

EXPERIENCES OF INJECTION FOR DEOXIDATION AND DESULPHURISATION OF STEEL

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INTRODUCTION

The object of ladle refining of steel is to enable us to carry out some metallurgical refining operations:

- faster,
- with higher yields,
- with better reproducibility,
- to meet special requirements for the products.

A very promising method for the treatment of liquid steel in the ladle is by powder injection. Since the beginning of MEFOS in 1965 and especially since 1972 work has been carried out on the development of this technique. This work has been done as a corporative research project for the Scandinavian steel industry.

The studies are nowadays directed towards clarifying the mechanism behind

the success of this method. Experience shows that no thermodynamic miracles can be achieved.

EXPERIMENTS

Most of the experiments were carried out at MEFOS, the procedure being as follows: Scrap was melted in a 10 t electric arc furnace (figure 1). The melt was pre-deoxidized and the temperature adjusted to 1680-1700°C. The melt was then tapped into the ladle. Additions, e.g. synthetic slag, deoxidants, alloying elements, were made during tapping.

On arrival at the injection station (figure 2), the temperature and oxygen activity were measured and both the slag and steel were sampled. Further deoxidants were added in order to achieve the prescribed oxygen activity. The experiments were then conducted. Modified mould samples of the Rudberg

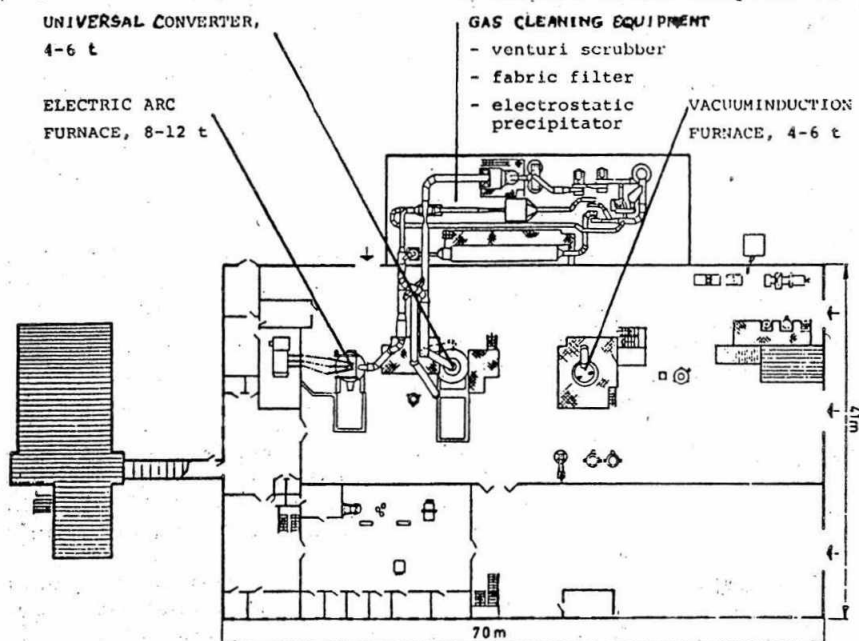


Fig. 1.: Main equipment of MEFOS, metallurgical research plant.

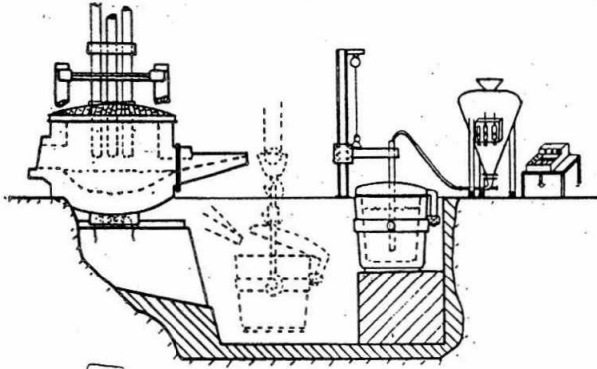


Fig. 2: Set up of MEFOS for injection experiments.

type were used. The steel samples were taken at the bottom of the ladle.

