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The Single-Stage Production of Low Zinc Pig Iron Nuggets from Basic Oxygen Furnace dust, using Blast Furnace Dust as a reductant

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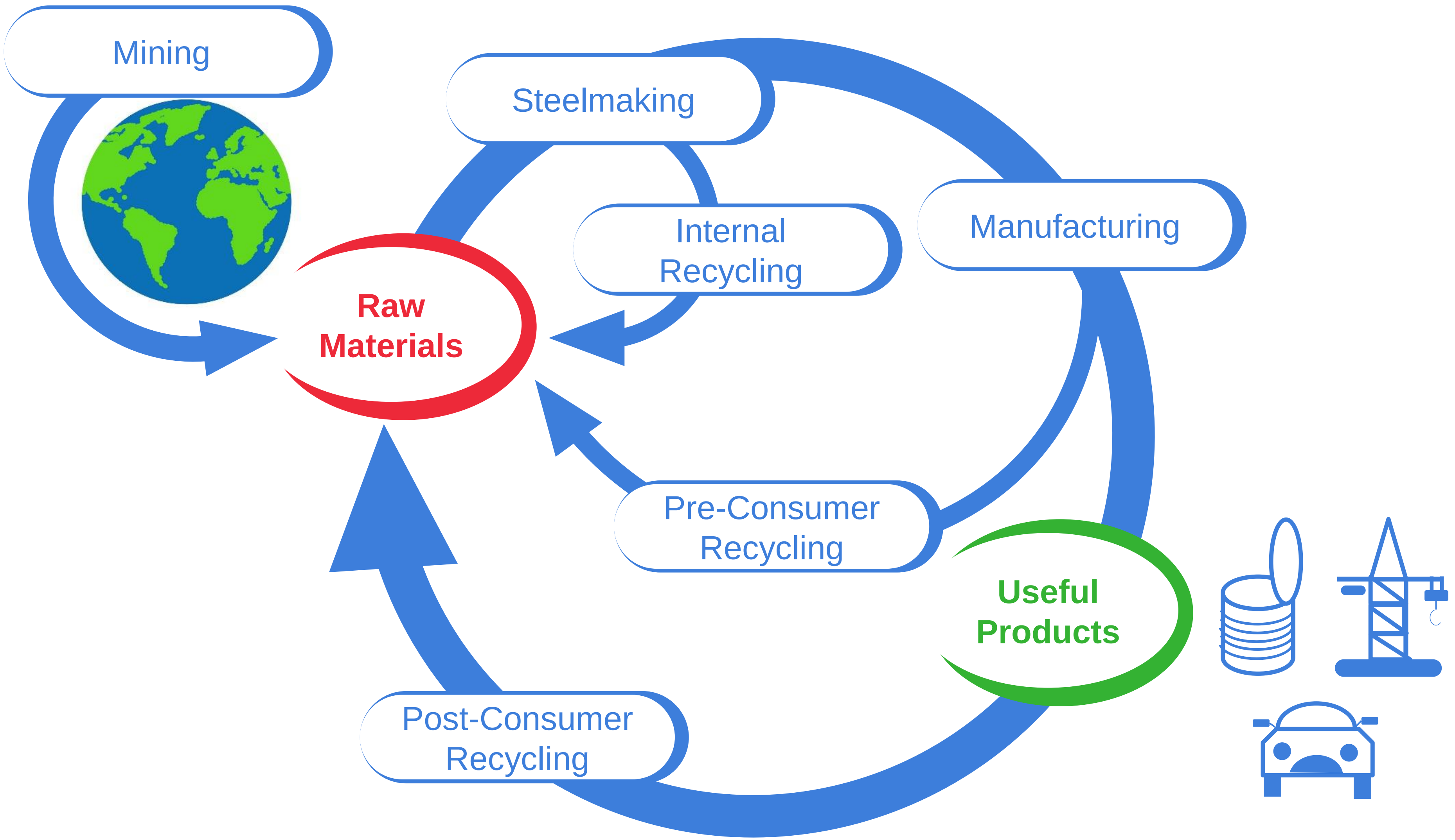
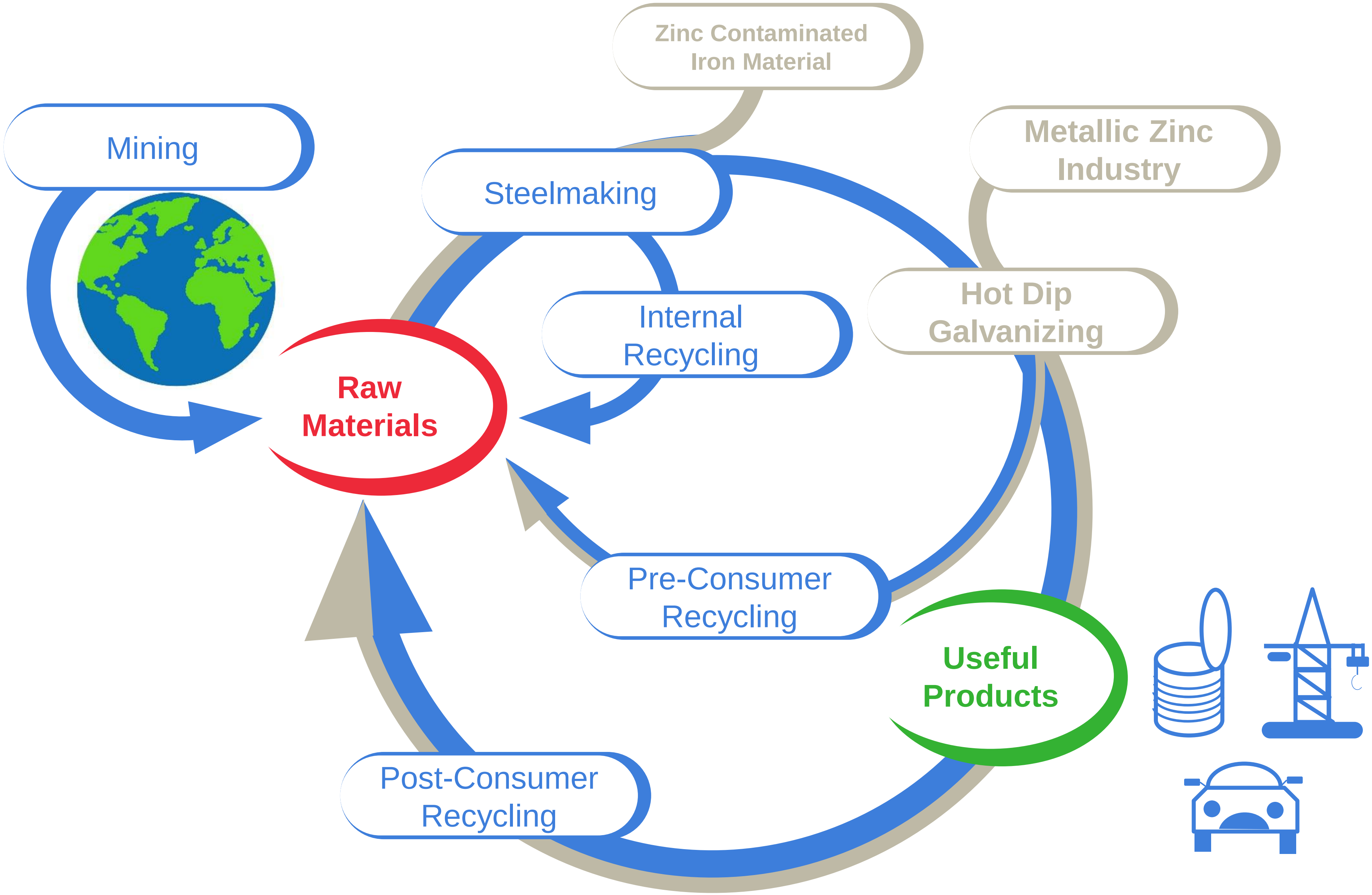
The Circular Economy of Steel



How does Hot Dip Galvanizing change this cycle?



Galvanizing - The Silver Bullet in the Battle against Corrosion

$$2Fe(s) + {}^{3}/_{2}\,O_2(g) \rightarrow Fe_2O_3(s)$$

$$\Delta_f G^{\circ} = -742.2\ \mathrm{kJmol^{-1}}$$

Very thermodynamically favourable!

