

**SYNTHETIC SLAGS**  
**FOR**  
**STEELMAKING**

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## **Introduction**

Slag making has always been a part of steel and iron making. After all, at least 10% of what is produced in the steel and iron making process is slag. In ancient times, the secret to steel and iron making was in the slag formulations. Today's steelmaker has a better understanding of the importance of slag compositions and their affects on steel economics and quality. In the past, slagmaking took place in primary melting units, but with changing technologies and the advantages of ladle stirring and LMFs, virtually all slag making takes place in secondary melt operations and no longer in the primary melting units.

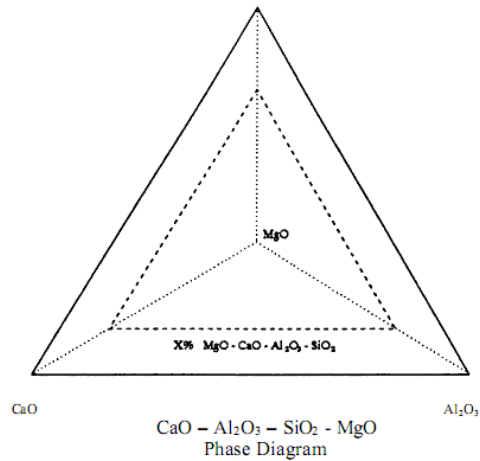
There is an old saying in steel making "Take care of the slag and it will take care of the metal". Slags are an important part of making steel quality. They remove unwanted oxides, sulphides, nitrides and phosphides. They provide a cover to protect refined steel from reoxidation and nitrogen and hydrogen pickup. Slags are also the basis for effective calcium treatment to improve castability and yields for continuous casters. However slag compositions must be closely controlled or else they will cause additional problems and become liabilities. Improper slag compositions can lead to harmful reversion of S, P, Si, and various oxide inclusions. If the slag liquidus is above the casting or teeming temperatures, they may require excess energy to flux and stabilize to a more liquid phase. Also there is the possibility of removing desired elements in the steel such as Al, Si, Ti, Mn, V, Nb, Cr, etc.

Instead of letting the steelmaking process determine the slag composition, it is possible and practical to engineer synthetic slags to improve steelmaking economics and quality. By understanding melt dynamics and the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  system, one can make an educated prediction of slag compositions which would be beneficial for individual steelmaking processes. Synthetic slags are a valuable and necessary tool for steelmakers to derive the maximum benefits by minimizing or eliminating the detrimental effects of process slag compositions. We will attempt to demonstrate how synthetic slags would apply in aluminum killed (AK) and silicon killed steels.

## **Steelmaking Slags**

Slags in the steelmaking process are complex single phase solutions in the molten state and multi-crystalline phases in the solid state. They serve to collect harmful impurities, provide a cover for the refined steel, and hopefully have minimal wear on refractories. By nature, they are less dense than steel which allows secondary refining to further improve metal quality by gathering inclusions that float out. The three properties of slag that we are interested in are: a) composition, b) melting point, and c) viscosity.<sup>1</sup>

Since steelmaking slags are mostly composed of oxides, fluorides, aluminates, and silicates, it is difficult to find phase diagrams that characterize a specific composition. Fortunately, in practical steelmaking, it is not crucial that we know all the compounds and complexes that are formed in slags. In steelmaking slags we will generally find CaO, MgO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, and MnO. Obviously, there are numerous other minor components but they have generally little effect on slag characteristics so we can discount them. One of our other objective for synthetic slags is extending refractory life, so calcium fluoride is eliminated from the slag making additives. By minimizing carryover slags from the furnaces to the tap ladles, we can also control the amount of FeO and MnO. Today's practices for aluminum killed and silicon killed steels also insures that FeO and MnO levels are relatively low (<6%) in the final slag compositions. That leaves us with the task of characterizing a CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>-MgO -slag. Unfortunately there are a limited number of phase diagrams of CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, systems at a specific MgO composition (Figure 1). MgO's presence in the slag composition is important and its primary function is refractory protection.



**Figure 1**

In practical steelmaking, according to Schuhmann, “it is satisfactory to assume that the behavior of MgO in slags is substantially the same as that of CaO.”<sup>1</sup> Which leads us to perhaps the most important phase diagram in AK steelmaking - the CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system (Figure 2).

