

SPL AND RED MUD: VALUE CREATION FROM HAZARDOUS WASTES

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Presenter's Biography

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Outline

SPL: Why should we care?

Applications / New Ideas

As flux for metal recovery in non-ferrous

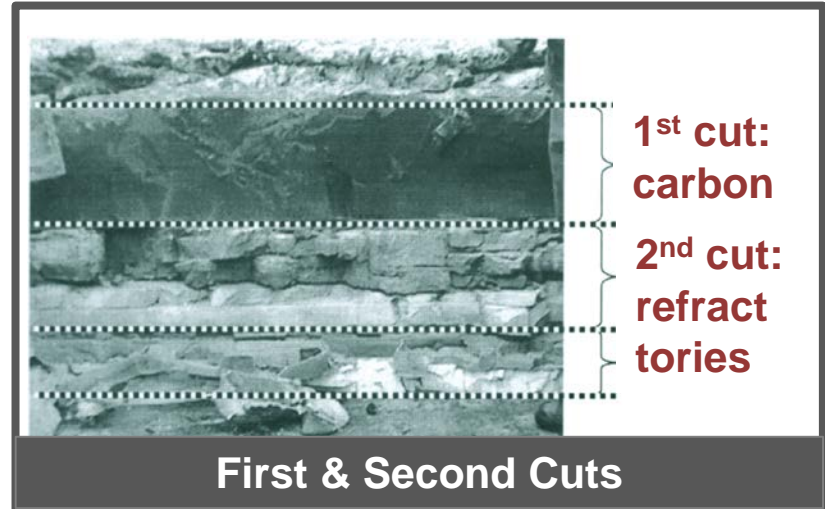
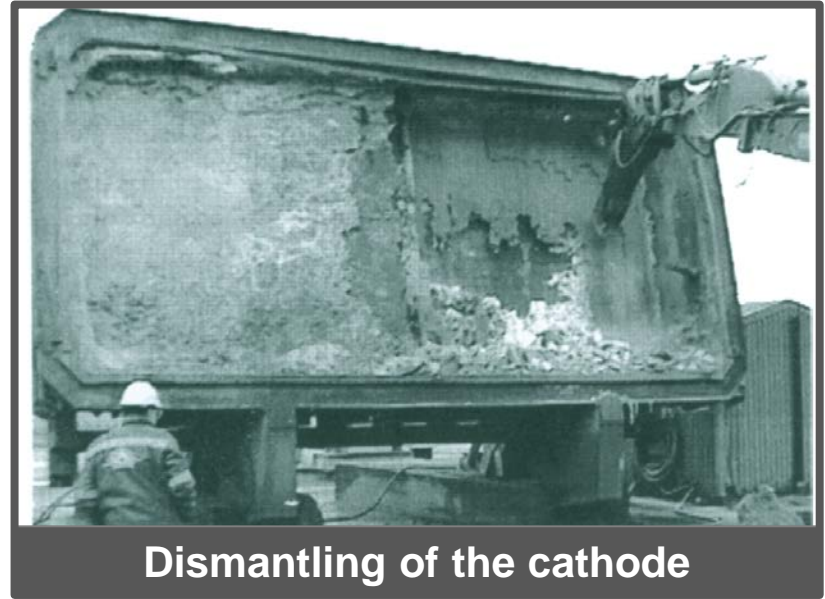
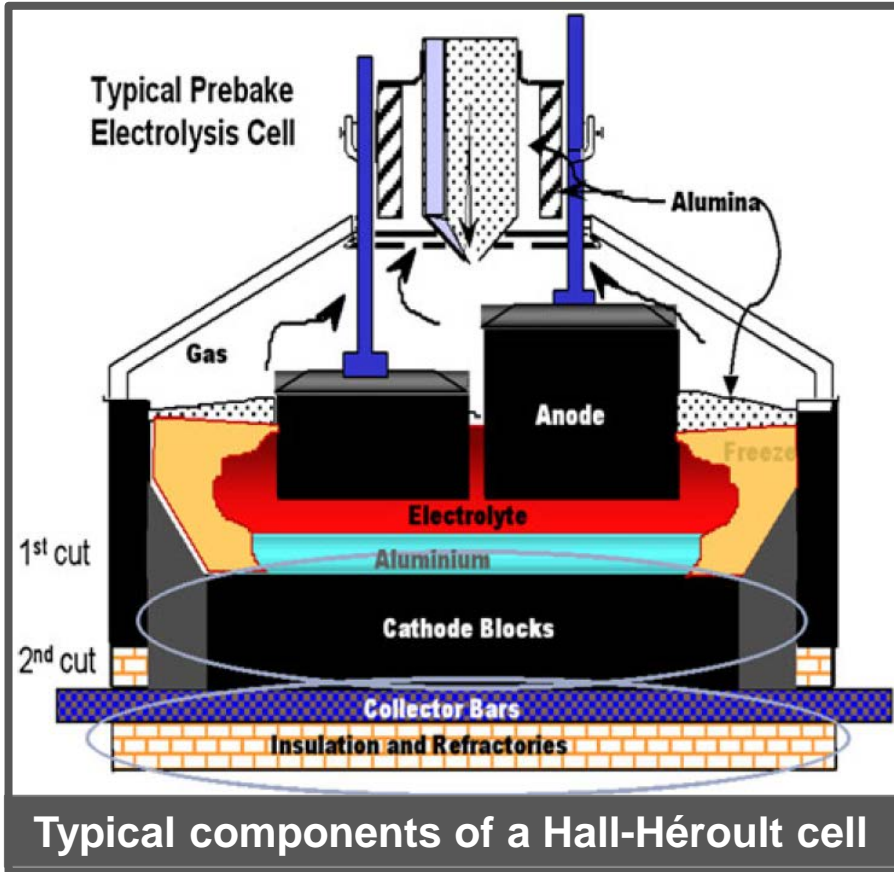
As alternative fuel in blast furnaces

**As carbon injection source in
steelmaking**

As flux additive in ferrous metallurgy

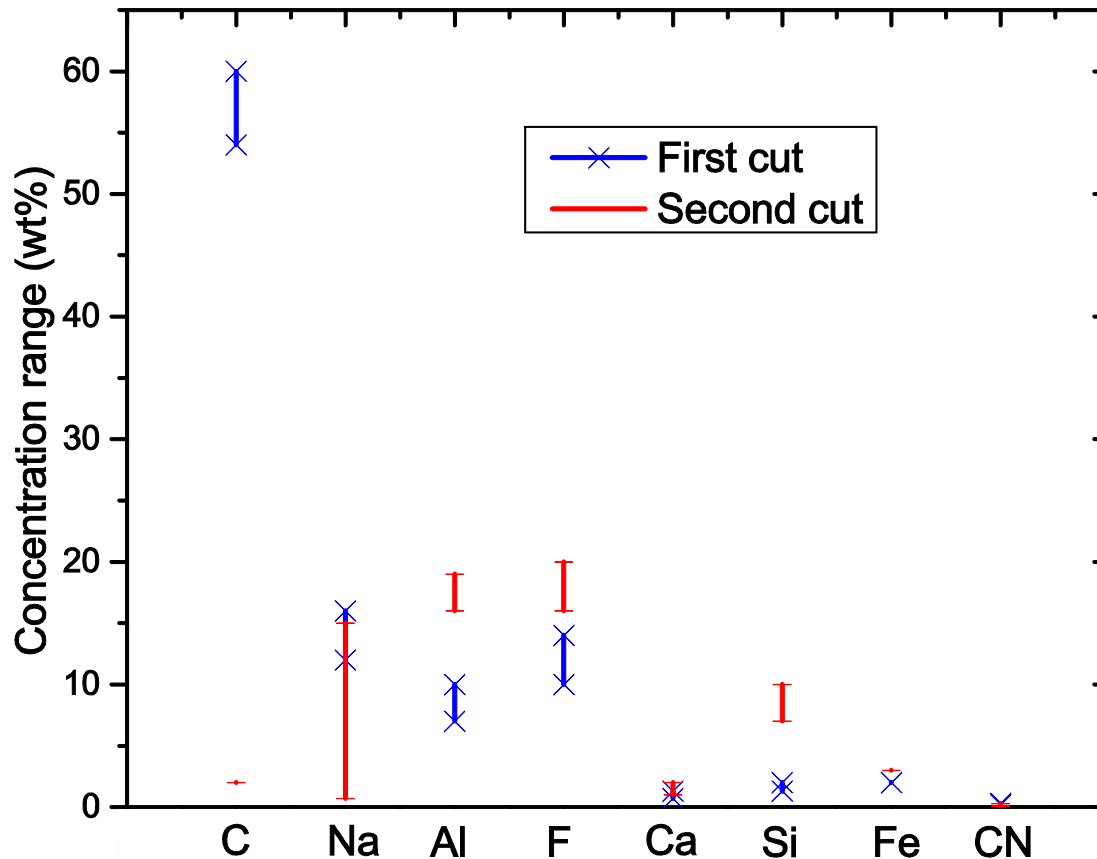
Summary of Key Insights

What is SPL?



Potlining life: 5 - 8 years

Chemical Composition of SPL



Major constituents

1st cut

- Graphite
- Na_3AlF_6
- NaF
- Al_2O_3
- CaF_2
- Fe_2O_3
- NaCN
- $\text{NaFe}(\text{CN})_6$

2nd cut

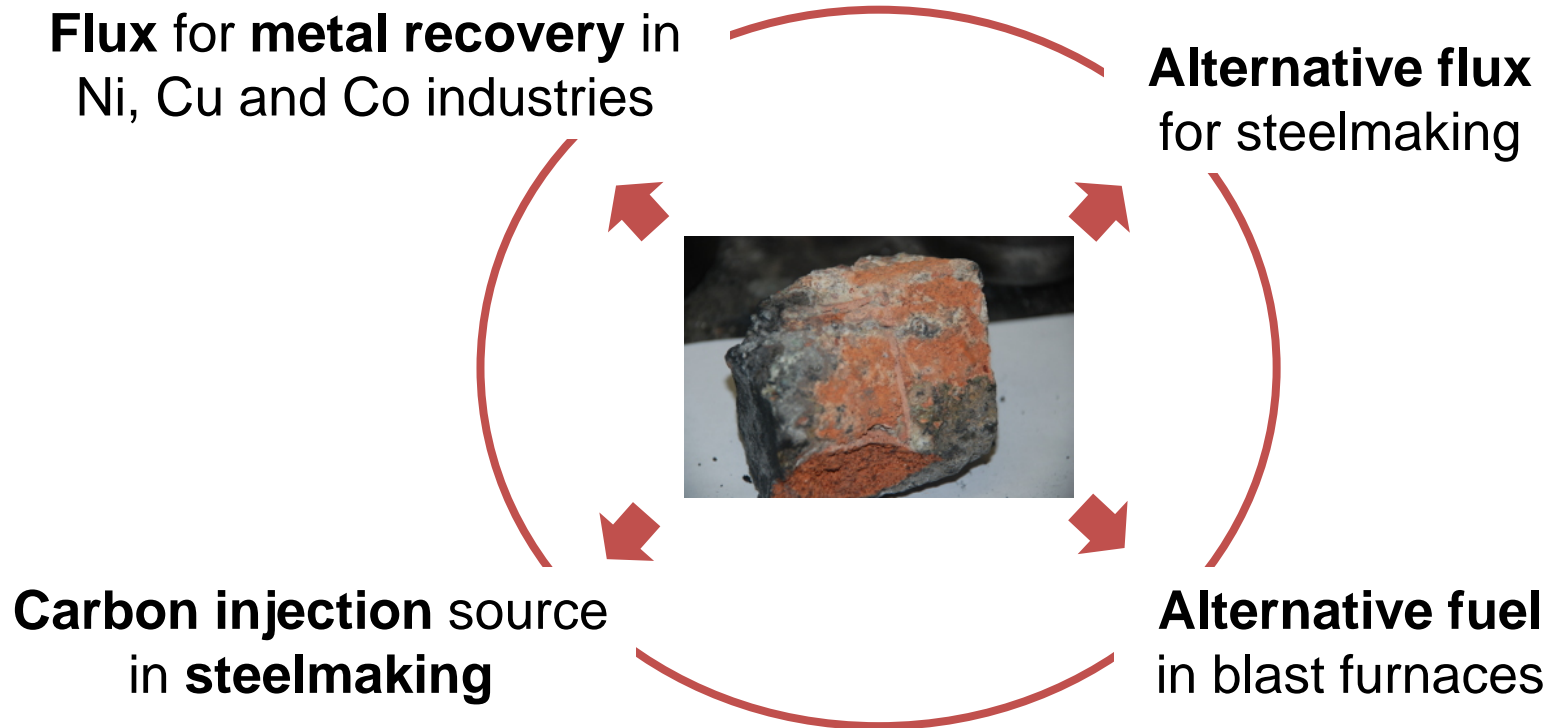
- SiO_2
- Al_2O_3
- Na_2O
- CaO
- Fe_2O_3
- MgO
- K_2O
- F

