2. Fundamentals of LF technology

Fundamental of ladle furnace technology

Steel is an alloy comprised mostly of iron, with a carbon content between 0.02 % and 1.7 % by weight, depending on grade. Carbon is the most cost-effective alloying material for iron, but various other alloying elements are used such as manganese and tungsten

The maximum solubility of carbon in iron is 1.7 % by weight, occurring at 1130 °C; higher concentrations of carbon or lower temperatures will produce cementite which will reduce the material's strength.

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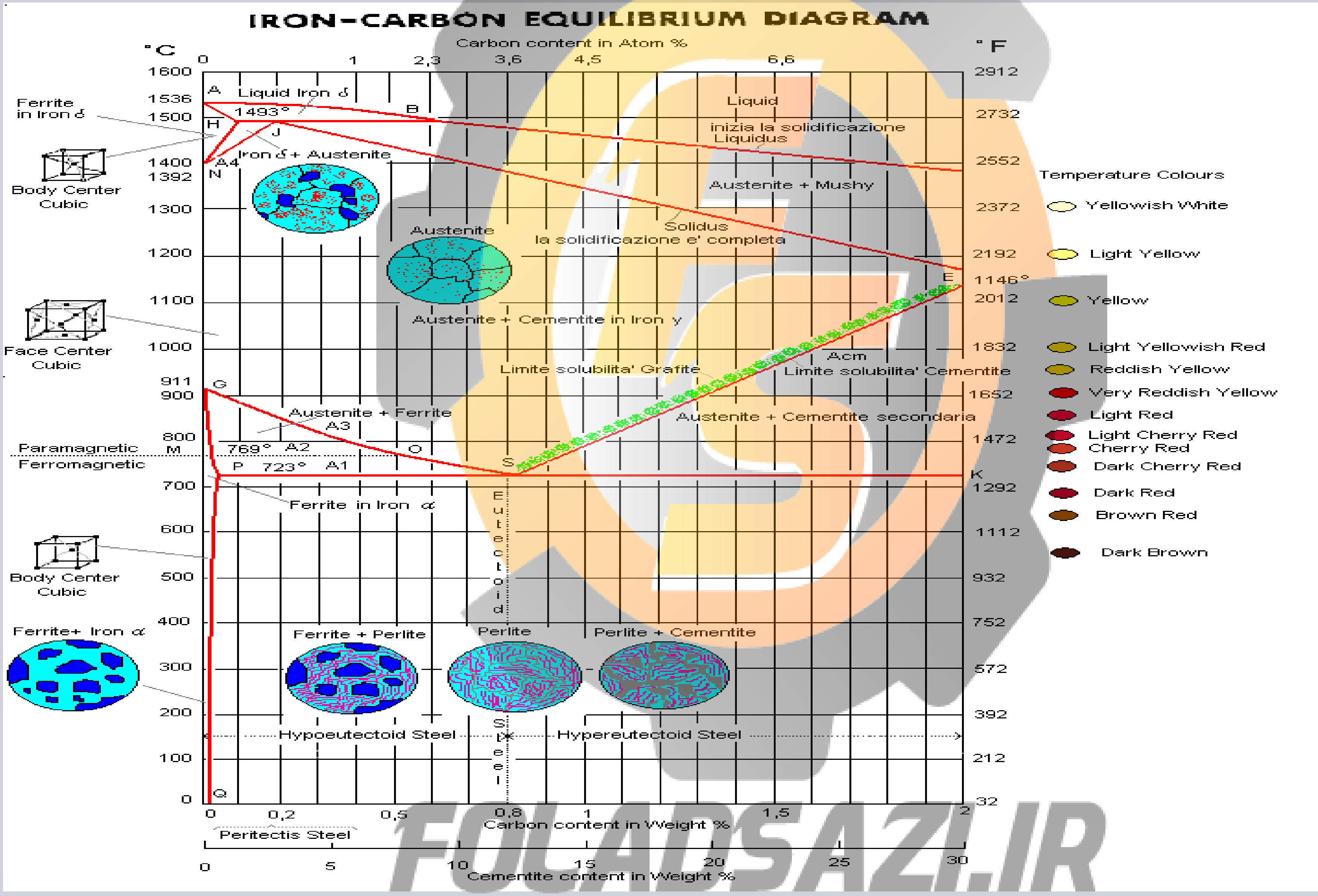
LIQUIDUS AND SOLIDUS TEMPERATURE

- Pure Fe melts at 1536°C.
- If the liquid iron contains other elements, it will no longer have a fixed melting point, but will rather melt within a solidification interval, determined by a solidus and liquidus temperature.
- Fe is typically alloyed with Carbon, which changes the melting point from pure iron to a liquidus line

Fundamental of ladle furnace technology



Fundamental of ladle furnace technology

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The calculation method considers the presence of alloyed elements in the steel

(The logarithm, widely used for calculation, is based on statistically evaluated results of metallurgical laboratories).

$$T_{liq} = 1536{,}6 - (\%C * Z) - (\%E * W)$$

C%	Z	E	W
0.06-0.10	89	Si	8
0.11 -0.50	88	Mn	5
0.51-0.60	86	P	30
0.61-0.70	84	S	25
0.71-0.80	83	Cr	1.5
0.81-0.90	82	Ni	4
		Cu	5
		Mo	2
		V	2
		Al	5.1

Tliq = liquidus temperature

%C = carbon content

Z = multiplying factor for carbon

%E = content of elements listed in the table

W = multiplying factor for the listed elements

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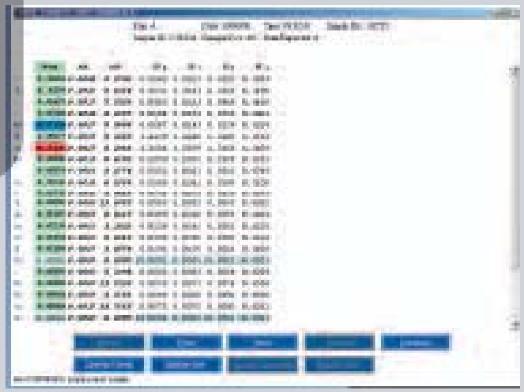
The steel analyses is obtained using the optical emission spectrometer assuming that each element has an individual spectrum.



From steel sample to Spectrometer until Results

5 minutes process time

Fundamental of ladle furnace technology

STEEL ANALYSIS SAMPLES								
ELEMENTS	*MIN*	*MAX*	*AIM*	*11:08*	*10:28*	*10:20*	*07:36*	*06:23*
				A	*A*	*A*	*A*	*M*
C	0,120	0,200	0,150	0.178	0.178	0.163	0.155	0.160
Si	0,120	0,300	0,150	0.195	0.195	0.150	0.145	0.160
Mn	0,300	0,700	0,420	0.430	0.430	0.415	0.410	0.400
P	0,000	0,045	0,030	0.011	0.011	0.011	0.010	0.013
S	0,000	0,045	0,030	0.016	0.016	0.017	0.018	0.017
Cr	0,000	0,300	0,000	0.030	0.030	0.030	0.030	0.030
Mo	0,000	0,000	0,000	0.001	0.001	0.001	0.001	0.001
Ni	0,000	0,300	0,000	0.030	0.030	0.030	0.030	0.030
Al	0,015	0,040	0,020	0.024	0.027	0.001	0.001	0.025
As	0,015	0,040	0,020	0.000				
Ca	0,000	0,000	0,000	0.004	0.004	0.001	0.001	0.004
Cu	0,000	0,300	0,000	0.015	0.015	0.010	0.010	0.010
Nb	0,000	0,000	0,000	0.010	0.010	0.006	0.006	0.007
Ti	0,000	0,000	0,000	0.001	0.001	0.001	0.001	0.001
V	0,000	0,000	0,000	0.005	0.005	0.003	0.004	0.004
Alt	0,000	0,000	0,000	-99.999				

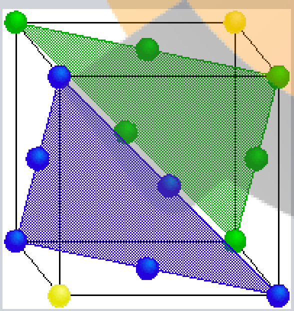
Typical process analyses results database for one heat

Fundamental of ladle furnace technology

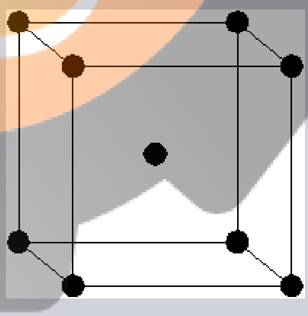
- The C-Fe diagram defines the existence two crystalline structure:

- Ferrite: solid solution of carbon in α-iron and δ-iron (b.c.c. structure)
- Austenite: solid solution of carbon in γ-iron (f.c.c structure)

$$\alpha\text{-Fe(krz)} \xrightleftharpoons{906^\circ C} \gamma\text{-Fe(kdp)} \xrightleftharpoons{1401^\circ C} \delta\text{-Fe(krz)} \xrightleftharpoons{1563^\circ C} \text{Schmelze}$$



face-centered-cubic



body-centered cubic

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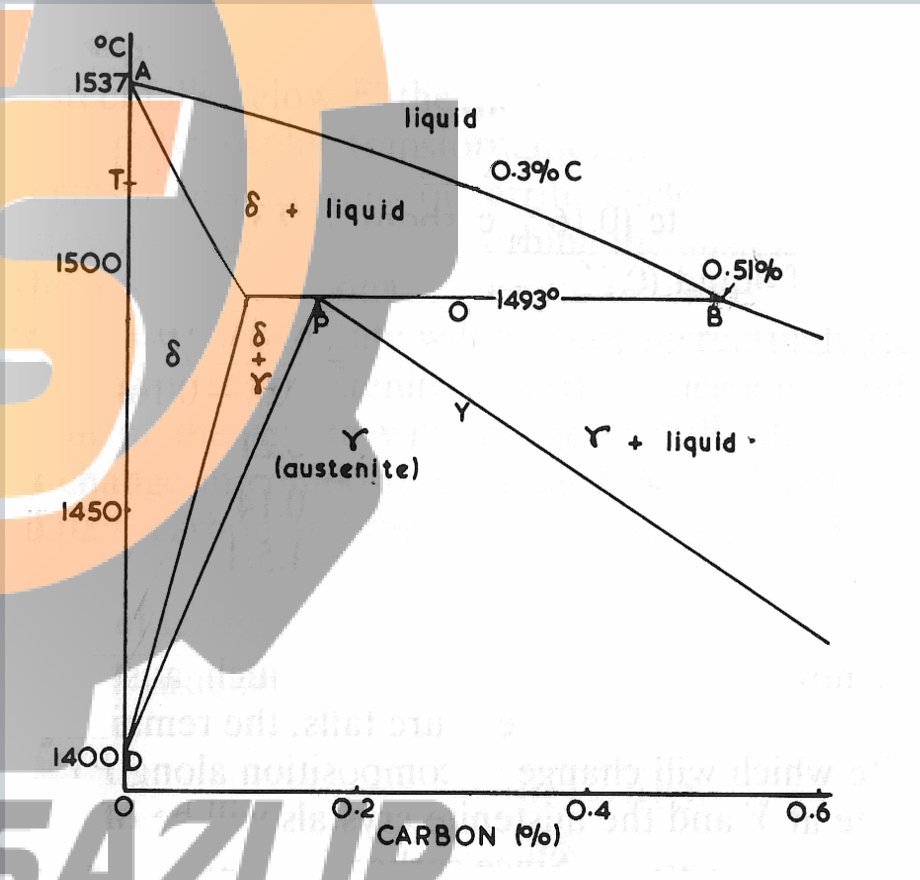
The C-Fe diagram shows three characteristic transformations: Peritectic, Eutectic (not important in our study) and Eutectoid.

Peritectic:

At the temperature of 1493°C, in the carbon range 0.1<%C<0.51, the solid solution of carbon in delta iron reacts with the liquid steel, during solidification, to give origin to a solid solution of carbon in gamma iron

In particular way for peritectic transformation around of 0.1%C the contraction is very high



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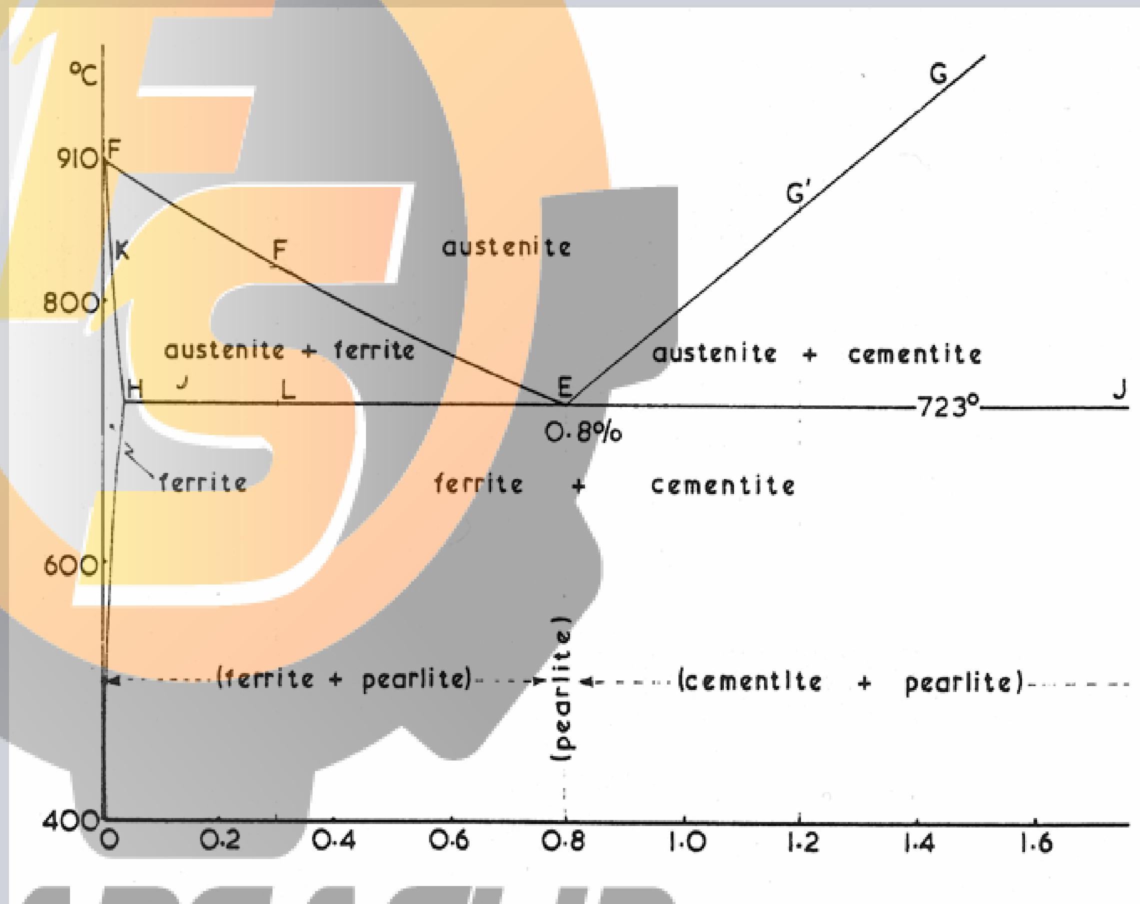
Eutectoid:

At the temperature of 723°C the austenite transform itself in pearlite

At room temperature is the result of different mix of ferrite, pearlite and cementite in function of carbon and other alloy elements. Some steel grade however has an austenitic structure



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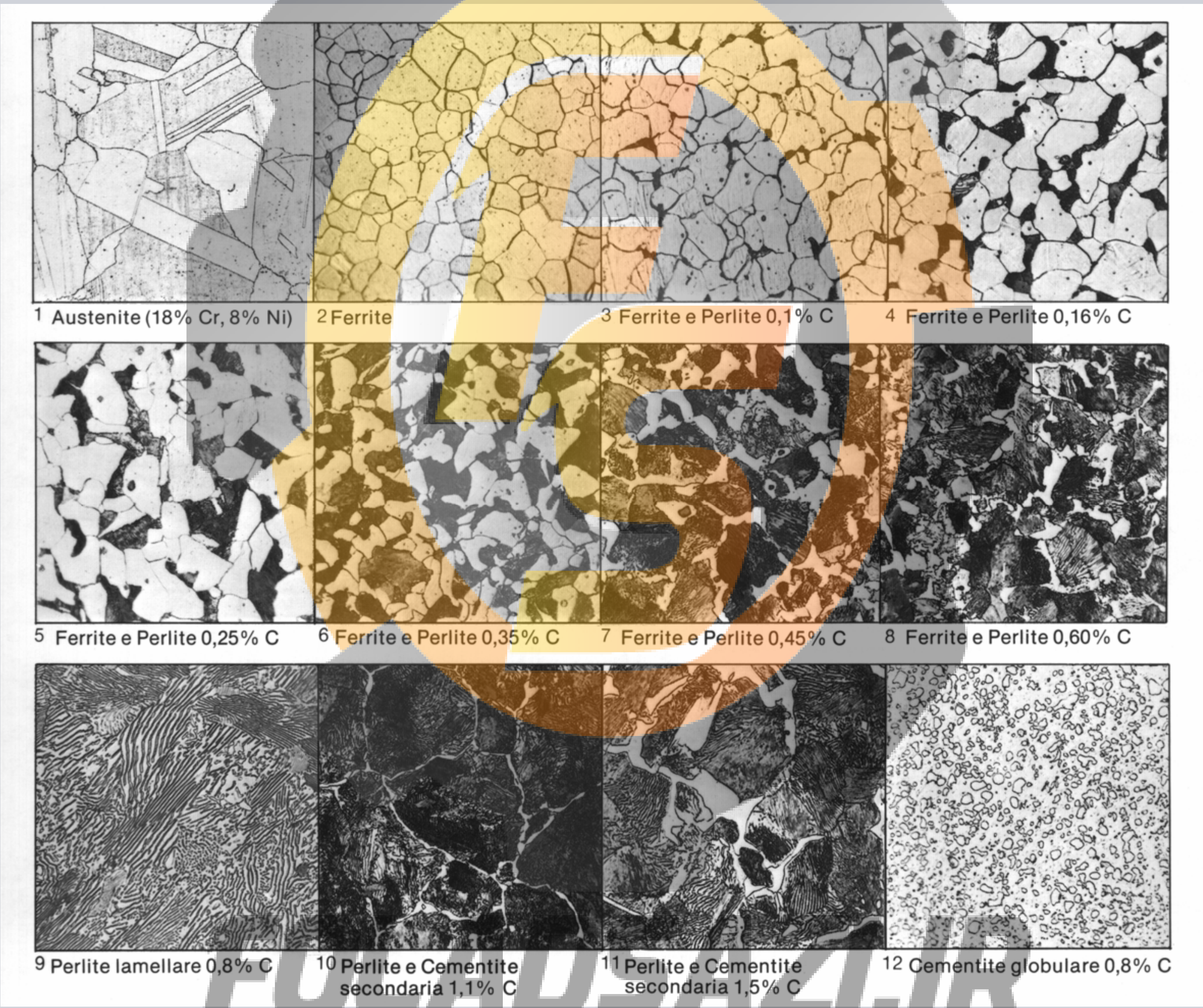

