Yield Improvements During Iron Desulfurization When Utilizing "Flow Aided" Compounds for Modifying Slag Characteristics

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INTRODUCTION

The importance of sulfur management in treatment of hot metal has given rise to various technologies that incorporate plant operational techniques, delivery systems using a combination of reagents to optimize slag management for improved yield and desulfurization of iron. It is well known that effective desulfurization of hot metal is based on three factors which are: 1) Low oxygen content of the metal, 2) High slag basicity, and 3) reasonable slag fluidity. The desulfurization reaction that is related to the lime based reagents can be shown by the following reaction:[9]

$$(CaO) + [S] = (CaS) + [O] \qquad \text{Where } K1 = \frac{(a_{CaS})\,[a_O]}{(a_{CaS})\,[a_S]}$$

The (CaO) indicates this component in the slag phase and the [S] indicates this component in the metal phase. This implies simply, that for effective levels of desulfurization, the (a_{CaO}) should be as high as possible and the [a_O] should be as low as possible. As shown in studies by Dr. Ian Sommerville and Y.D. Yang , Univeristy of Toronto, sulfide capacity is one of the most important parameters for the molten slag to absorb the highest level of sulfur from the metal. Slag characteristics also impact the iron yield as a result of the desulfurization process where iron particles can be trapped in the slag itself as well as the reduction of iron oxide from the slag.

Evidence can be shown to an improved approach for producing a carrier material for use with particulate passivated magnesium for injection into a ladle contained molten iron. The blended carrier material and passivated magnesium improves the characteristics of the slag to increase iron yield while providing effective desulfurization of the hot metal. The key points are characteristics of the blended carrier material that influence the injection techniques and the slag properties to achieve these results. What is more important in the development of these reagents are the benefits to the steel plant. This paper tries to provide data and discussions that are evidence of this improvement in the hot metal treatment.

Background Information

Desulfurization technology developed as a result of the need to reduce cost and increase productivity in the hot metal process. Slag management and sulfur management became key in these improvements. Use of reagents introduced into the hot metal had been through mechanical stirrers and by dunking materials filled with magnesium into the ladle. These conditions created environmental problems due to the fuming of the reagents.

The next critical step to desulfurization technology was the development of subsurface pneumatic injection of reagents blended with pulverized lime in a mono-injection lance system. Further improvements were achieved with co-injection which allowed for injection of a magnesium reagent with multiple combinations of lime blended products stored in silos and controlled mixing of the reagents in the transport system. (Fig. 1.)[3] This allowed for adjustments in the ratios of reagents and delivery rates as needed. The benefit of blended reagents is the elimination of segregation due to consistency in sizing and density of the improved flow aided blends.