In the process of producing AK Steels, the oxygen levels in EAF heats after decarb are around 1000 ppm (a little higher in BOF’s). Aluminum is added to the tap ladle along with CaO, MgO, Mn, Si and various microalloy elements for deoxidation, slag making, and steel specification. The purpose of the Al is to deoxidize the steel and improve alloy recoveries. It also deoxidizes carry over slag and modifies refractory contaminants. The slag making components are there to absorb the oxidation products, provide a cover, and have the capacity to absorb sulphides. Of the four major slagmaking components (Al<sub>2</sub>O<sub>3</sub>, CaO, MgO, and SiO<sub>2</sub>), Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> levels are dictated by the steel's oxygen content and specification, which does not always place the slag's composition in the most beneficial region x of the CaO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system (Figure 3).

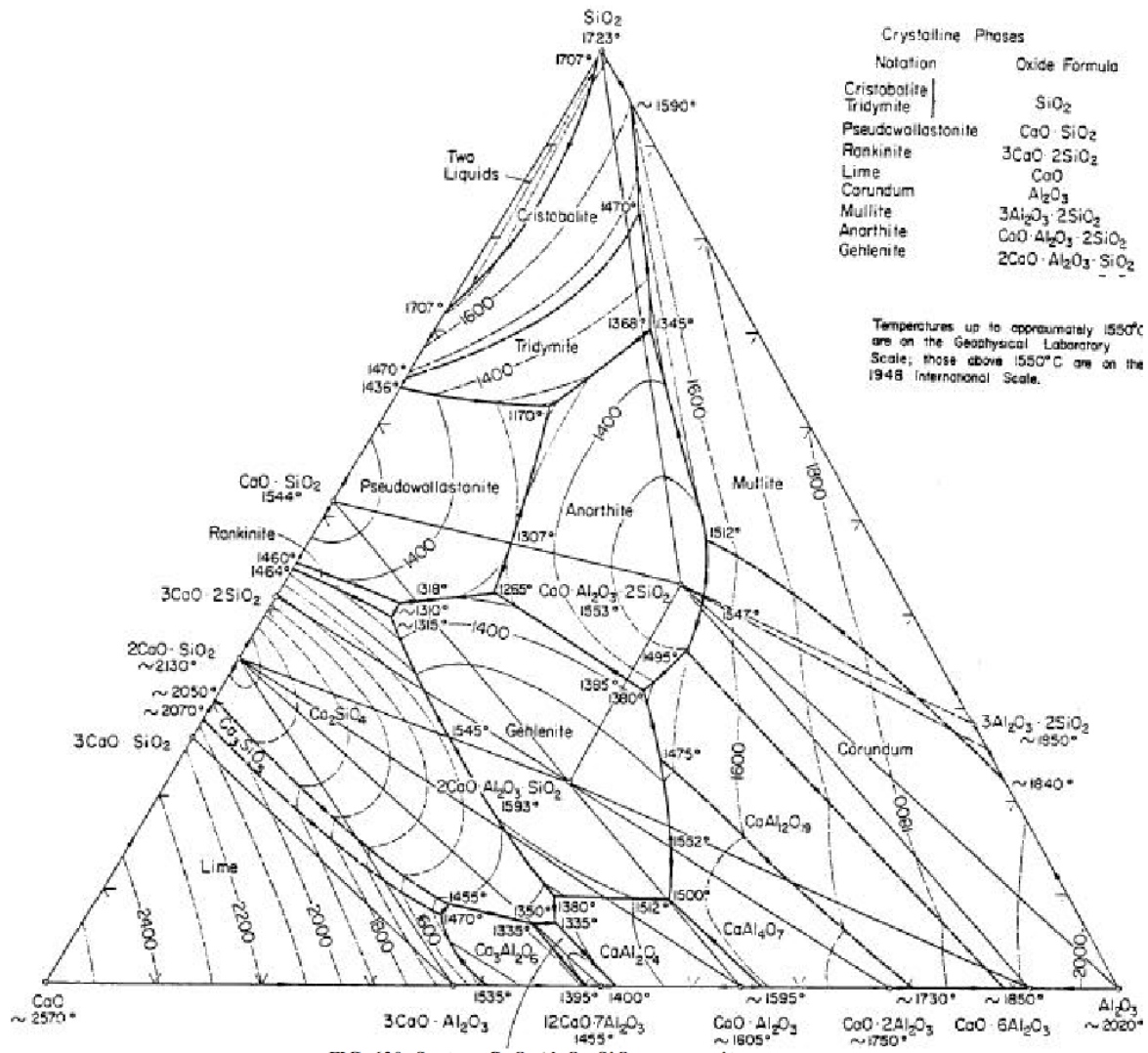


FIG. 630.-System CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>; composite.