- Hot dip galvanized material has become critical in automotive and construction sectors due to its ability to resist this reaction for longer
- Corrosion has been estimated to directly cost the US economy **$276 billion per annum**

G. Koch, M. Brongers, N. Thompson, Y. Virmani and J. Payer, *Handbook of Environmental Degradation of Materials*, 2005, 3-24.

Where does this Zinc end up?

Steelmaking Revert Materials

- Almost every stage in steelmaking has an associated dust by-product
  - **Fines** generated during the handling of bulk material
  - **Off-gas Dusts** when process gases are cleaned before discharge to atmosphere, dust is recovering in the form of slurry, sludge or dry dusts
  - **Mill scales** formed from the flaking of iron oxide from the hot surfaces of slabs in casters/hot strip mill
- These products are too fine for direct recycling into the blast furnace, so require agglomeration
- Usual process route is to agglomerate the fines in the Sinter Plant **but** this process **does not separate zinc from the ferrous material.**

The usual solution to Zinc bearing wastes? Dilution

Zinc loading in a Blast Furnace

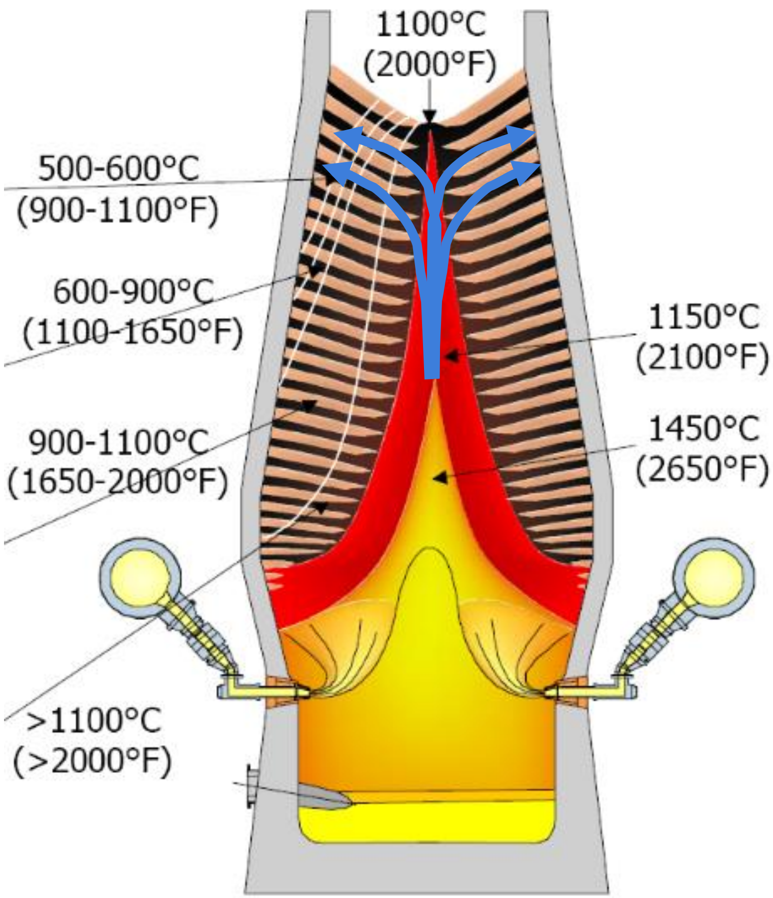


Image Courtesy of Tata Steel UK

- High levels of Zn in the blast furnace can have deleterious effects on furnace performance
  - This is due to cycling of Zn within the stack and the formation of scaffolds
- Zinc in input materials is therefore tightly controlled, around 200g Zn/tonne of hot metal
- Therefore a 3.5mt steel plant could only process around **700 tonnes** of zinc per year through the furnaces
- This limit on the amount of zinc permissible in the furnace can result in surplus revert material that is **unable to re-enter the process economically.**
- Some of the zinc within the furnace exits with the off-gas dust, this is the source of our first difficult to recycle material – **Blast Furnace Dust**

The introduction of Zinc into the revert cycle – BOS Slurry

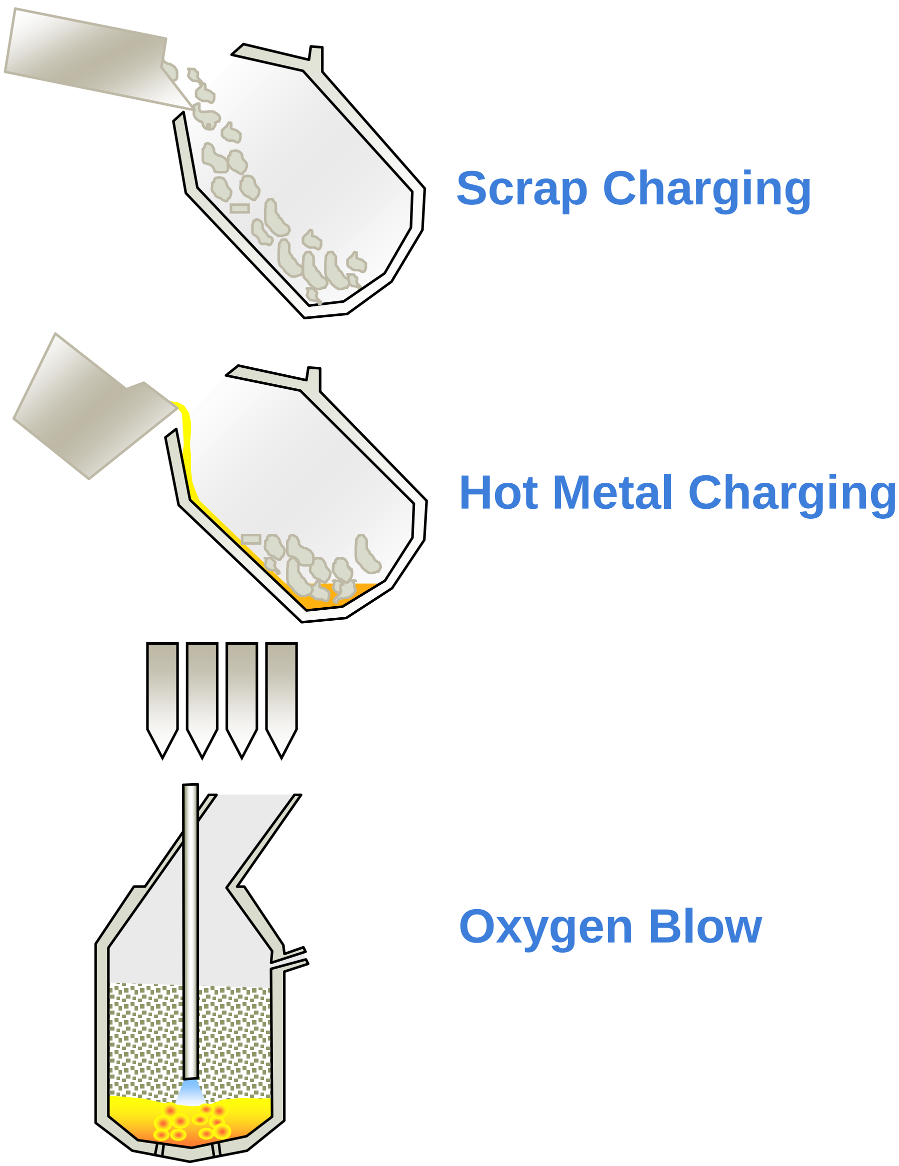


Image Courtesy of Tata Steel UK

Galvanized Scrap

- Around 25% of the iron produced in a BOS converter is sourced from scrap
- Any Zinc present within this scrap charge immediately vaporizes and reoxidizes in the off-gas
- The off-gas dust is collected via a de-dusting system to give BOS Slurry, **our second key high zinc material**
- The levels of zinc in BOS slurry can be managed by **excluding** galvanized scrap from charges
- However, non-galvanized scrap is **more expensive** and simply not recycling galvanized material is not a long term solution

Blast Furnace Dust and Basic Oxygen Steelmaking Dust

Blast Furnace Dust

- From **20%-30% carbon**, originating from the coke charged to the blast furnace
- Produced as a wet slurry as a result of being wet scrubbed from off-gas

SiO_2	Al_2O_3	TiO_2	CaO	MgO	Fe_{Tot}	FeO	Fe_2O_3	C_{fix}	Zn
7.60	4.07	0.30	12.87	3.045	28.57	1.87	38.83	30.83	1.31

Typical chemical analysis of blast furnace dust

Basic Oxygen Steelmaking Dust

- Much more metallized due to origin in steel plant, high Fe content
- Typically has a **higher Zn content (2% - 8%)** than BF dust, negligible amounts of fixed carbon