After finishing the trials the melt was poured back into the EAF, to adjust the composition of the melt, temperature etc. A low-alloy steel with the following composition was used:

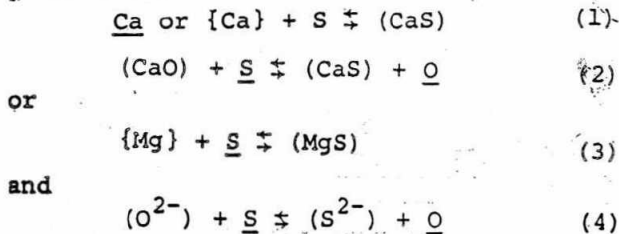
C Si Mn S_o Al_{sol}
 ~ 0.2% ~ 0.3% ~ 0.6% < 0.035% 0.001 - 0.200

Reoxidation experiments were carried out by either adding a batch of iron ore or continuously feeding iron ore to the top slag. This was followed by a rapid sampling of both the steel and slag.

The off-gas analysis, together with our process data systems, is of great help in preventing excessive oxidation of carbon. The actual injection time in the 7 t ladle is about 5-10 minutes.

DESULPHURISATION

The aim of the treatment of liquid steel by powder injection is often desulphurisation, or control of the sulphur content. This can hardly be done with good reproducibility in various vessels without knowing anything about thermodynamics and rate phenomena involved. For the desulphurisation of liquid steel the following reactions have to be considered.



It is not yet clearly shown that reactions (1) and (3) really take place when injecting calcium or magnesium in steel melts at 1600°C. Anyway the product of the reaction has to be dissolved in the slag on the top in order to avoid sulphur reversal. The maximum desulphurising result is thus controlled by (1).

- the attainable sulphur distribution, $\frac{(S)}{S}$
- the relative amount of slag, $\frac{m_s}{m_{Fe}}$

The product $\frac{m_s}{m_{Fe}} \cdot \frac{(S)}{S}$ is called relative sulphur capacity of slag.

Calculated and analysed sulphur distributions from samples taken after vigorous argon purging or powder injection in pilot plant trials, show good agreement (figure 3). For high sulphur distribution values well-reduced lime-rich slags are necessary.

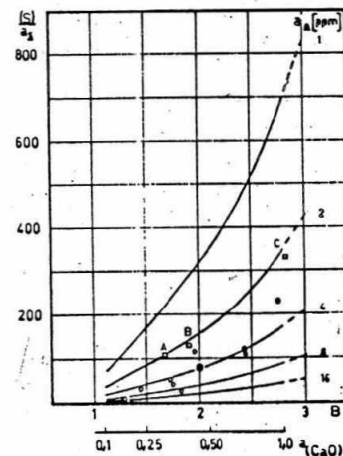


Fig. 3: Sulphur distribution as a function of slag basicity and oxygen activity (1)

$$B = \frac{{}^nCaO + {}^nCaF_2}{{}^nSiO_2 + {}^nAl_2O_3}$$

Studies on rate phenomena in desulphurisation may begin at a macroscopic level [1,2]. Three types of reactor behaviour could be observed:

- permanent reactor,
- transitoric reactor,
- combination of permanent and transitoric.

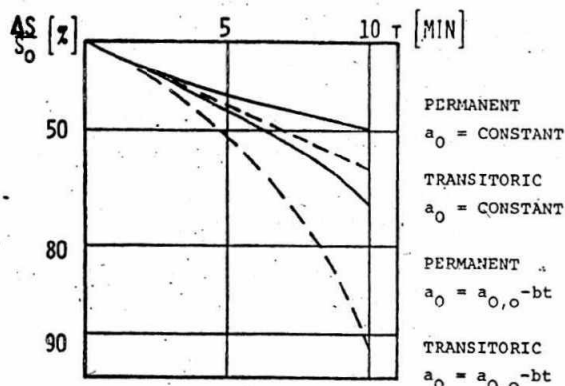


Fig. 4: Influence of types of reactors and t the change of oxygen activity on desulphurisation. (11).

The motivation for this type of study is illustrated in figure 4 and might be abstracted as: Save money!