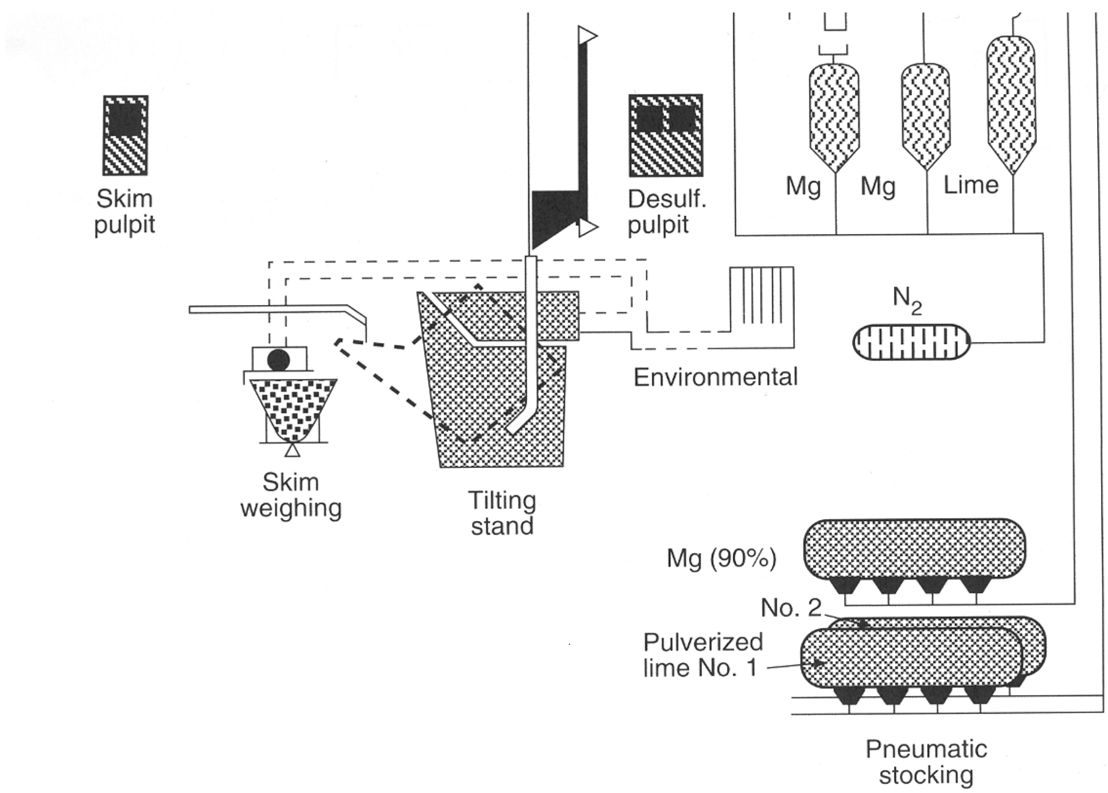

Fig. 1 Diagram of hot metal treatment station using co-injection technology – LTV

Some recent developments and current status of hot metal desulfurization as well as new improvements in technology continue to impact hot metal desulfurization listed in Table 1:[6]

Table 1: Recent Developments and Current Status for Hot Metal Desulfurization

Product Specs	Auxiliary Equipment & Services	Reagents	Process Control	New Technologies
Low Sulfur metal less than 0.010%. Increasing demand from customers.	Dual port & dual lances for injection Contract desulfurization services and technical support at the plant.	"Flow aid treated blends" Use of slag fluidizers in lime blends for slag conditioning to improve metallic yield.	Process controlled injection systems for least cost and consistency in the production process.	Mini-mill evaluating technologies for the scrap replacement with iron production Hismelt, AusIron, and other technologies.

Discussion on Characteristics of "Flow Aided" Carrier Materials

The carrier material of choice for injection with magnesium metal is a lime base product blended with various reagents that typically include calcium aluminate and spar. (Table 2.)[1]

Table 2

Carrier Material Composition

Compound	Formula	wt %
Calcium Oxide	CaO	54 - 74
Aluminum Oxide	Al_2O_3	19 – 32
Magnesium Oxide	MgO	4 max
Calcium Fluoride	CaF_2	10 max
Silicon Dioxide	SiO_2	2.5 max
Iron Oxide	Fe_2O_3	1.0 max
Phosphorus Dioxide	P_2O_5	0.025 max
Titanium Dioxide	TiO_2	0.025 max
Manganese Oxide	MnO	0.5 max
Sulfur	S	0.05 max
Polymethyl Hydrosiloxane	$(CH_3)3SiO[(CH_3)HSiO]x\ Si\ (CH3)_3$	0.01 – 0.02
Combined LOI/Moisture		1.5 max
Particle sizing		200 Mesh

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The presence of oxygen decreases the chemical efficiency of the magnesium which is the predominant component for sulfur removal. Therefore severe turbulence during injection is not desired where exposure to the atmosphere can influence the magnesium. However, a moderate amount of turbulence is beneficial for the desulfurization process because of the slag metal interaction.

It is also important to consider which reagents can decrease the oxidation potential in the process. Low quality reagents can unfortunately provide an oxygen source even though the reagent appears to be cost effective. A balance has to be made on pricing versus the impact of the composition on the desulfurization process.

Some of the primary reasons to utilize calcium aluminate with lime in the hot metal desulfurization process are:[2]

- Improved desulfurization efficiency
    - increases fluidity of the top slag and enhances the sulfur partition ratio of the steel/slag exhange
- Reduced iron losses
    - reduces quantities of iron particles in the slag because of improved slag viscosity
    - reduces splashing of slag and iron during skimming of the ladle

The binary diagram below shows the low melting point (less than 2525 ^{o}F) of calcium aluminate which has a direct influence on the fluxing of the finer lime particles in the flow aid blend (fig.2):[5]