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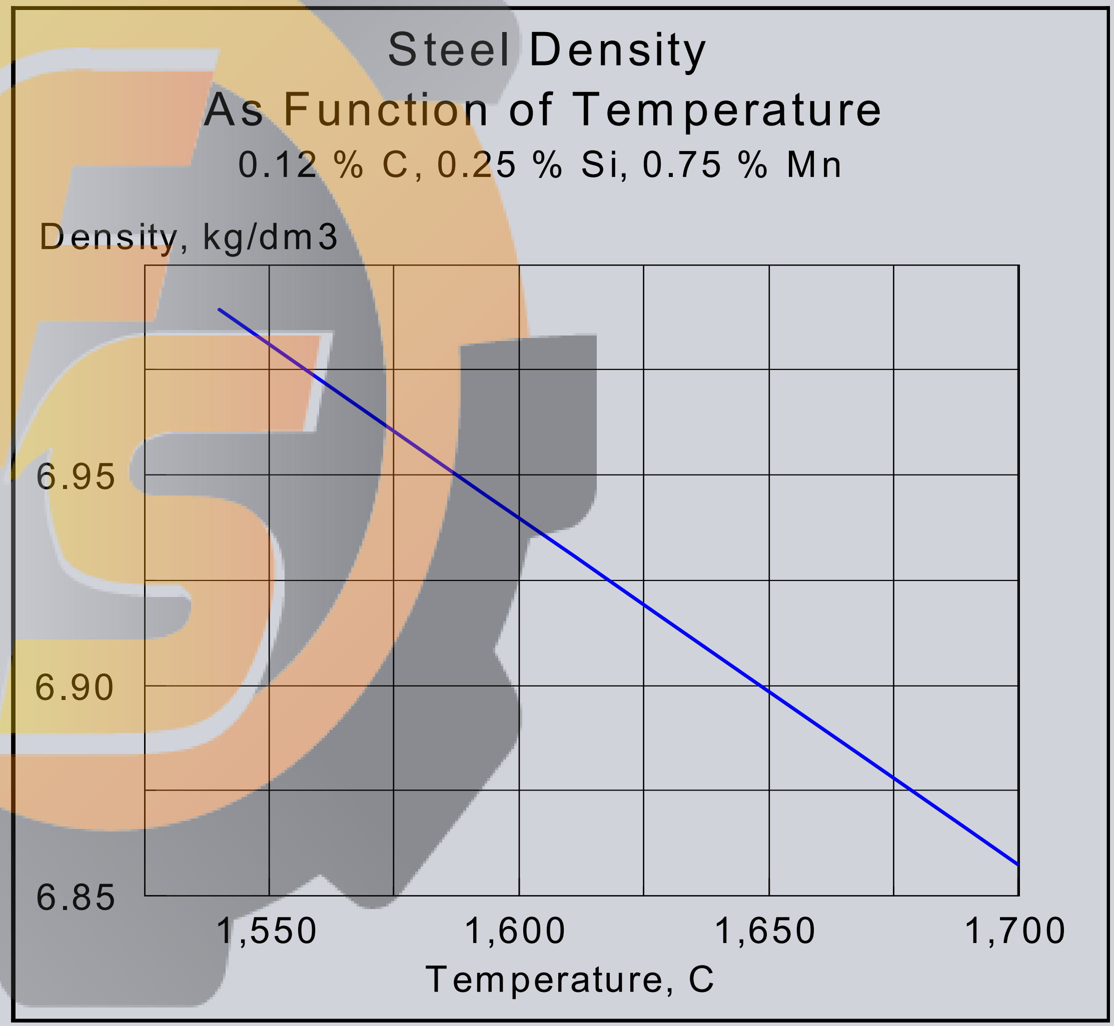
HEAT CAPACITY

The specific heat of liquid steel is relatively independent of its composition and temperature. For ordinary steel it has the value 0.22 kWh/(ton,°C).



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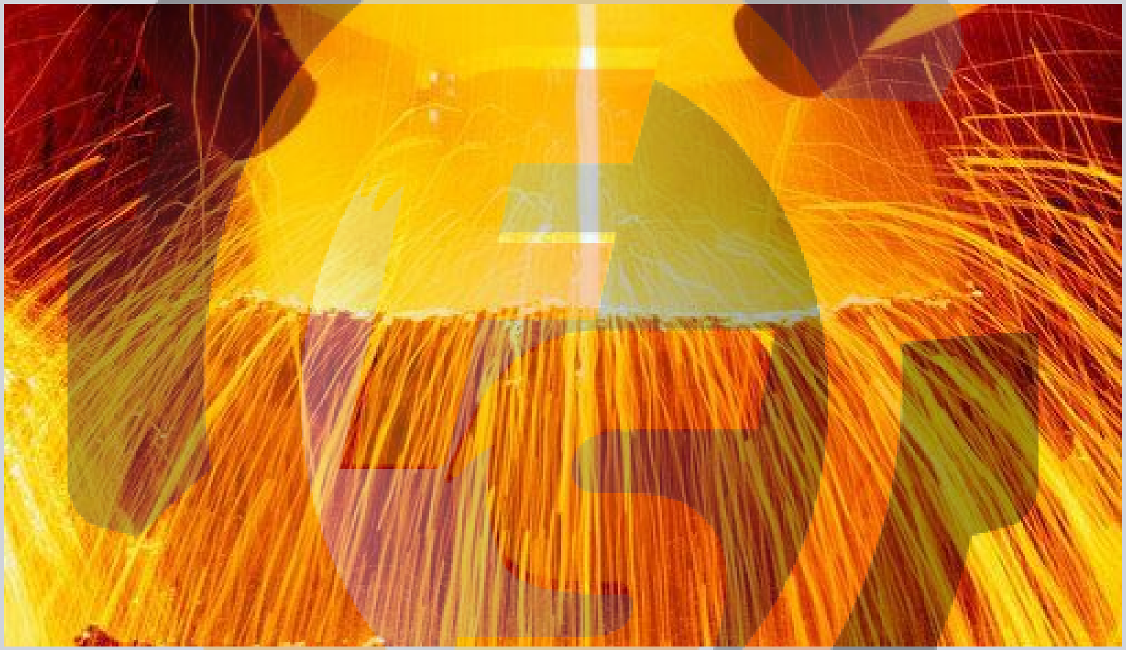


STEEL MAKING IS A PROCESS OF CONTROLLED OXIDATION

LF FURNACE IS PART OF THE SECONDARY METALLURGY

Fundamental of ladle furnace technology

Secondary metallurgy is divided into two steps.

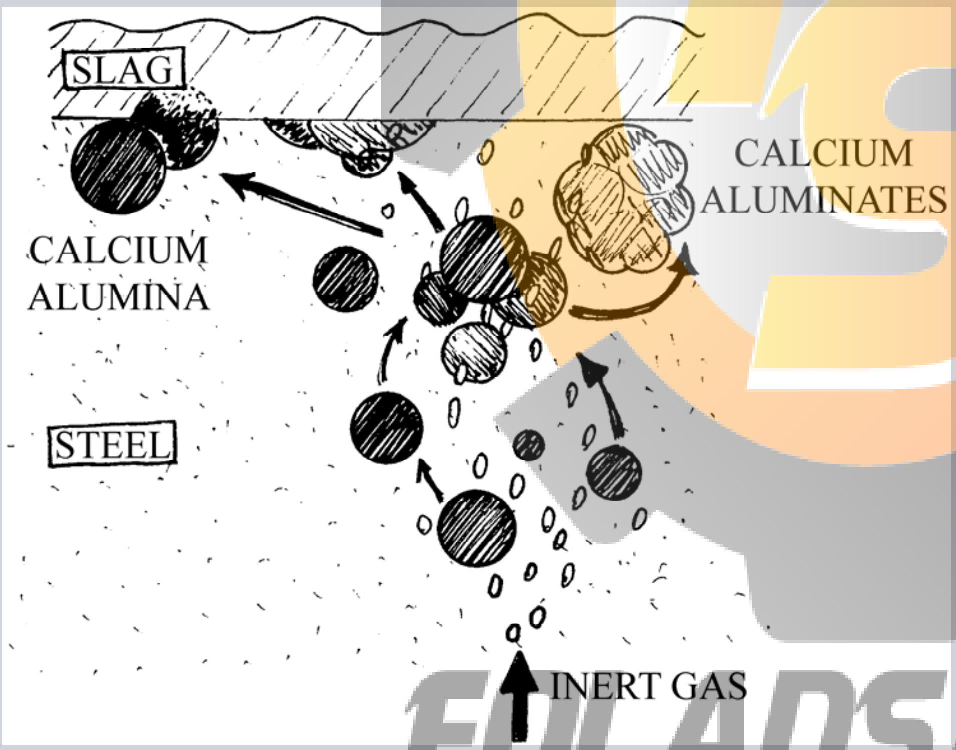
- Operating steps
- Techniques

The basic steps are as follows

1. Mixing and homogenization
2. Temperature adjustment (heating by chemical and/or electrical sources)
3. Charging of additives (deox., fe-alloys, slag building materials)
4. Desulphurization
5. Inclusions removal

REFINING REACTIONS.

Refining of steel normally means the removal of one or several elements from the metal bath.Such refining is brought about by slag metal reactions,gas-metal reactions or metal bulk reactions. Refining of the following elements will be discussed: S, H, N, C, O.



Inclusion modification

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DEOXIDATION.

Deoxidation is the process by which the content of dissolved oxygen is reduced in the metal. One distinguishes between three different techniques for bringing about deoxidation

1. PRECIPITATION DEOXIDATION
2. TOP SLAG DEOXIDATION.
3. VACUUM CARBON DEOXIDATION.

Single Element

$$\underline{Si} + 2\underline{O} = SiO_2$$

$$2\,\underline{Al} + 3\underline{O} = Al_2O_3$$

Note, soluble versus total oxygen, soluble is determined from O-sensor. Total by chemical analyses.

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PRECIPITATION DEOXIDATION - REMOVAL OF SLAG INCLUSIONS.

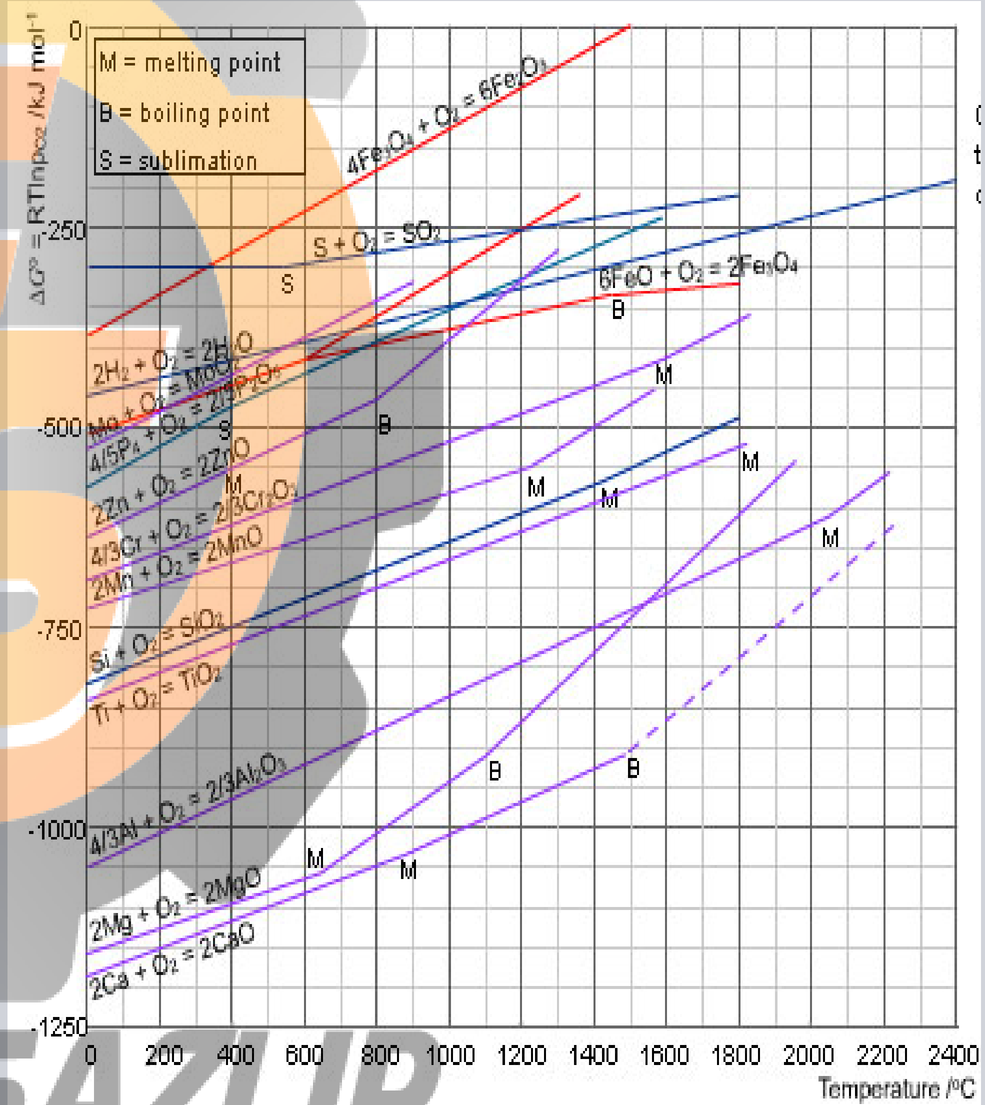
Precipitation deoxidation is by far the most common deoxidation method. As the name suggests,a deoxidiser normally Al, Si, Si-Mn or Ca is added to the metal bath.

The precipitation deoxidation in itself does not reduce the oxygen content but just transforms the dissolved oxygen into oxidic oxygen. Next ,the oxidic oxygen particles must be removed from the metal bath by flotation.

$2[Al]+3[O] \rightarrow (Al_2O_3)$

$[Si]+ 2[O] \rightarrow (SiO2)$

$[Mn] + [O] \rightarrow (MnO)$



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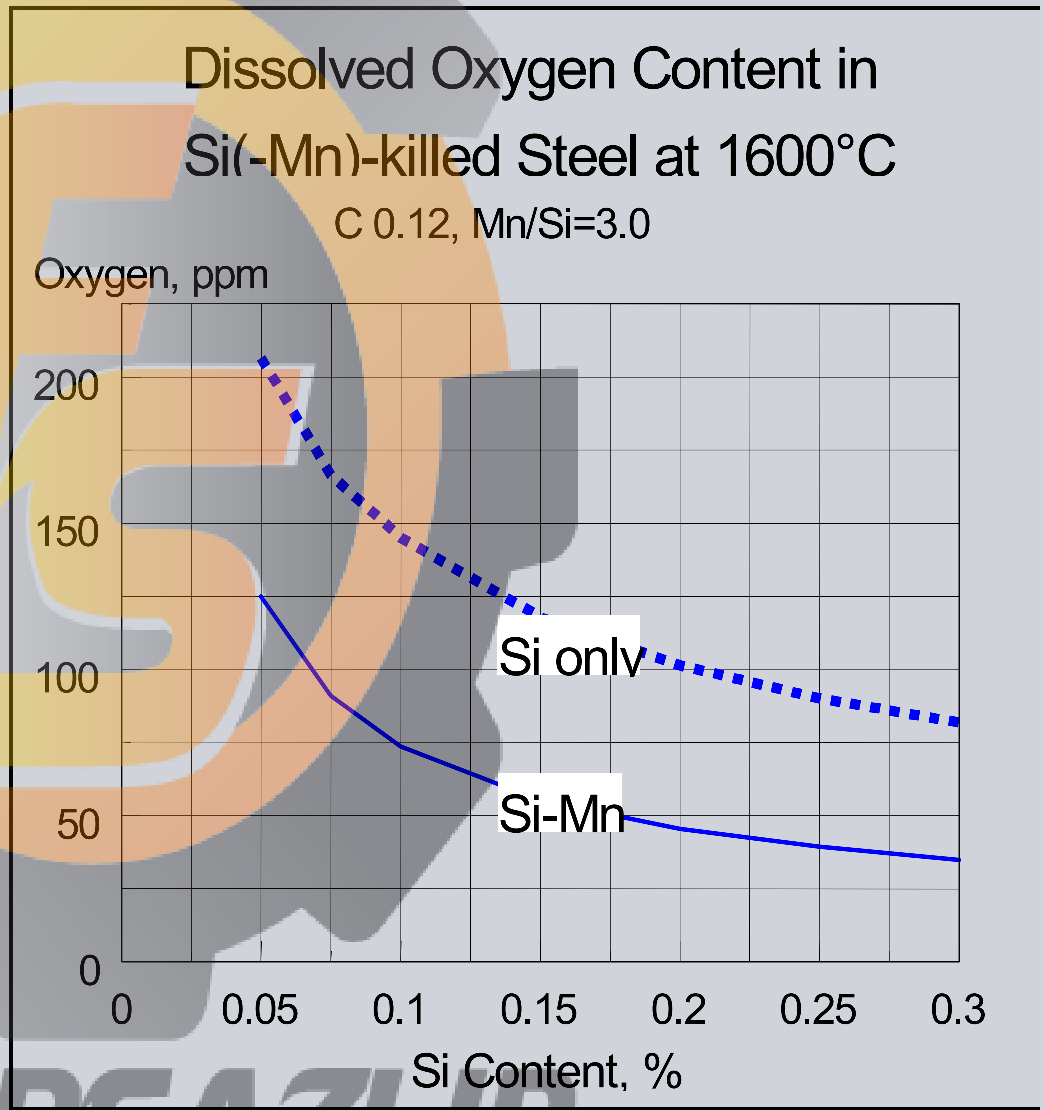
Si and Si-Mn deoxidation

One normally aims at an Mn/Si ratio after deoxidation of >3.This ensures that the manganese formed silicate is liquid at steelmaking temperatures.



