $123\mu\text{m}$.

During this investigation the mould flux surface dosage on the contaminated slabs varied between 0.05 kg/m^2 and 0.35 kg/m^2 (see Table 4.1 and Table 4.9).

2.1.4 Implications for this Work

From the literature survey, it is clear that the removal of scales is mostly linked to the scale-metal adhesion, which depends on the interfacial nature, characteristics of the scale after reheating and the segregation of numerous elements at the interface steel-scale.

Residual mould flux contaminant on steel before reheating may act to decrease or to increase steel-scale adhesion. Residual mould flux and alloying elements may act to decrease scale-metal adhesion as follows:

The presence at the interface of an oxide layer or dispersoids (that contain SiO_2 , CaO , Na_2O and Cr_2O_3 in the inner layer) may act as the inhibitor of grain boundary diffusion (Nagai, 1989) and so reduce internal oxidation which acts as a key between scale and the underlying metal substrate when developing sticky scales with nodules deeply incrustated in the underlying alloy (Riquier & Dumortier, 1997).

The presence of MgO and SiO_2 in the scale during descaling can significantly increase the spallation of the scale and improve the descaling effectiveness (Nagai, 1989).

Acid and alkali oxides (Na_2O , K_2O , SiO_2) and fluorides can form some low melting mixtures. The presence of liquid at the scale/steel interface during high temperature descaling is expected to improve hydraulic descaling.

Residual mould flux and alloying elements may also act to increase scale-metal adhesion as follows:

- a. Molten phases formed at the interface due to the presence of mould flux may break down the interface and accelerate internal oxidation.



- b. Beside the electronic conduction in the solid-oxides, ionic conduction may occur through the liquid phase and increase the internal oxidation (Kubaschewski, & Hopkins, 1962).
- c. The presence of Al_2O_3 and some molten oxide dispersions at the interface may improve scale adherence and minimize the porosity of the scale (Moon & Bennett, 1989).

2.2 REHEATING OF STAINLESS STEELS

2.2.1 Introduction

Reheating of steel before hot rolling is an essential step, which is not totally controlled and optimised despite the various improvements made in the last two decades (Bockel-Mac & Zamuner, 2002). Reheating aims to facilitate subsequent hot forming and to oxidize away some surface imperfections (Li *et al.*, 2005).

2.2.2 Influence of Reheating Parameters on Descalability

The microstructure of the scale close to the interface, which affects the scale-steel adhesion and hence the descalability, is influenced not only by the steel chemical composition, but also by the heating parameters (reheating temperature, reheating time and composition of the gas in the furnace atmosphere) (Dénes *et al.*, 2003).

After reheating followed by mechanical descaling of the stainless steels grade 412 and 304, it was found that:

The descalability of the steel type 412 was very sensitive to the reheating parameters (mainly reheating time and the excess of oxygen in the furnace gas atmosphere). For this steel grade, the extent of the entangled region which arose at the interface scale-steel and made descaling quite difficult was found to increase for longer reheating times and higher excess oxygen contents.

In contrast, for the steel grade 304, the descalability was found to be mostly linked to the microstructure of phases formed close to the interface, the austenite grain structure, and not primarily on the conditions in the reheating furnace. For this steel grade, descaling proceeds along chromite layers (paths in the scale which consisted of oxide only without Ni-metal enriched tendrils) formed on the austenite grain boundaries. The formation of this chromite was enhanced for reheating with higher excess oxygen, longer reheating times and at high temperature (Pistorius *et al.*, 2003).

2.2.2 Effect of Water Vapour

Tuck *et al.* (1969) found that the oxidation rate of most steels at a given temperature is greater in steam than in air or oxygen after long exposure times; and this effect can

be increased if water vapour is present with O₂. It follows therefore that the scaling rate would be greater in oxygen/water vapour mixture than it would be in either of the gases separately (Tuck & Barlow, 1972). However, at temperatures lower than 950°C and higher O₂ concentrations, increasing the water vapour content of the gas mixture had no effect on scaling rate (Sachs and Tuck, 1970). In oxidizing gas mixtures (oxygen containing more than 10 vol % H₂O) at 950°C, the scale remained attached to the metal surface for considerably longer reaction times than in the absence of water vapour, and the scale growth progressed in accordance with the parabolic rate for pure Fe (Sheasby *et al.*, 1984). The presence of water vapour leads to greater plasticity in the scale and consequently greater scale adherence to the substrate (Kofstad, 1988) whereas adherence was lost in samples scaled in oxygen alone. At 950°C, thicker and more compact scale was formed on mild steel. These observations have been attributed to the penetration of pores in the scale by H₂/H₂O mixture, which enhances inward migration of oxygen (Tuck *et al.*, 1969). Therefore in order to achieve scale growth that is comparable to that in reheating furnaces, the presence of water vapour in the laboratory furnace atmosphere is vital [(Sheasby *et al.*, 1984), (Kizu *et al.*, 2002)]. The concentration of water vapour required in the gas mixture to obtain product gas containing 3% excess oxygen, for example was calculated to be about 16.3 % (Appendix 1).