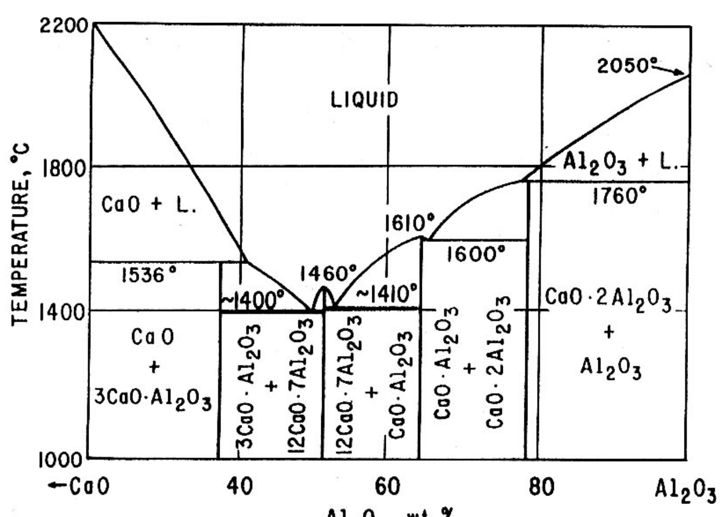
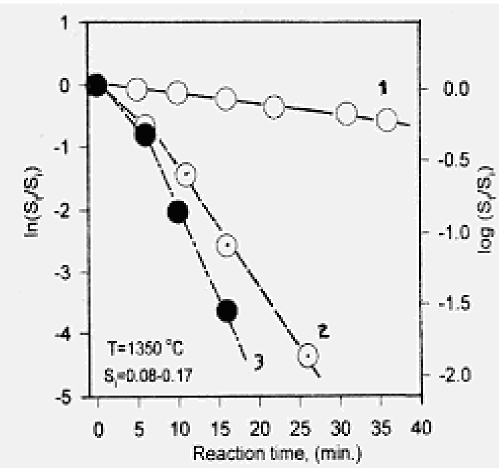


Fig. 2 Phase-equilibrium diagram for CaO-Al_2O_3 system.

The carrier material is delivered through a lance using an inert transport gas and passivated magnesium particles that are introduced into the stream for mixing during injection into the ladle. The ratio of the carrier material to the passivated magnesium being injected into the molten iron is in a range of (2.5 to 6):1. The pressure of the inert gas in the dense phase system is adjusted in a range of 100 to 200 psi where approximately 150 psi is typical. In the dilute phase system pressures are as low as 70 psi. In a paper presented by Dr. Peter Koros, R. Petrushka of LTV Steel Company and T.R. George of TG Associates on the "Flowability of Powder Materials" show that "powders which tend to flow tend not to pack, and powders which tend not pack tend to flow."[3] The treatment of lime with the flow aid prevents the tendency to pack as is normally experienced in powdered lime.

Particle sizing impacts the efficiency of the injection systems which are designed on consistency of delivered material. Common experience and scientific fact shows that smaller particles will go into solution faster than larger particles of the same product.

Particle size has a definite effect on desulfurization rates in the ladle. When comparing lump lime (12-20mm) with the same composition of pulverized lime (<0.124mm), Dr. Sommerville and Y.D. Yang indicted that additional pulverized reagents blended with the lime have dramatic effects in the increased desulfurization rates. Fig. 3 shows the comparison of particle size on the desulfurization rate.[9]



Effect of particle size and CaF_2 addition on desulfurization rates at 1350°C,(50g flux mixture containing 60% total lime).

1. Flux A+lime, $d_{P,flux\ A}$<5mm, $d_{P,lime}$<15mm,
2. Flux A+lime, $d_{P\ for\ all}$<0.124mm,
3. Flux A+lime+CaF_2, $d_{P\ for\ all}$<0.124mm.

Fig. 3 Effect of particle size and additions on desulfurization rates.

When producing smaller sizes of product for injection, problems occur related to the physical and chemical attractions that occur between particles. This causes compaction and caking actions that are not conducive for transport using inert gases. It requires very high volumes of gas in order to fluidize material such as this. The "flow aid" concept is associated with the reaction of the siloxane derivative that is added with the finely pulverized blended product. It produces a product that does not allow adherence of the blended pulverized particles with lower gas volumes. The main interactions between fine powder particles can be seen by:[3]

- **Mechanical** – forces that include surface tensions which causes interlocking of irregular shapes.
- **Electrical** – forces can hold particles together by attraction of positive to negative charges or repulse because of similar charges.
- **Molecular forces** – Van der Waals –which are chemical forces between molecules that are relative weak which are usually dipole-dipole forces.

What forces are involved in a particular solid are dependant on the materials involved, size and shape and conditions such as temperature and pressure. Particles with sizing around 200 mesh tend to agglomerate because of the increased surface energy related to the larger surface area.

In the case of pulverized lime particles, surface charges tend to be associated to electrostatic interactions that become dipolar in nature. Whereby, on one side of the lime particle there are positive charges and on the opposite side of the lime particle there are negative charges. Polar compounds can dissolve in water and are usually not soluble in non-polar solvents. Lime tends to be polar in nature which is why it can dissolve in water. However, with the addition of the flow aid, the dynamic flexibility of the long chained non-polar molecule attaches to the lime powder in a chemical bond that changes the characteristic of the powder to non-polar so that it reduces the inter-particle attractions that are associated with powdered lime. This treated lime will not dissolve in water, but will react with other non-polar material. An example of how the structure influences the surface attractions can be characterized in Fig 4.