E. F. Osborn and Arnulf Muua, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 1, published by the American Ceramic Society and the Edward Orton, jr., Ceramic Foundation, 1960.

Figure 2  
CaO - Al<sub>2</sub>O<sub>3</sub> - SiO<sub>2</sub> System<sup>3</sup>

Region x is beneficial for AK steel since it has the best sulphide capacity<sup>4</sup>, melting points below steelmaking temperatures, compositions compatible with calcium treatment, and cause minimal wear on most ladle refractories. AK steels for galvanizing, tin plating, and paint adherence have low Si requirements and therefore the residual SiO<sub>2</sub> in the carry over slag must be kept low. It is possible in region x (Figure 3) to achieve a fluid slag with less than 10% SiO<sub>2</sub> and still have good sulphide capacity (Figure 4).<sup>4</sup>

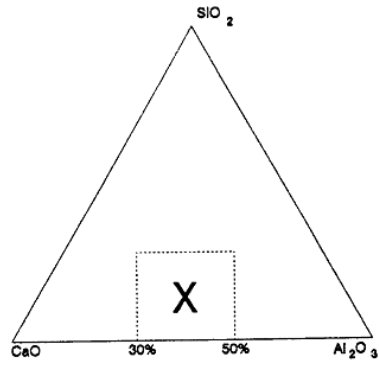
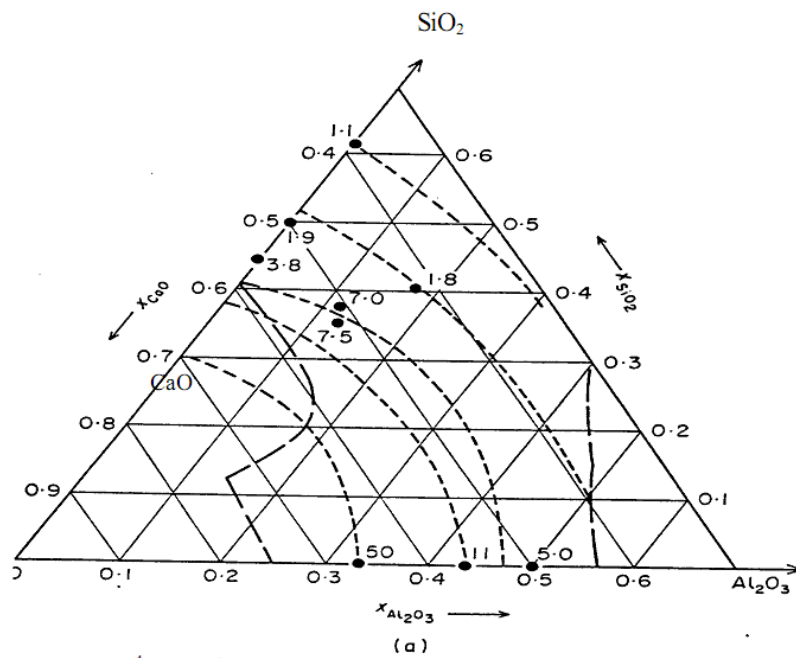


Figure 3  
Beneficial region in CaO – Al<sub>2</sub>O<sub>3</sub>– SiO<sub>2</sub> for AK Steel



(a)  
Sulphide capacities  $\times 10^4$  at 1650°C in CaO+SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub> melts (2). Broken lines show iso-capacity contours; heavy dash lines show liquid composition limits at this temperature.

