



Steel Revolution



2. The Thomas - Gilchrist Process

Many iron ores contain some phosphorous and so does the pig iron smelted from them. Blowing the oxygen contained in air through liquid pig iron in the Bessemer process obviously did not remove the phosphorous. It neither bubbled out as a component of a gas like the carbon in carbon monoxide (CO), nor did it become part of slag or dross swimming on top. But you must catch the phosphorous in some slag in order to remove it. The question to consider is simple: Why was phosphorous not incorporated as some kind of oxide in the slag formed during the blowing? With hindsight, a different but closely related question is: why did the phosphorous problem not come up during [puddling](#)?

- We have an exceedingly difficult question here. This becomes obvious as soon as one checks the Net for answers. There aren't any - just a lot of confusion; I'll get to that.
If we look at "the question" in a broader context, it becomes clear that we ask for the equilibrium between a lot of chemical processes that can happen in liquid iron at very high temperatures. At the minimum iron, oxygen, nitrogen, carbon, silicon, phosphorous, sulfur and manganese are involved, plus calcium, magnesium and aluminum if we add the oxides of these elements as flux or as part of the lining.
The reaction products could be gaseous, liquid or solid. Some of the solids might dissolve in the essentially liquid iron, some might not.
- The naive approach we took so far (without being aware of that!) was to assume that carbon, silicon, and so on oxidize during the air blast *independently* of each other according to

Si + O ₂	⇌	SiO ₂
C + ½O ₂	⇌	CO
2 P + 2.5 O ₂	⇌	P ₂ O ₅
Mn + ½O ₂	⇌	MnO
Fe + ½O ₂	⇌	FeO

- Not completely naive, actually. All these reactions *do* happen, and they can go in both directions as the double arrow (⇌) signifies. They are, however, *not* independent and there are far more reactions that must also be taken into account.
- The first thing to realize is that all the reactions above release energy at high temperatures - but in different specific amounts. I have actually given you a diagram for this already - in [this link](#). Running through numbers makes clear that most of the energy released during an air blast comes from silicon and phosphorous. That explains the old and puzzling observation to the practitioners that in the *acidic* Bessemer process you need to have about 2% silicon in the pig iron, while the *basic* Thomas process depends on 1,5 % -2 % phosphorus in the mix. Otherwise your converter "blows cold", not a good thing.
And now I have mentioned the magic words: *acidic* and *basic* that invariably turn up when steel making with the Bessemer or Thomas process is discussed. At the same time a problem turns up, even for the small minority of elite people who are not chemically challenged:

What makes a brick acidic or basic?

- I'm not sure I know the answer. Just like (hopefully) almost everybody else, I know that acids and bases in common chemistry relate to the concentrations of H⁺ (hydrogen) or OH⁻ (hydroxide) ions in some (watery) solution. If H⁺ dominates, like when you pour some hydrochloric *acid* into water, you call that an acid. The H⁺ concentration goes up according to HCl → H⁺ + Cl⁻. Likewise, sodium hydroxide raises the OH⁻ concentration according to NaOH →

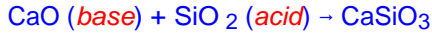
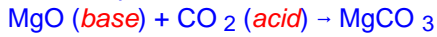
$\text{Na}^+ + \text{OH}^-$; it is a *base*. React an acid and a base and you get a salt: $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$

I do know a bit more about the issue - but not enough. Most likely the whole notion of acidic - basic bricks goes back to chemical concepts predating the modern definition hinted at above (and going back to [Svante Arrhenius](#); Nobel prize in 1903). There are, however, about as many concepts for acidic - basic (Wikipedia mentions 8) as there are sexy chemists, and most likely the so-called *Lux-Flood definition* is at the root of things here. What is that? To quote Wikipedia:

This acid-base theory was a revival of oxygen theory of acids and bases, proposed by German chemist Hermann Lux in 1939, further improved by Håkon Flood circa 1947. It is still used in modern geochemistry and electrochemistry of *molten* salts. This definition describes

- an acid as an oxide ion (O^{2-}) *acceptor*;
- a base as an oxide ion *donor*

For example:



That might be interpreted simply as: a (solid oxide) *acid* and (solid oxide) *base* can react and form a *salt*.