CN & F makes SPL toxic, and difficult for direct recycling

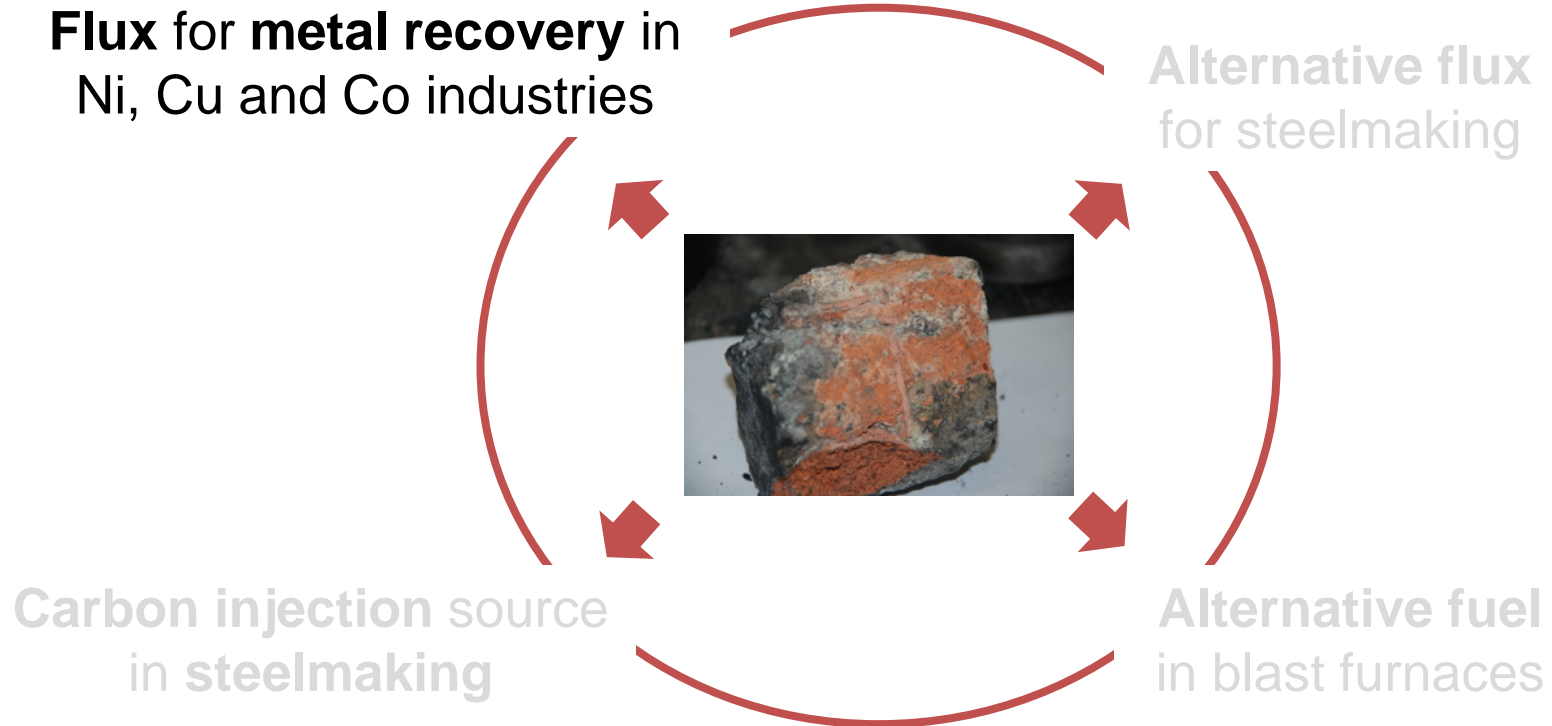
Motivation

- ▶ **Hazardous** solid waste discharged from the aluminum smelter with a generation rate of **1 – 1.5 Mtpa**
 - ▶ High treatment **cost**: \$400 – \$1200 per ton
 - ▶ **Current practice**: Stored at the aluminum smelter sites or placed in landfills
 - ▶ **Environmental impact**: Leached materials from SPL may contaminate the earth's crust and underground water.

Applications



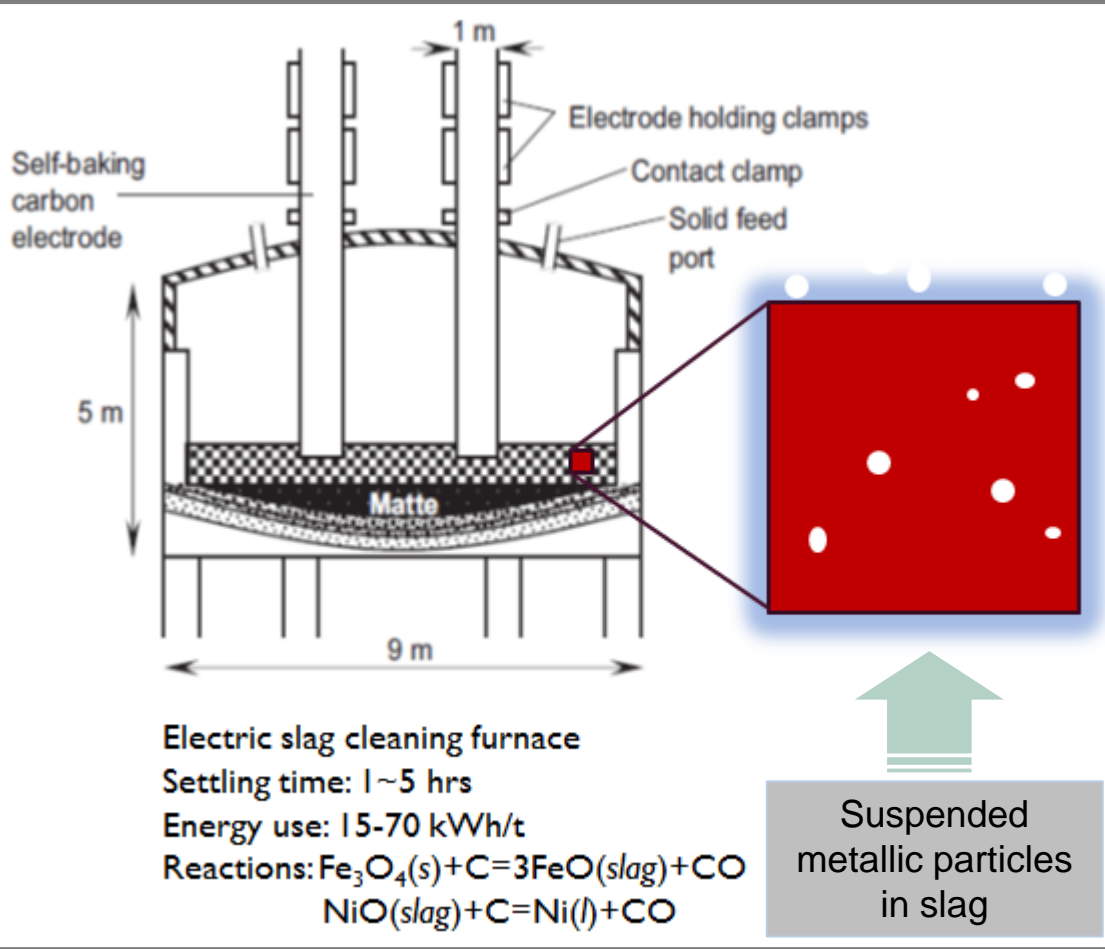
Applications



Cu/Ni/Co Converter Slag Cleaning

1960s - Present

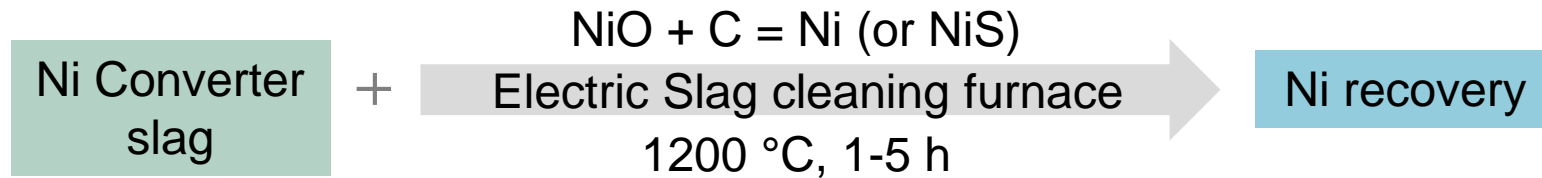
Separation/slag cleaning furnace



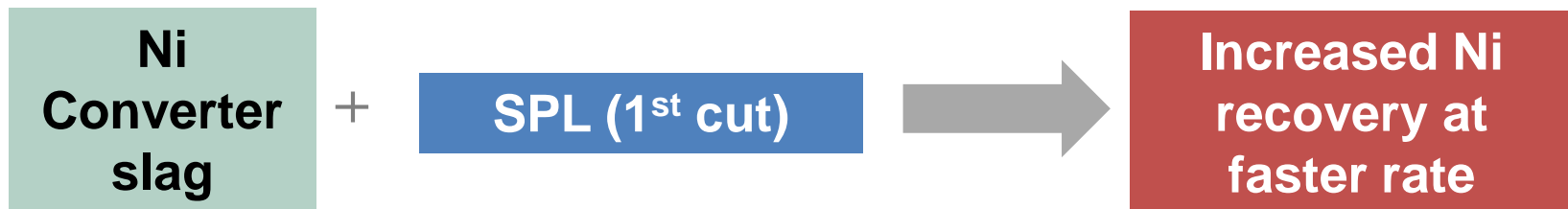
- $t = 1 - 5$ hours
- $T = 1200 - 1300$ °C
- **Electrode heating** necessary for settling of matte/metal droplets
- $E = 15 - 70$ kWh/t
- **Reduction** of spinel & Ni/Co/Cu oxides to suspended Ni/Co/Cu sulfide drops