2.2.5 Surface Finish and Surface Structure

The structure and composition of the surface of the slab depend on the solidification mode and reheating conditions, and can change from one slab to another. This makes it difficult to simulate exactly industrial operating conditions (Riquier & Dumortier 1997).

Polished or ground surfaces are often used during oxidation studies, to provide a reproducible starting condition. However, it has been found that the nature of the surface finish does always affect the scaling process. Studies were carried out to find the influence of surface roughness on the adherence of oxides formed on type 1018, 304, and 430 steels, and it was found that oxide adherence could be enhanced by smooth surface or hindered by a rough finish (Sherwood *et al.*, 1984).

Sherwood *et al.* (1984) found that deep scratches on a coarsely finished metal may act as stress raisers and set up high compressive stresses at the steel/scale interface, giving rise to scale fracture and subsequent spallation. When a scale grows by cationic diffusion, the new scale grows on the top of the old, which implies that the original surface is trapped at the scale/metal interface. Only in the case of extensive internal oxidation, is the surface finish expected to be less important.

2.3 DESCALING

2.3.1 Introduction

The primary scale formed on the slab during reheating (prior to roughing rolling) and secondary scale formed on steel during roughing rolling are often removed with high-pressure water sprays (hydraulic descaling), while the tertiary scale which forms during finishing rolling is removed by acid pickling prior to other processing steps (Chen *et al.*, 2001).

2.3.2 Hydraulic Descaling

2.3.2.1 Principle

Hydraulic descaling systems consist of a pump, which delivers high pressure water to a header bar over the steel, from which water is sprayed through a series of nozzles. In flat products each nozzle is designed to spray water in a flat sheet, allowing the jet from a nozzle to strike the steel in a straight line; the nozzles are angled, so that the impingement patterns from adjacent nozzles do not overlap, and the force of impact is not reduced. The jets are also generally directed towards the approaching steel (Morris *et al.*, 1996).

In Figure 2.3, the scale is removed from the front to the back while the slab is moved from the back to the front. The scale is removed on both sides of the slab, and the rear part of the slab is not yet descaled.

Hydraulic descaling is affected by the scale thickness, jet angle, jet velocity, steel temperature and time of exposure to water jet (Sheppard & Steen, 1970).

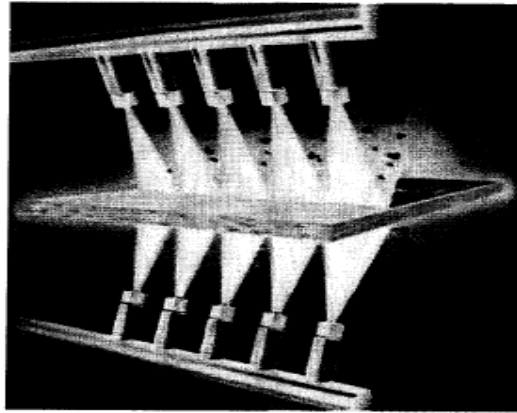
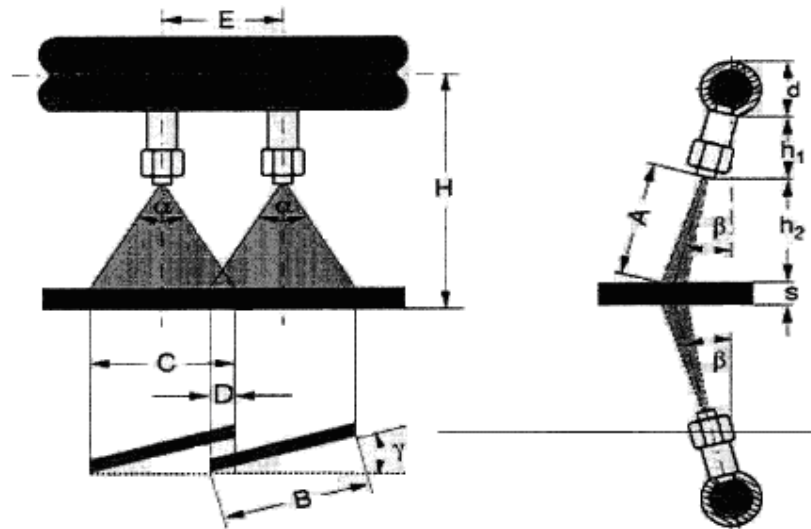