SiO_2	Al_2O_3	TiO_2	CaO	MgO	Fe_{Tot}	FeO	Fe_2O_3	C_{fix}	Zn
1.83	0.39	0.05	11.18	2.13	58.93	57.3	20.55	-	6.3

Typical chemical analysis of basic oxygen steelmaking slurry

Barriers to Zinc Separation

The Zinc Recovery Gap

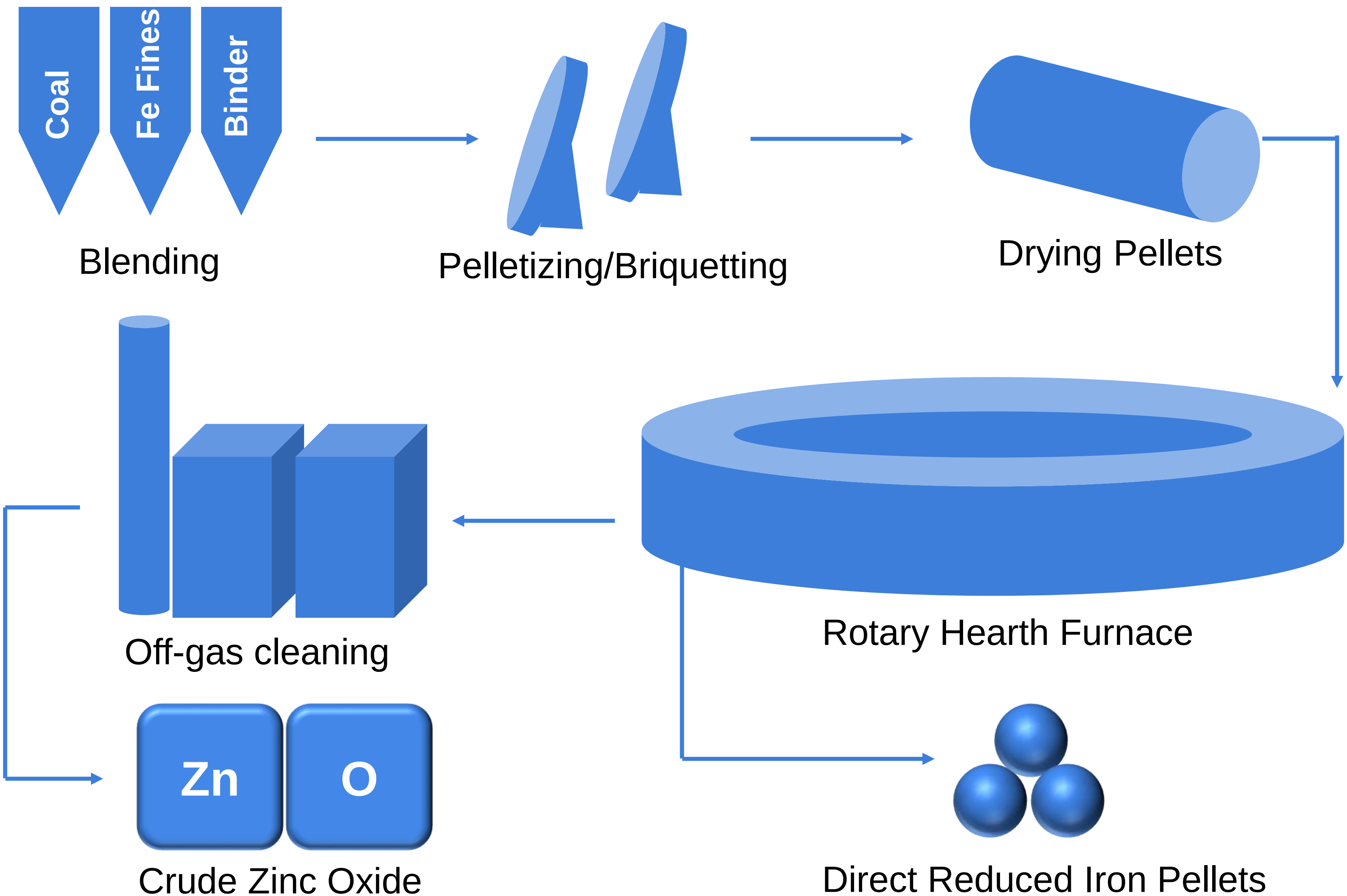
- Iron is considered a tramp element with regards to zinc extraction, therefore the value of any zinc bearing dusts decreases rapidly with higher Fe% and lower Zn%

- High zinc materials (12-15wt%) can be sold or economically processed in a number of ways including – Waelz Kiln, Hydrometallurgical leaching etc. The zinc's high value offsets the large operational costs of these processes

- Low zinc material (<0.3wt%) generated at a steelworks can typically be **recycled within existing processes** by dilution with other material, dependent on volumes

- This leaves a gap in material recycling viability that unfortunately BOS dust and BF dust fall into; the best available technology for processing these medium zinc content materials is the **rotary hearth furnace.**

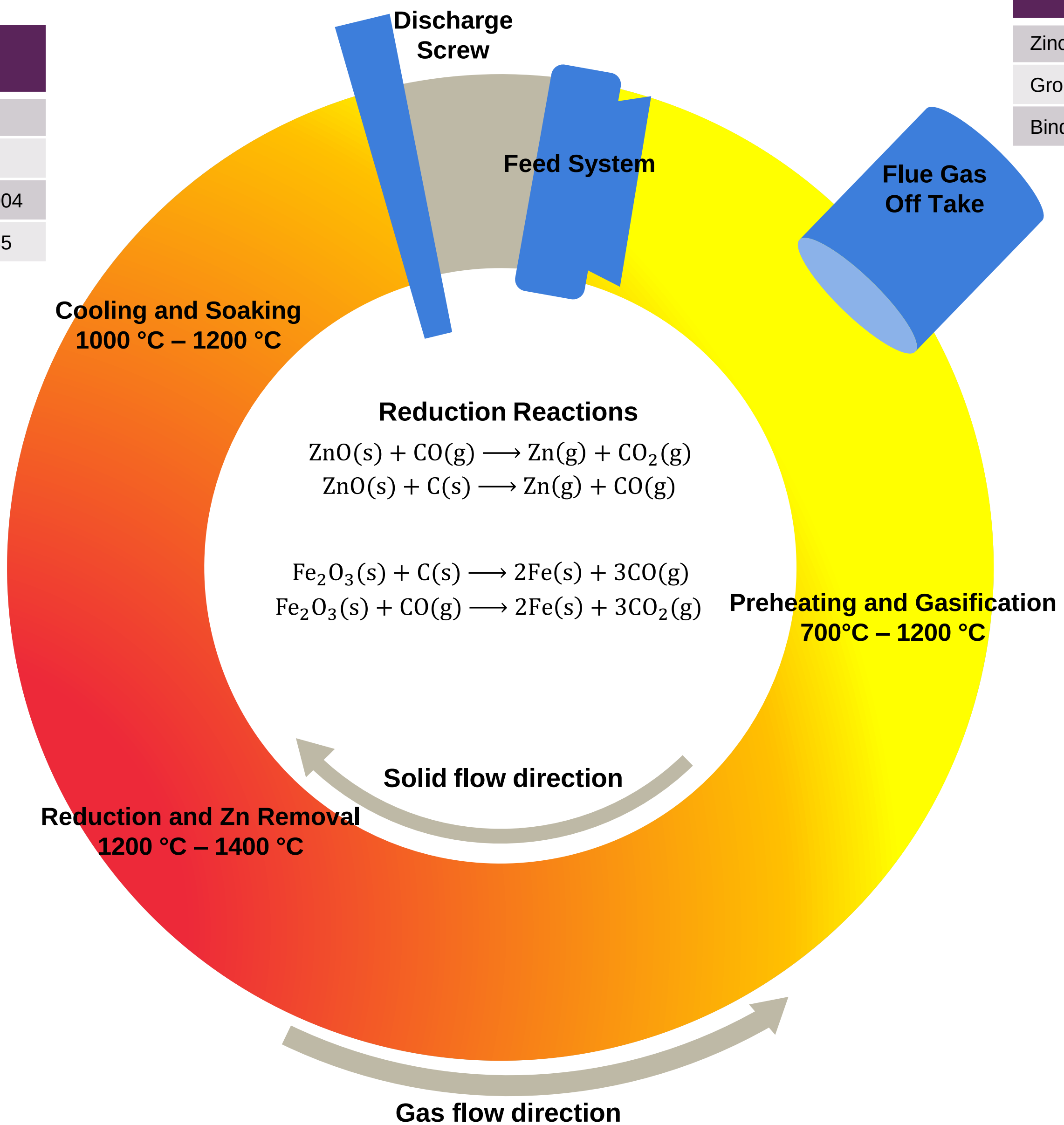
Process Flow for the RHF – general outline of Fastmet®, DryIron® etc.