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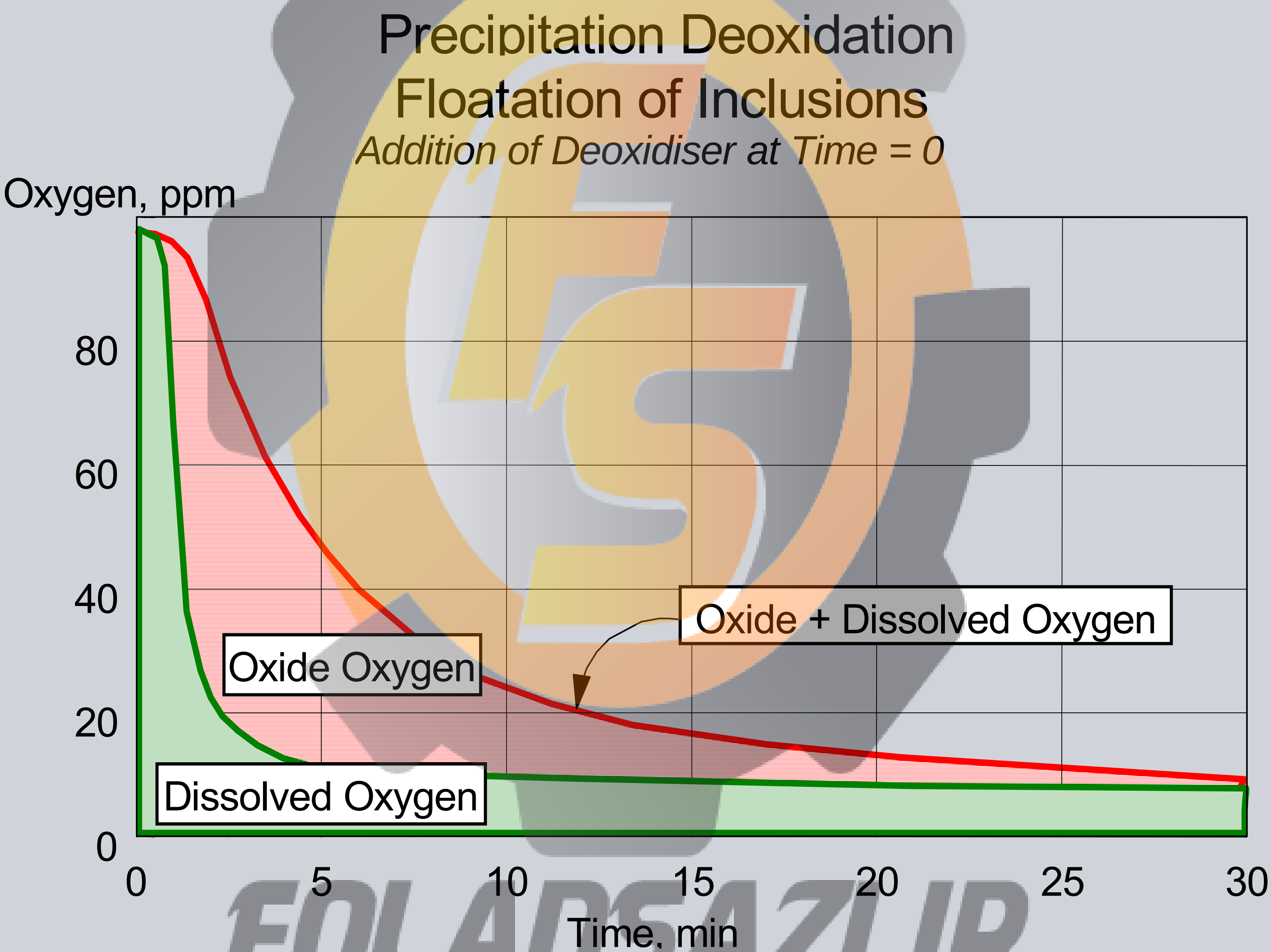

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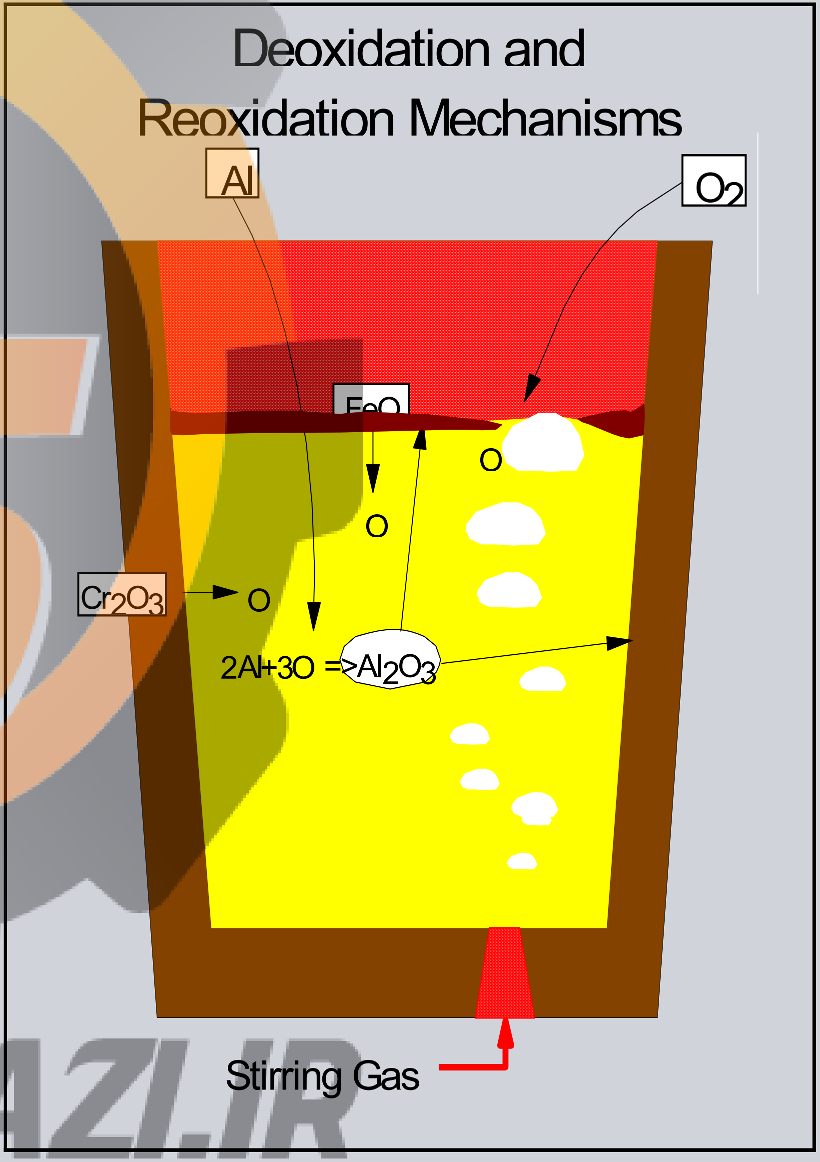
The metal bath is always exposed to reoxidation,which generates new precipitates.

Such reoxidation is caused by FeO, MnO and Cr_2O_3 in the top slag refractories. It is also caused by direct oxidation with atmospheric oxygen



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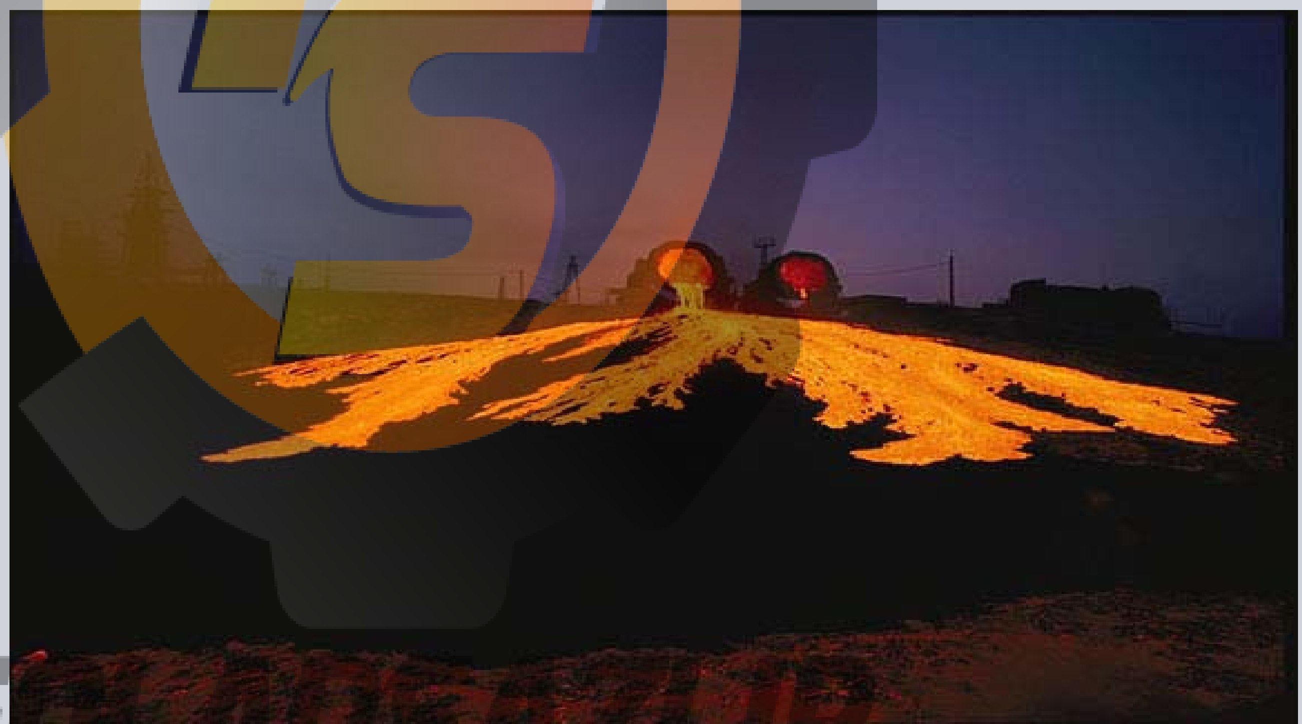
SLAG IN THE LADLE FURNACE

Slag is a desired product of refining, new refining slag is prepared at the LF furnace with a function of:

- thermal insulation layer
- protect layer from the atmosphere
- refining purpose
- inclusion removal



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FUNDAMENTAL PROCESS REQUIREMENTS:

Primary slag (coming from EAF and BOF during tapping) must be avoided in order to:

- minimize the phosphorus reversion into the steel
- minimize the amount of oxygen entering the ladle.
- minimize the ladle refractory lining wear
- increases (FeO + MnO) in the ladle
- increases Al Consumption
- Reduces Steel Cleanliness
- Reduces Desulphurisation

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Slag Control

- Control Slag on tapping
  - EBT
  - Slag Stoppers
- Slag Modifiers
  - Al – CaO
  - CaC_2 – CaO

What is Clean Steel ?

„Clean Steel is steel for which the composition and inclusions are closely controlled to improve properties or production of steel." In particular, we are concerned with one or more of the following:

1. Low Oxygen or oxides
2. Oxide Shape Control
3. Low Sulphur
4. Sulphide Shape Control
5. Low Hydrogen
6. Low Nitrogen
7. Low Phosphorous
8. Tight control of alloying elements, such as Al, Mn, Si, etc.

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Clean Steel Processes

- Tapping
- Slag Control
- Deoxidation
- Gas Bubbling
- Desulphurisation
- Inclusion Modification
- Ladle Furnace
- Vacuum Degassing
- Tundish Practices
- Transfer Practices
- Mould Reactions and Processes

Note, clean steel is not made in the primary furnace

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After tapping into the ladle ,the steel is normally pre-deoxidized but it still contains a high oxygen content ,and the oxygen potential of the slag is very high. In order to prevent the primary furnace slag from entering the ladle furnace there are three possible ways to deslag:

1. DESLAGGING OF THE PRIMARY FURNACE BEFORE TAPPING.
2. DESLAGGING OF THE LADLE BEFORE STARTING TREATMENT..
3. RELADLING.

The method used mostly today is to deslag before treatment, this can be done by tilting the ladle, simply running off via a slag spout, or by the most popular method of using a slag rake

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CHEMICAL COMPOSITION.

Refining slag are composed of the main constituents from the Ca0-SiO2-Al2O3 - MgO system.

CaO comes from the added lime and the slag should normally be saturated with it.

SiO2 and Al2O3 come from the primary furnace slag, deoxidation products and, to some extent from the refractory wear, Al2O3 is also an important flux in many synthetic slag.

The MgO content normally comes from the dissolution of MgO in the ladle and roof refractory.

Al killed		Si killed	
CaO	56-62%	CaO	56-62%
SiO_2	6-10%	SiO_2	15-20%
Al_2O_3	20-25%	Al_2O_3	5-8%
$FeO+MnO+Cr_2O_3$	<2%	$FeO+MnO+Cr_2O_3$	<2
MgO	6-8%	MgO	6-8%
S	0.3-2.0%	S	0.3-1%

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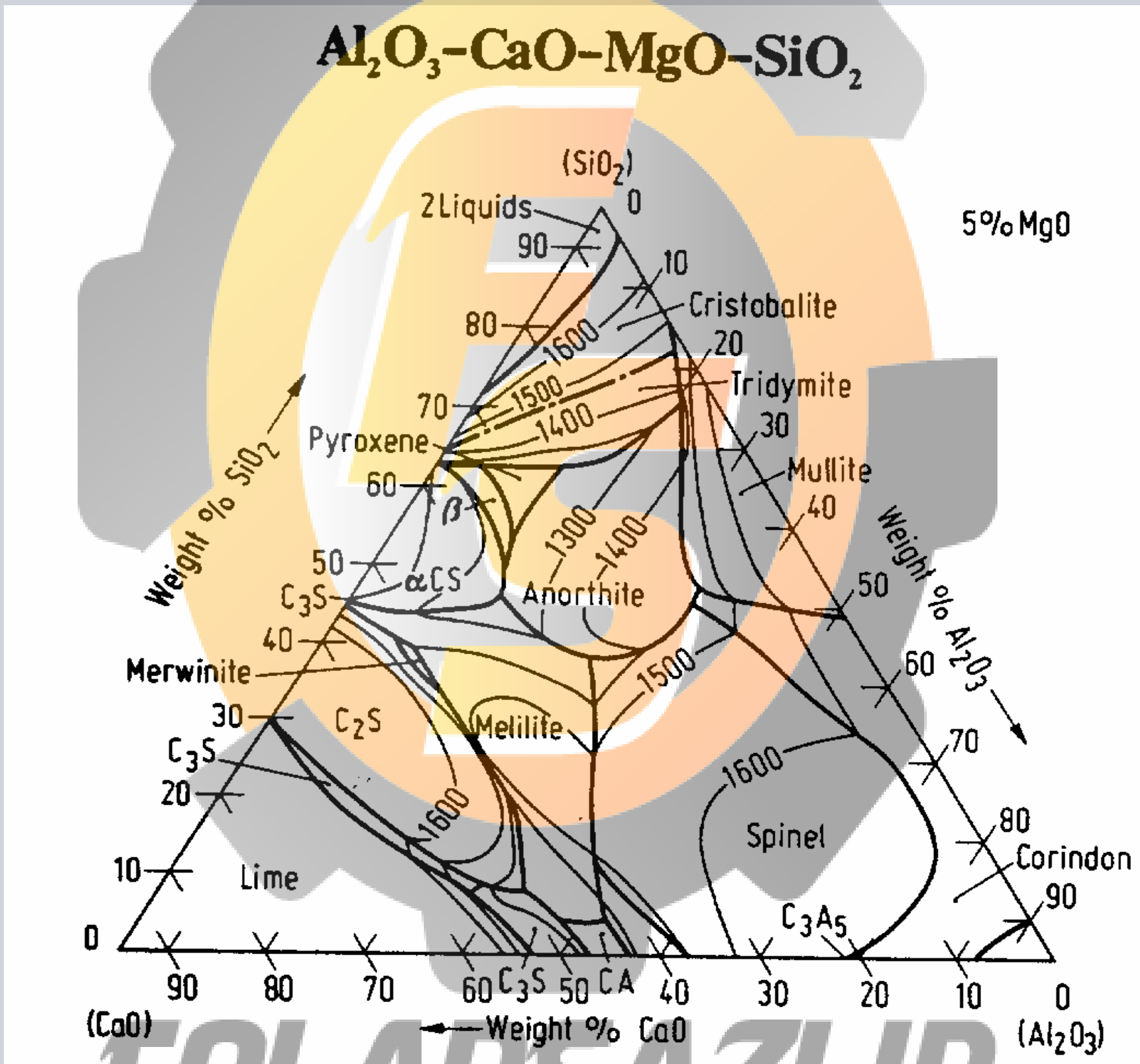

Ladle Slag Mass Balance

Component	Amount (kg/tonne)					Percentage
	Steelmaking	Ladle Addition	Reactions	Refractory	Total	
CaO	1,29	4,5	0	0,50	6,29	59
SiO_2	0,60	0	0	0	0,60	6
MgO	0,21	0	0	0,50	0,71	7
Al_2O_3	0,12	0	2,83	0	2,95	28

10,55 kg/tonne (Total)

1,00 kg/tonne (Dolomite refractory)

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HEAT CAPACITY

The heat capacity for the aforementioned slags is 0.41kWh/(tonne,K) and practically independent of temperature within the 1500 - 1700 °C range.