FIGURE 2.3: Double- sided industrial descaling process using several nozzles (Schürmann, 2000).

2.3.2.2. Descaling Header Designs

Figure 2.4 shows the typical nozzle arrangement with the list of terms and symbols.

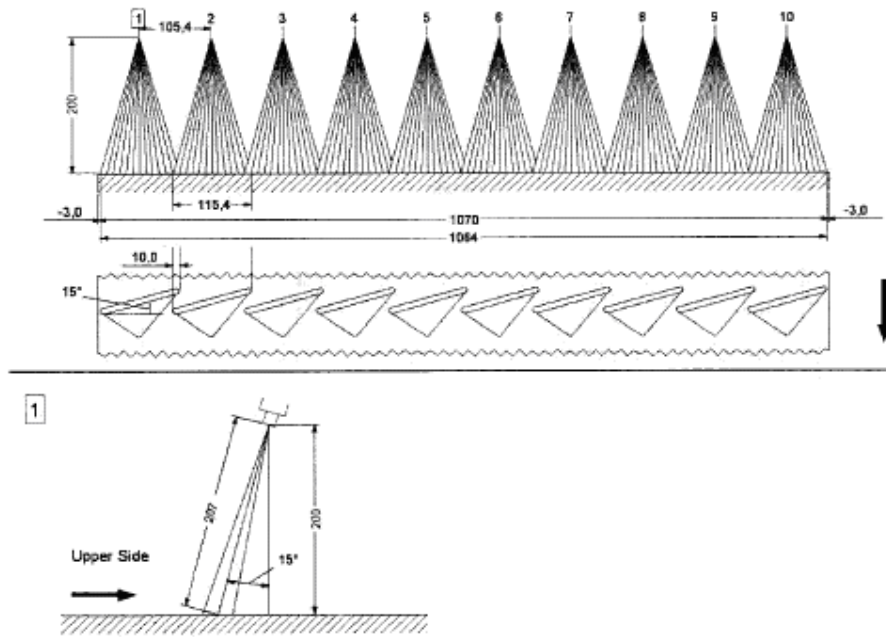


A = jet length
B = jet width
C = jet width in jet direction
D = overlapping
E = nozzle distance
H = distance from mid-spray beam
to lower edge of strip

S = strip thickness
d = outer diameter of pipe
h₁ = vertical height of nozzle
h₂ = vertical spray height
 α = nozzle spray angle
 β = angle of inclination
 γ = offset angle of nozzle
against pipe rotation axis

FIGURE 2.4: Typical nozzle arrangement with list of terms and symbols (Frick, 2003).

Computer simulation software enables the prediction of the optimum nozzle arrangement as a function of variables which influence the design of a descaling nozzle arrangement. These variables are water pressure; total water flow; spray height; the slab width and thickness (Boulton *et al.*, 2004). The Figure 2.5 below shows an example of the output of a computer simulation program for a proposed nozzle arrangement.



Nozzle part number:	642.887	Spray width (B):	120mm
Nozzle spray angle (α):	30°	Spray depth:	8.61mm
Pressure:	200 bar	Total force:	521 N
Flow rate:	158.39 l/min	Impact, av 85%:	0.74N/mm ²
Inclination angle (β):	15°	Max. impact:	0.97N/mm ²
Offset angle (γ):	15°	Total flow rate:	1583.9 l/min
Vertical spray height (h_2):	200mm	Overlap (D):	10.0 mm

FIGURE 2.5: Proposal of a typical descaling installation carried out by means of Lechler Descale program (Boulton *et al.*, 2004).

a) Nozzle spray characteristics

Descaling nozzles can have orifices of different shapes but the best results are obtained with elliptically shaped ones, because a relatively constant impact pressure can be maintained across the jet (Sheridan & Simon, 1995). Impact pressure, which is a measure of the force with which the water impacts the steel stock, is a maximum when the nozzle geometry is vertical due to its scouring action on the chipped scale, so removing the scale (Sheppard & Steen, 1970).