The Chemistry of the RHF – Plan View

Typical DRI from Waste	
Fe_{Tot} / wt%	70
Metallization / %	95
Zn / wt%	0.004
S / wt%	0.35

Input Material	
Zinc Bearing Waste	70%
Ground Coal	29.5%
Binder	0.5%

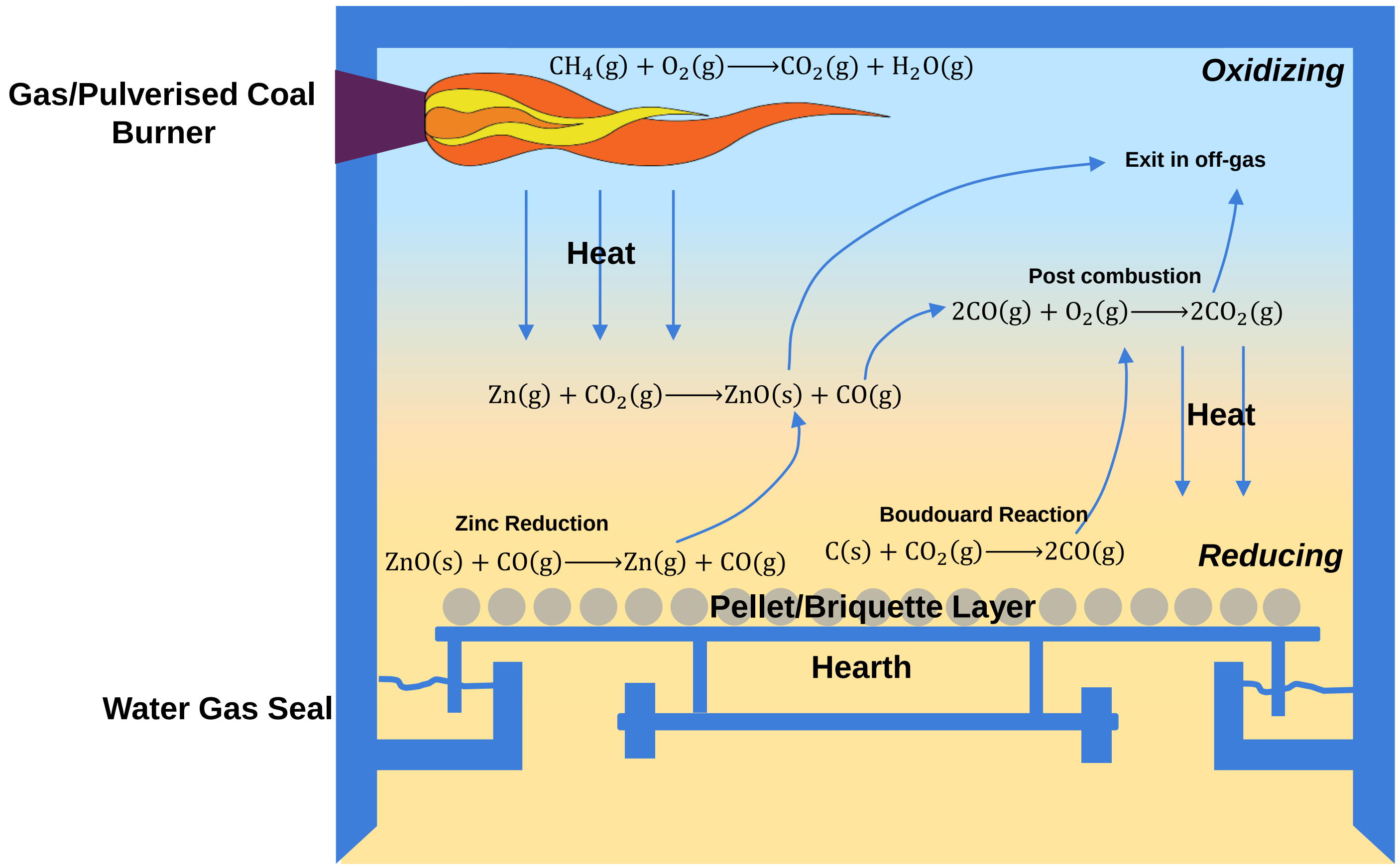


Reduction Reactions

$$ZnO(s) + CO(g) \longrightarrow Zn(g) + CO_2(g)$$
$$ZnO(s) + C(s) \longrightarrow Zn(g) + CO(g)$$

$$Fe_2O_3(s) + C(s) \longrightarrow 2Fe(s) + 3CO(g)$$
$$Fe_2O_3(s) + CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$$

Cross Sectional View – Full Post Combustion and Zn Reoxidation



The Rotary Hearth Furnace

Rapid Processing

Very high thermal efficiency

Able to use inexpensive non-coking coals

Saleable ZnO product

Large initial capital expense

High and flexible Zn removal

High temperature and carbon source required

Low CO_2 emission

DRI product useful on site

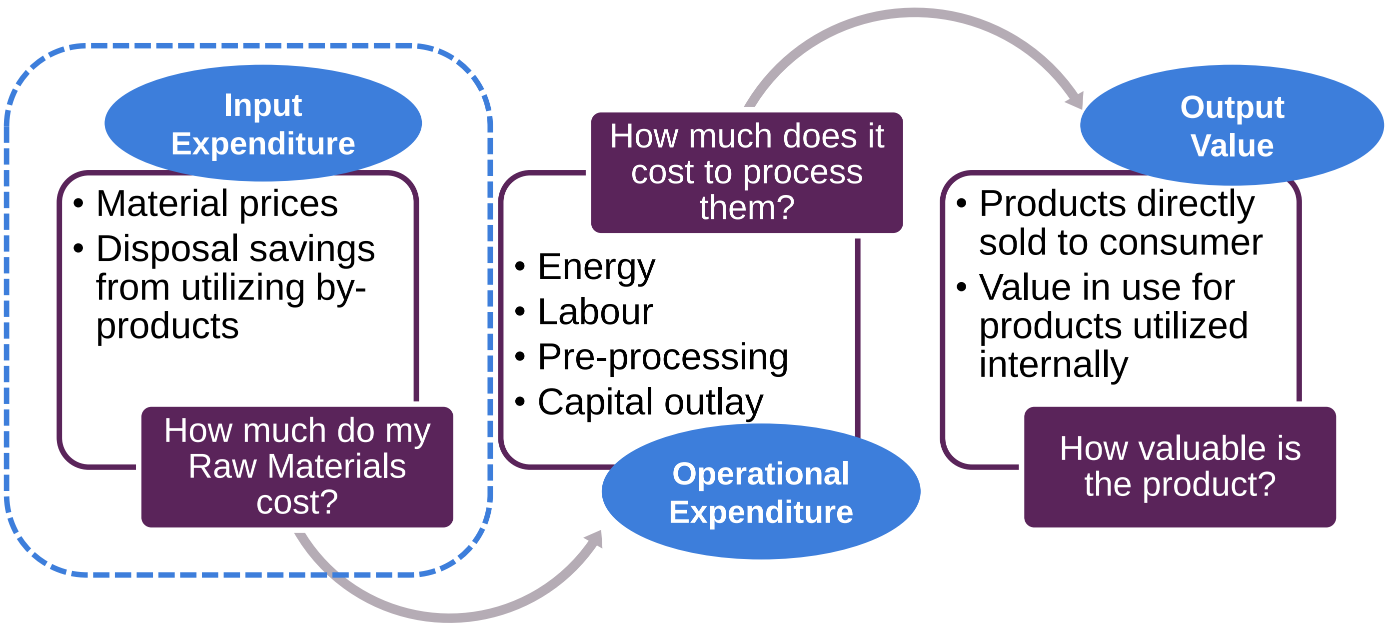
Relatively immature technology

Requires support plant

So what's the problem? The RHF seems like the ideal technological solution

The value of the ZnO and Direct Reduced Iron produced isn't high enough

- When accounting for the operational costs of an RHF and the input material costs (coal as a reducing agent, binder) the units don't generate enough value to offset the large investment