DENSITY

The density of refining slags can be calculated with fair precision on the basis of empirical models.Densities for the two aforementioned slags are in the 2.7 to 2.8 kg/dm³ range for temperatures within the 1500 to 1700°C.

SLAG BASICITY

The single most important numerical index which summarizes the composition of a slag and serves as a single parameter with which its chemical character can be correlated, is the BASICITY INDEX.

The simplest and most widespread definition is the one by Herty in the 1920,s called V -RATIO and defined as :

V-ratio =(WT-% Ca O) / (WT-% SiO2) [1,8-3,5]

The V-ratio ignores the effects of the other basic (FeO,MnO, MgO) and acid (Fe_2O_3,Al2O3,P2O5).

Fundamental of ladle furnace technology

Removal of S from steel into the slag is conventionally illustrate by the reaction

$$[S] + CaO \rightarrow CaS + [O]$$

To achieve a good desulphurisation it is first of all necessary that three fundamental conditions be satisfied.

1. Basic Slag.
2. High Temperature (60-80deg greater than delta T sl).
3. De -oxidation of the bath(aO2 less than 40ppm).

The stirring of the bath and the reactivity of the slag are important to speed up the formation of Ca Sulphide.

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Desulphurisation is mathematically represented by the formula

$$S_{final} = S_{initial} * e^{-ks *(A/V)* t}$$

A = bath area m^2

V = metal volume m^3

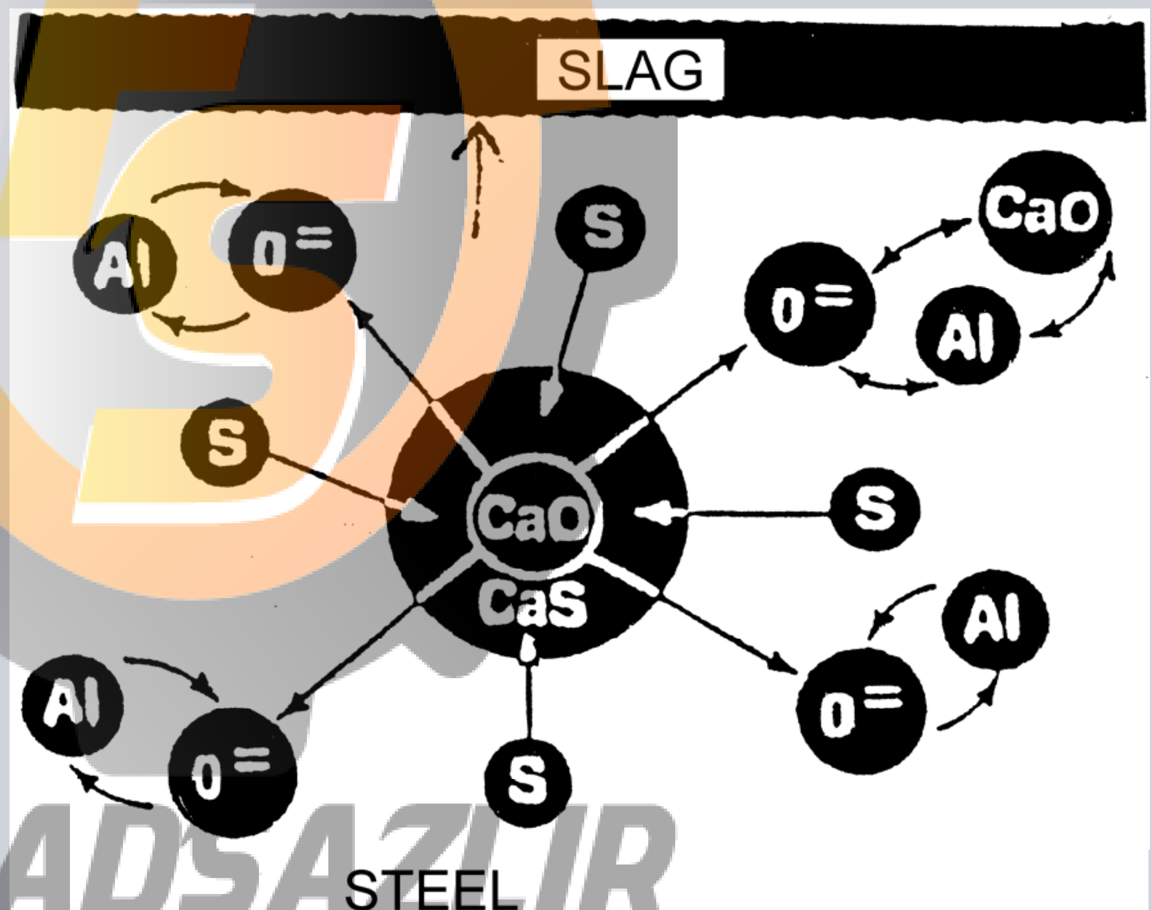
Ks = deS rate constant m/min

t = process time

Ks in the LF = 0.08

(0.8-1.2 Nl/ton min)

Ks in the VD = 0.20



Ladle Desulphurisation

- Mature, well understood process
- Desulphurisation equilibrium depends on
  - Sulphide capacity of slag
  - Oxygen activity (Al or Si)
  - Slag Weight
- Basic Reaction
  $3\underline{S}+2\underline{Al}+3(CaO)=(Al_2O_3)+3(CaS)$
- Kinetics
  - Equilibrium sulphur
  - Stirring energy

<u>Desulphurisation is, therefore, favoured by</u>

- High basicity
- High level of Al or Si, Al is generally more effective.

$$3\underline{S}+3(CaO)+2\underline{Al}=3(CaS)+(Al_2O_3)$$
$$2\underline{S}+2(CaO)+2\underline{Si}=2(CaS+(SiO_2))$$

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Ladle Desulphurisation

$3(CaO) + 2\underline{Al} + 3\underline{S} = 3(CaS) + Al_2O_3$

- High CaO and Al
- Optimum slag
- (S)/[S] as high as 500

However, kinetics are not fast enough for simple ladle, Ladle furnace is required for optimum results.

2CaO + Si + 2S = (SiO2) + (CaS)

(S)/[S] ~ 50

Desulphurisation is limited

$$L_S = \frac{(\%S)\ \ (slag)}{[\%S]\ \ (metal)}$$

The higher L_S, the more effective is desulphurisation

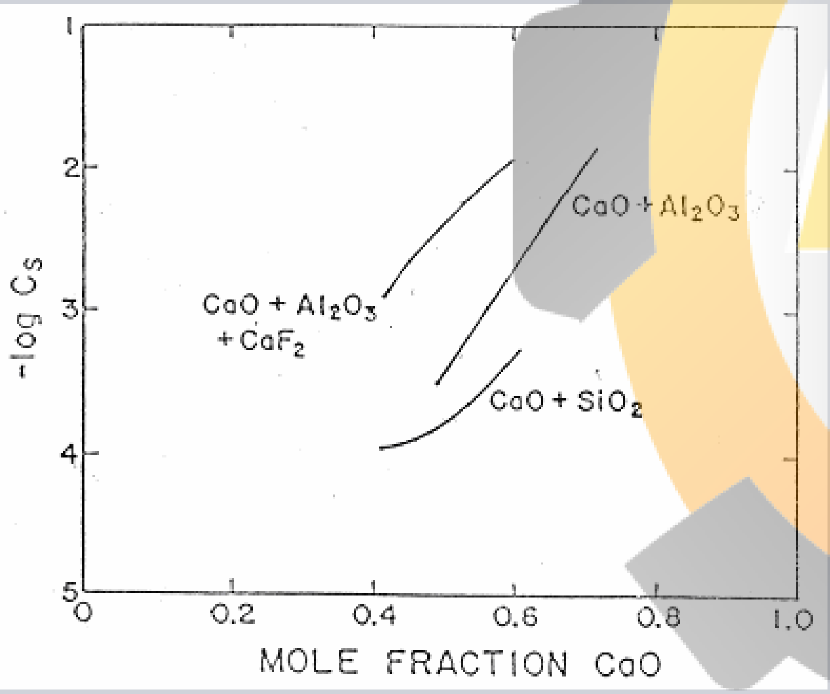
Process Kinetics

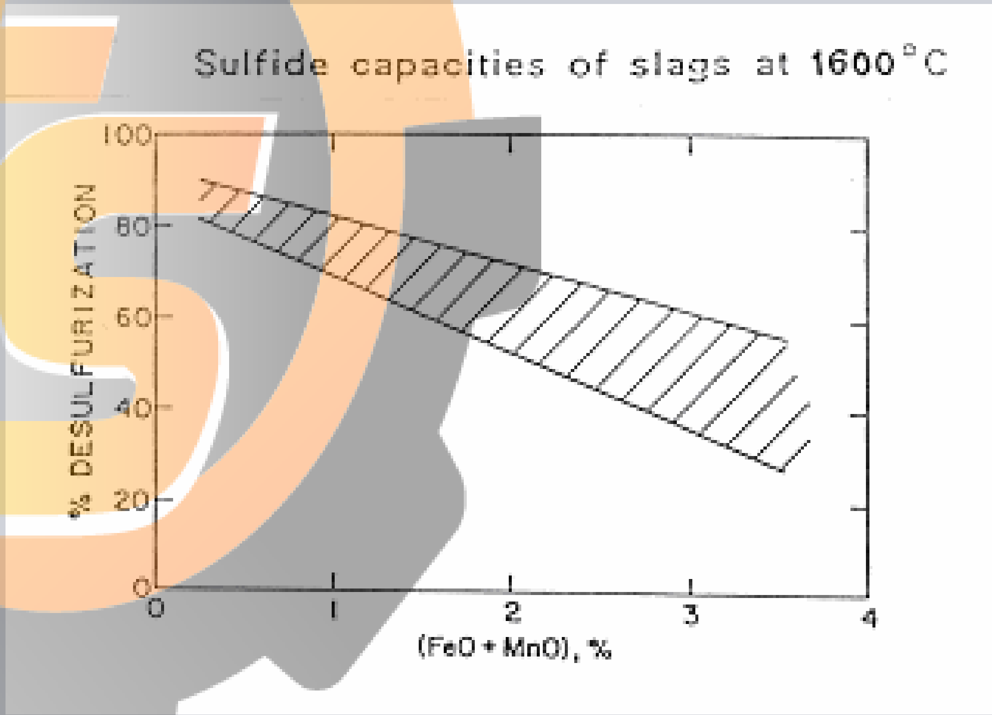
The rate of desulphurisation is controlled by liquid phase mass transfer and favoured by:

- Stirring
- Fluid Slag (CaF_2)
- Low [%S]
- High L_S
- High W_S

Example shown in the next two figure.

Effect of FeO and MnO on Desulphurisation





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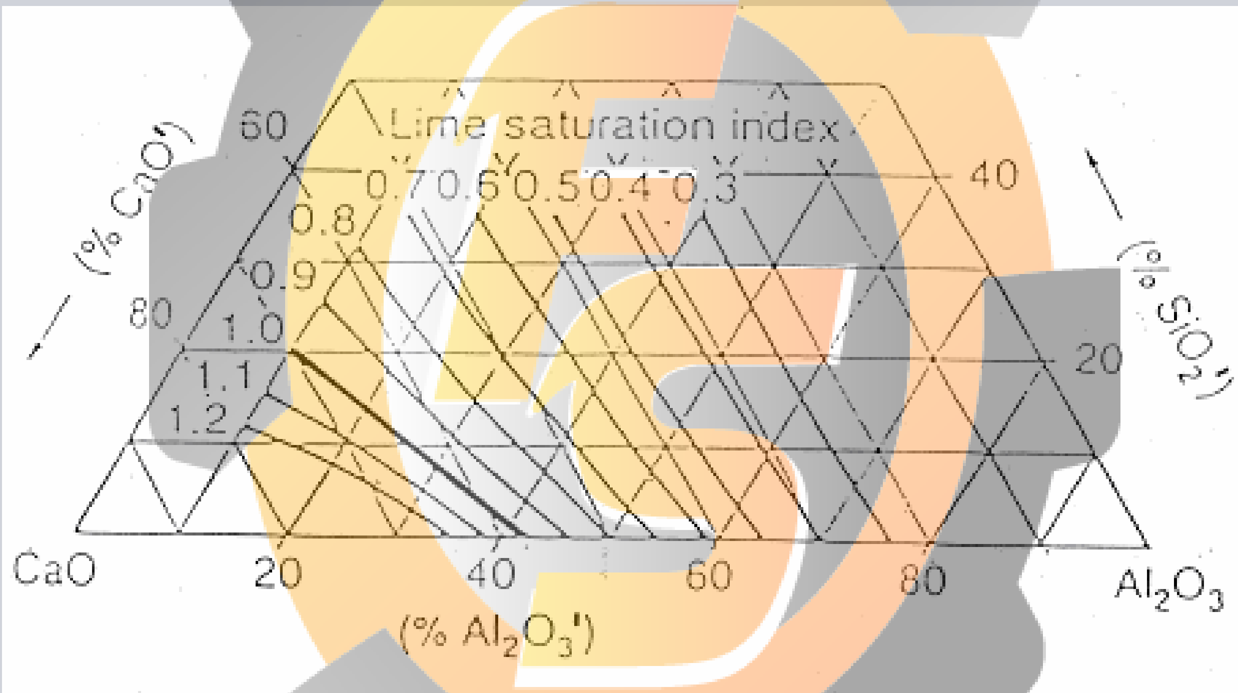
Lime Saturation index



Ladle Slag formation and lime saturation index in the system $CaO – Al_2O_3 – SiO_2$

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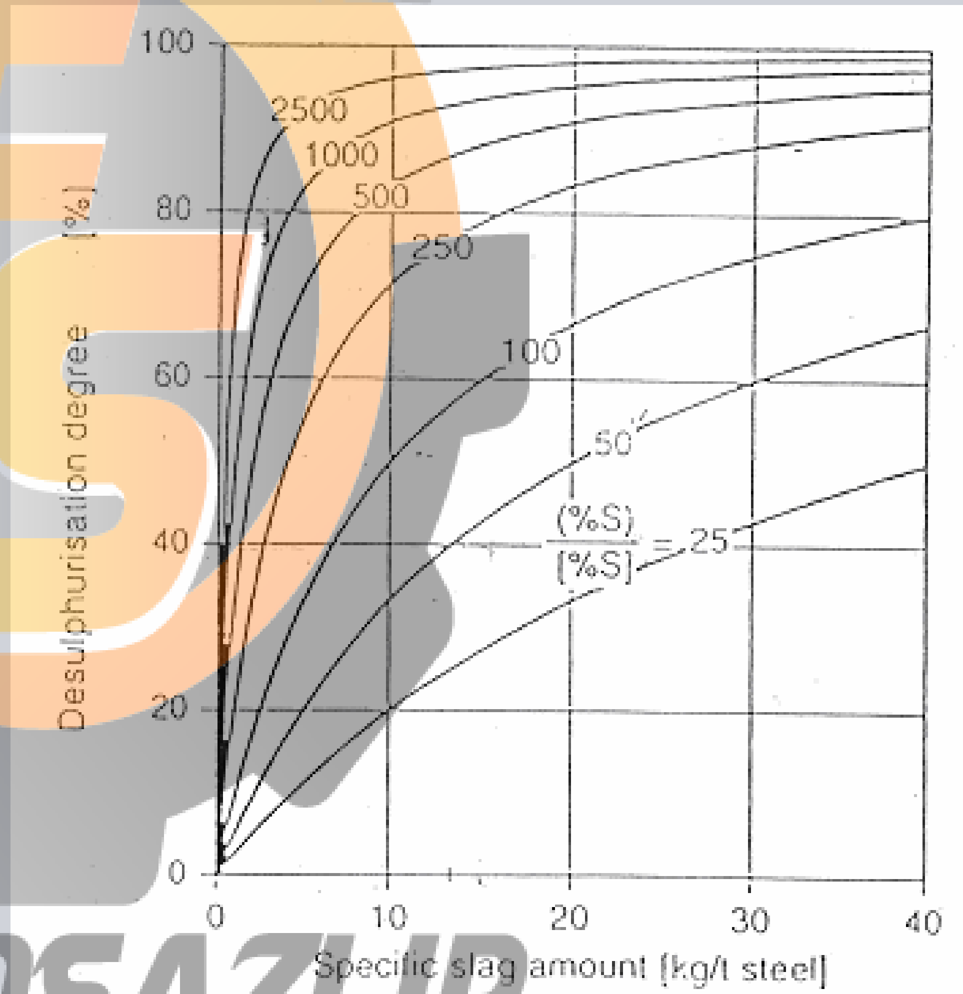
Desulphurisation versus Slag Amount