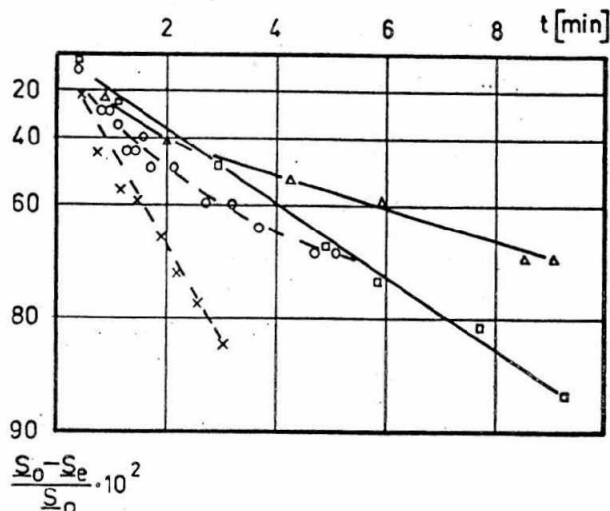
Investigations of the results from pilot plant trials show that the desulphurisation can be either transitoric or permanent, depending on the powder flow rate (figure 5). According to Burder [3], there is desulphurisation when sulphur content is under 0.015%, transitoric. Contrary to Burden's opinion that a calcium-injection always shows transitoric behaviour, research at MEFOS has shown that both permanent and transitoric reactors may occur. During a calcium-injection the oxygen activity is changing.

The behaviour of oxygen activity ($a_0 = f(\text{time})$) influences the observed desulphurisation. Thus even the permanent reactor can display straight time behaviour and even the accelerated course is possible and has been observed (figure 6). Thus the question of permanent or transitoric reactor is not easily confirmed. Without the possibility of continuously measuring the oxygen activity during injection, a pertinent conclusion about the reactor model cannot be drawn.

Studies at MEFOS have shown that reduction of slag via the melt is a slow reaction (4). The oxygen transport from the slag into the melt influences the desulphurisation and also the deoxidation.

After finishing the injection, the system is close to equilibrium. The sulphur distribution can be described as [5]

$$\frac{(S)}{S} = \frac{118.4 B - 205}{FeO_t} \quad (5)$$



	SYNTHETIC SLAG ADDED			ALUMINIUM		SULPHUR	
	INJECTION	TOP	TOTAL	INITIAL	FINAL	INITIAL	FINAL
	KG MIN	KG	KG TON	10 ⁻³ %	10 ⁻³ %	10 ⁻³ %	10 ⁻³ %
x---	23	69	35	14.0	106	46	64
o---	10	48	31	13.2	68	9	20
Δ---	12	104	330	10.3	5	6	17
□---	27	240	220	11.0	2	2	16

Fig. 5: Desulphurisation with lime-fluorspar-injection (12)

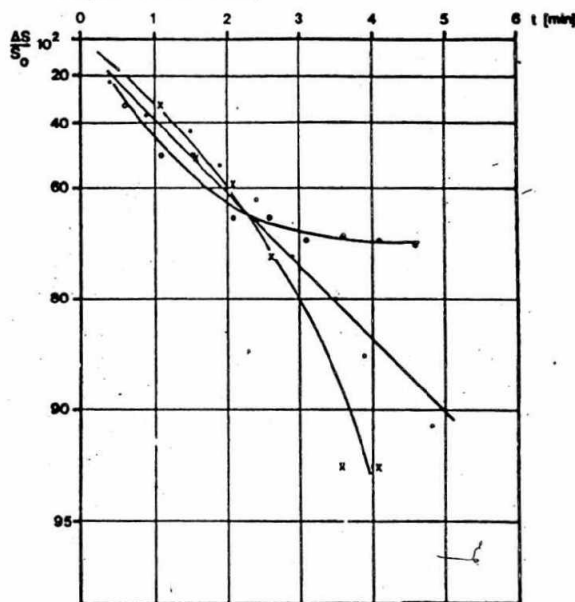


Fig. 6: Desulphurising by CaSi-injection as a function of injection time.

and

$$B = \frac{CaO + 1.4 MgO}{SiO_2} \quad (6)$$

An analysis of the hit rate of the desulphurisation can be made by an error calculation [6]. Two suggestions have to be made:

1. The desulphurisation is permanent.
2. The sulphur distribution is given by equations (5) and (6).

For a permanent reactor, the desulphurisation can be written:

$$w_s = \frac{S_o}{S_e} = 1 + \frac{(S)}{S} \cdot \frac{m_s}{m_{Fe}} = 1 + \left(\frac{118.4 B - 205}{FeO_t} \right) \frac{m_s}{m_{Fe}} \quad (7)$$