The Idea

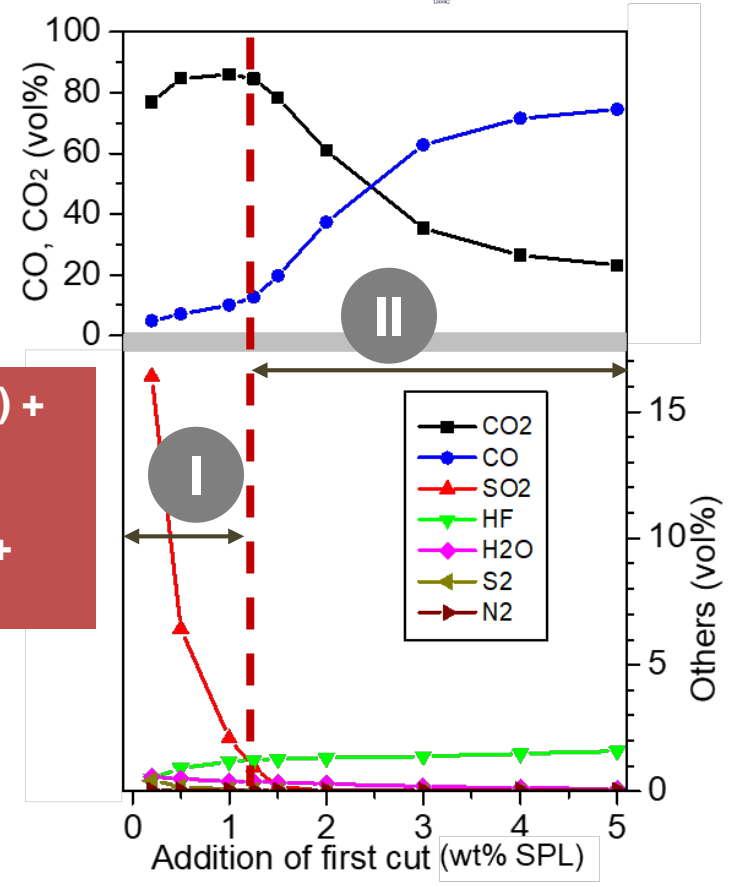
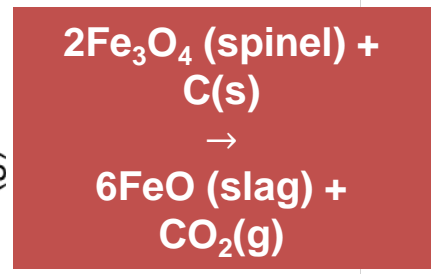
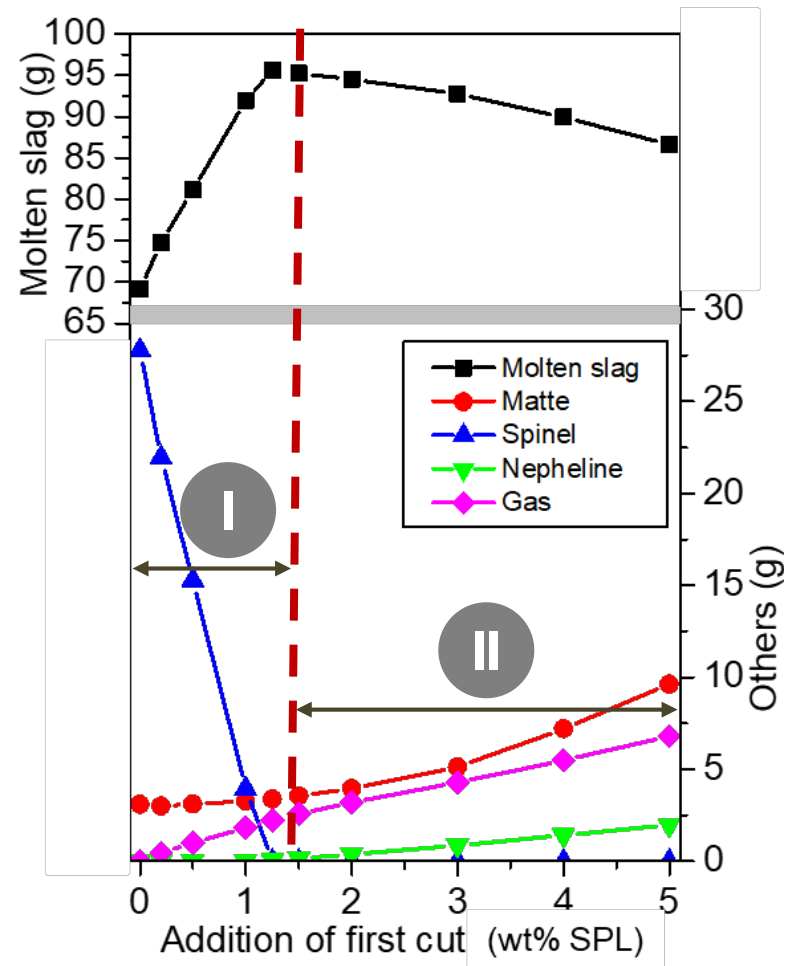
Conventional route:



Proposed Route:



Our Findings: Process Model



I Spinel ↓ Slag/Gas ↑

II (Oxides)_{slag} / Slag ↓ Matte / Gas ↑

I p_{O2} ↑ CO₂ ↑

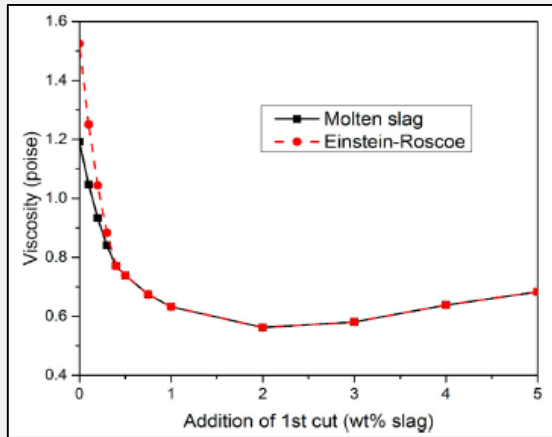
II p_{O2} ↓ CO / HF ↑

Our Findings: Process Model

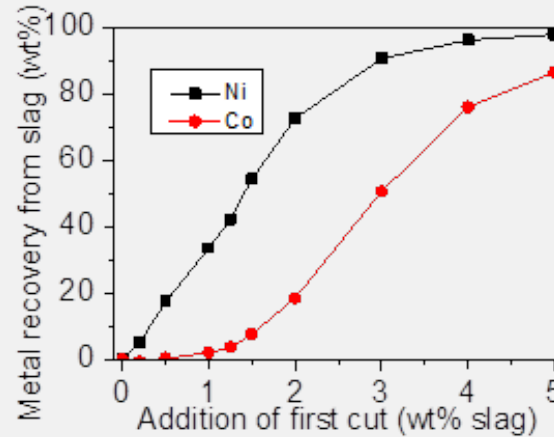
Ni converter slag +

SPL
(1st cut)

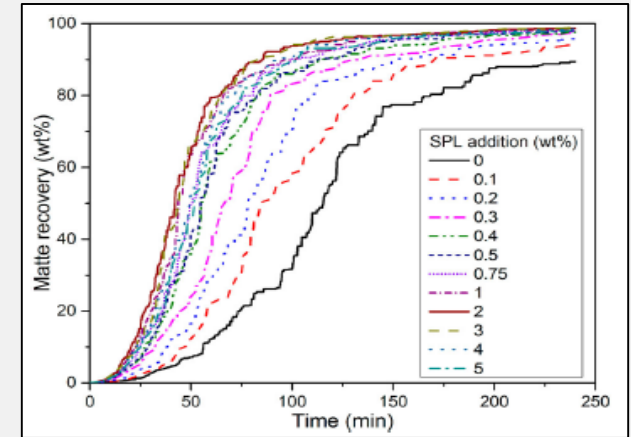
Increased matte
recovery at faster rate



Slag Viscosity ↓



Metal recovery ↑

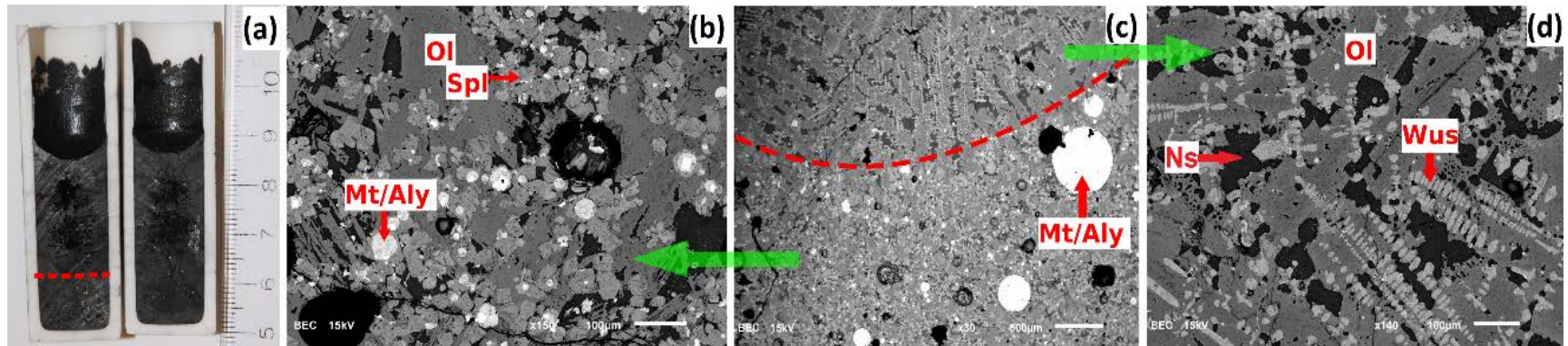
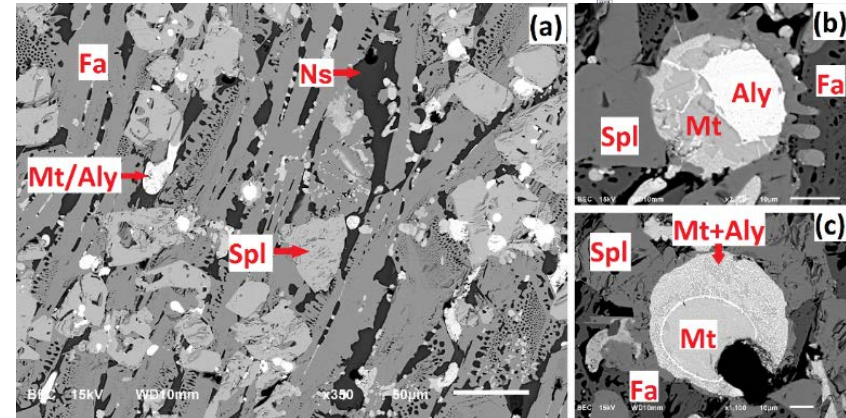


Metal recovery vs time ↑

- ▶ Fluorides in SPL reduce slag viscosity
- ▶ Increased matte settling rates → Greater metal recovery

Our Findings: Experiments without SPL Addition

- Mechanism of **matte entrainment** in the converter slag → **attachment** of the matte or metal droplets to the solid spinel particles
- Solid spinel particles in slag **hinders the coalescence and settling** of matte/ alloy droplets in the absence of SPL addition.