Desulphurisation degree for different Sulphur distributions as a function of specific slag amount



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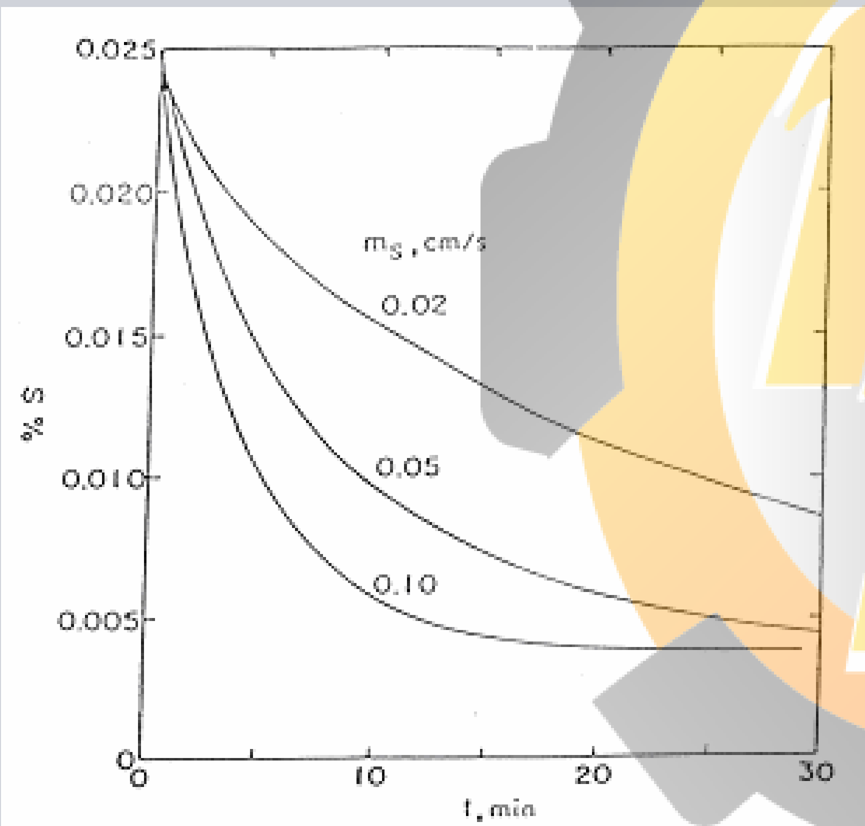
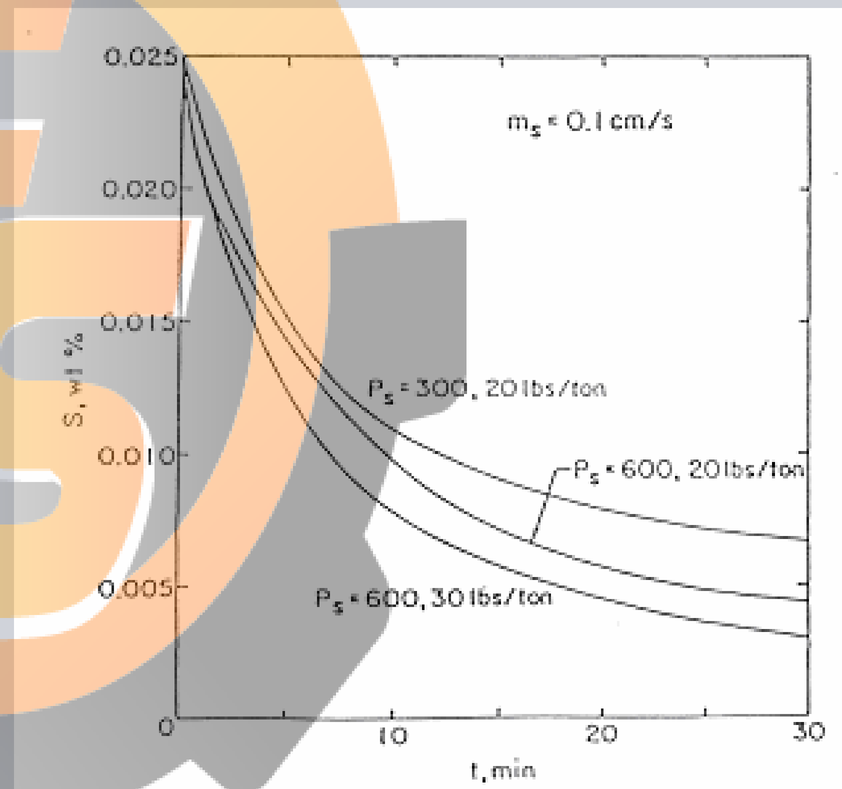
Desulphurisation



Effect of stirring on desulphurisation
(Figure 10)



Effect of (S)/[S] and W_S on desulphurisation
(Figure 11)

Kinetics

The rate of desulphurisation is controlled by liquid phase mass transfer and favoured by:

- Stirring
- Fluid slag (CaF2)
- Low [%S]

High LS
High WS

Examples shown in Figures (10-11)

Percentage Desulphurisation $\frac{[\%S]_i - [\%S]_f}{[\%S]_i} \times 100$	Stirring (SCFM)	Time (minutes)
70%	10	10
85%	10	20
70%	30	5
95%	30	15

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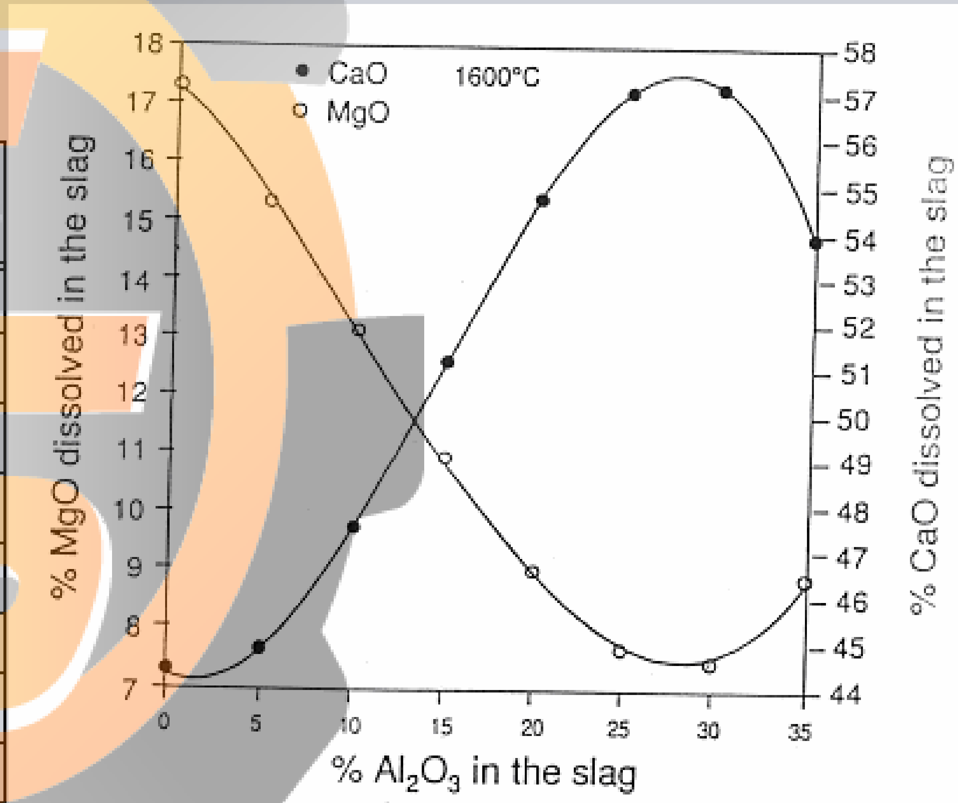
Optimum Slag at 1600°C

$\%Al_2O_3$	$\%MgO$	$\%CaO$	$\%SiO_2$	C/S ratio	Opt.Bas (Λ)	$-\log C_S$
0	17,32	44,31	38,37	1,15	0,696	3,042
5	15,19	44,79	34,92	1,28	0,700	2,982
10	13,11	47,45	29,44	1,61	0,715	2,763
15	10,92	51,13	22,95	2,23	0,737	2,458
20	8,99	54,69	16,32	3,35	0,759	2,132
25	7,68	57,05	7,68	5,56	0,778	1,856
30	7,47	57,15	5,38	10,62	0,789	1,702
35	8,92	53,88	2,20	24,49	0,786	1,742



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Desulphurisation efficiency

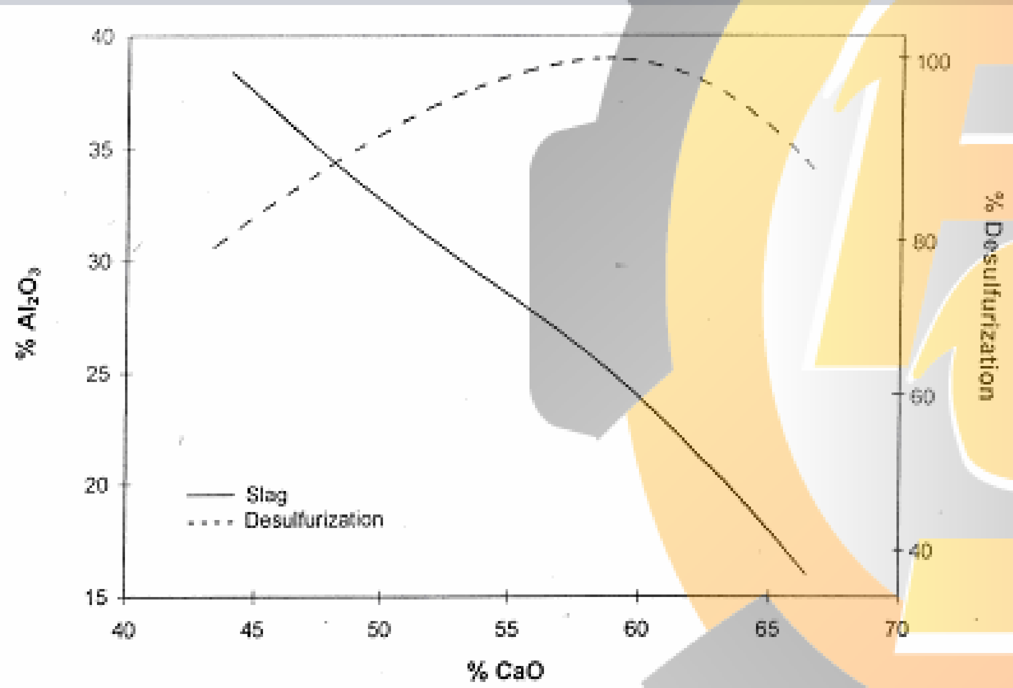

Fig. 2 - Plot of %CaO versus %Al_2O_3 in the slags and the desulfurising efficiency of the slags

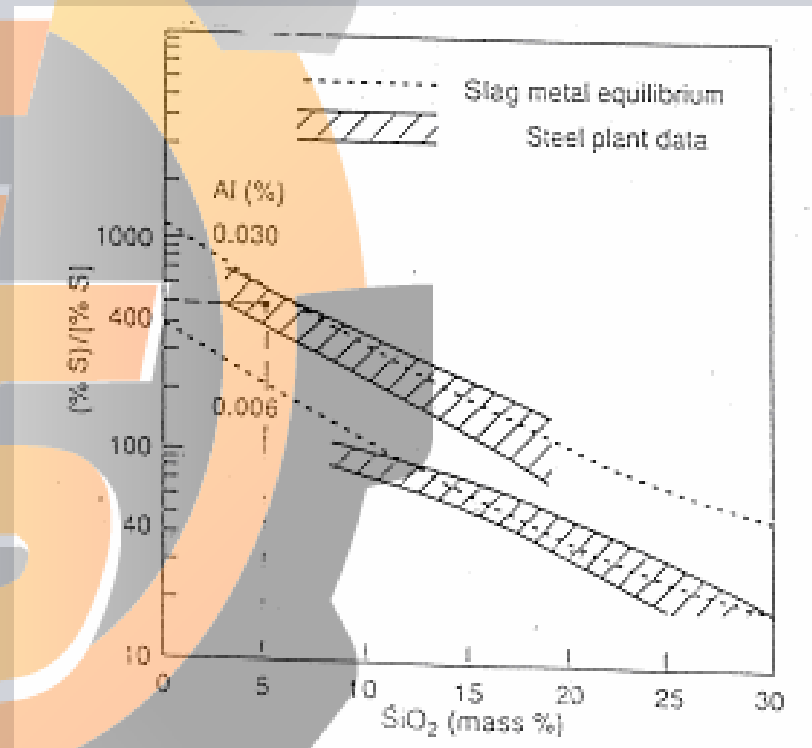

Fig. 3 – Slag/steel sulphur distribution ratios after desulphurisation with lime-saturated CaO – MgO – Al_2O_3 – SiO_2 slags at 1600 ± 15°C with steels containing residual 0,006% Al and 0,03% Al are compared with the equilibrium values.

Slag Color

Since slags cannot be analysed as quickly as steel, it is necessary to adapt the slag conditions according to other information, which is given by the appearance of the slag. The slag have to be cooled prior the appearance can be analysed.
The colour of the slag can be black, brown, grey, green, yellow or white with a lot of nuances in between. The slag colour changes from black to white with the rate of slag reduction.

Black: FeO + MnO > 5% to be reduced either by Al, CaC_2 or FeSi.

Dark to green: FeO + MnO = 4% to be reduced either by Al, CaC_2 or FeSi.

Dark to grey: FeO + MnO = 3% to be reduced either by Al, CaC_2 or FeSi.

White to yellow: FeO + MnO < 2%.

This slag is well reduced. The yellow colour indicates that desulphurisation has taken place. This slag should disintegrated to powder when cooled down.

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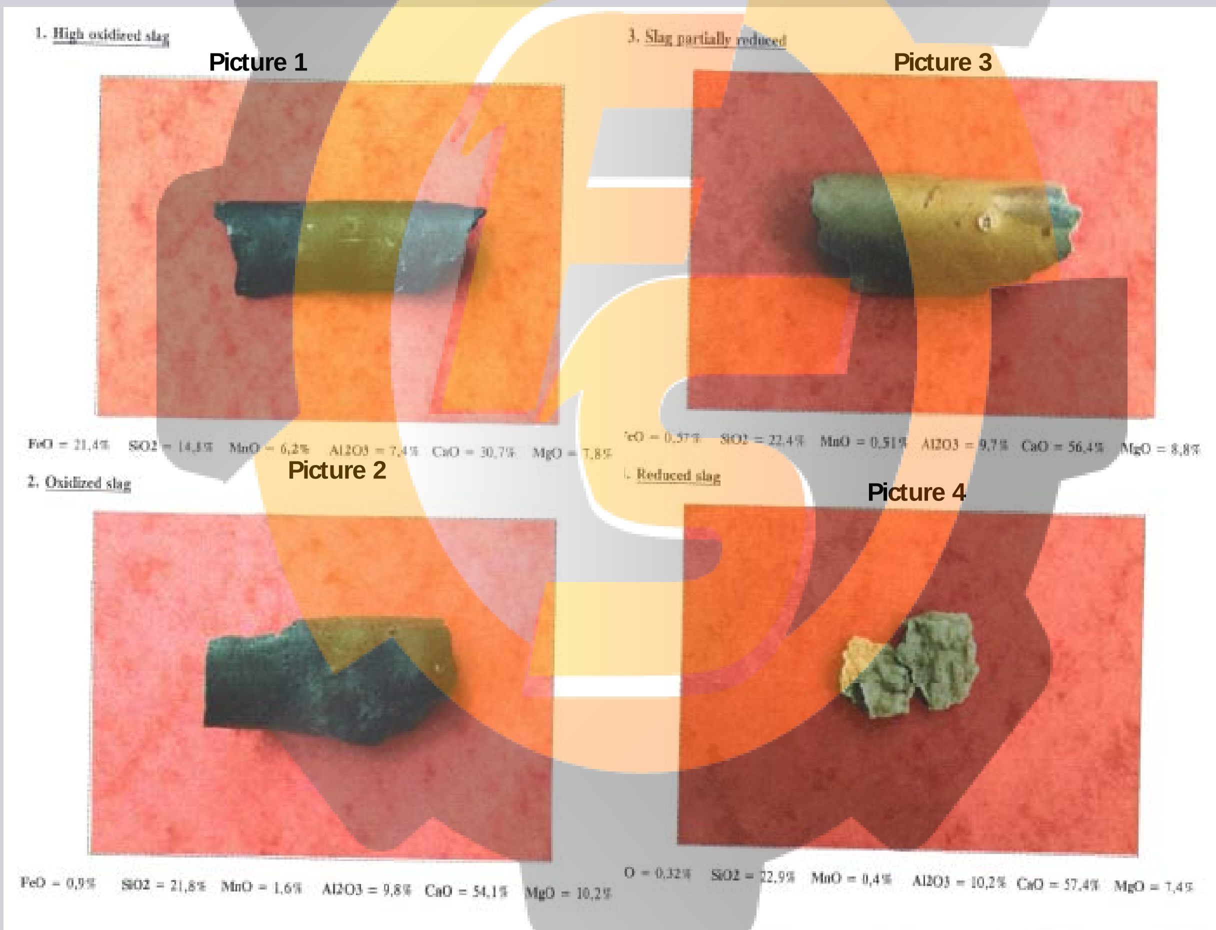
LADLE SLAG REFERENCE PICTURES



Ladle Slag Colours {typical}

Slag Surfaces

The slag surface can be glassy, smooth or brittle, depending on the different components in the slag.