As mentioned, the rolling mill descaling stations are usually designed with the nozzles inclined towards the approaching steel. The main reason is that detached scale is directed away from the rolling stand. If the stand is a sufficient distance from the

descaler so it will not be affected by the detached scale, most efficient descaling is achieved with vertical nozzle geometry. The jet width and thickness increase linearly with nozzle stand-off distance (height) (Morris *et al.*, 1996). At a constant water flow rate and for given impact width, maximum impact pressure decreases linearly with nozzle height (Sheridan & Simon, 1995).

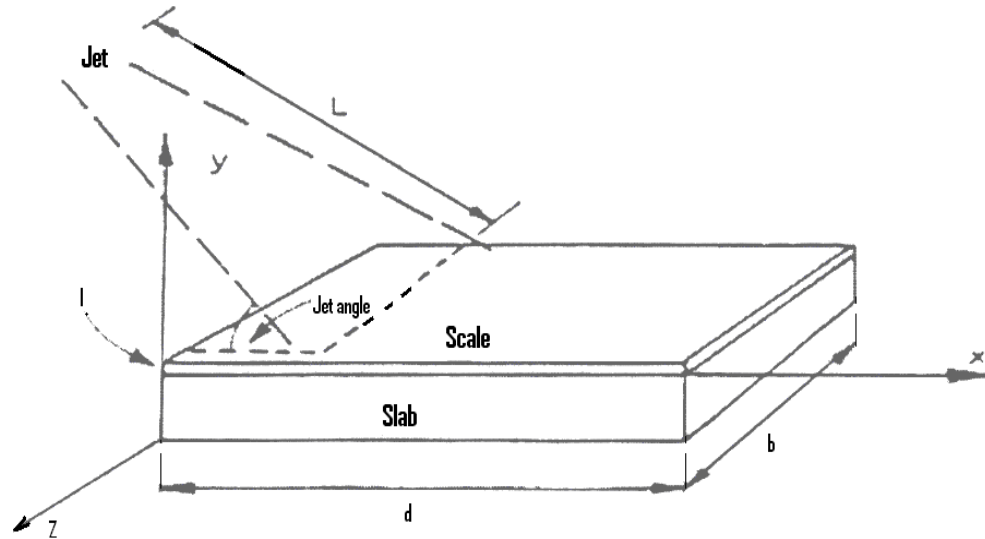


FIGURE 2.6: Geometry of the offset angle of the cooling jet (Sheppard and Steen, 1970).

It was found that the descaling capacity increases with the nozzle diameter but the efficiency is better with smaller nozzles. Hence, it is best to use a larger number of nozzles of smaller diameter with a reduced pitch between nozzles (Sheridan & Simon, 1995). Four nominal spray angles describing the width of spray are now very common. These are 22°, 26°, 30° and 40° nozzle tips, each are available in 13 standard flow sizes in order to achieve design flexibility; the spray width is identical for all nozzle tip sizes at identical pressures and spray heights (Frick, 2004).

In modern installations with spray heights around 80mm spray depths range between 3 and 4mm only (Sheridan & Simon, 1995). The water pressure and the water flow are approximately proportional to the impact. Table 2.3 shows the influence of water pressure on the impact for a spray height of 128mm.

TABLE 2.3: Influence of the system water pressure and the flow rate on the impact pressure (Frick, 2004).

Scale-master type	Spray angle [°]	Water pressure [bars]	Water Flow [l/min]	Spray jet width [mm]	Spray Jet Thickness [mm]	Total force [N]	Max Impact [N/mm ²]
694.566.27	26	100	18.00	57	3.80	42	0.26
694.566.27	26	200	25.50	58	3.60	84	0.54
694.566.27	26	300	31.20	58	3.40	126	0.84
694.566.27	26	400	36.00	59	3.20	167	1.17

Descaling jet impact pressure decreases when the jet thickness increases as shown in the graph below.

