# MECHANISM AND REDUCTION OF INSOLUBLE SLAG OR DROSS FOR CLEANER METAL

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## Article Takeaways:

1. Increasing cell count in grey iron, especially for thin section castings
2. Understanding the sulfur effect in treated ductile iron for a given magnesium content
3. Why you should improve standard calcium bearing 75% ferrosilicon inoculation in cast irons

For many years, ferrous and nonferrous metalcasters have been tackling the issue of insoluble slag or dross on a daily, continuous basis during their melting and pouring process. Depending on the industry segment, cleaning fluxes have been a vital part of achieving clean, quality metal. Others are slowly adapting flux technology as a cleansing tool.

Cast iron foundries have managed slag build-up in many facets of melting and pouring of the molten metal. Whether coreless induction, channel induction or cupola melting, fluxes have become necessary as charge materials quality and metallurgical treatments dictate. In pouring applications, fluxing has helped alleviate buildup in poor thermal conditions of the vessel or ladle.

## WHAT IS THE MECHANISM OF INSOLUBLE BUILD-UP IN MOLTEN METAL

Buildup of slag on furnace walls and inductor loops from emulsified slag phases in molten metal is a classical crystal nucleation and growth process. It can be somewhat simplified into two explanations: thermodynamic and mechanical theories.

A thermodynamic explanation of buildup formation:

When considering the reasons for the initial formation of buildup, both sedimentation and thermodynamics are essential. The phenomenon of the buildup in a channel furnace is related to the type of insoluble oxides that are formed or introduced within the molten metal. Thermodynamic considerations are of obvious importance in predicting the complex mineralogical compounds present in the buildup.

As the metallic charge is melted, and after the initial liquid slag phases start to precipitate as the initial nuclei, followed by a thin solid film or substrate on any furnace refractory surface. Thus, typical crystallization growth of insoluble buildup proceeds quite easily and rapidly. It is a valid assumption that insoluble buildup will initially begin to deposit, based on the Gibb's

Free Energy of Formation values for each complex compound present. This liquid glass or slag phase will nucleate and grow on the deposited buildup because the surface of the initial buildup or solid slag phase is similar to the liquefied slag or glass phase attempting to precipitate out of solution.

The order of precipitation of ceramic compounds can be predicted by thermodynamic calculations but this is extremely difficult due to the complex chemistry of the systems involved. This concept has seemingly been verified by observation of the order, orientation and morphology of buildups observed in previous research.

Another factor in the formation of buildup can be considered similar to the general principles of ceramic crystallization. At the melting point of a ceramic material (or any material), the Gibbs's Free Energy of Formation ($\Delta G_f$) for a given quantity is the same whether it is crystalline or liquid. At lower temperatures, the crystalline form that has a lowest free energy, will precipitate out first. However, this does not readily happen unless there are nucleation sites.

In the absence of nuclei, crystallization does not occur unless the system is cooled to a point below a critical temperature at which crystallization is spontaneous. Unfortunately, very little is known about the thermodynamic properties of the complex systems involved so it is not possible to develop a method to predict critical temperatures for this crystallization theory. However the behavior of this formation can be compared to other ceramic formations.