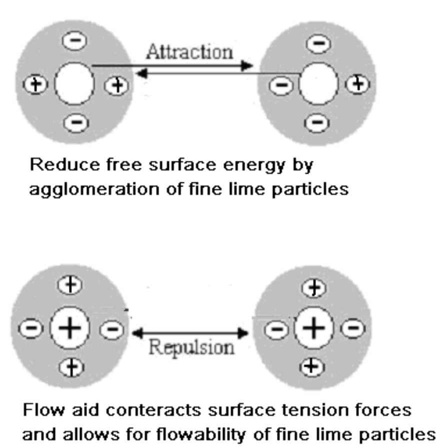


Fig. 4 Flow aided ingredient influences electrical charges on the particles to repel other particles.

The characteristics of the "flow aided" carrier material which provides for the solid blend product to flow with a "milk like" viscosity provides the following advantages for the hot metal desulfurization process:[1]

- produce a more homogenous mixture of material being injected
- reduce desulfurization agent surging during injections
- reduce molten iron splashing related to surging
- reduce environmental issues from molten iron splashing
- reduce the iron yield reduction related to splashing of molten iron
- reduce the iron yield reduction related to the slag characteristics which retains metallic iron and prevents efficient slag raking.

Discussion on slag characteristics and yield improvements

Slag management encompasses chemistry of the slag to achieve the following:

- Lower iron losses
- Improved desulfurization
- Characteristics of the slag to accommodate slag removal after injection.

Final slag formation and slag volume is achieved by controlled injection of a specific lime blend to achieve the characteristics which are related to the chemistry of the arriving slag and also the chemistry of the blended reagent used for desulfurization.

Previous recommended basicity for desulfurization of hot metal was between 3 and 4 as defined by N.A Voronova using the formula (CaO + MgO+ MnO) / (SiO2 + Al2O3).[7] A highly basic slag is required as noted previously but it must be fluid enough to avoid trapping iron particles. Other elements which impact fluidity of the slag are iron oxide, silica and titanium oxide content of the slag. When comparing the use of prior art material (flow aided lime only as the carrier material) versus the blended carrier material, it can be seen in Table 3. that the total iron content of the slag is reduced in the carrier blend compared to the basicity ratio of the two slags after desulfurization:

Table 3. Comparison of after injection slag chemistry

Element	Prior Art Material	Flow Aided Blend
CaO	13.42%	19.9%
Al2O3	0.37%	6.04%
SiO2	5.35%	15.43%
MgO	2.31%	18.5%
MnO	0.42%	1.63%
C	6.13%	5.04%
S	0.99%	2.62%
Total Iron	70.78%	30.24%

The practice for injection techniques of one of the trial plants involved combining the carrier material of 200 mesh and magnesium metal of 14 to 20 mesh as one desulfurization agent. Approximately 50 – 100 pounds of flow aided blend is pre-injected into the molten iron prior to injecting the combined magnesium / flow aided blend. Following completion of injection for the required Mg / flow aided blend, an additional 300 - 500 pounds of flow aided blend is injected.

This practice results in a slag conditioned so that it ”crumbles” and releases the entrapped iron. From the slag chemistry in Table 3. the basicity of the slags using Voronova’s formula for “prior art material”is about 2.82 versus the lower basicity of the “flow aided blend” of 1.86. The nature of the higher basicity is a slag that is higher viscosity and can easily trap iron particles from the injection process. The improved slag’s characteristic is that it appears to form a granulated “patty” that is easily skimmed off with a raking machine. This results in a 42.7 % reduction in time required for skimming as compared to use of prior art material injection only. This also translates into less heat loss from the molten iron and increased productivity.

Trials at several plants has yielded data that show the improvement in iron loss related to slag skim weights as seen in Fig 5.