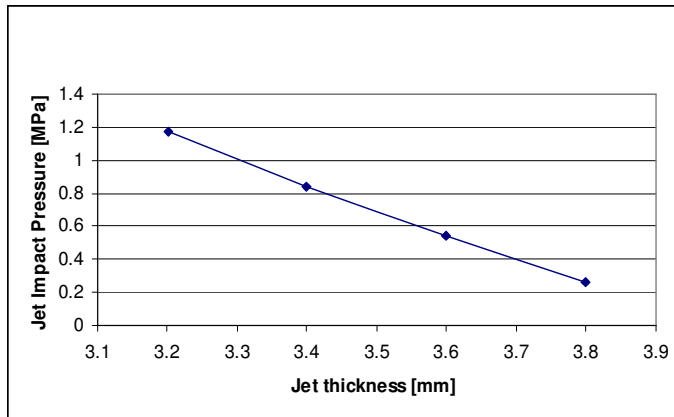


FIGURE 2.7: Variation of impact pressure trough the jet thickness at a system pressure (Scale-master type 694.566.27 nozzle 26° spray angle at 128 mm distance) (Frick, 2004).

The speed of the stock under the descaling spray and the water flow from the spray determine the volume of water applied to the steel surface. These two parameters and the width of the descaling spray are used to calculate the specific water impingement (U).

$$U(\text{litre} / \text{m}^2) = \frac{Q(\text{litre} / \text{s})}{B(\text{m}) \cdot v(\text{m} / \text{s})} \quad (18)$$

The specific water impingement influences the rate of cooling of the steel surface and the effectiveness of the descaling process (Morris *et al.*, 1996).

b) Header diameter

For pipes with fixed flow rate and water pressure larger header diameters (150mm) yield lower velocities, and bring less turbulent flow than those with smaller diameter heads. Less turbulence gives better descaling action since more kinetic energy remains in the spray. Modern descaling systems endeavour to achieve an optimum velocity of 1.2 m/s in the header (Grigg *et al.*, 1987).

2.3.3 Mechanisms of High Pressure Water Descaling

2.3.3.1 Introduction

Hydraulic removal of the scale is dependent on both the impact pressure and quantity of applied water per unit area, the total stress produced by cooling action of water jets, the stress due to the impact force of the jet and the depositional compression stress (the oxidation stress) (Matsuno, 1980).

The theoretical possible mechanisms of high pressure water spray descaling are:

- Thermal gradient within scale (scale bending away),
- Differential contraction effect (scale breaking away),
- Disruption of scale by steam (scale rupture),
- Mechanical pressure effect (force of water crushes & fragments scale) (Morris *et al.*, 1996).

2.3.3.2 Thermal Effects

Thermal effects arise from water cooling and mechanical pressure effects. The scale on steel slabs, to greater or lesser extent, has the tendency to crack due to water-cooling. Scales on Si-killed steels are more susceptible to cracking into small pieces in air whereas scale on semi-killed steels do not crack easily on air-cooling (Fukutsuka *et al.*, 1981). The scale is subsequently washed away along the cracks due to the effect of the water.

During descaling, there exists a thermal gradient within the scale that leads to thermal contraction stresses and bending of the scale away from the steel. This thermal gradient arises as a result of the difference in temperature between the descaling water

and the scaled steel or the scale when the steel is removed from the furnace (Morris *et al.*, 1996). The cooling and contraction of the scale cause it to curl and break away (Sheridan & Simon, 1995). Reducing the sample speed under the descaling water spray increases the effective volume of water directed to a given area of steel, which leads to a further reduction of the temperature and consequently increasing the descaling action. Formation of steam leading to disruption of the scale has the ability to supply sufficient energy to the scale for fracturing of the metal/scale interface. However, this mechanism is dependent on the ability of the water to penetrate pores and fissures within the scale and produce an undercutting effect (Morris *et al.*, 1996).

2.3.3.3 Mechanical Pressure Effects

On the other hand, when considering the effects of the mechanical pressure, it should be noted that the force exerted by the water jets on the surface of the scale could produce displacement of the scale if porosity or detachment exist. This mechanism would be expected in friable scale and its effectiveness would increase at higher water pressures. Furthermore, the scale may be crushed and shattered due to the pressure of the water jet on it and subsequently washed away (Morris *et al.*, 1996).