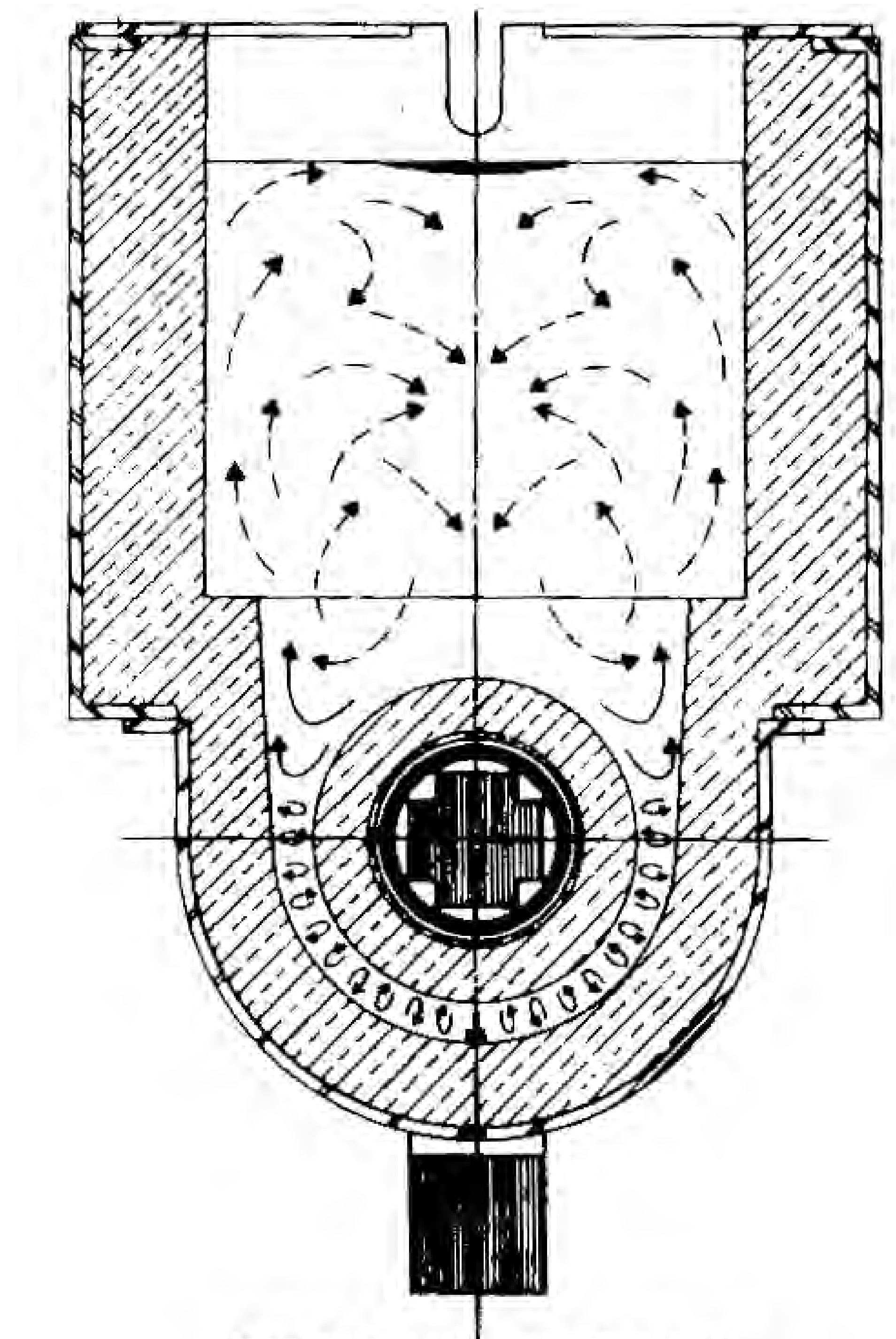
A mechanical explanation of buildup formation:

Prominent research has proven the mechanisms for the formation of alumina buildup in pouring tubes and referred to three basic conditions that had to be satisfied: (1) particles have to come in contact with the refractory surface, (2) particles have to adhere to the refractory surface, and (3) particles have to adhere to each other so as to sinter and form a network. This work explained the importance of metal velocity, especially in areas close to the surface where flow velocity is a function of the frictional force between the refractory surface and the molten metal. If the metal flow is kept at a high velocity and not allowed to remain in an idle or slow-moving state, the tendency for buildups to occur is usually reduced.