Aha! The phosphorous pentoxide P_2O_5 formed according to our first naive view then is also an *acid*. It can form a *salt* with a base like CaO ($\text{Ca}_3(\text{PO}_4)_2$) according to that - just like SiO_2 . Same thing for the wüstite, FeO , that also is a base. If we now realize that the components of slag are *salts* like *fayalite* (Fe_2SiO_4), the usual question concerning competing chemical reactions comes up: *who wins*? The answer is simple: silicon! Phosphorous always loses to silicon and that means that the P_2O_5 formed will not make it into the slag but decomposes again (with the help of the carbon monoxide produced), and elemental phosphorous remains in the iron - provided it is still liquid after everything has reacted and the air blast is stopped. That will be so as long as there is still some unreacted silica around, and that will be so as long as the silica-containing lining of the converter is in place.

As a corollary it becomes clear why phosphorous is not a big problem at puddling. The temperatures are too low for the reduction, gases do not bubble through the stuff but are formed at the surface, and chemistry is different anyway when solid iron / steel is present.

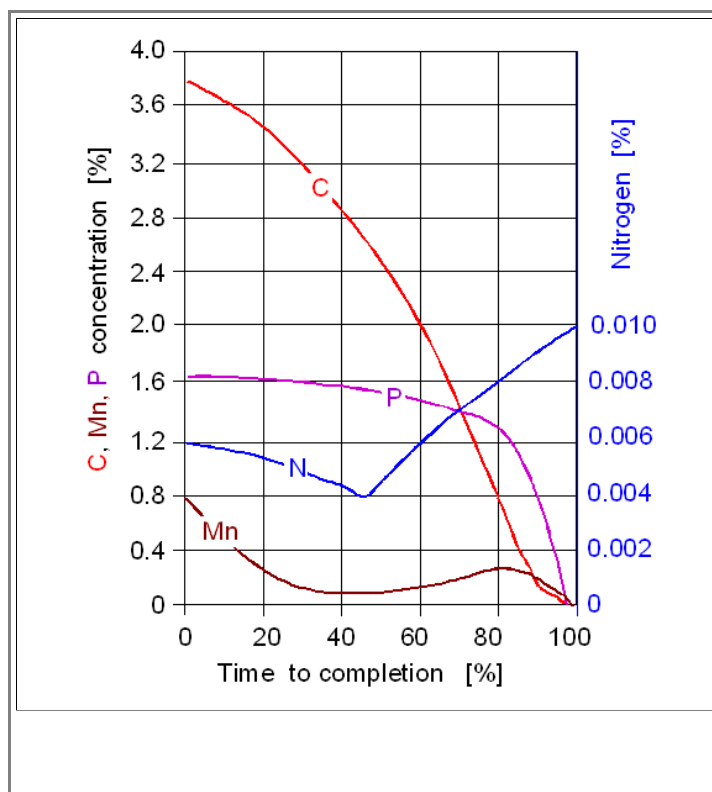
It is far more complicated, of course. But I will spare you more details (mostly because I don't know them myself).

As a final conclusion a recipe emerges: Use basic fluxes like quicklime (CaO) *and* basic bricks for the lining of the converter. As long as you have acidic silica bricks, you have a source of silicon / silica and phosphorous loses. Adding basic flux to a converter with acidic bricks simply encourages salt formation between the two, and that means your bricks dissolve and your lining crumbles.

You can't afford that. Relining a big converter is time consuming and expensive and the whole point of the exercise, after all, is to [boost production](#).

It was thus quite remarkable that already in 1857 a German chemist (Grüner) pointed out that Bessemer's silica-based bricks could not possibly "absorb" phosphorous. **Sidney Gilchrist Thomas** became obsessed with the topic, and with the help of his cousin **Percy Carlyle Gilchrist** got the "basic" process going. I have recounted that in the [main part](#) and won't repeat it here.

Let's instead look at what happens in a Thomas converter a little bit more closely:



Measured concentration change of some impurities during blasting in the Thomas process

Source; Redrawn from a figure in [Buchwald's second book](#).

- The phosphorous concentration only goes down *after* the carbon concentration is almost zero. Manganese behaves a bit oddly, and nitrogen positively strange. Try to calculate these curves and you will appreciate that there are a lot of interconnected reactions at work.
- ▶ We see once more that having a good idea is one thing, making it work another. The Thomas process worked and has changed the world quite a bit before it succumbed to the even better Siemens-Martin process and its followers.
- There is still a lot of Thomas steel out there. A lot of the steel towers or high-voltage cables in Germany were made from Thomas steel - and there might be a problem now. Thomas steel (and Bessemer steel) contains small but appreciable amounts of nitrogen, and in time this may lead to **nitrogen embrittlement**. Consequences might be severe:



Massive power interruption 2005 in Germany due to a snow storm

Source: Newspaper

- This may or may not have been due to nitrogen embrittlement; I haven't heard the final word yet. Black-outs by the way, are very rare in Germany but this one lasted 5 days!