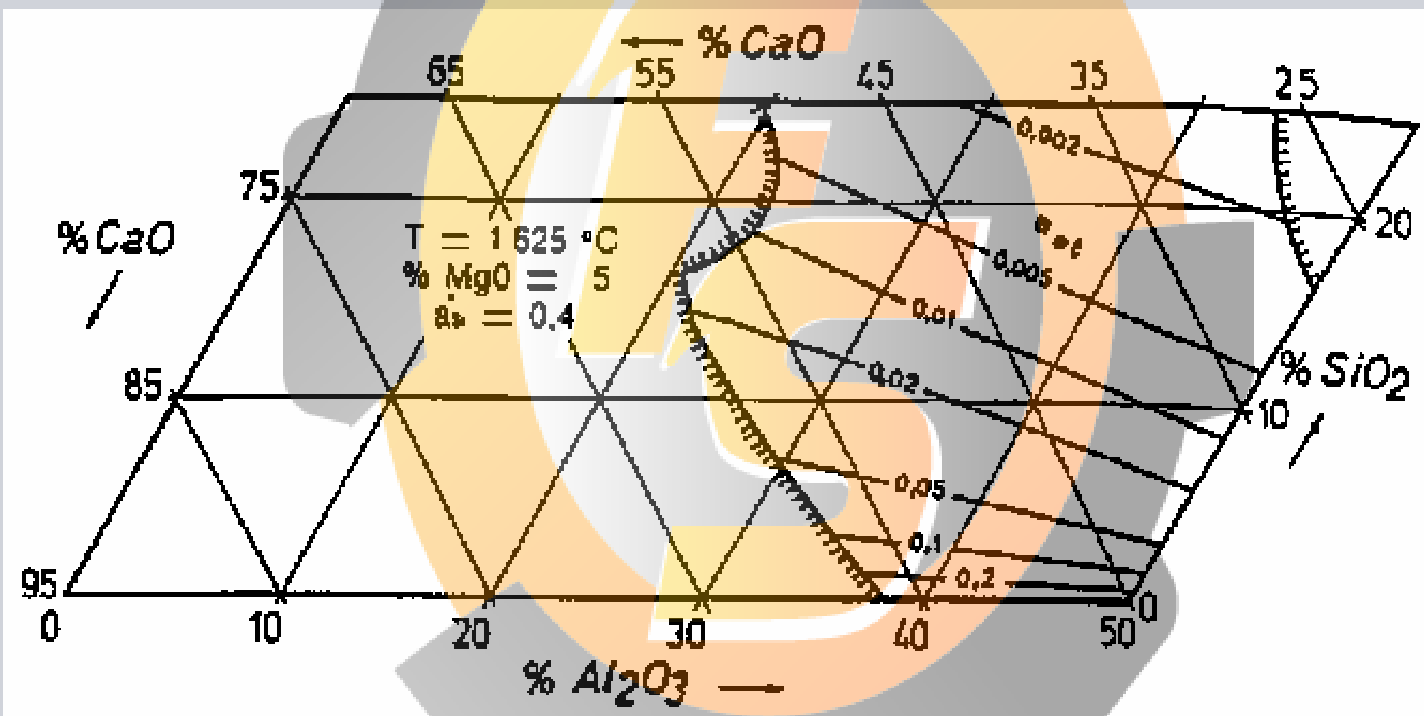
Glassy and thin: This indicates that the SiO_2, Al_2O_3 or CaF_2 content are too high. Lime should be added in this case, not more than 1,0 kg/t steel at a time. After dissolving it should be tested once more.

Smooth and thick: This slag should normally disintegrate to powder when cold. Slag condition seems ideal. In case it does not disintegrate, the SiO_2, Al_2O_3 or CaF_2 may be high. Desulphurisation may cause problems in this case. More lime shall be added, as indicated above.

Rough and thick: The amount of lime is too high. In case undissolved lime particles are found, Al_2O_3 or CaF_2 shall be added. Not more than 0,5 kg/t at a time should be added and dissolved prior new test.

The above mentioned can only be a rough indication, how to react on different situations.

CaO-Al2O3-SiO2-5%MgO with Si-0,4%



Al content in the metal in equilibrium with CaO-Al_2O_3-SiO_2 and 5% MgO slag with a Si activity = 0,4%.

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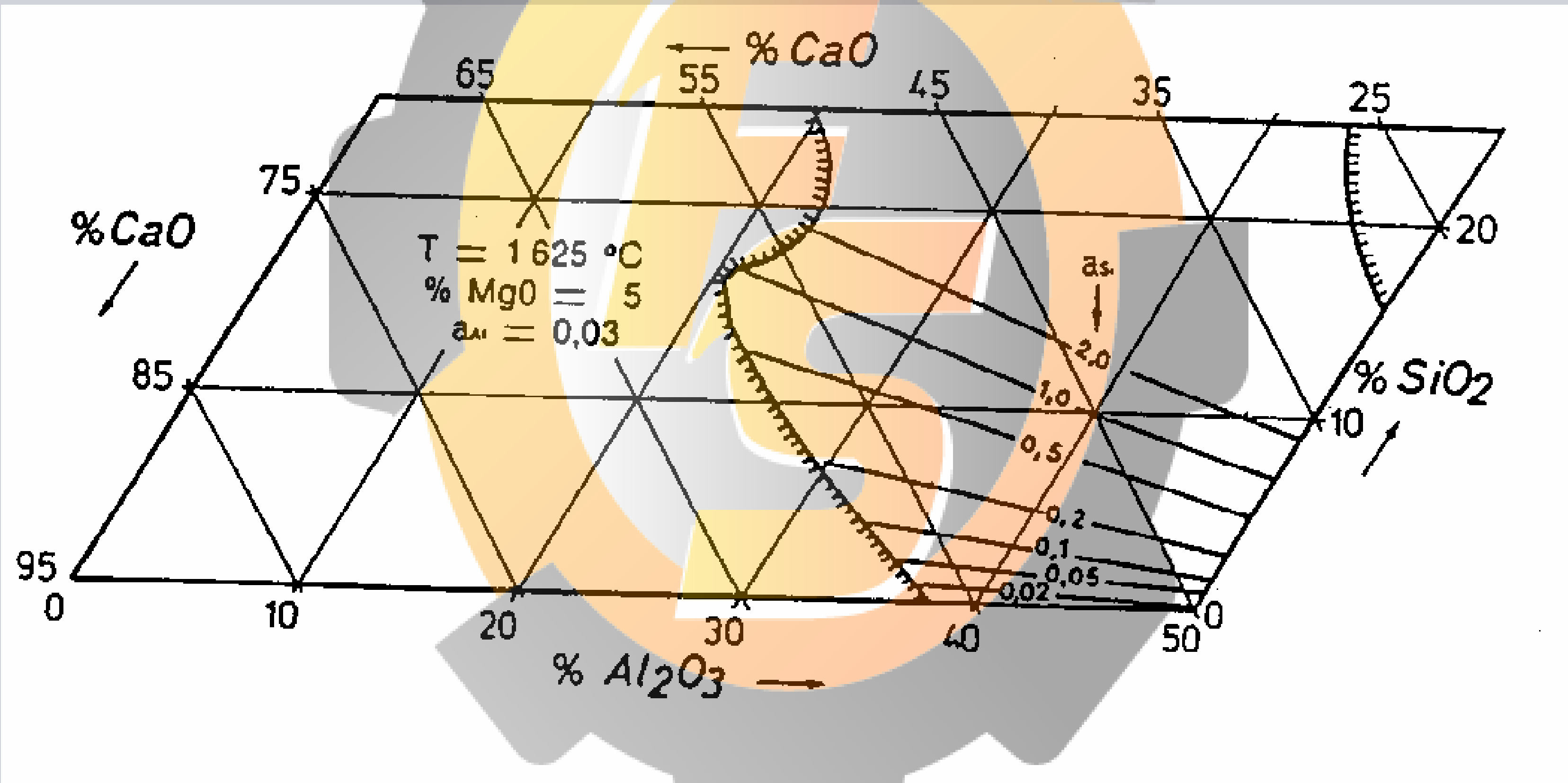
$CaO-Al_2O_3-SiO_2$-5%MgO with Al 0,03%



Si activity in the metal in equilibrium with $CaO-Al_2O_3-SiO_2$ and 5% MgO slag with a Al activity = 0,03 (0,03% Al).

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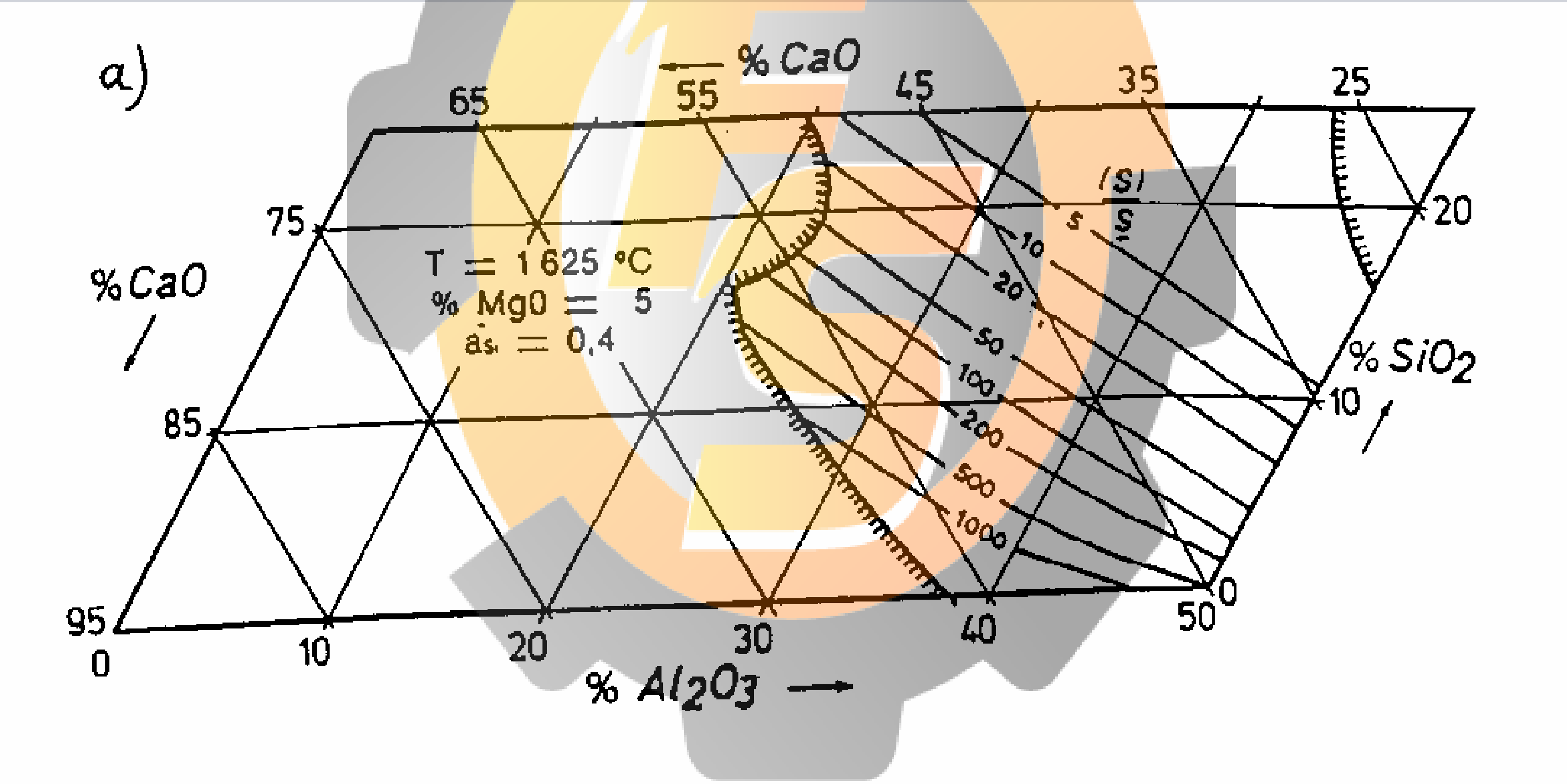
L_S for Si-killed Steel



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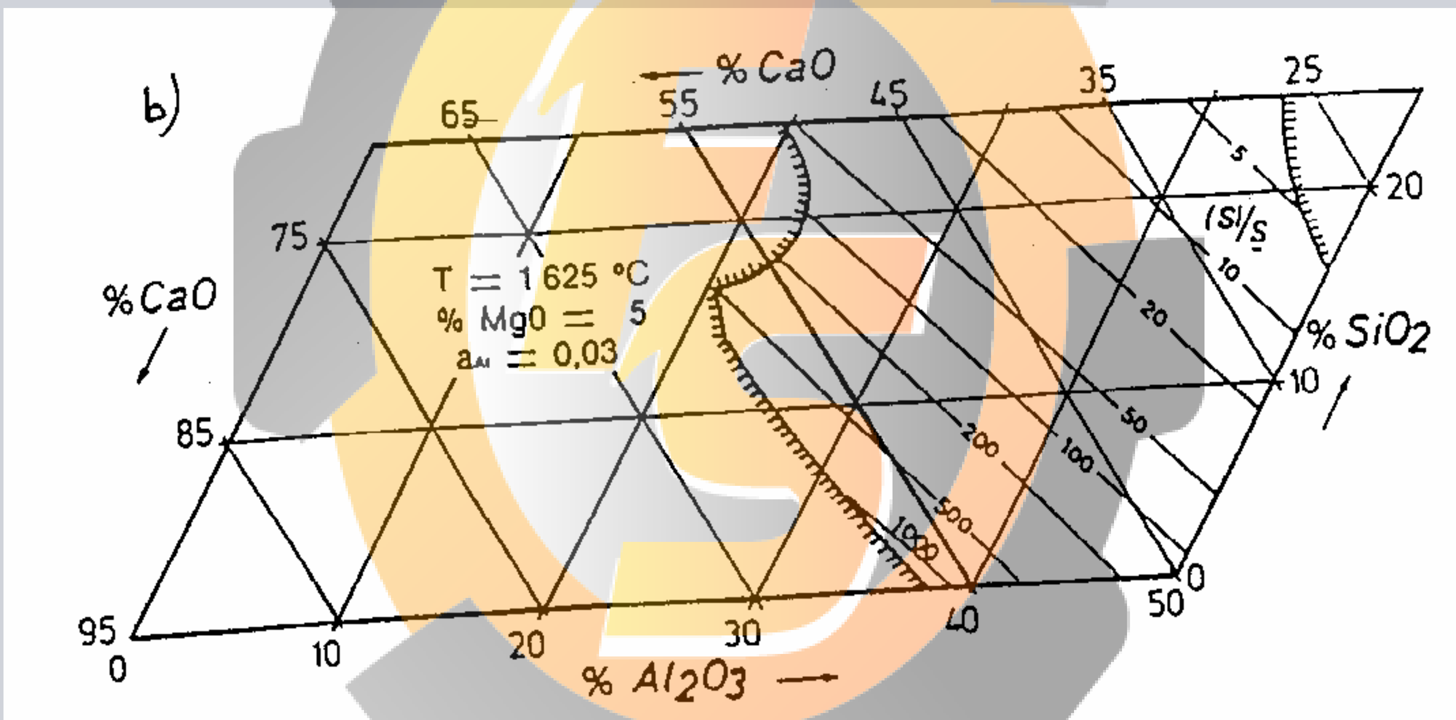
L_S for Al-killed Steel



Sulphur partition ratio for a steel with

- a Si activity of 0,4
- an Al activity of 0,03 (0,03% Al)

In equilibrium with CaO-Al_2O_3-SiO_2 and 5% MgO slag

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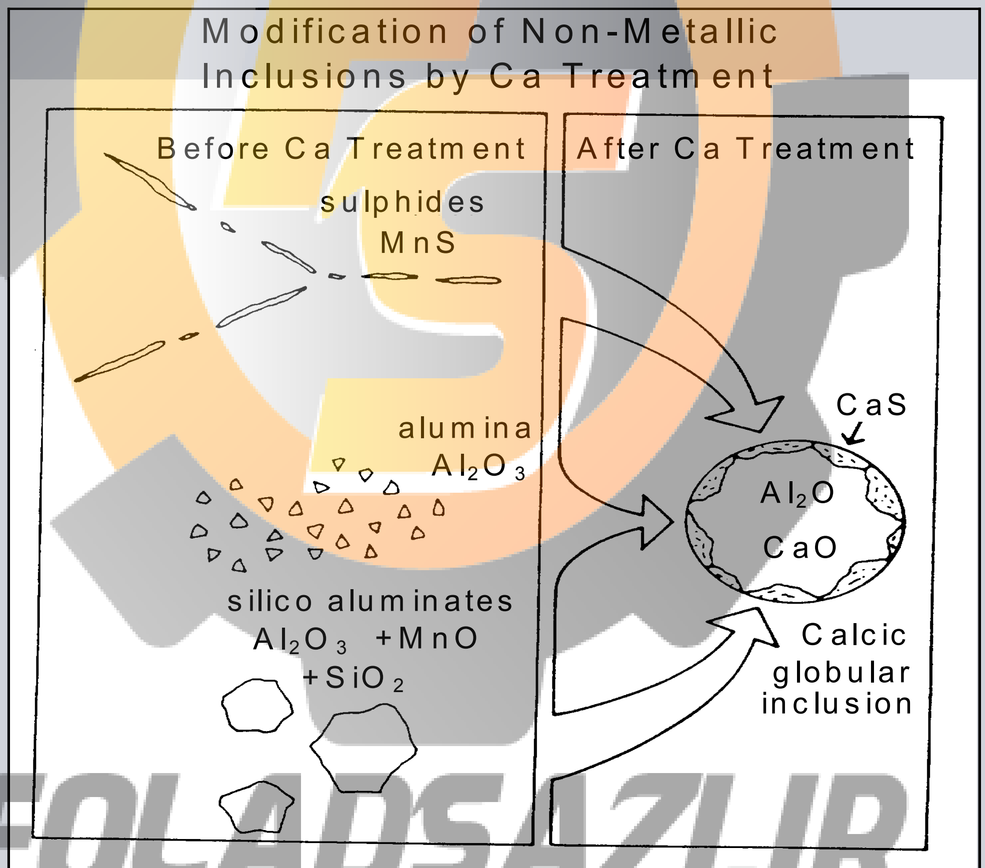
CALCIUM TREATED STEELS

The aim of calcium treatment is in most cases to improve castability, by modifying the sharp edged, solid Al2O3 particles into spherical liquid calcium aluminates.