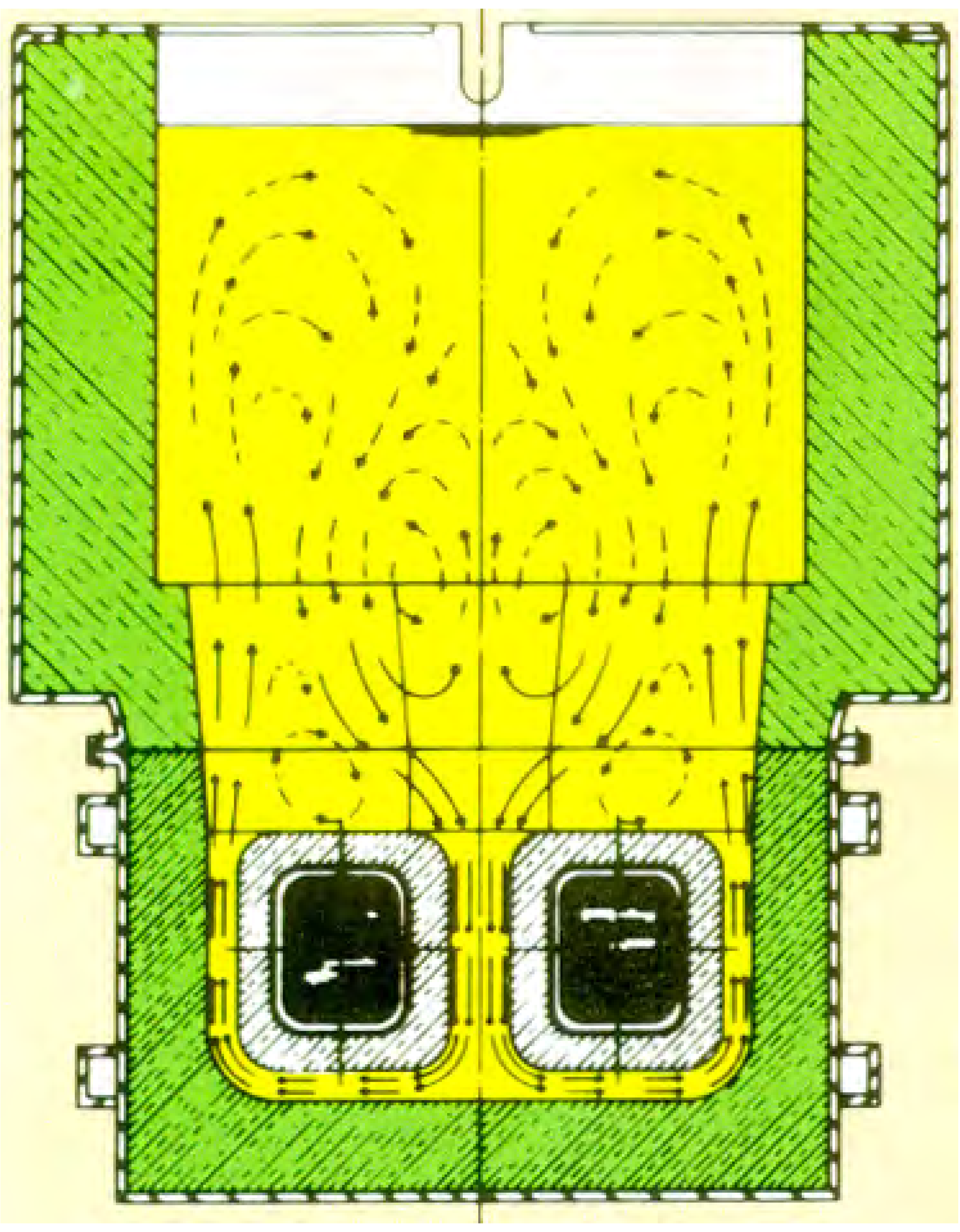
Stirring action of an inductor is pronounced when the inductor is placed on high power. This "stirring action" refers to the actual metal flow through the inductor channels. Whether in a single loop or a double loop inductor, the molten metal is superheated within the inductor channels and enters the upper body through the throat.

## Circulation of Molten Metal in a Channel Induction Furnace

In either inductor case, the "stirring action" is not as well defined when the furnace is left on low hold power such as during an idle weekend operation. During these periods, the areas of minimal flow occur in the boat section (the transition section between the channels at the top of the inductor) or in the refractory areas in the throat that are adjacent to the molten metal stream emanating from each channel. These represent the "dead" zones where metal does not circulate as effectively as it does within the channel. The mechanical mechanism for buildup can be further supported by sedimentation of the insoluble oxides in the low flow areas. This is helpful in explaining initial buildup.



STIRRING PATTERN



## TWO EXAMPLES OF CAST IRON INSOLUBLE BUILDUP, THE IDENTIFICATION OF COMPONENTS AND FLUX TREATMENTS:

### Example #1

### Treated Ductile Iron Magnesium Fade in Holding Pouring Applications

Since the introduction of ductile iron, foundries have managed the inevitable problem of loss of magnesium, i.e., "mag fade" when holding and pouring treated ductile. The magnesium fade often creates insoluble build-up which will result in significant capacity loss for ladles / unheated pouring boxes, and inductor/throat failure for operating pressure pour furnaces. Significant downtime can be attributed to insoluble build-up and the required cleaning maintenance.

An example of a Magnesium Silicate build-up in the presence of a magnesia matrix is shown below. This is a typical build-up scenario for Magnesium fade in treated ductile iron.