(a) Solidified slag sample

(b) Lower region: high proportion of spinel & matte/alloy particles; **increased viscosity**

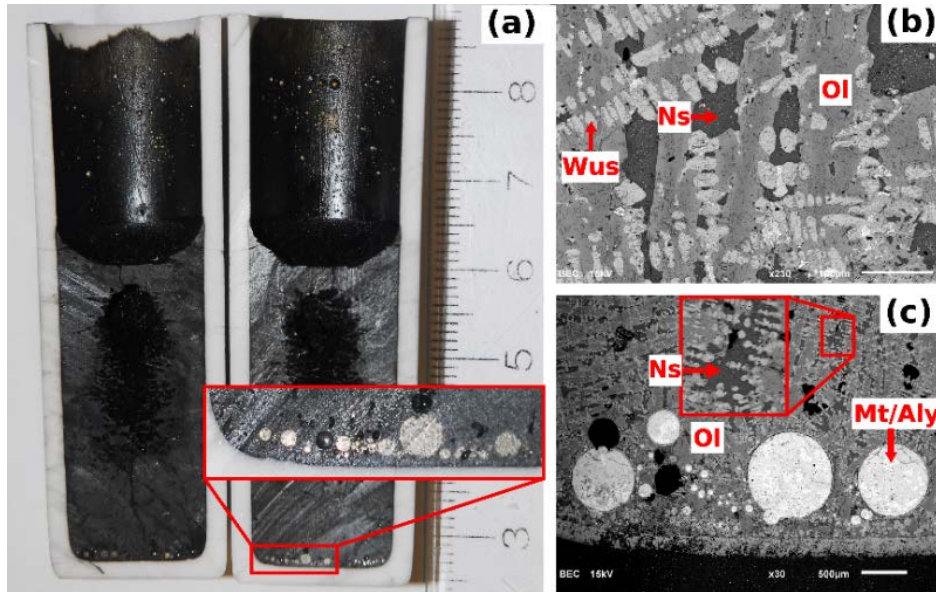
(c) Boundary b/w upper & lower regions

(d) Upper region: Almost no matte particles

**Fa: Fayalite (Fe_2SiO_4); Ol: olivine; Spl: Spinel (Fe_3O_4); Mt: Matte (Fe,NiS); Wus: Wustite; Aly: Ni-Fe alloy; and Ns: alkaline-bearing ferro-aluminosilicate

Our Findings: Experiments with SPL Addition

- Matte particles **settle to the bottom** due to the **complete reduction of solid spinel** particles by the carbonaceous component of SPL



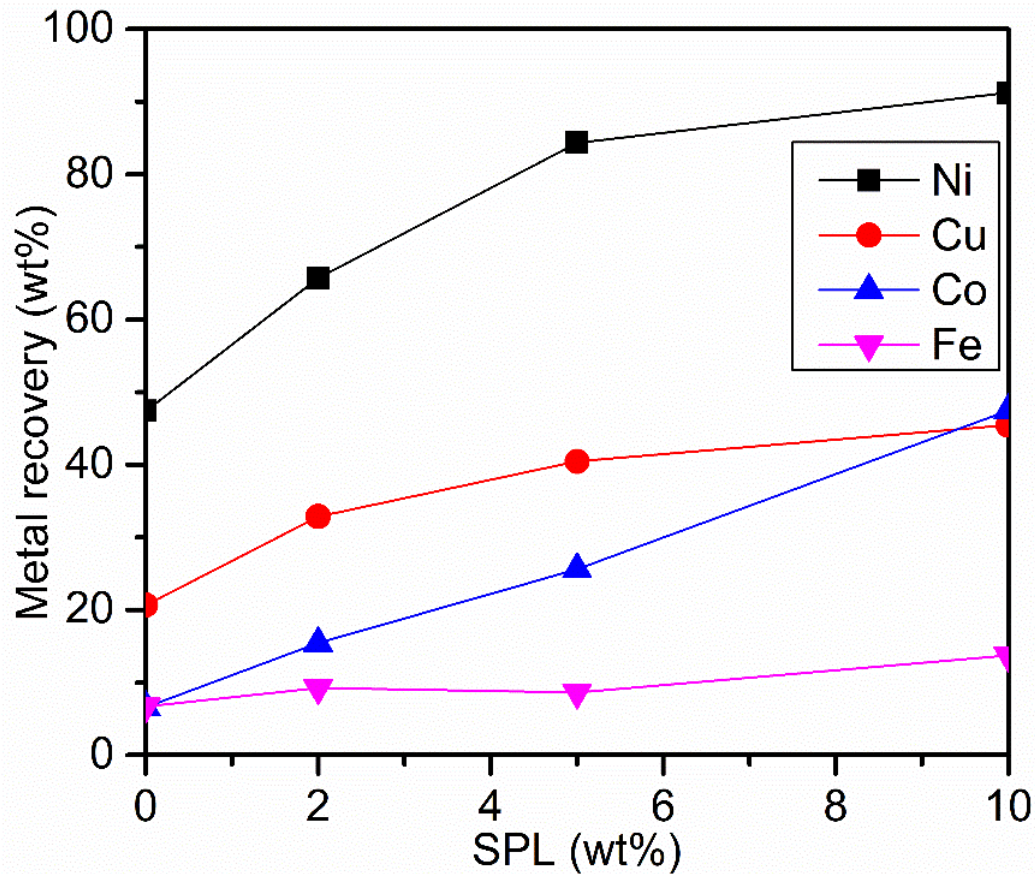
- Higher metal recoveries are achieved at higher SPL additions due to **further reduction of the dissolved oxides in the molten slag**, forming metals that report to the matte/alloy phase

**OI: olivine; Mt: Matte (Fe,Ni)S; Aly: Ni-Fe alloy; Wus: Wustite; and Ns: alkaline-bearing ferro-aluminosilicate

- ~ **9 wt% of total fluorine** contained in the SPL gasifies
 - Carried by CO/CO₂ gas
 - Lost in gas stream

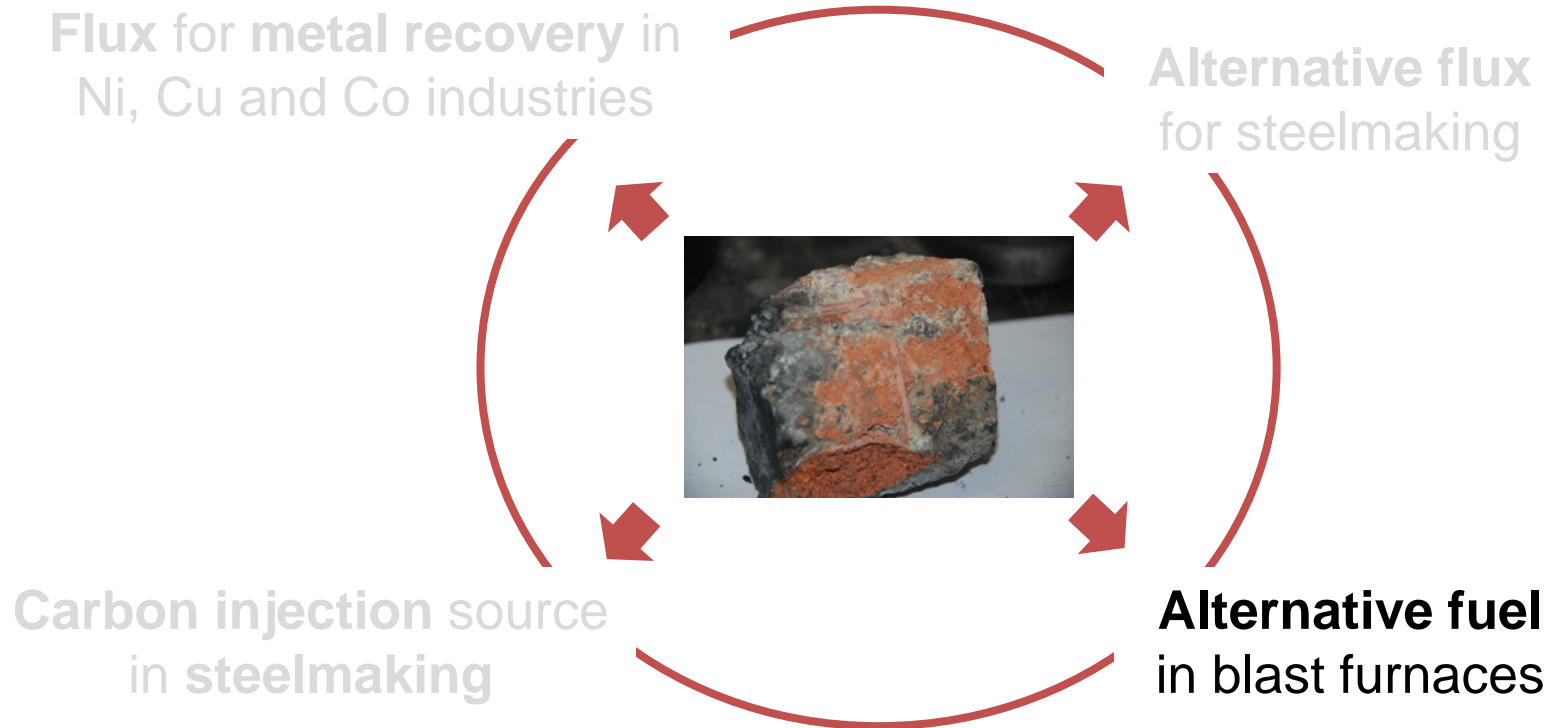
- Remaining fluoride and Na-bearing components (e.g. NaF, and nepheline (Na-K-Al-Si-O)) **dissolves in the molten slag**
 - Reduces slag viscosity
 - Enhances the matte settling process

Our findings: Experiments with SPL Addition



Metal recoveries of **91 % Ni, 45 % Cu and 47 % Co** were achieved with the addition of **10 wt% SPL**