Calcium Reaction

1. Reacts with oxygen (O) , Steel must be deoxidised
2. Reacts with sulphur or Al_2O_3 inclusions
   If sulphur is high sulphur first

%Al	%S
0,01	0,015
0,03	0,010
0,05	0,006

   $CaS + Al_2O_3 = (CaO - Al_2O_3) + \underline{S} + \underline{Al}$
3. If sulphur is low during solidification Ca prevents MnS formation
   S $\rightarrow$ (CaO – Al2O3) into solution   Ca + S = CaS
4. For re-sulfurised steel
   - Remove as much Al2O3 as possible
   - Add Ca
   - Add wire just prior to casting

Oxide Shape Control

- Liquid ($MnO - SiO_2$) Ca may help
- Liquid ($CaO - Al_2O_3$)

Ca Reacts

Oxygen
Sulphur
Inclusion

$$(CaS) + (Al_2O_3) = (CaO - Al_2O_3) + \underline{Al} + \underline{S}$$

Al and S must be below curve

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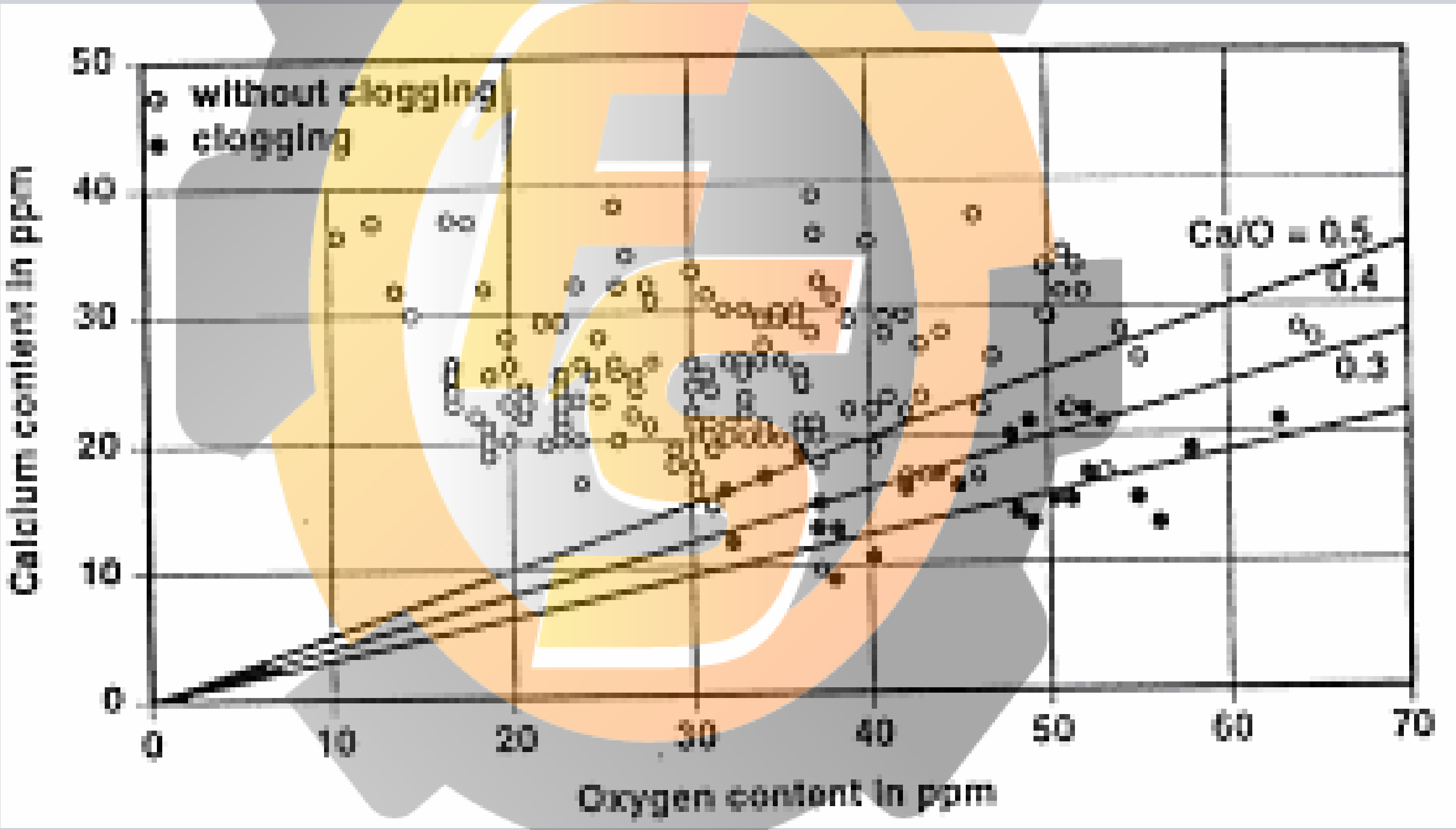
Clogging behaviour



Clogging behaviour dependent on the oxygen and calcium of the steel for Fe – Ca – Al treated heats

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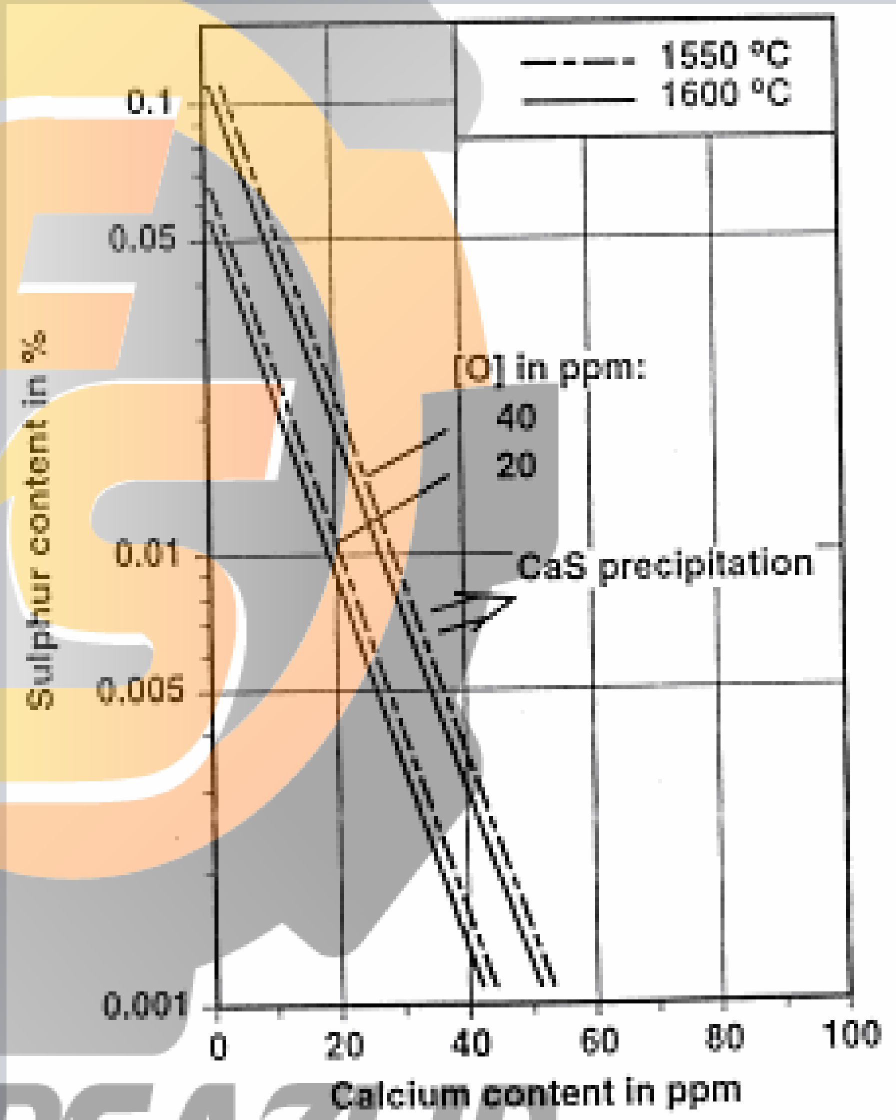
CaS precipitation

CaS precipitation dependent on calcium, oxygen sulphur content.



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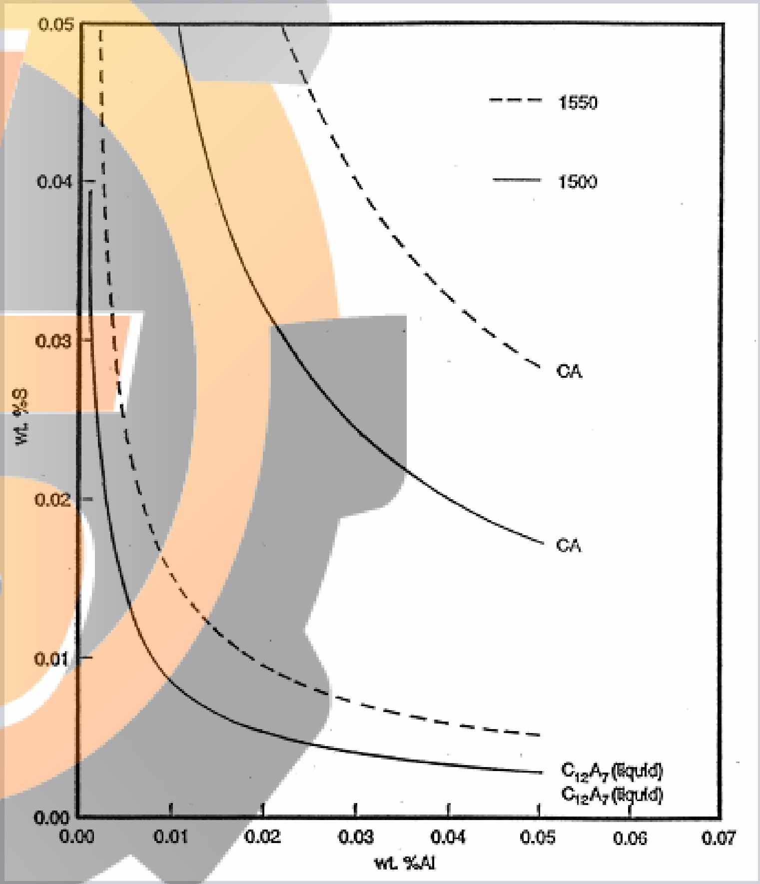
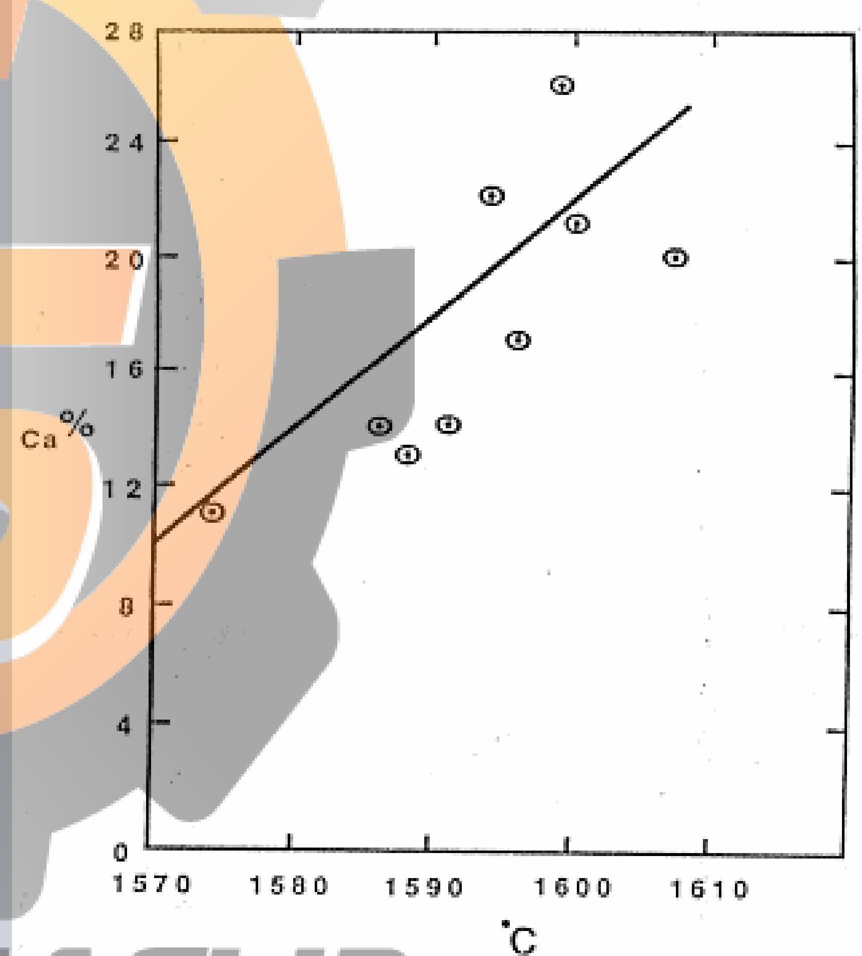
Equilibrium for CaS and $C_{12}A_7$



Univariant equilibrium for CaS (a_{CAS} = 0,74) and $C_{12}A_7$ or CA as a function of %Al and %S at 1550 and 1500°C

Calcium Retention Efficiency

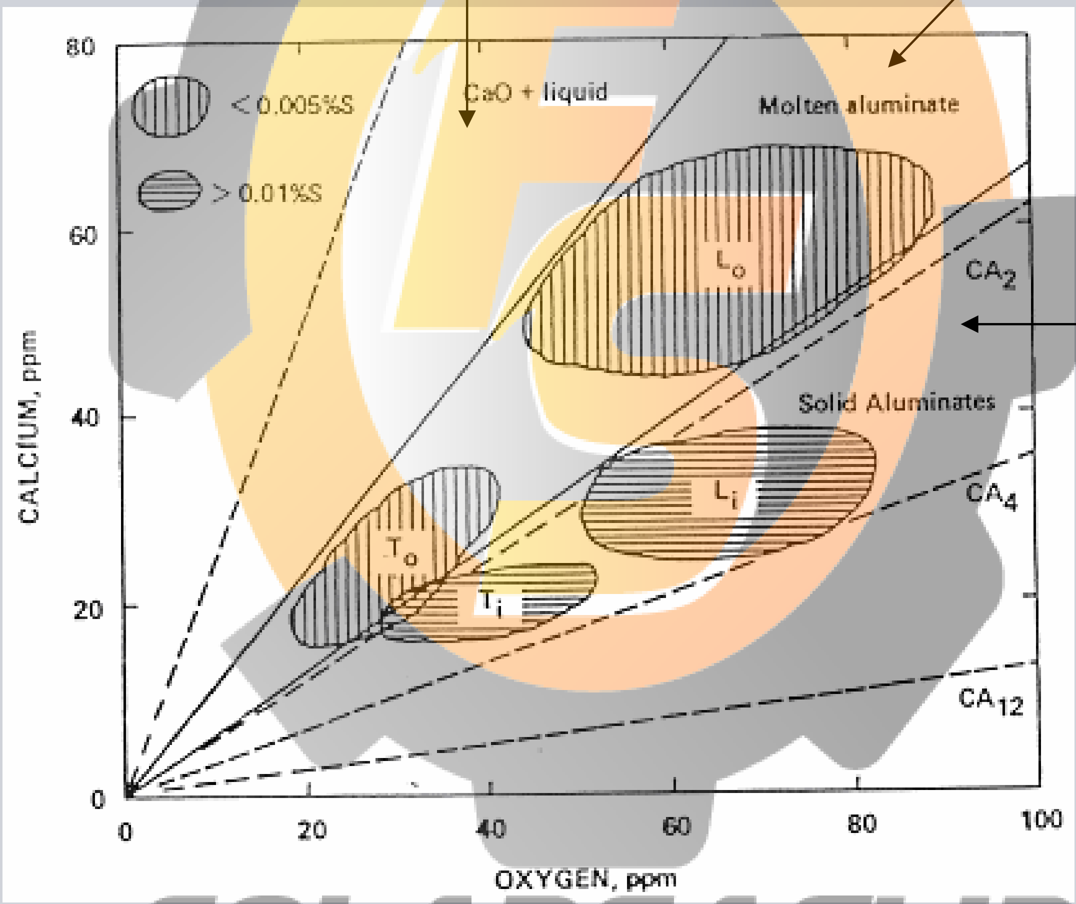
Calcium retention efficiency in the steel after wire feeding of CaSi (~30%Ca) at an average rate of about 180 m/min (~10kg Ca/min) into (123 ± 5), tonnes heats (~0,5 kg Ca/tonne total added). This figure shows the observed calcium retention efficiency in (123 ± 5) tonne heats as determined from the known quantity of calcium added and the calcium content of a sample taken after the calcium addition. Although the data show some scatter, there is a clear trend showing that the retention efficiency increases with increasing bath temperature, the net effect of a bath temperature increase is an increase in calcium retention efficiency, presumably because of faster reaction rates between calcium and the reactive constituents present in the steel.