Magnesium Silicates, $2MgO \cdot SiO_2$ (Forsterite)
Melt temp 3,434oF(1890C), $\Delta G$form@2,700 oF = -13,017 Cal/mole
$2MgO + SiO_2 \Rightarrow 2MgO \cdot SiO_2$

From the Gibbs Free Energy of Formation calculation, at 2700 F magnesium silicate is quite stable. (A moderate low negative value for the $\Delta G$) When holding or pouring treated ductile iron, molten metal temperatures will be less, which would translate into more stability for this compound. In the presence of a flouride-free flux, Calcium Oxide can react as follows:

Calcium Oxide on Forsterite,
$2CaO \cdot SiO_2 + 2MgO \cdot SiO_2 \Rightarrow 2(CaOMgO) \cdot 2SiO_2$ (Diopside) @2,700°F
Melt temp 2,536°F(1,391°C) $\Delta G$form = -33,922 Cal/mole

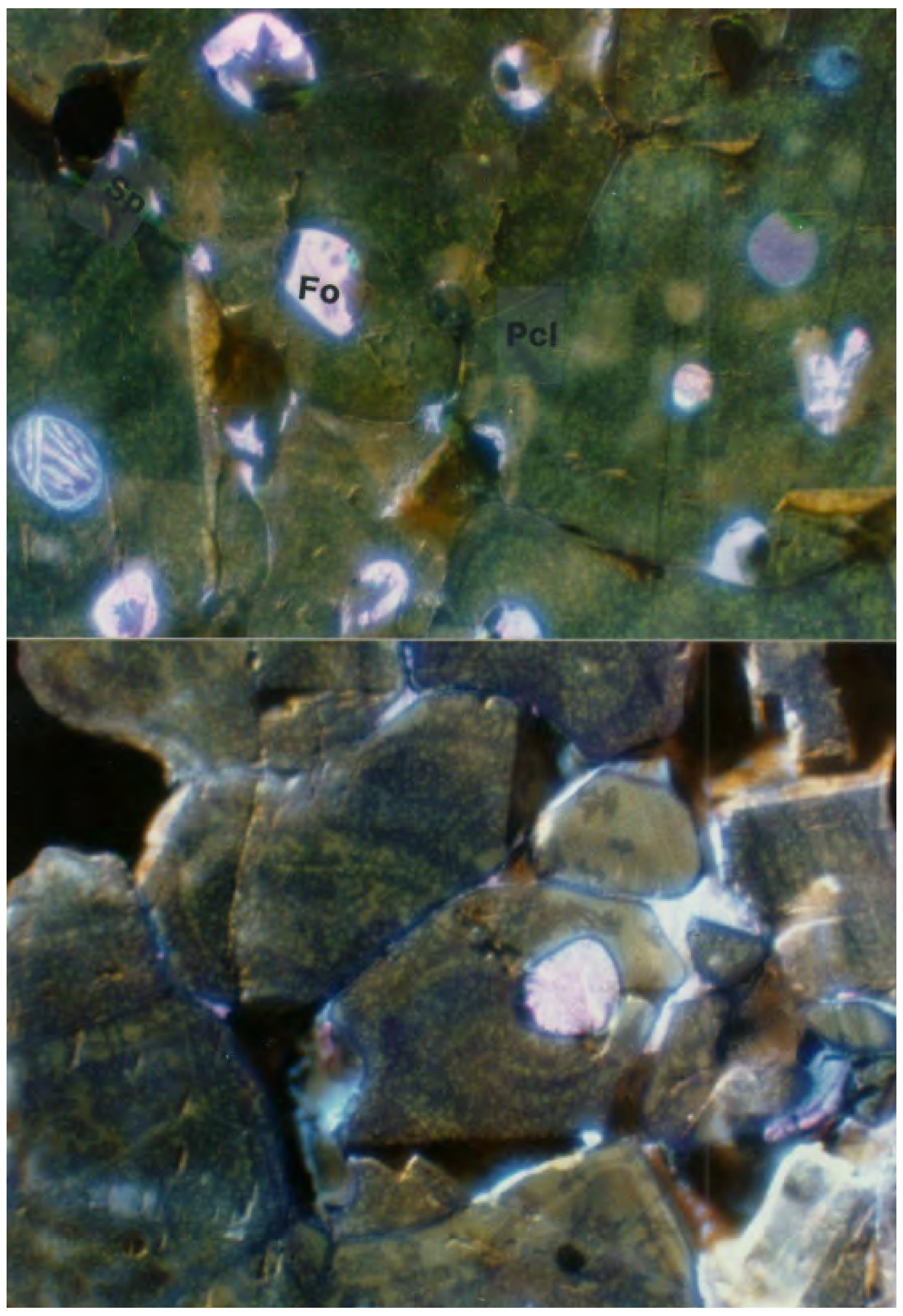
When considering buildup obtained from fading treated ductile iron, the chemical analyses will reflect major presence of MgO along with MgS. While it is impossible to stop this "fade," how foundries can maintain daily and weekly cleaning can help prolong the service hours of the pouring and treatment equipment.