Applications

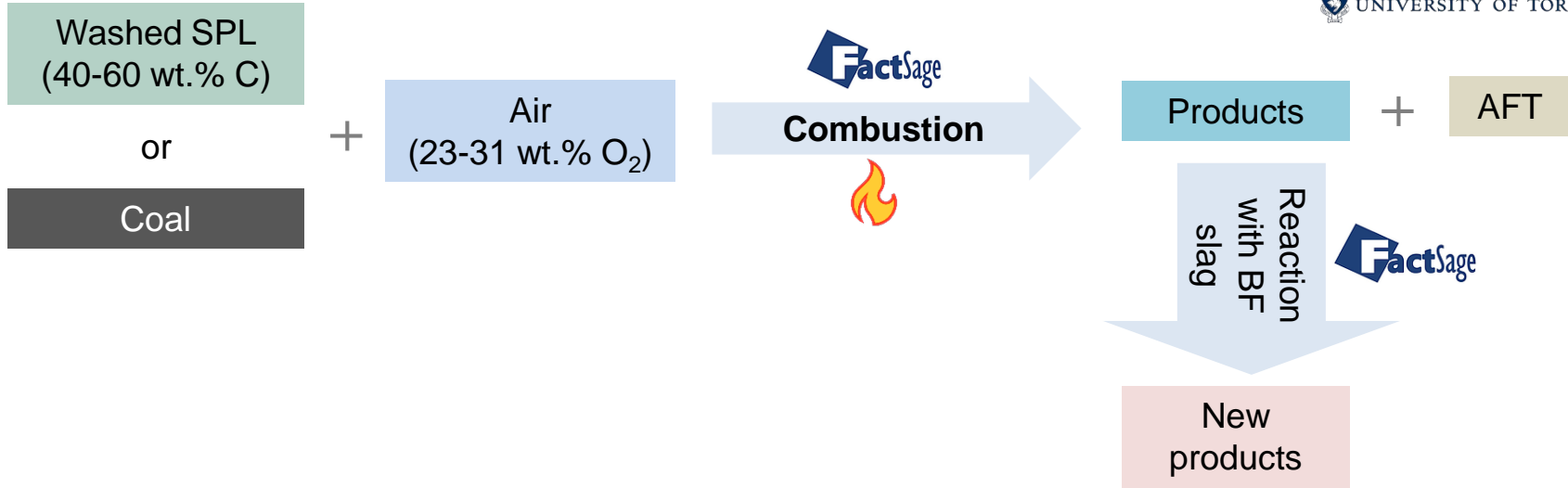


Basis of Proposed Work

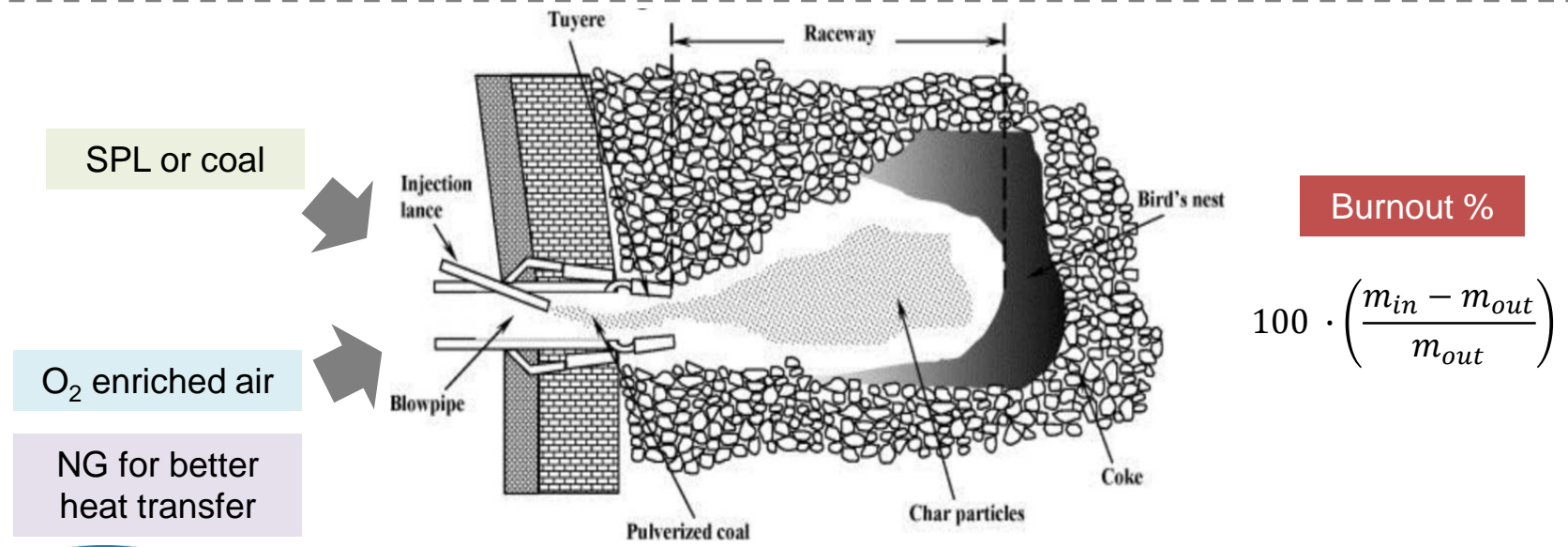
- ▶ Coke production: excessive **emission of greenhouse gases** and energy wastage
- ▶ Coke ovens: major source of **pollution** in the steel plants
- ▶ Coke price: constitutes **>60% of total burden cost**. Variable market price of coke: \$130 to \$800/ton in 2010
- ▶ Trend: **replace coke** with other carbonaceous materials such as PCI, NG, Hydrogen and Oil
- ▶ SPL: 50% graphitic carbon; can be recycled as an **alternative fuel** in the blast furnace to reduce coke rates
- ▶ Combustion of SPL: CN decompose into C & N; **energy released can be used in furnace**

Calculations Performed

Equilibrium calculations



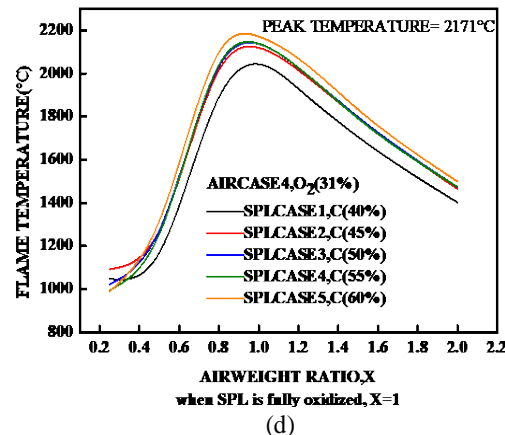
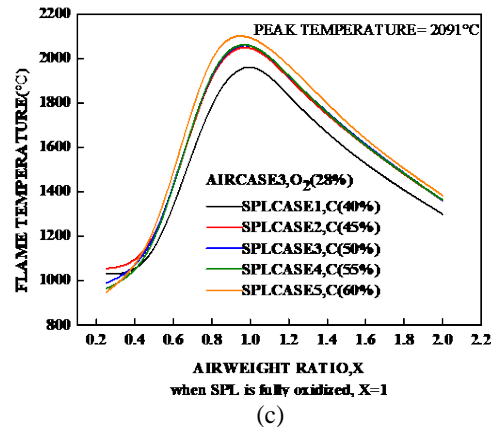
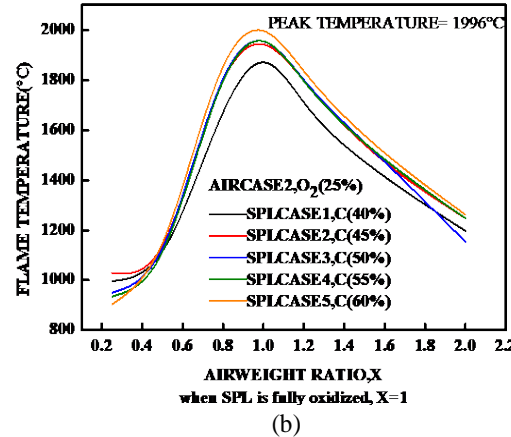
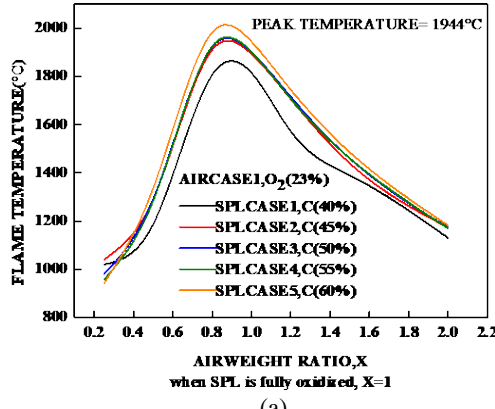
CFD calculations



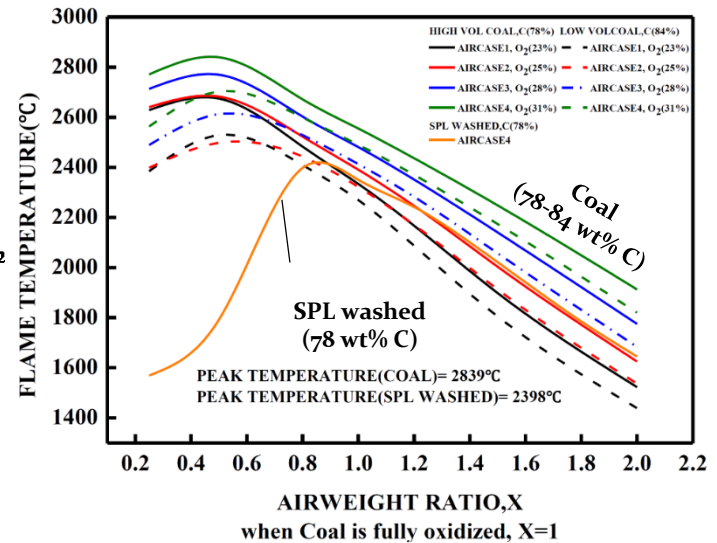
Equilibrium Thermochemical Calculations

SPL

Coal



Peak AFT_{SPL} ~ 2200-2400 °C



** Air Wt ratio (X) =
Fuel sample wt / Air wt

Peak AFT_{coal} ~ 2800 °C

SPL has potential to be used as an alternative BF fuel

Our Findings: Equilibrium Thermochemical Calculations

SPL combustion

Washed SPL
(40-60 wt.% C)

+

Air
(23-31 wt.% O₂)

FactSage

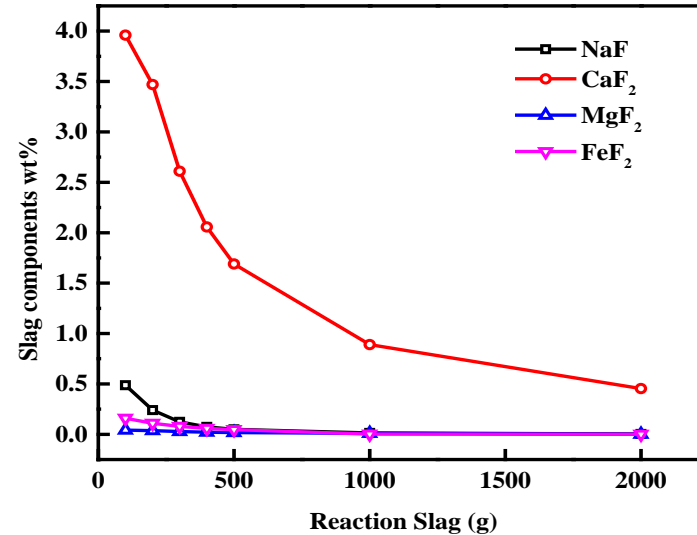
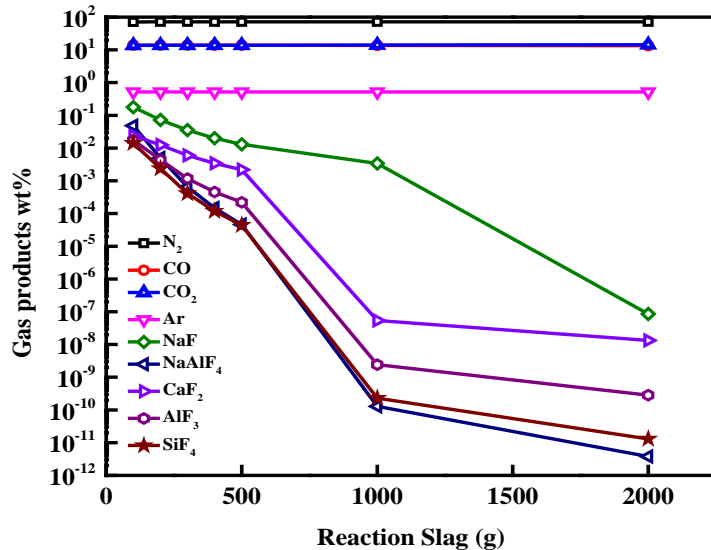
Combustion