Increasing the water pressure means an increase of the kinetic energy and the impact pressure. Hence, more scale will be removed from the steel at shorter dwell time under the jets. This is illustrated further with the aid of the figure below:

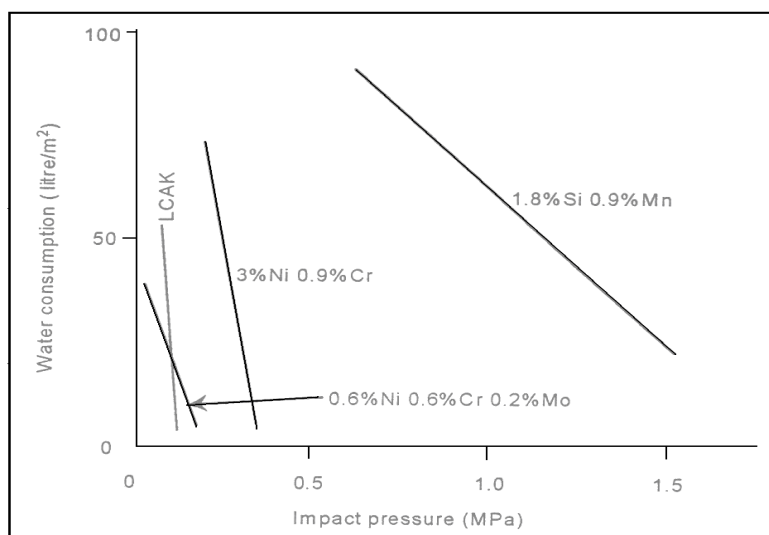


FIGURE 2.8: Conditions required for the effective descaling of different steel grades (Sheridan & Simon, 1995).

Figure 2.8 shows that plain carbon steels (labelled "LCAK" in the figure) are the most easily descaled whereas those containing considerable amounts of silicon or nickel are much more difficult to descale, that is they form more adherent scale. The effectiveness of the descaling of the low carbon steel depends on the impact pressure being high enough. This goes to confirm the mechanism of descaling by mechanical effects, whereas in the case of the steels that are more difficult to descale, especially the high silicon one, there is a compromise between the specific water consumption and the impact pressure. At low impact pressure ($\sim 0.8\text{MPa}$), descaling this steel effectively required a large amount of water. This translates to longer dwell time of this steel under the water jets. At an impact of about 1.5MPa , a low amount of water ($\sim 25\text{l/m}^2$) was consumed, hence with a shorter dwell time. This effect of dwell time indicates that a comparatively slow process such as heat transfer through the scale may influence the descaling of steels (Sheridan & Simon, 1995).

Heat is transferred from the steel slab by conduction to the scale surface and by convection and radiation to the water spray. By assuming that heat conduction through the scale contributes to the scale removal on the steel surface, the descaling header pressure (Δp) and the time (t) required to obtain successful descaling for given reheating conditions would be linked to the square of the scale thickness (l^2) by the parameter $\Delta p t / l^2$. The predicted effect of the heat transfer is to quench the scale thereby leading to contraction, scale failure being as a result of thermal shock (Sheppard & Steen, 1970).

The thermal shock effect can be evaluated by estimating the time required to cool the scale to a given depth. If conduction through the scale is assumed to be the determining step, the time to cool the scale can be expressed by l^2/δ (where l and δ are the scale thickness and thermal diffusivity respectively). The heat capacity value of wustite from FactSage and thermal conductivity and density from Akiyama *et al.* (1992) were used to estimate the scale thermal diffusivity at 1100°C ; the estimated value is $8.5 \times 10^{-7} \text{ m}^2/\text{s}$

For a typical water jet thickness of 5mm and slab speeds of 0.1 to 1 m/s (Morris *et al.*, 1996), the time that the scale is exposed to water jet is between 5 and 50 ms. Based on the thermal diffusivity value, this time is only sufficient to quench 0.06 – 0.2 mm of

the scale (compared to total thickness of the scale which after reheating, may be 5mm or more).

The above results suggest that thermal shock effect will be less effective than mechanical effect under hydraulic descaling conditions, as proposed by Blazevic (1987).

2.4. CONCLUSIONS ON EXPERIMENTAL APPROACH

From the above literature and based on the two legs of this project (i.e. the descaling efficiency and the effect of mould flux on scale-steel adhesion after reheating), the experimental approach therefore involved scale growth on contaminated slabs under gas mass transfer conditions similar to those in reheating furnaces, followed by the laboratory high pressure hydraulic descaling of the sample while hot. The evaluation of the residual scale amount and the characterisation of the structure and composition of the scale oxide layers were performed by means of scanning electron microscopy and X-ray microanalyses.

The reheating variables considered were temperature, time, excess oxygen and mould flux surface concentration.

The descaling variables considered were the water flow rate and the system pressure. The descaling spray height and the descaling speed were maintained constant.

The experimental techniques and procedures that were used are detailed in the next chapter.