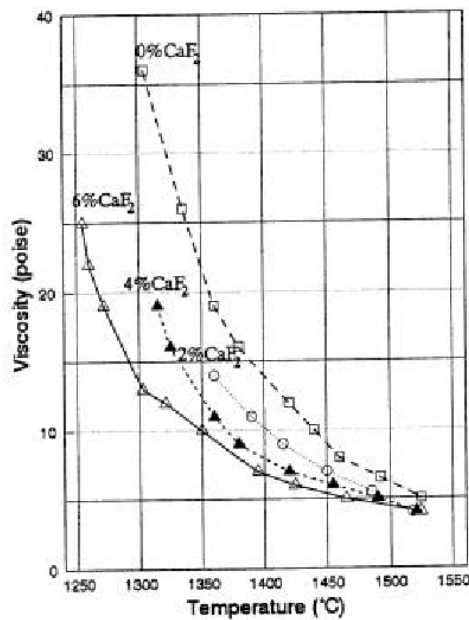
Figure 4  
Sulphide Capacities at 1650°C in CaO – Al<sub>2</sub>O<sub>3</sub> – SiO<sub>2</sub> System<sup>4</sup>

Secondary steelmaking LMFs are nothing more than low powered EAFs. They operate by heating up the slag which in turn heat up the steel. This is to prevent reoxidation and recarburization, along with a cover protection from nitrogen and hydrogen. If the slag is crusty and viscous, energy must first be expended to fluidize the slag at a higher temperature before the reheat and inclusion absorption process by the slag can occur.<sup>5</sup>

Often slag viscosity is confused with its melting point since temperature does affect it, but it is possible to lower a slag's viscosity without changing its melting point (Figure 5).

We are familiar with the effects of  $\text{CaF}_2$  when it is added to crusty and viscous slag. Unfortunately, we also know what it does to our ladle slag lines. Not only does  $\text{CaF}_2$  lower the slag's melting point, it also weakens the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  bonds - hence the lower viscosities that are observed. This is the same mechanism that erodes ladle slag lines.

Since the Al and Si additions are process determined, there may not be enough  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  generated to place the slag composition in the beneficial range. This is when a prefused synthetic slag addition can be used to modify the process slag into beneficial range x. Synthetic slags can be engineered with the proper  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  balance, taking into account the oxidation products of the AK steelmaking process, to achieve final ladle slags that have a good sulphide capacities, ability to absorb inclusions, low viscosities, lower melting points than steelmaking temperatures, and have minimal refractory wear. The properly engineered synthetic slag should be prefused to minimize energy consumption at LMFs and possess a low melting point so it can be introduced into the tap ladle early to take advantage of a longer refining period.



**Figure 5**  
**Effects of CaF<sub>2</sub> on Slag Viscosities (after Kozakevitch)<sup>2</sup>**  
**(44% SiO<sub>2</sub> - 12% Al<sub>2</sub>O<sub>3</sub> - 41% CaO - 3% MgO)**

Silicon killed steels are usually low in Al (<.006%) and except for structural steels, most of the end products are bar, rod and wire. They are normally continuously casted as round or square billets and through small diameter nozzles (<25 mm). Al is avoided since Al<sub>2</sub>O<sub>3</sub> is notorious for clogging nozzles and are nucleation sites for stress failures. Since there is little Al<sub>2</sub>O<sub>3</sub> available except for contaminations in the charge materials, alloys, and refractories, Si killed steelmaking slags are characterized by the CaO - MgO - SiO<sub>2</sub> system (Figure 6). The lowest melting region in this system is when the CaO - MgO - SiO<sub>2</sub> ratios are approximately 2:1:2. However from a steelmaking perspective, this region has poor sulphide capacity and very corrosive to refractories. To solve these problems, most melt shops add enough lime or dolomitic lime to make the slag more basic and less corrosive. The penalty is the possible addition of fluorspar to lower the slag viscosity and increase energy consumption at LMFs without any great sulphide capacity increases.