Combustion products	N ₂	CO ₂	CO	NaF	Ar	AlF ₃	Na	FeF ₃	FeF ₂	NO
wt%	64.44	19.36	12.62	1.46	0.67	0.24	0.19	0.12	0.11	0.1

Fluorides_{off-gas}
~ 1.5-2 wt%

Environmental concern

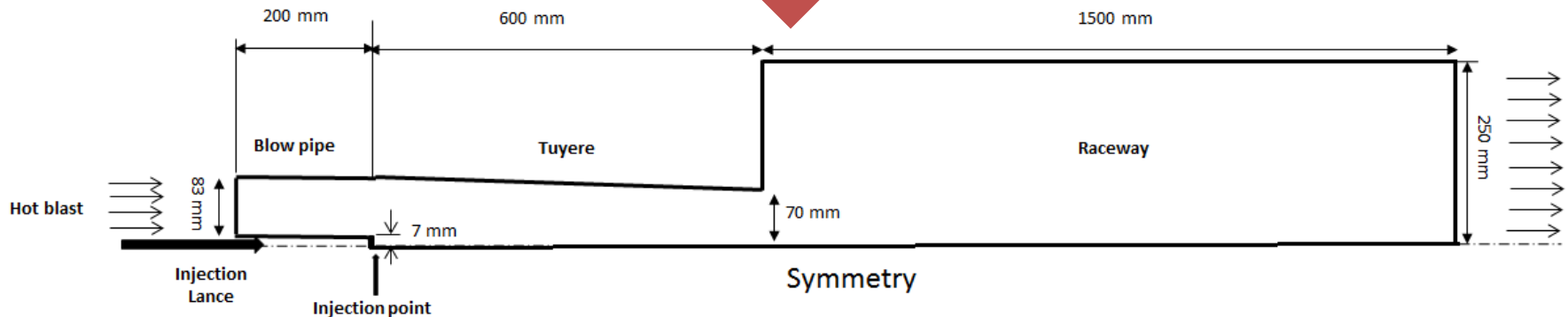
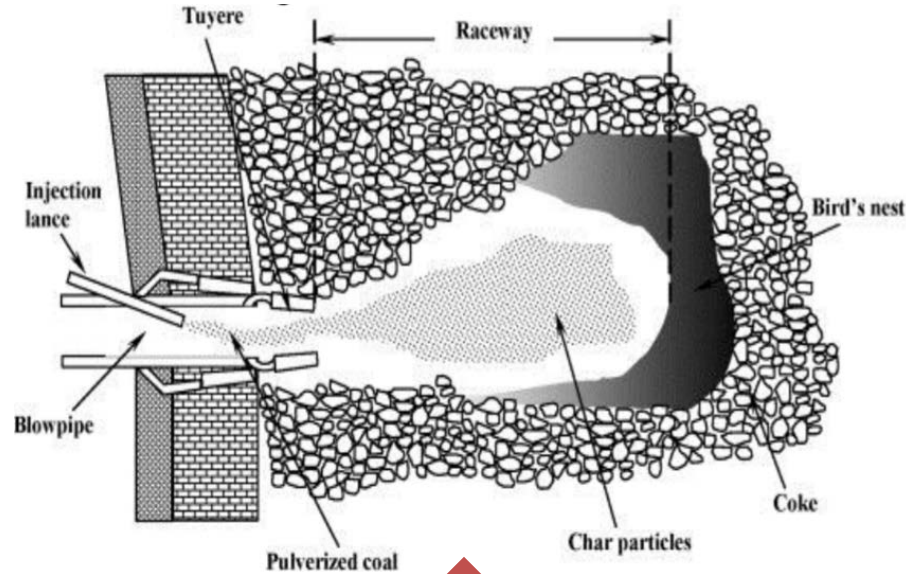
Reaction with BF slag



Fluorides can be captured in BF slag

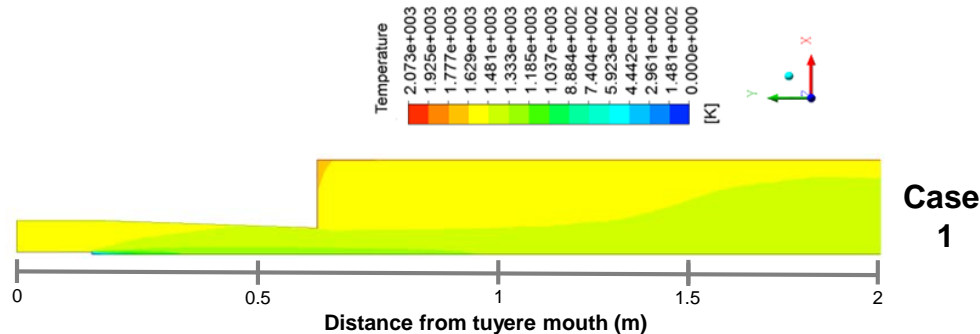
Our Findings: Simplified CFD Calculation Domain

Tuyere
raceway
system



Our Findings: CFD Calculations

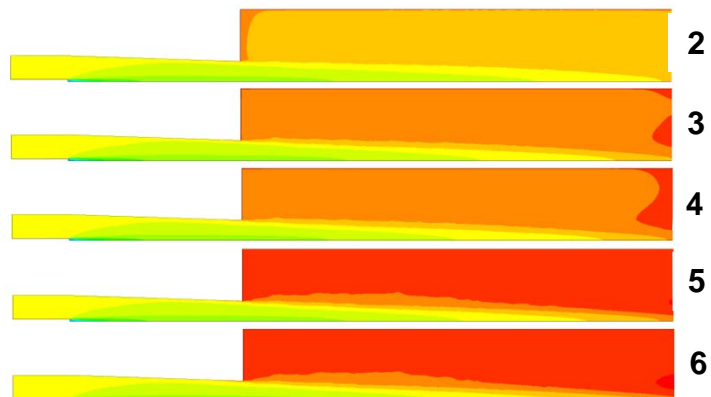
Air combustion



Case	Solid	Injectant Gaseous	O ₂ level (wt%)	Burnout%
Base	High vol	X	23	74
Case1	SPL washed	X	23	2.89

SPL remains unburnt (due to lesser residence time on account of higher ρ & C_p than coal)

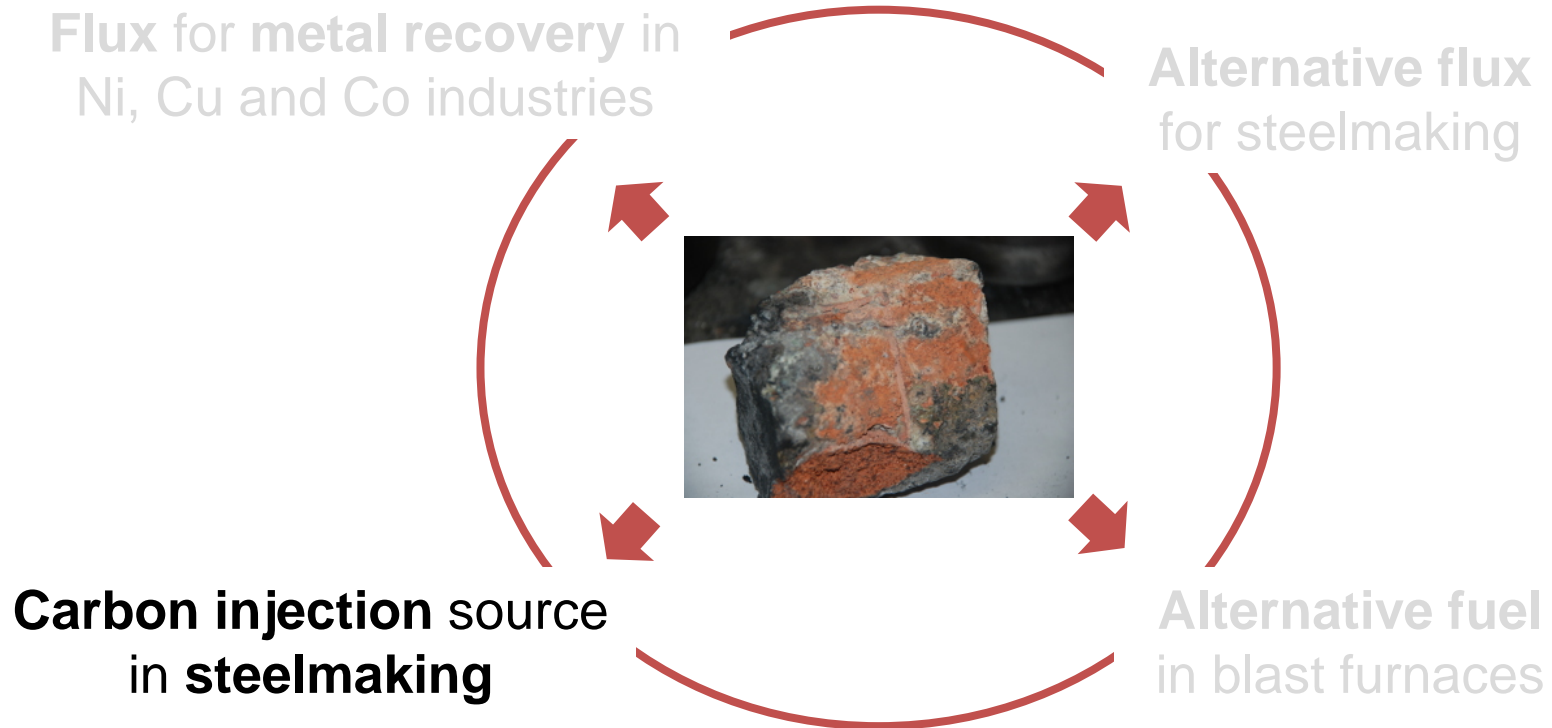
Using NG with carrier as N₂



Case	Solid	Injectant Gaseous	O ₂ level (wt%)	Burnout%
Case2	SPL washed	25 wt% NG (carrier N ₂)	23	8.78
Case3	SPL washed	50 wt% NG (carrier N ₂)	23	12.36
Case4	SPL washed	50 wt% NG (carrier N ₂)	25	14.39
Case5	SPL washed	75 wt% NG (carrier N ₂)	23	14.52
Case6	SPL washed	75 wt% NG (carrier N ₂)	25	18.17