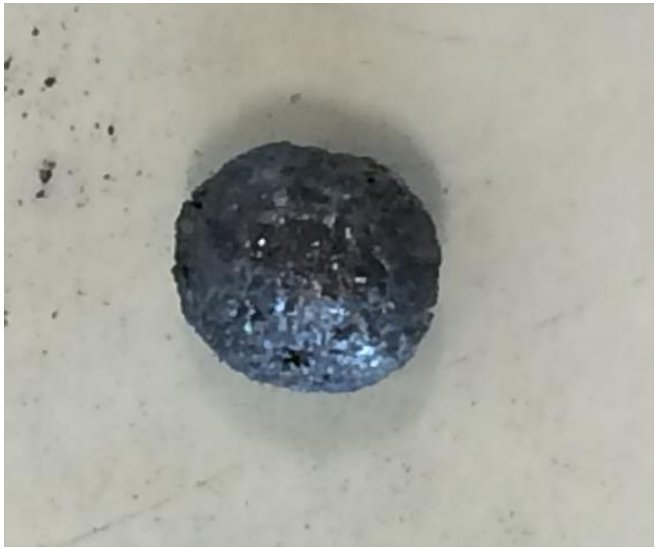
Displacing coal from the RHF

Utilizing the C_{fix} of BF dust

- Theoretically, to fully reduce the zinc and iron within a pellet, the blend should satisfy the stoichiometric relationship

$$\frac{C_{fix}}{O_{Fe}+O_{Zn}}=1$$

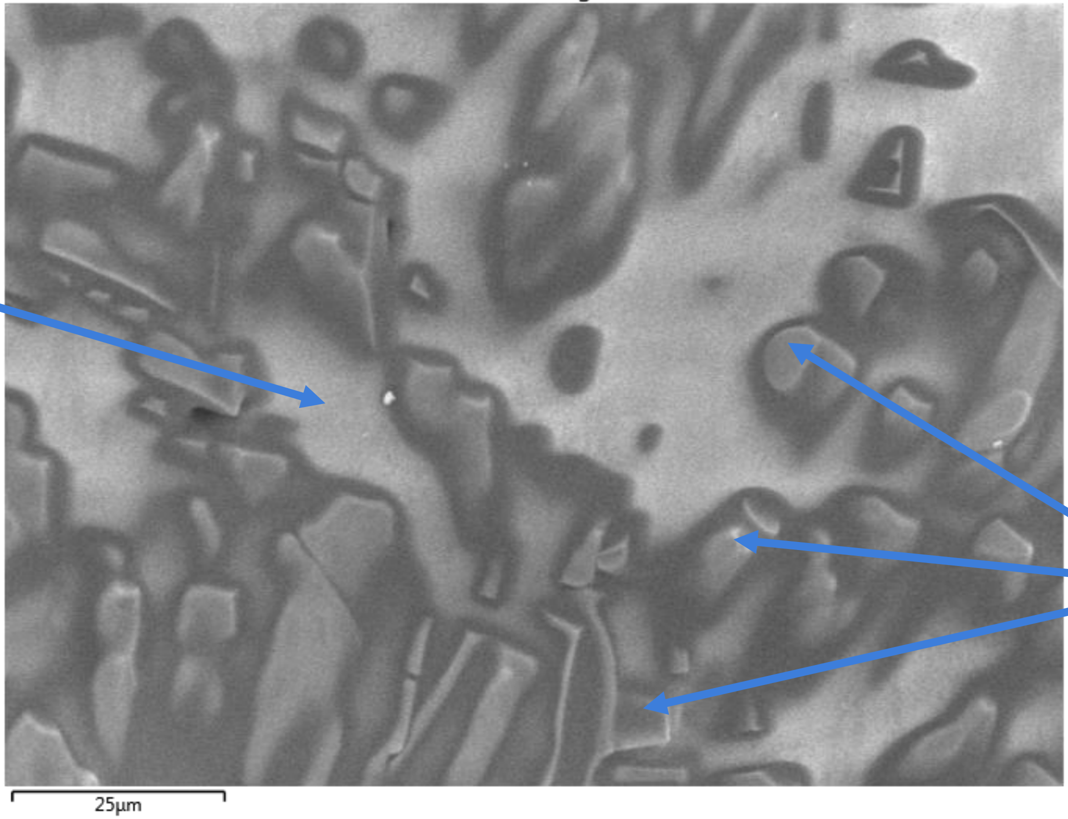
- Therefore a blend of around 50% BF dust and 50% BOS slurry should be sufficient to fully reduce and dezinc both materials
- Experimentally, **95% Zn removal** and ~**80% metallization of Fe** is achievable at realistic RHF temperatures (1300 °C) and hold times (22 mins) for a 50:50 pellet in a **non-inert atmosphere**
- The result is a crude ZnO powder and a lump of direct reduced iron, however – the DRI produced in initial experimentation was physically weak and would be unsuitable for use in the BF



A closer look at the DRI Product

Scanning Electron Microscopy

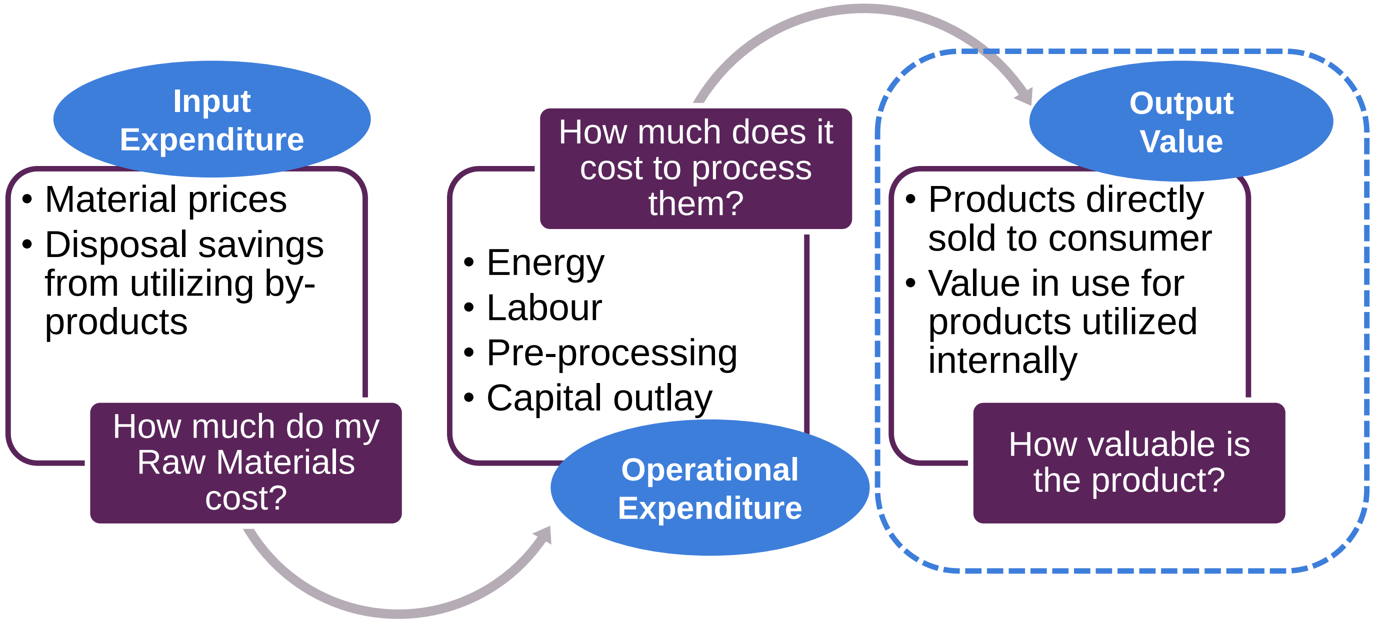
Electron Image 4



Slaggy matrix containing $CaO/SiO_2/MgO$

Metallic iron grains

Can the output value of the RHF be increased without drastically changing the other two variables?



ITmk3 and the Mesabi Plant

A new spin on the RHF

- Developed by Kobe Steel in the 2000s, ITmk3 is a variant of the RHF whereby pellets achieve a fully molten state and slag and iron separate to form distinct iron nuggets all within an adapted RHF.