Calcium and Tot. [O] content in Ca treated steels

Tundish

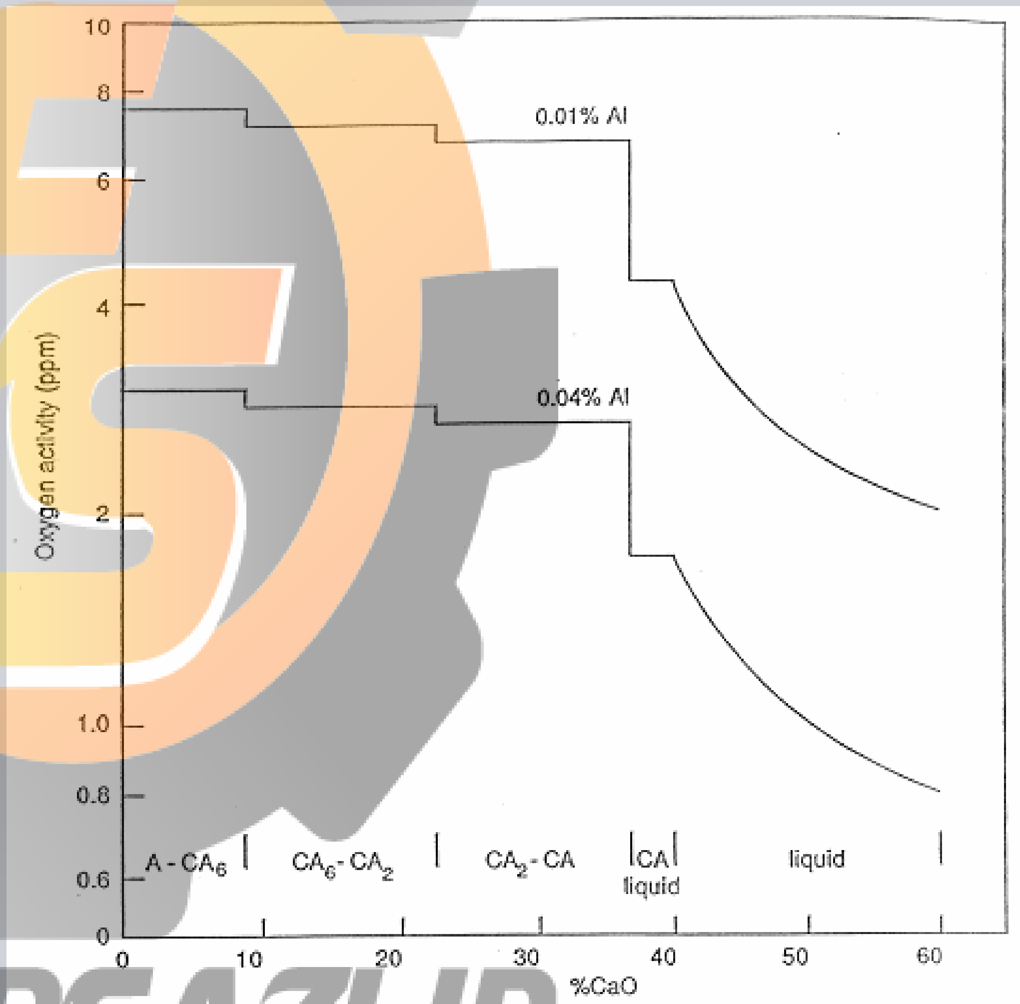
Ladle after De-S



Bad De-S

Oxygen Activities after Ca-treatment

Oxygen activity in Iron containing 0,01% Al and 0,04% Al in equilibrium with calcium aluminates at 1600°C.



Inclusion removal

•Low flow for removal

- 5 SCFM for 200 tonnes
- 5 – 6 minutes

• For cooling higher flows can be used but should finish with gentle stir.

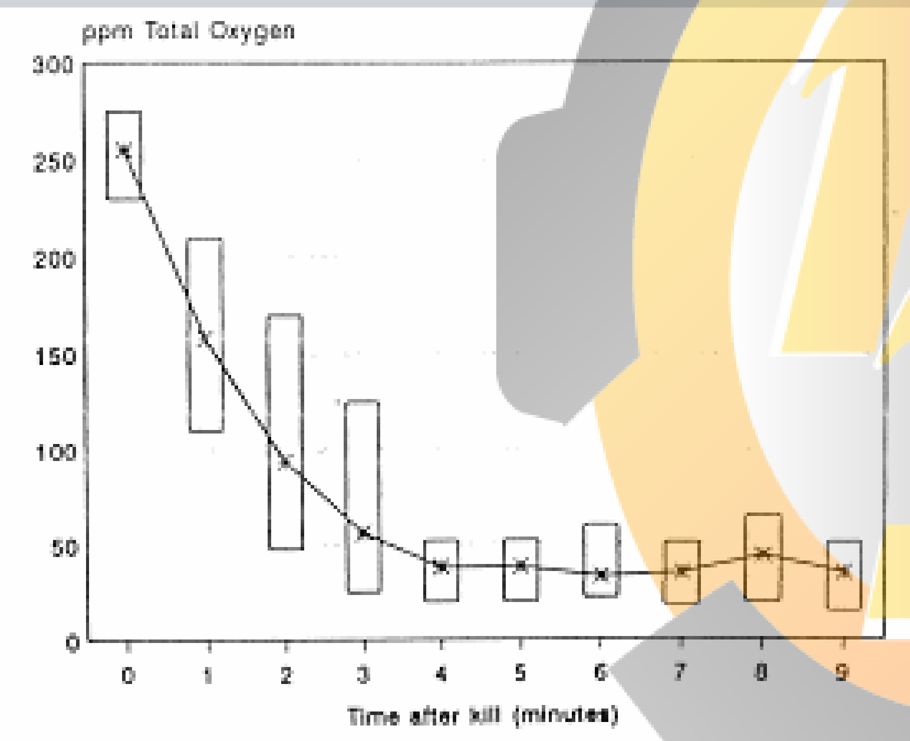
• Plugs are best.

• Lance can be used but more difficult to control and usually higher cost.

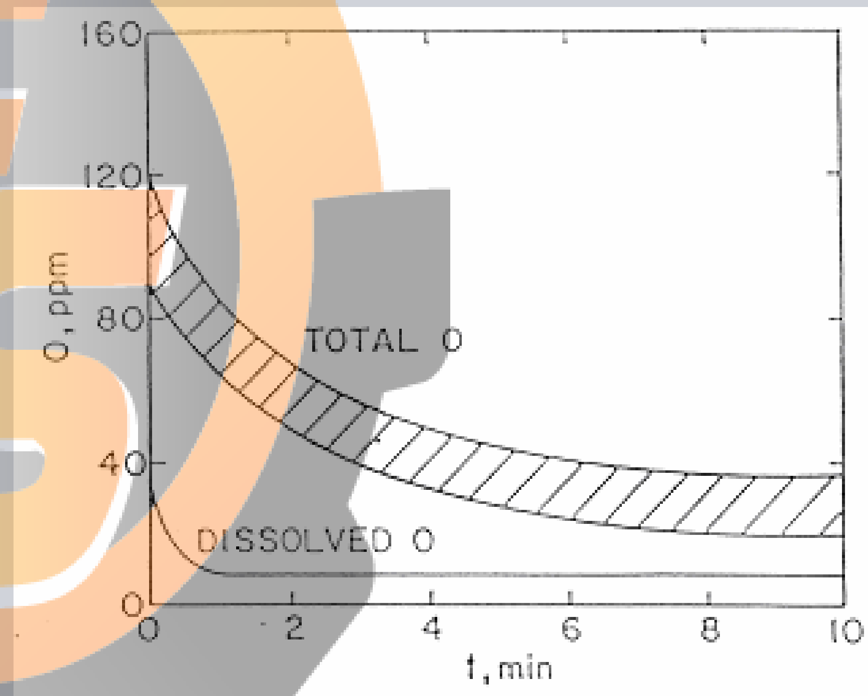
• Large inclusions float out easily.

• Gas helps make larger inclusions, provides fluid flow and inclusions attach to bubbles.

Total Oxygen



Total oxygen of LCAK heats during stirring after final aluminium deoxidation addition.



Rate of alumina inclusion removal with Ar bubbling.

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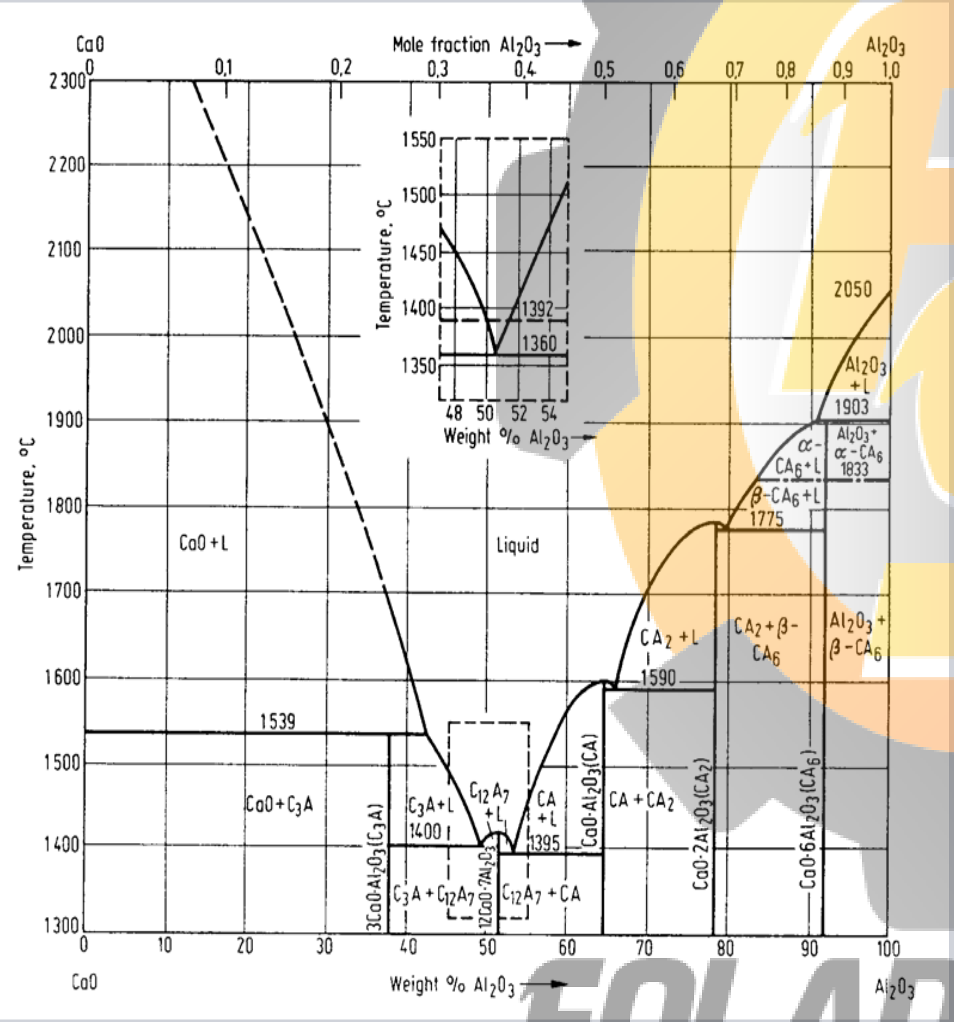
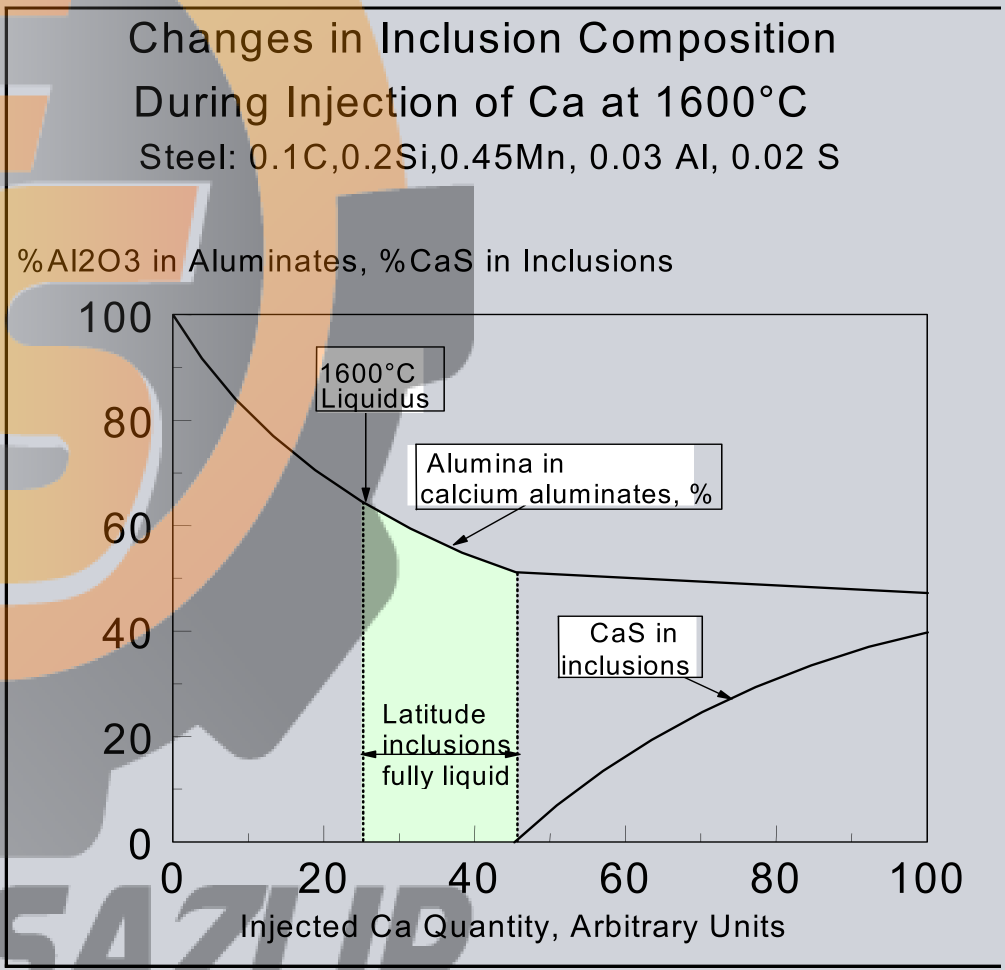
Al_2O_3-CaO





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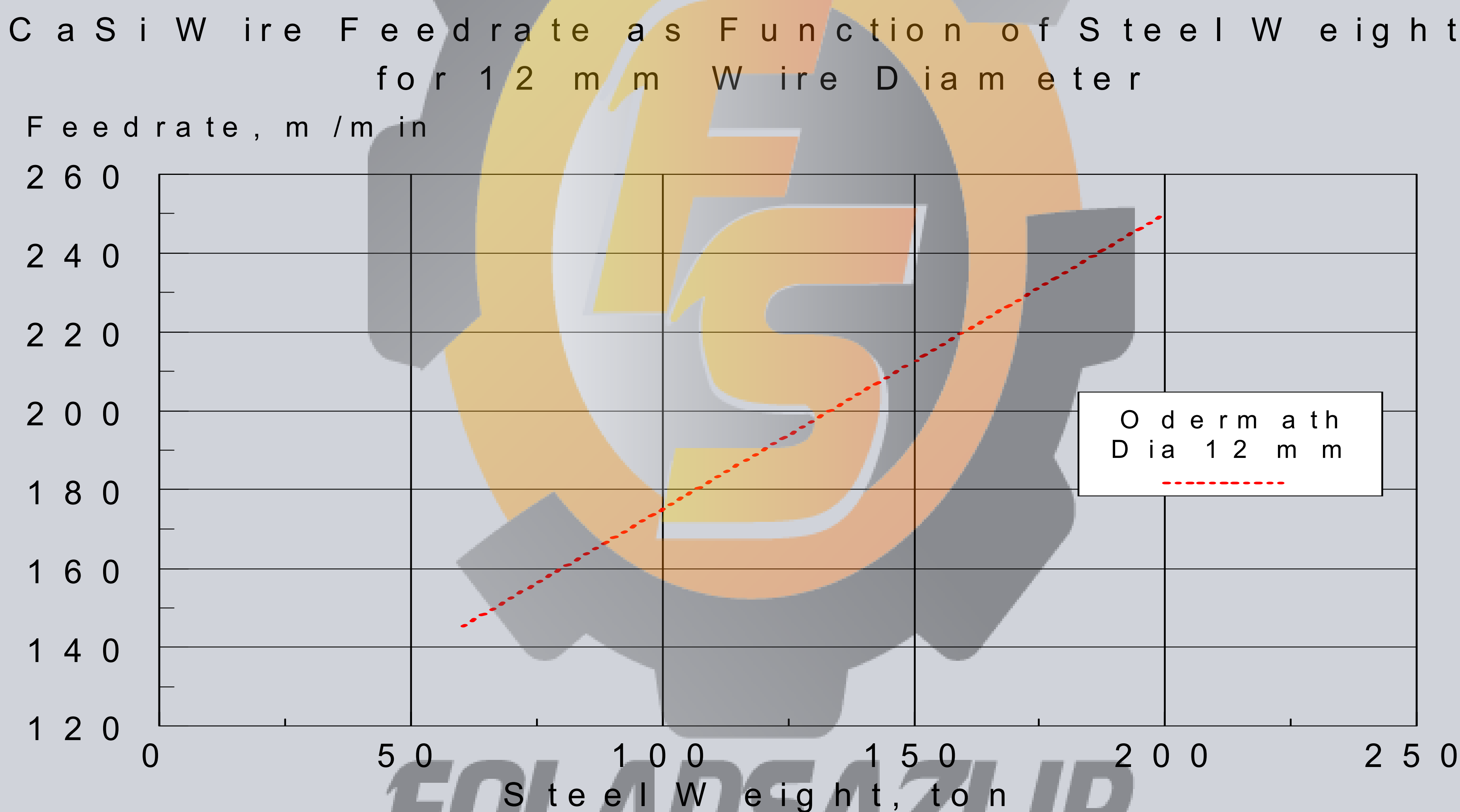

End

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