Introduction of NG results in increase of T_{raceway} , heat transfer to SPL particles & burnout

Applications



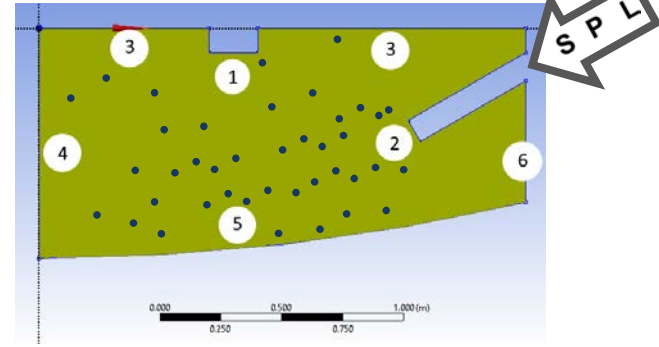
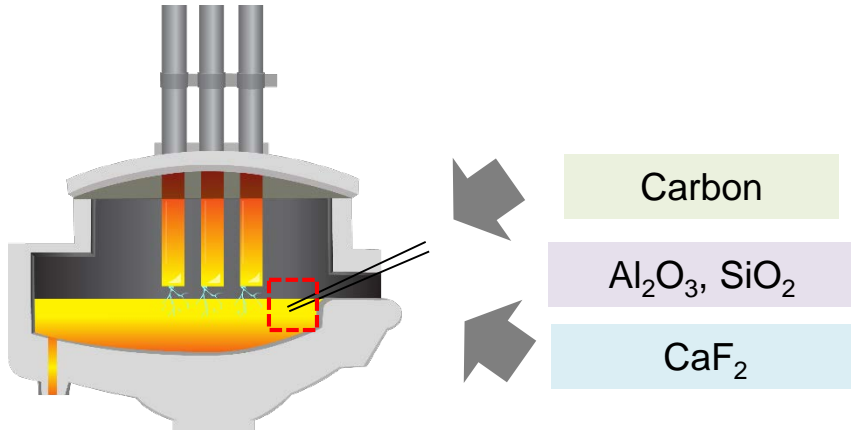
Basis of Proposed Work

- ▶ Electric Arc Furnaces (EAF) requires carbon:
 - to **reduce** oxidized Fe & other oxides
 - to act as a **fuel source** (heat released via combustion)
 - to **adjust the** $[C]_{\text{final}}$ → liquidus & quality of the finished product

- ▶ SPL: primarily carbonaceous material containing significant amount of SiO_2 and Al_2O_3 → replenish slag with flux

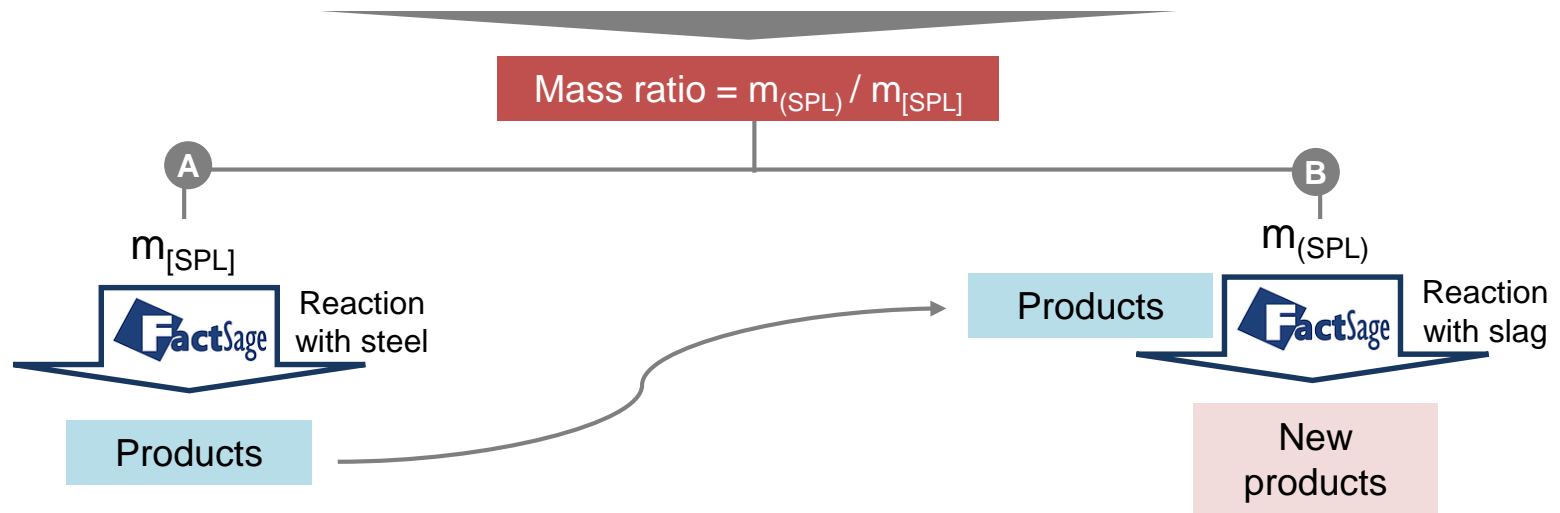
Calculations Performed

CFD calculations



- 1 Arc spot
- 2 Injection lance (Cu)
- 3 Steel/Slag interface
- 4 Symmetry plane
- 5 Water cooled
- 6 refractory walls

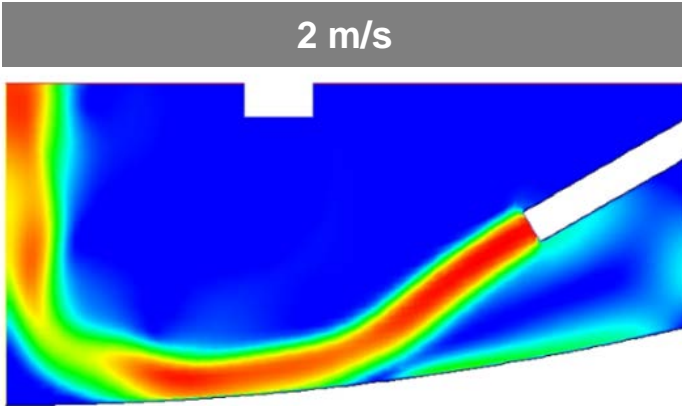
Equilibrium calculations



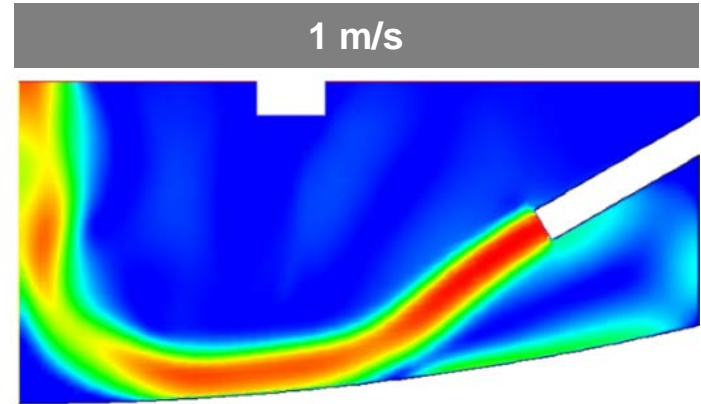
Our Findings: CFD Calculations for Different Injection Velocities