ITmk3 – 1400 °C

Fastmet – 1300 °C

Gasification

$$\mathrm{Coal} \xrightarrow{\mathrm{Heat}} \mathrm{H_2, CH_4, CO, H_2O, N_2, C_nH_m, C}$$
$$\mathrm{C + O_2 \longleftrightarrow CO_2}$$
$$\mathrm{CO_2 + C \longleftrightarrow 2CO}$$
$$\mathrm{C + {}^1/_2\, O_2 \longleftrightarrow CO}$$
$$\mathrm{CH_4 + CO_2 \longleftrightarrow 2CO + 2H_2}$$
$$\mathrm{C + H_2O \longleftrightarrow CO + H_2}$$
$$\mathrm{CaCO_3 \longrightarrow CaO + CO_2}$$

Reduction

$$\mathrm{Fe_3O_4 + C \longleftrightarrow 3FeO + CO}$$
$$\mathrm{FeO + C \longleftrightarrow Fe + CO}$$
$$\mathrm{Fe_3O_4 + CO \longleftrightarrow 3FeO + CO_2}$$
$$\mathrm{FeO + CO \longleftrightarrow Fe + CO_2}$$
$$\mathrm{Fe_3O_4 + H_2 \longleftrightarrow 3FeO + H_2O}$$
$$\mathrm{FeO + H_2 \longleftrightarrow Fe + H_2O}$$

DRI

Slag Forming*

$$\mathrm{CaO + SiO_2 \longleftrightarrow CaSiO_3}$$
$$\mathrm{SiO_2 + 2C \longleftrightarrow Si + 2CO}$$
$$\mathrm{FeO + SiO_2 \longleftrightarrow FeSiO_3}$$
$$\mathrm{CaO + FeSiO_3 \longleftrightarrow CaSiO_4 + FeO}$$
$$\mathrm{FeS + CaO + CO \longleftrightarrow CaS + FeO + CO}$$

Carburization and Melting

$$\mathrm{Fe} + C \longleftrightarrow [C]_{Fe}$$
$$\mathrm{C} + 3Fe \longleftrightarrow Fe_3C$$
$$Fe(s) \longrightarrow Fe(l)$$

Pig Iron Nugget

ITmk3 and the Mesabi Plant

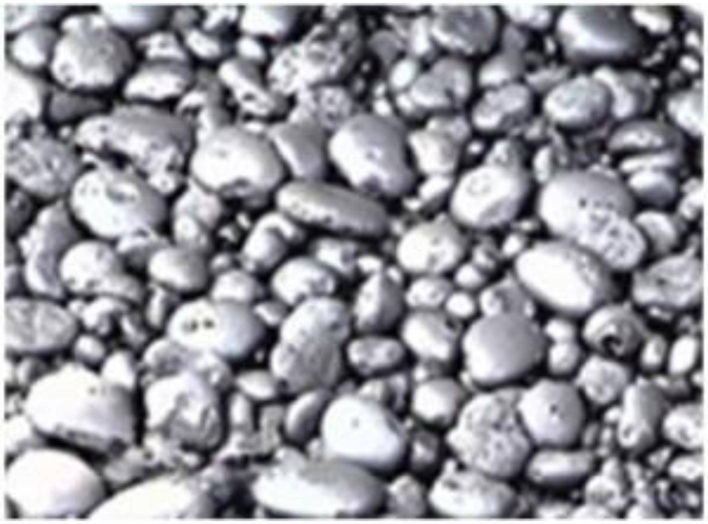
A high value added product from iron ore

Aerial view of the 500kt/year ITmk3 plant in Minnesota operated by Steel Dynamics Inc. The plant was mothballed in 2015-2016.
Image used with permission courtesy of Aaron Brown, www.minnesotabrown.com

RHF Direct Reduced Iron versus Pig Iron Nuggets

Direct Reduced Iron

- 60-70% $Fe_{Tot,}$ mostly recycled to BF
- No slag separation, increase in slag volume and heat loss during recycling
- Propensity to reoxidation, **pyrophoric** unless hot briquetted
- Highly metallized



Pig Iron Nuggets

- >95% Fe_{Tot}, scrap replacement
- No entrained slag
- Completely metallized, similar structure to blast furnace pig iron
- High density, easy to store and transport due to oxidative stability
- Do not generate fines and are exceptionally easy to remelt

ITmk3 and the Mesabi Plant

An alternative use for ITmk3

- The plant in MN was unsuccessful for a number of reasons including
  - EAF customer issues related to residual S from reductant coal in pig iron nuggets
  - Difficult economic circumstances related to global steel crisis 2015-2016

- Instead of using it at the source of iron to generate a higher value Fe product than ore pellets/DRI, can it be introduced into the **Zn recovery process at an integrated steelworks?**

- ❑ **Removal of Zinc**
- ❑ **Generation of a low melting temperature slag**
- ❑ **Low temperature melting of iron**
- ❑ **Immiscibility between Fe and slag phases**

CaO - Al_2O_3 - SiO_2 - MgO

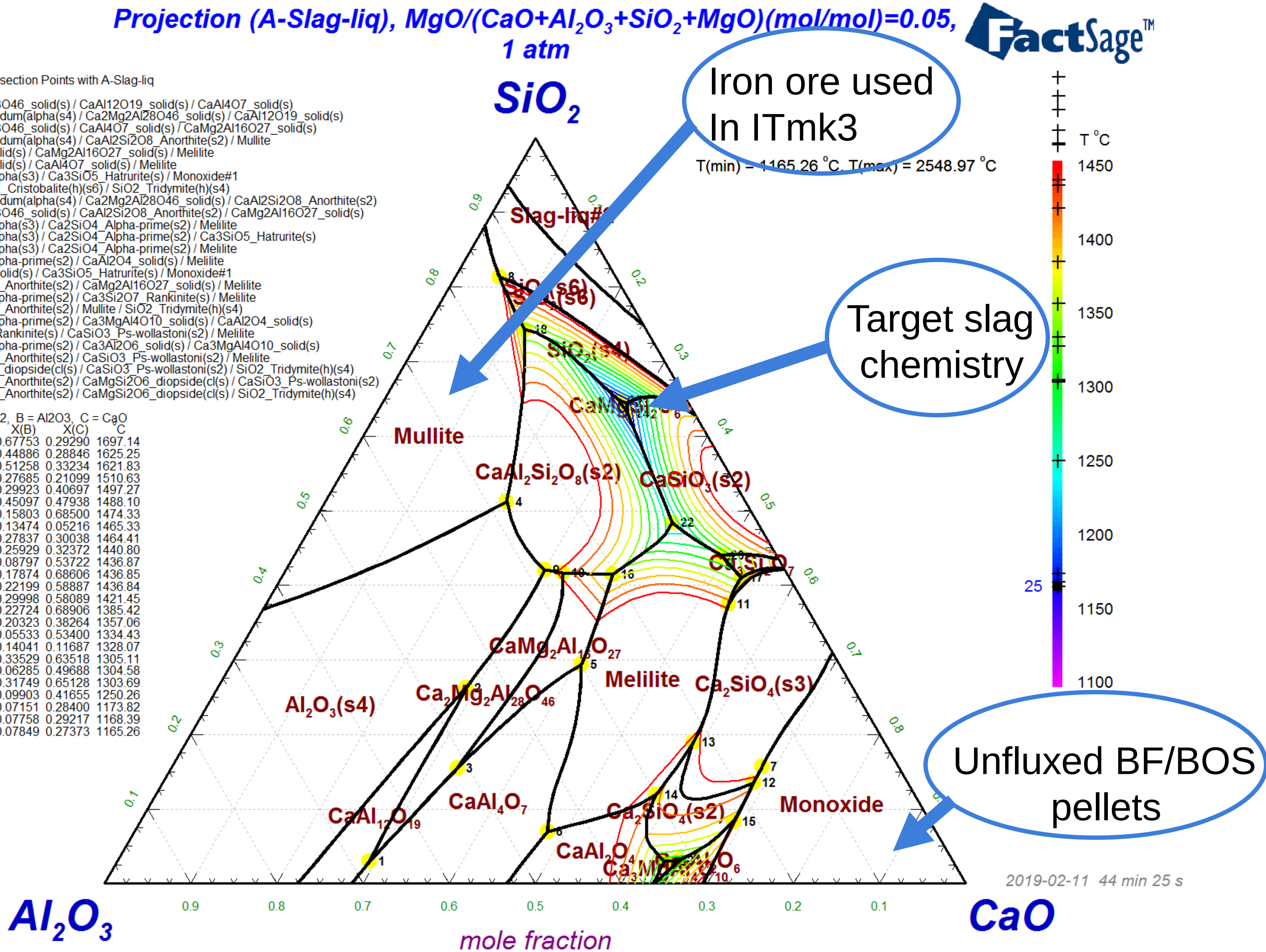
Projection (A-Slag-liq), MgO/(CaO+Al_2O_3+SiO_2+MgO)(mol/mol)=0.05, 1 atm