To help to control the insoluble MgO and MgS from "mag fade", an addition of ½ to 1 pound of flouride-free flux to every ton of molten metal in a treatment vessel or ladle, is an improvement and will allow for increased service life.

### Example #2

### Channel Induction Furnace – throat buildup in cast iron, grey or ductile-base.

Many cast iron foundries utilize a channel induction furnace for melting or holding/pouring molten metal continuously. As charge or molten metal continuously enters into the channel furnace, the presence of slag and insoluble remnants is floating within the metal. When the metal level is dropped to minimum heel level, the likelihood of this slag to reach the throat opening is inevitable. Below is an example of a severe clogging of the throat opening of a typical channel furnace melter.



This furnace is a 35 ton vertical channel furnace melting grey and ductile-base iron. A common insoluble precipitate in initial build-up formation is an Alumino Silicate, $3Al2O3\cdot 2SiO2$ ( Mullite)

Alumino Silicate, (Mullite)
$3Al_2O_3\cdot 2SiO_2$
Melt temp 3,380°F(1860°C),ΔGform @2,700°F = -3,177 Cal/mole
$3Al_2O_3 + 2SiO_2 \Rightarrow 3\ Al_2O_3\cdot 2SiO_2$

The addition of ½ to 1 pound of flouride-free flux to every furnace charge is extremely beneficial in preventing buildup, evenly distributed throughout. If a flouride-free flux isn't used, slag buildup will usually proceed more rapidly once the first stages of buildup appear on furnace refractory.

For channel holders or pressure pour furnaces, the addition of a flouride-free flux to every transfer ladle will assist in keeping those ladles clean as well as cleanse the metal in the ladle and remove various slag phases from the metal. For such applications, EF40LP in 1 pound bags are recommended.

Other considerations for flouride-free flux are on current build up constituents in cast iron applications are shown below. As was previously mentioned, Gibbs Free Energy of Formation helps to identify the possible reactions that can occur first followed by other reactions.

Here are some examples of Calcium Oxide reacting with various insoluble build-up components.

Calcium Oxide on Mullite, $3Al_2O_3\cdot 2SiO_2$
$3CaO + 3Al_2O_3\cdot 2SiO_2 \Rightarrow 3(CaOAl_2O_3)\cdot 2SiO_2$ Anorthite @2,700°F
Melt temp 2835°F(1557°C) ΔGform = -33564 Cal/mole
Calcium Oxide on Forsterite, $2MgO\cdot SiO_2$
$2CaO\cdot SiO_2 + 2MgO\cdot SiO_2 \Rightarrow 2(CaOMgO)\cdot 2SiO_2$ Diopside @2,700°F
Melt temp 2,536°F(1,391°C) ΔGform = -33,922 Cal/mole
Calcium Oxide on Sulfur , $2CaO + 2S \Rightarrow 2CaS + O_2$ (Oldhamite)
Melt temp 4,577°F(2,525°C) ΔGform = -86,573 Cal/mole

When considering a flouride-free flux, similar reactions can occur with Sodium Oxide as well.

$Na_2CO_3 + SiO_2\ \Delta\ Na_2SiO_3 + CO_2$
$Na_2O + SiO_2 \rightarrow Na_2O\cdot SiO_2$
Melt Temp 1,990°F (1,088°C)
$Na_2O + Al_2O_3 \rightarrow NaAlO_2$
Melt temp 3,002°F(1,650°C)
$Na_2O + Al_2O_3 \rightarrow Na_2O\cdot Al_2O_3$
Melt temp 2,469°F(1,353°C)

As observed, this fluoride-free flux can readily react with insoluble build-up when used as prescribed.

Cast iron foundries can now understand some formation criteria for the daily buildup that they are challenged with. Included were two examples for iron melting and pouring that are common in many cast iron foundries. No longer should there be a negative stigma towards flux usage in cast iron foundries as there are definite benefits for cleaner metal.

When used properly, Redux EF40 flouride-free flux can assist cast iron foundries to achieve improved furnace capacity, extended service life and improve metal cleanliness. Improved metal cleanliness directly correlates to improved mechanical properties for the castings.

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