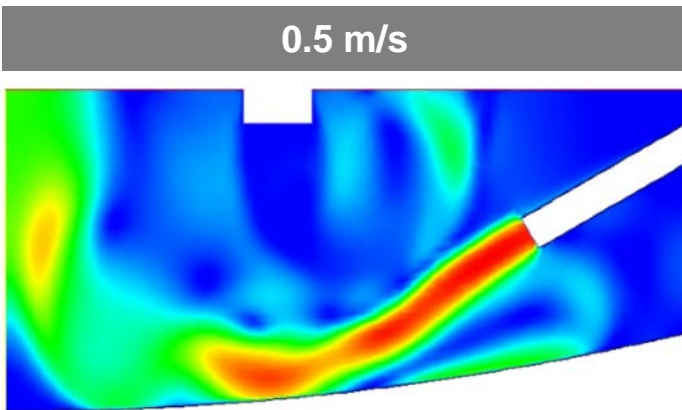
2 m/s



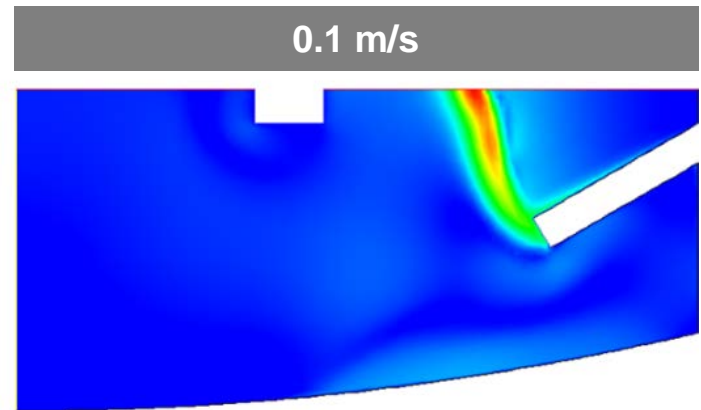
1 m/s



0.5 m/s

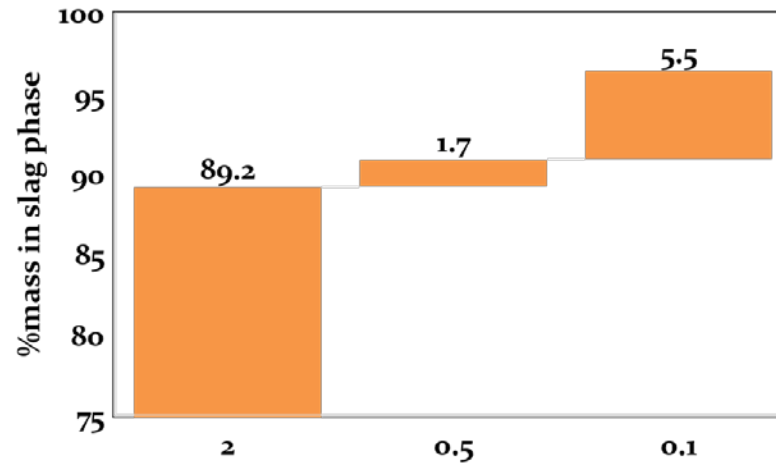


0.1 m/s



Our Findings: CFD and Thermochemical Calculations

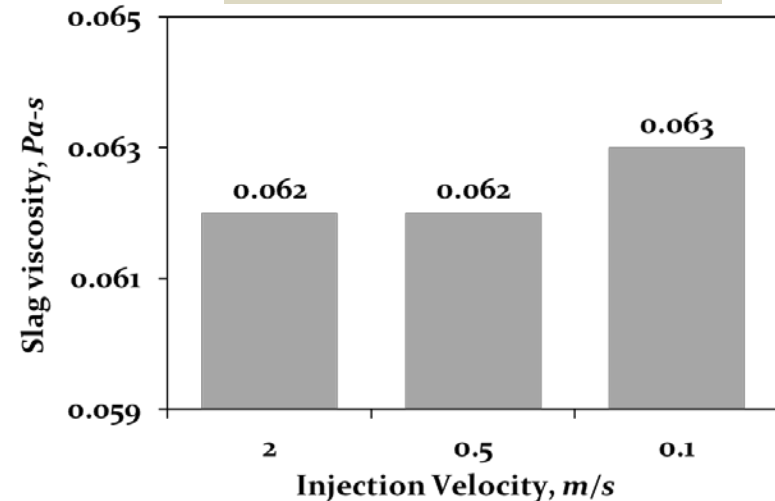
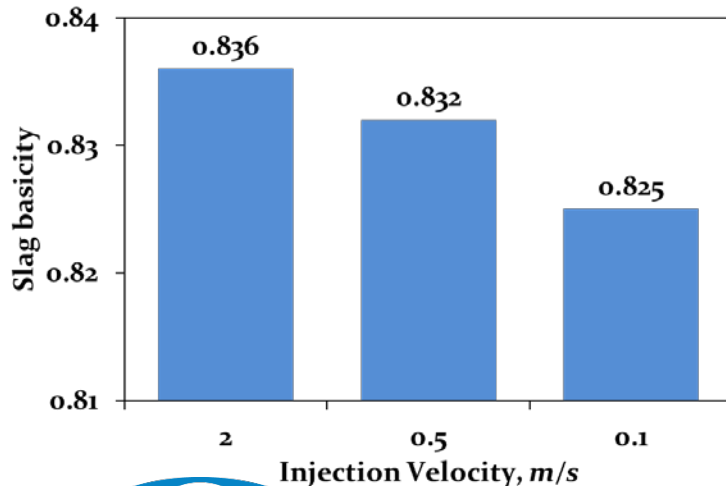
%SPL mass in slag phase

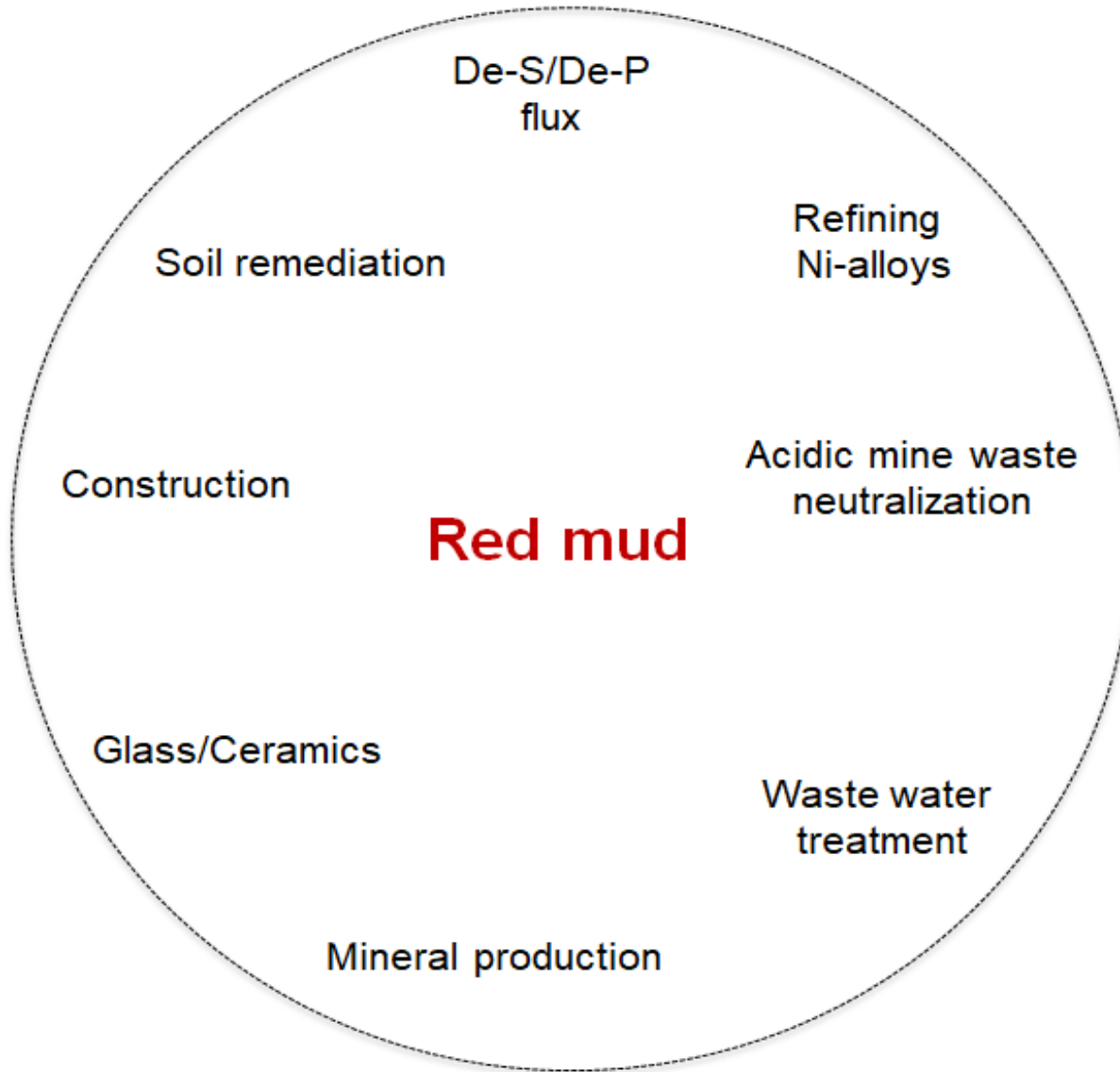


Slag basicity

Injection Velocity, m/s

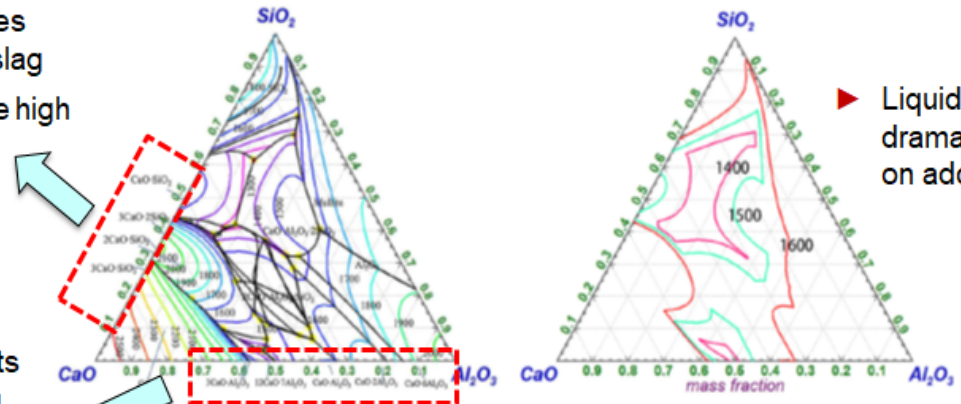
Slag viscosity





CaO-SiO₂-Al₂O₃

- ▶ CaO flux generates CaO-SiO₂-Al₂O₃ slag
- ▶ Components have high MP (> 1550 °C)

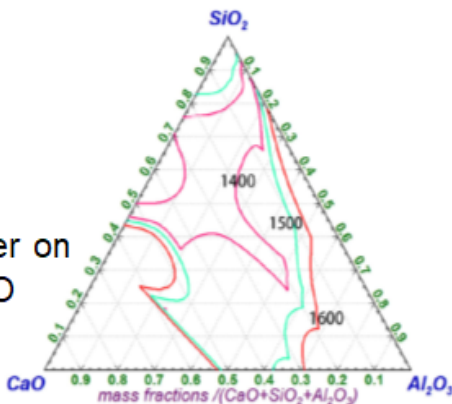


- ▶ Liquid region dramatically increases on addition of Al₂O₃

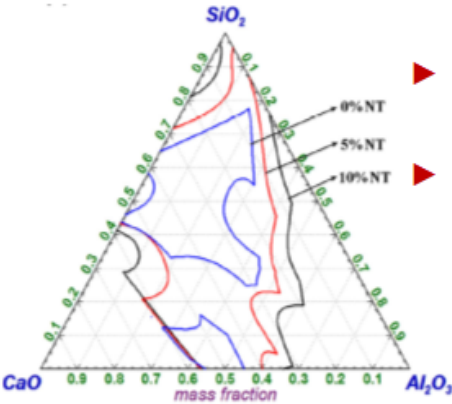
- ▶ Low MP components produced on adding Al₂O₃ → reduce MP of slag & improve its fluidity

CaO-SiO₂-Al₂O₃-5% Na₂O

CaO-SiO₂-Al₂O₃-Na₂O-Ti₂O



- ▶ Liquid region increases further on addition of Na₂O



- ▶ NT: Na₂O + TiO₂ mixture (2:1)
- ▶ Slag fluidity increases on adding red mud

Our Findings: Thermochemical Analysis

Major Reaction	MP of Product Phase
$12(\text{CaO})_{\text{slag}} + 7(\text{Al}_2\text{O}_3)_{\text{RM}} \leftrightarrow \text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$	1363°C
$(\text{CaO})_{\text{slag}} + 3(\text{SiO}_2)_{\text{slag}} + 2(\text{Na}_2\text{O})_{\text{RM}} \leftrightarrow \text{Na}_4\text{CaSi}_3\text{O}_9$	1183°C

Our Findings: Economic Case Study

Reagents Used	Units	Present				With Red Mud (2:1)		
		CaO	CaC ₂	Mg	Total	Red Mud	CaO	Total
Annual Production of Hot Metal	million tonnes / year	5				5		
Reagent Consumption	ton / year	5000	15000	2000	22000	335000	165000	500000
Market Price (USD/T)	USD/ton	64.29	714.29	2428.57		0	64.29	
Total expenditure on reagents	M USD/ year	0.32	10.71	4.86	15.89	0.00	10.61	10.61

Total savings	5.29 M USD /year
---------------	-------------------------

Summary

- ▶ **Reduction:** Spinel + (oxides)_{slag}
- ▶ **Emission:** ~ 9 wt% F + zero CN
- ▶ **Slag:** Rest F & Na-bearing components reduce slag viscosity for faster recovery

- ▶ **Slag Improvement:** Lower Viscosity Yields Improved Reactivity
- ▶ **Economics:** Viable Feedstock for Flux Compounds

Flux for metal recovery in Ni, Cu and Co industries

Alternative flux for steelmaking



Carbon injection source in steelmaking

Alternative fuel in blast furnaces

- ▶ **Yield improvement:** (FeO)_{slag} to [Fe]_{steel}
- ▶ Lime addition required

- ▶ **Combustion:** releases energy; AFT comparable to coal
- ▶ **Emission:** CN decompose
- ▶ **Fluorides:** captured in BF slag

Thank you for your attention.

Any questions?