Four-Phase Intersection Points with A-Slag-liq

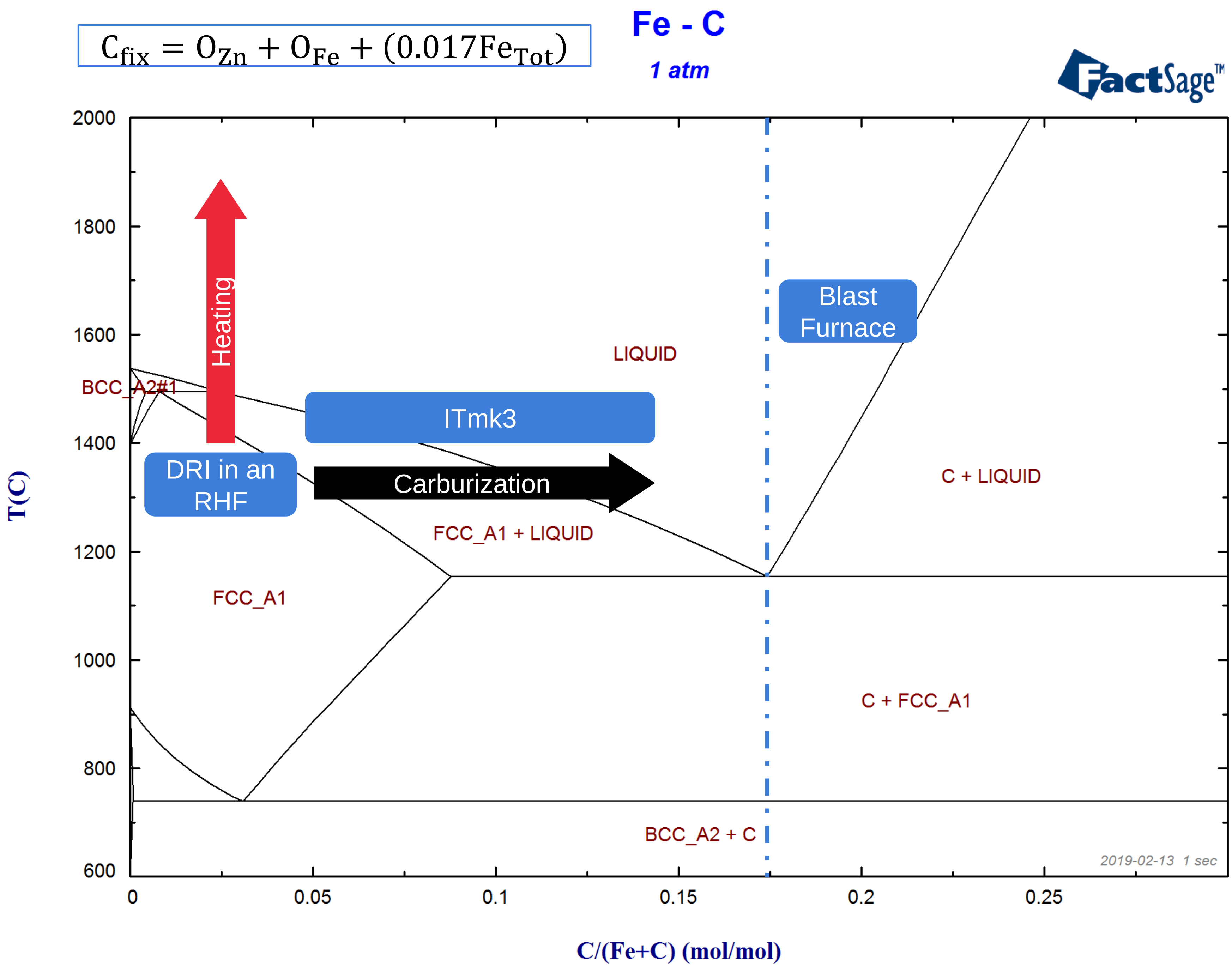
1: Ca2Mg2Al28O46_solid(s) / CaAl12O19_solid(s) / CaAl4O7_solid(s)
2: Al2O3_corundum(alpha(s4) / Ca2Mg2Al28O46_solid(s) / CaAl12O19_solid(s)
3: Ca2Mg2Al28O46_solid(s) / CaAl4O7_solid(s) / CaMg2Al16O27_solid(s)
4: Al2O3_corundum(alpha(s4) / CaAl2Si2O8_Anorthite(s2) / Mullite
5: CaAl4O7_solid(s) / CaMg2Al16O27_solid(s) / Melilite
6: CaAl2O4_solid(s) / CaAl4O7_solid(s) / Melilite
7: Ca2SiO4_Alpha(s3) / Ca3SiO5_Hatrurite(s) / Monoxide#1
8: Mullite / SiO2_Cristobalite(h)(s6) / SiO2_Tridymite(h)(s4)
9: Al2O3_corundum(alpha(s4) / Ca2Mg2Al28O46_solid(s) / CaAl2Si2O8_Anorthite(s2)
10: Ca2Mg2Al28O46_solid(s) / CaAl2Si2O8_Anorthite(s2) / CaMg2Al16O27_solid(s)
11: Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Melilite
12: Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Ca3SiO5_Hatrurite(s)
13: Ca2SiO4_Alpha(s3) / Ca2SiO4_Alpha-prime(s2) / Melilite
14: Ca2SiO4_Alpha-prime(s2) / CaAl2O4_solid(s) / Melilite
15: Ca3Al2O6_solid(s) / Ca3SiO5_Hatrurite(s) / Monoxide#1
16: CaAl2Si2O8_Anorthite(s2) / CaMg2Al16O27_solid(s) / Melilite
17: Ca2SiO4_Alpha-prime(s2) / Ca3Si2O7_Rankinite(s) / Melilite
18: CaAl2Si2O8_Anorthite(s2) / Mullite / SiO2_Tridymite(h)(s4)
19: Ca2SiO4_Alpha-prime(s2) / Ca3MgAl4O10_solid(s) / CaAl2O4_solid(s)
20: Ca3Si2O7_Rankinite(s) / CaSiO3_Ps-wollastoni(s2) / Melilite
21: Ca2SiO4_Alpha-prime(s2) / Ca3Al2O6_solid(s) / Ca3MgAl4O10_solid(s)
22: CaAl2Si2O8_Anorthite(s2) / CaSiO3_Ps-wollastoni(s2) / Melilite
23: CaMgSi2O6_diopside(cl(s) / CaSiO3_Ps-wollastoni(s2) / SiO2_Tridymite(h)(s4)
24: CaAl2Si2O8_Anorthite(s2) / CaMgSi2O6_diopside(cl(s) / CaSiO3_Ps-wollastoni(s2)
25: CaAl2Si2O8_Anorthite(s2) / CaMgSi2O6_diopside(cl(s) / SiO2_Tridymite(h)(s4)

A = SiO2, B = Al2O3, C = CaO

	X(A)	X(B)	X(C)	°C
1:	0.02957	0.67753	0.29290	1697.14
2:	0.26268	0.44886	0.28846	1625.25
3:	0.15508	0.51258	0.33234	1621.83
4:	0.51215	0.27685	0.21099	1510.63
5:	0.29381	0.29923	0.40697	1497.27
6:	0.06965	0.45097	0.47938	1488.10
7:	0.15697	0.15803	0.68500	1474.33
8:	0.81310	0.13474	0.05216	1465.33
9:	0.42124	0.27837	0.30038	1464.41
10:	0.41700	0.25929	0.32372	1440.80
11:	0.37481	0.08797	0.53722	1436.87
12:	0.13520	0.17874	0.68606	1436.85
13:	0.18915	0.22199	0.58887	1436.84
14:	0.11914	0.29998	0.58089	1421.45
15:	0.08371	0.22724	0.68906	1385.42
16:	0.41412	0.20323	0.38264	1357.06
17:	0.41067	0.05533	0.53400	1334.43
18:	0.74272	0.14041	0.11687	1328.07
19:	0.02953	0.33529	0.63518	1305.11
20:	0.44027	0.06285	0.49688	1304.58
21:	0.03123	0.31749	0.65128	1303.69
22:	0.48443	0.09903	0.41655	1250.26
23:	0.64449	0.07151	0.28400	1173.82
24:	0.63025	0.07758	0.29217	1168.39
25:	0.64778	0.07849	0.27373	1165.26