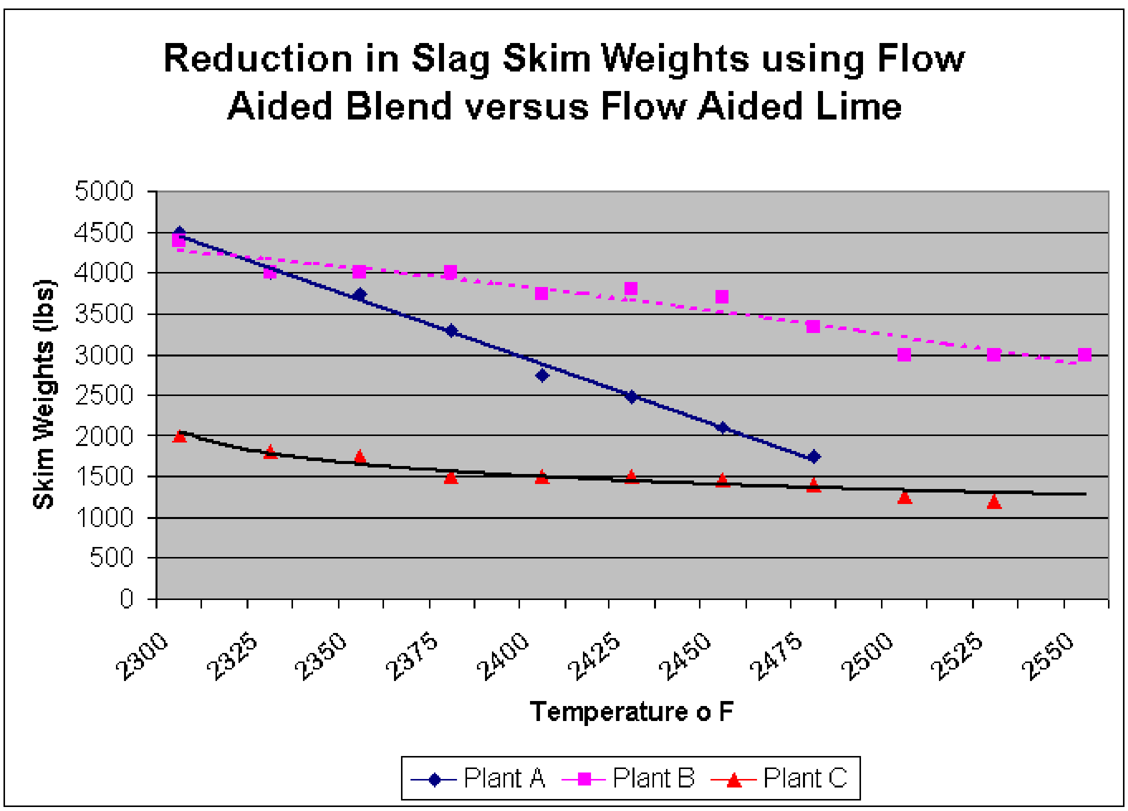


Fig. 5. Graph of trial plants showing reduction in amount of slag skimmed using “flow aided blend” as compared to the prior art material (flow aided lime).

It can be noted that the data is normalized for presentation and that any scatter in the raw data can be related to the variability of the skimming process. It is affected by technique of the operator, positioning of the ladle and conditions of the equipment utilized in raking the slag off the ladle. The characteristic of the improved slag as compared to the previous slag conditions clearly impacts the skimming weights and the retention of iron particles in the slag influencing yield improvements.

Iron Losses

Analysis of slags showed a typical average analysis of total metallic iron content of the lime / spar blend injected slag to be approximately 65% Fe and for the calcium aluminate / lime / spar flow aided blend to be approximately 30.2% Fe. An example of possible cost savings can be calculated with the understanding that each plant has differences in equipment, delivery cost of materials and operational practices. The calculation is only used as an indication of what savings is possible for this steelmakers example:

Lime /Spar blend: 10,500 lbs slag skimmed * 65% Fe in slag = 6,825 lbs Fe in the slag.
Flow aided blend: 7,100 lbs slag skimmed * 30.2% Fe in slag = 2,144 lbs Fe in the slag.
Difference of Fe savings = 4,681 lbs

At \$140 per ton cost of hot metal * 40 heats per day * 4,681 lbs Fe = \$ 13,107 per day! If iron yield savings were based on an annual production, this steelmaker would realized a savings of \$4,613,664! A slight decrease in this number would be related to raw material costs at the plant and cost associated with the operational philosophy of a particular plant.

Summary:

1. The characteristics of the improved blended carrier material provides homogeneity of fine particle sized reagents with excellent flowability and consistency in injection parameters for controlled hot metal treatment.
2. Consistent desulfurization of the hot metal can be attributed to the characteristics of the top slag which is due to the fluidity of the slag for metal / slag interactions.
3. Significant improvements in iron yield can be realized because of the slag chemistry at iron making temperatures that provides a slag that prevents retention of iron particles entrapped in the slag.
4. Physical slag characteristics related to slag chemistry improves skimming of slag from the ladle reducing the loss of hot metal from the ladle.
5. Cost savings to the steelmaker are seen in time savings during treatment, efficient use of reagents and improved iron yield.

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