An error calculation according to

$$dw_s = \left[\sum \left(\frac{\partial w_s}{\partial x_i} \right)^2 \Delta x_i^2 \right]^{1/2} \quad (8)$$

with the following

i	\bar{x}_i	Δx_i
B	3.3	± 0.3
FeO _t	2.0	± 1.0
m _s	1 500	± 500
m _{Fe}	165 000	$\pm 2 000$

results in the following sum:

$$dw_s = (0.026 + 0.178 + 0.002 + 3.10 \cdot 10^{-6})^{1/2} \quad (9)$$

\uparrow \uparrow \uparrow \uparrow
 B FeO_t m_s m_{Fe}

This calculation shows the influence of slag-basicity, FeO_t-content of the slag, amount of slag and amount of metal on the result of desulphurisation. From equation (9) the following conclusion can be drawn: The two main parameters to be controlled are FeO_t-content and slag-basicity. But, the amount of slag has such an influence that we cannot neglect it. It is important that the right amount of top slag with the right composition is added. As mentioned above, the reduction of slag via the melt is a slow reaction and it is therefore important that the top slag has a correct composition for desulphurization.

Figures 5-6 show some desulphurisation results from pilot plant trials at MEFOS. The following conclusions may be drawn:

With lime-fluorspar injection, higher powder feeding rate gives a higher degree of desulphurisation when the other parameters are constant

(figure 5). This supports the predominance of a transitoric reactor model by injection of powdered slag.

DEOXIDATION

The work deoxidation can be used, meaning:

1. Lowering the dissolved oxygen content.
2. Lowering the total oxygen content.
3. Inclusion shape control. The composition of the inclusions are then changed so that
 - they are easier to remove,
 - they are less harmful for the mechanical properties of the steel.

The dissolved oxygen content may readily be lowered by deoxidants e.g. Si, Al. Here the outstanding possibility exists for a direct measurement, namely by using the oxygen probe. The oxygen activities shown in Table I have been measured by Celox Lo probes. Typical oxygen activities before the start of powder injection treatment at MEFOS are below 5 ppm.

Many studies have shown that deoxidation reactions of the first kind are quick, whereas the physiochemical reactions involved in the second type of deoxidation are rather slow. The final level of total oxygen achieved in 75% Al₂O₃-lined ladles is circa 20-40 ppm. This low oxygen content in the melt manifests itself in the form of a high degree of cleanliness in the steel product.

Figure 7 shows typical tracks of total oxygen content during argon purging. From different start levels the total oxygen content tends towards a final level, O_∞, which clearly differs from the dissolved oxygen content; the difference being oxygen contained in non-metallic inclusions.

The rate of removal of non-metallic inclusions is heavily influenced by the fluid dynamics of the system. Work is in progress to study the influence of different working parameters on deoxidation rates and to clarify the mechanisms involved. The following mechanisms may be put forward, separately or

Table I - Deoxidation and reoxidation in 7 t melts.

Type of treatment	Gas flow rate [dm ³ n/sec]	k ₁ [sec ⁻¹]	k ₂ [sec ⁻¹]	α
Argon stirring	3,3	~0,1	1,7	0,01
Argon stirring	8,3	0,36	1,4	0,01
Powder injection	11,4	0,36	2,7	0,01

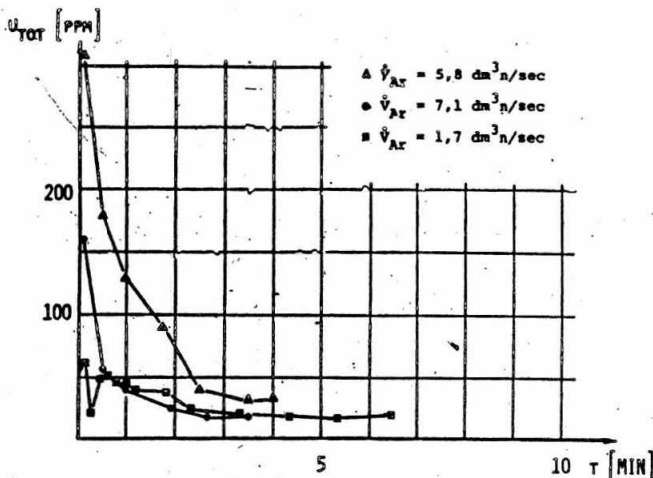


Fig. 7: Deoxidation of Al-killed steel with Ar stirring.

in combination, to explain deoxidation in a gas stirred ladle,

- flotation by gas bubbles,
- coagulation,
- rise by buoyancy,
- turbulent deposition,
- diffusioforetical deposition (surface tension gradients).

But the only evidence that we have today is that gas purging is a very efficient way of removing non-metallic inclusions.