$$C_{fix} = O_{Zn} + O_{Fe} + (0.017Fe_{Tot})$$



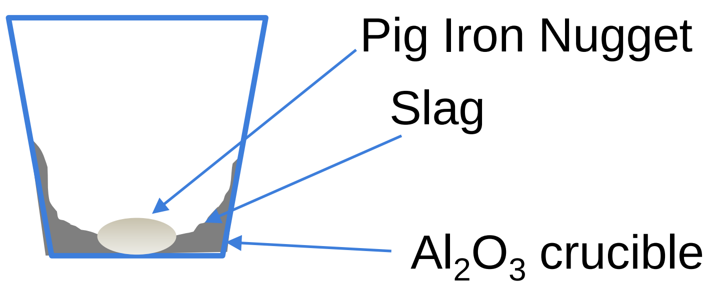
Trials

Fluxing BOS/BF dust pellets using SiO_2

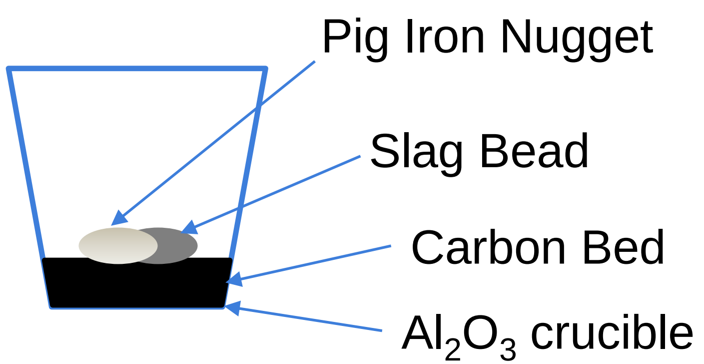
- 1450 °C for 22 minutes in air using alumina crucibles in a laboratory box furnace.
  - Pellets were hot charged into preheated crucibles and replaced into furnace. Furnace temperature stabilized after 5 minutes. Incomplete separation can be observed in as little as 10 minutes
- Control pellets without SiO_2 addition showed good reduction and zinc removal but no melting and slag separation
- Fluxed pellets rapidly underwent melting and separation **however** the molten slag attacked and destroyed crucibles through diffusion and alloying.
  - Recovery of Fe and Slag extremely challenging!

Mitigating the aggressive slag formed through the process

Slag Wetting onto Crucible Walls



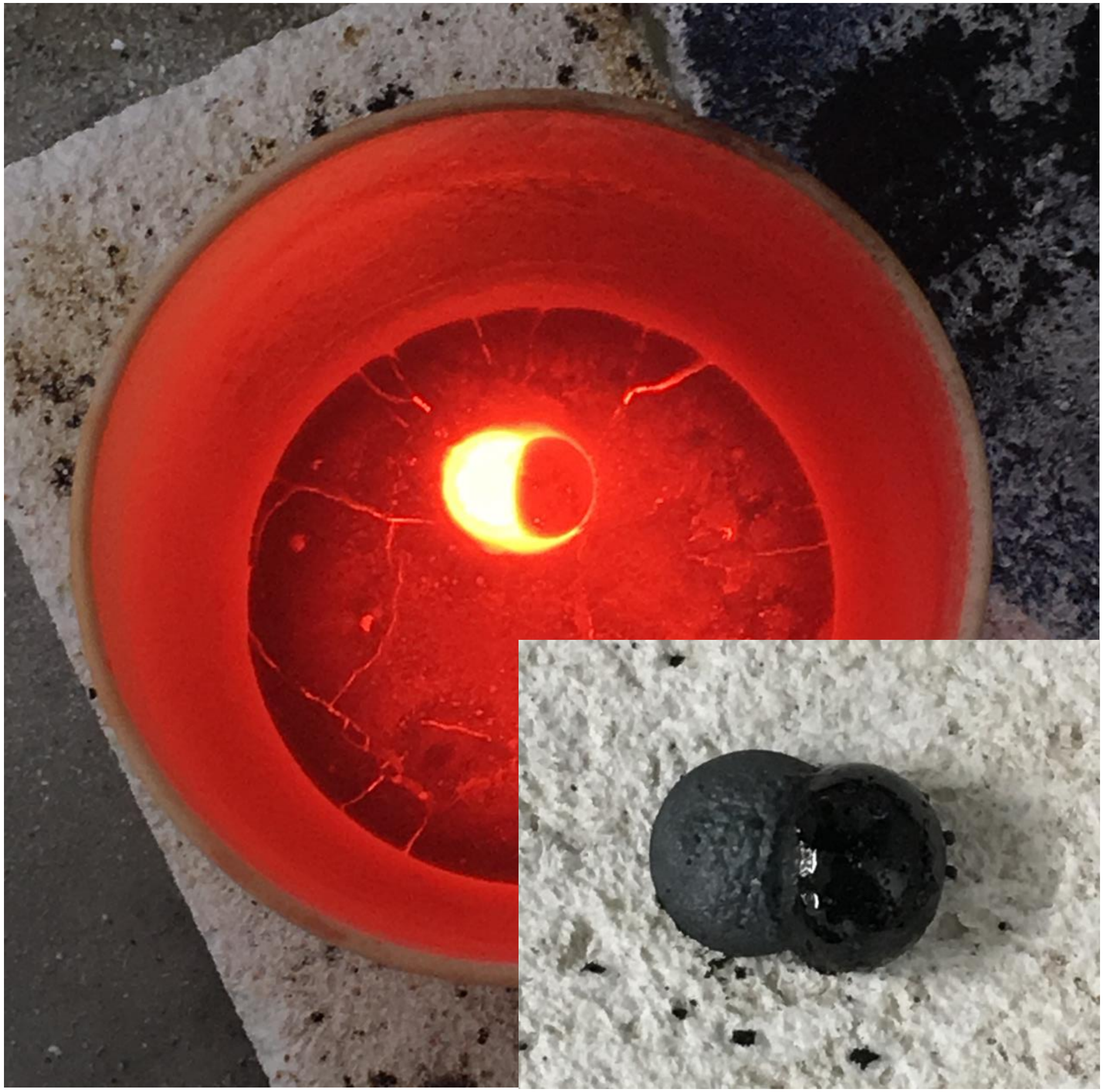
Proposed Solution



Material selection for Crucibles

- The slag adhesion to the crucible causes a number of concerns
  - Alloying and thinning of crucible walls
  - Extremely short lived crucibles
  - Difficult to extract products for analysis
- Experiments with synthetic slag suggested that slag would not wet a graphitic surface
  - However, graphite oxidizes at a high rate at working temperatures and would still consume refractory at unacceptable rates in oxidizing atmosphere
- Trial of using a compacted bed of graphite within an Al_2O_3 crucible

Success!



Notes

- The yield of metallic pig iron was 91% from the starting pellet
    - Dust loses during initial heating and gasification
    - Emulsion loss to slag
    - FeO dissolved within slag
- Slag and iron physically separated with ease
- Zn in pig iron nugget at 0.01% initial levels of green pellet as determined by ICP
    - Small crystals of ZnO are observable around rim of crucible

Benchtop proof of concept

Outcomes

- It is experimentally possible to use an RHF type process to rapidly dezinc, carburize and melt BOS dust using BF dust, yielding pig iron nuggets by fluxing with SiO_2
  - Silica can be sourced flexibly, from sand, iron ore fines etc.
- Production of Pig Iron Nuggets in this manner is similar in reaction times to traditional RHF DRI production (such as in Fastmet) and only 100 °C hotter
- Zinc removal performance is excellent, more than satisfactory for recycling Zn bearing steelmaking by-products
- A modified Pig Iron Nugget process would be less reliant on expensive pellet binding agents

Forward Focus

Benchtop Proof of Concept → **Extended Trials** → **Scalability Analysis** → **Commercially Viable Zn Separation Solution**

- In principle, Pig Iron Nugget Production through an RHF while simultaneously removing zinc from steelmaking reverts has been demonstrated

- Explore key process mechanisms and parameters
- Carburization, C_{fix}, Slag chemistry, heat treatment profile, pellet size etc.
- Refractory material selection

- Value in Use modelling
- Energy/Mass balance for commercial scale unit
- Feasibility
- Cost Benefit and Risk Reward analysis
- Raw materials selection

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Thank You for Listening

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