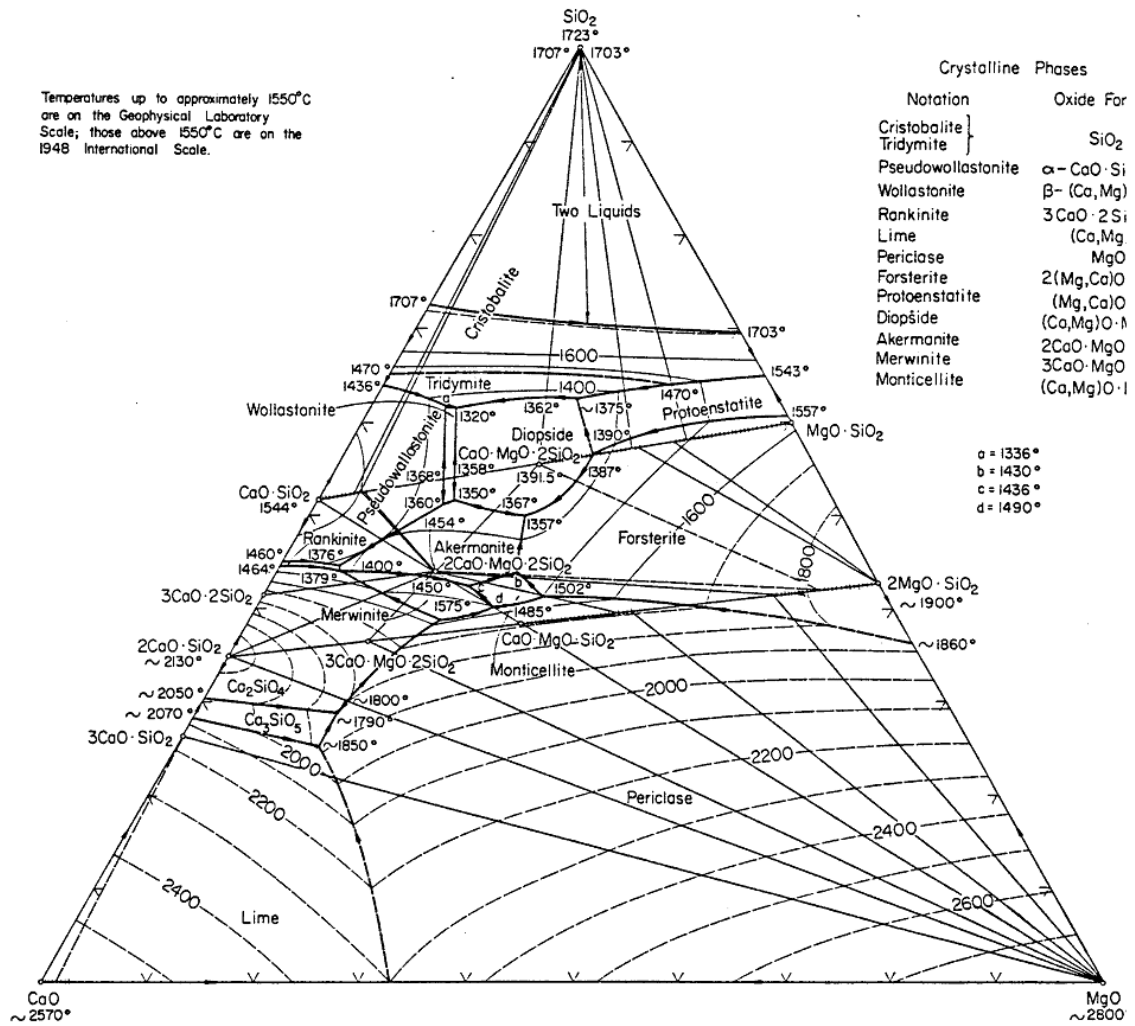


FIG. 598.—System CaO-MgO-SiO<sub>2</sub>; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 2, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

### Figure 6 CaO - MgO - SiO<sub>2</sub> System<sup>3</sup>

Hille and Papay provided conclusive evidence that a CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ladle slag produced cleaner billets, reduced nozzle clogging and increased ladle refractory life.<sup>6</sup> Since there is little Al<sub>2</sub>O<sub>3</sub> available in Si killed steels, synthetic slags were used to achieve a beneficial CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>3</sub> composition in their ladle slag and an aluminum

## Summary

Synthetic slags are a valuable and necessary tool for today's steelmakers. By understanding melt dynamics and engineering synthetic slags to shift ladle slags into the beneficial region of the  $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2$  systems, steelmakers derive the benefits of material and energy savings, fluid slags throughout the steelmaking process, good sulphur and inclusion removal, improved castability and overall yields, and increased refractory life. Steelmaking processes that do not generate  $\text{Al}_2\text{O}_3$  can also utilize synthetic slags to generate the same benefits.

## References

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