Lowering of the total oxygen content closer to the dissolved oxygen content can be speeded up by stirring of the melt. The dissolved oxygen content, for instance, in an aluminium killed steel is about 5 ppm. Such low levels can seldom be reached during normal time of treatment. The reason is re-oxidation, e.g. transport of oxygen into the melt. The lining used and the

top are two of the main sources of re-oxidation (7). Two primary sources of reoxidation are:

- 1 Reduction of unstable lining or top slag.
- 2 Mechanical erosion of lining or drawing in of slag into the melt and dispersion of these particles/droplets in the bath.

Pilot plant trials of MEFOS have been carried out to study the reoxidation. The technique is mentioned under the chapter on experiments. The results from these experiments lead to a combined deoxidation-reoxidation model [8, 9] describing the total oxygen content:

$$O_{tot}(t) = O_1^* + \frac{m_s}{m_{Fe}} \cdot \frac{k_2}{(k_1 - \alpha k_2)} (O_{2,0}^* - O_1^*) e^{-\alpha k_2 t} + (O_{tot,0} - O_1^* - \frac{m_s}{m_{Fe}} \cdot \frac{k_2}{(k_1 - \alpha k_2)} (O_{2,0}^* - O_1^*)) e^{-k_1 t}$$

Response of melt analysis on bath addition of oxygen to the slag is shown in figure 8. Experimental values of the deoxidation constant k , and the reoxidation constant k_2 for different types of treatment are presented in Table I. One conclusion is, that in cases with incomplete slag separation when tapping the primary furnace, the slag reduction via the melt B rate is a determining factor. The model also suggests two ways of meeting the problem:

1. By minimizing the amount of slag to be reduced ($\frac{m_s}{m_{Fe}}$).
2. By increasing k_2 during the slag reduction period.

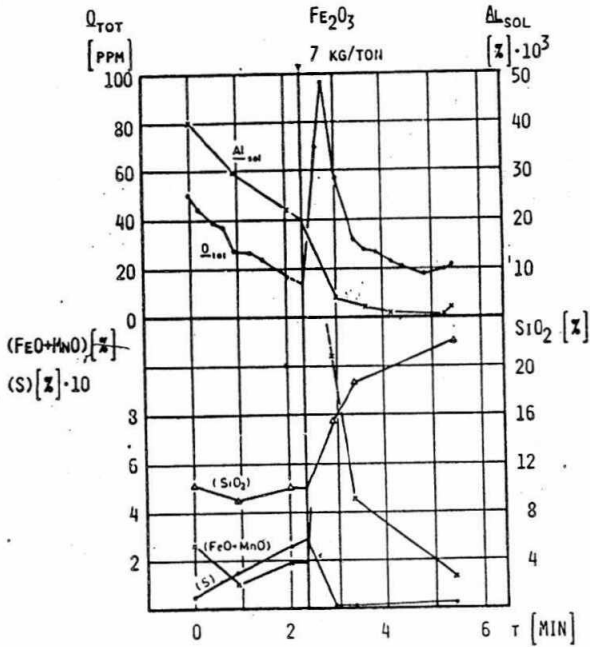


Fig. 8: Reoxidation of 7 ton melt with oxidizing slag during argon purging. $V_{Ar} = 7.5 \text{ dm}^3/\text{sec}$.

The conclusion from these two points is that a more stable surrounding should be used. A stable surrounding has been shown to be of the utmost importance to the final product and the reproducibility of ladle treatment.

CONCLUSIONS

Powder injection as a tool of ladle metallurgy has been studied at MEFOS in co-operation with Scandinavian steelworks. Good desulphurisation can be achieved by powder injection and argon stirring. To obtain reproducible results the thermodynamics of the system have to be under close control e.g. by a control of the amount of furnace slag transferred to the ladle. The amount of FeO in the slag should be low and the slag basicity high.

Deoxidation, here used to express the reduction of total oxygen content, has often been found to be a difference between large numbers. The deleterious influence of easily reducible oxides on the cleanliness of steel has been demonstrated.

The use of ladle injection metallurgy has grown dramatically during recent years. The benefits obtained from the process should insure its

continued development, growth and application.

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List of symbols

- B basicity
 k_1 deoxidation rate constant
 k_2 reoxidation rate constant
 m mass
 O_{tot} total oxygen content
 O dissolved oxygen content

Indices

Fe liquid steel
s slag
o at start ($t=0$)

*1 equilibrium in the melt
*2 equilibrium at slag-metal interface
∞ steady state