Optimized, zero waste pyrometallurgical processing of polymetallic nodules from the German CCZ license area

David Friedmann, Marcus Sommerfeld, Bernd Friedrich (RWTH Aachen), Thomas Kuhn, Carsten Rühlemann (BGR)

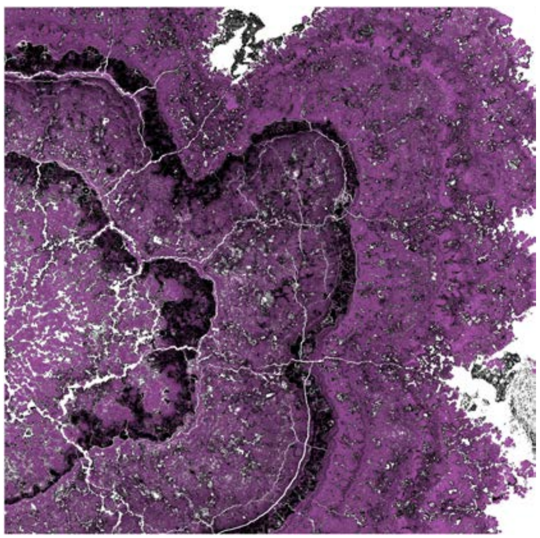
ISA - IOM Workshop,
Warsaw, Sept 3-5, 2018

Polymetallic nodule chemistry

Average chemical composition of nodules of the German territory:

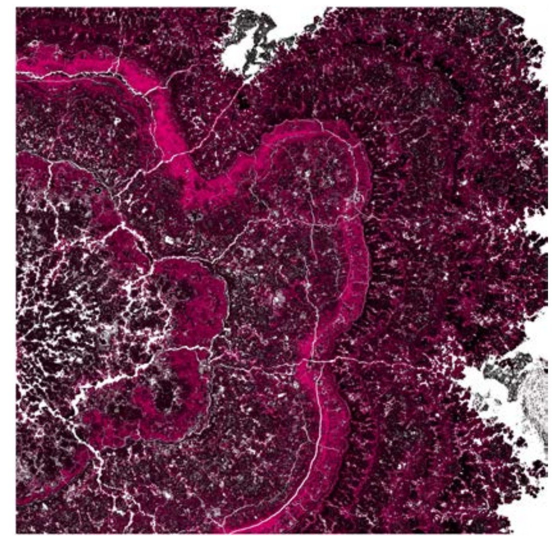
	Mn	Ni	Cu	Co	Mo	V	Fe	Si	Al	Mg	Ca	Zn
Wt.-%	31	1.4	1.2	0.16	0.06	0.06	6.2	5.9	2.3	1.9	1.6	0.15

Minerals are complex manganese and iron oxides and hydroxides (e.g. Buserite, Todorokite, Manganite or Goethite)



Manganese

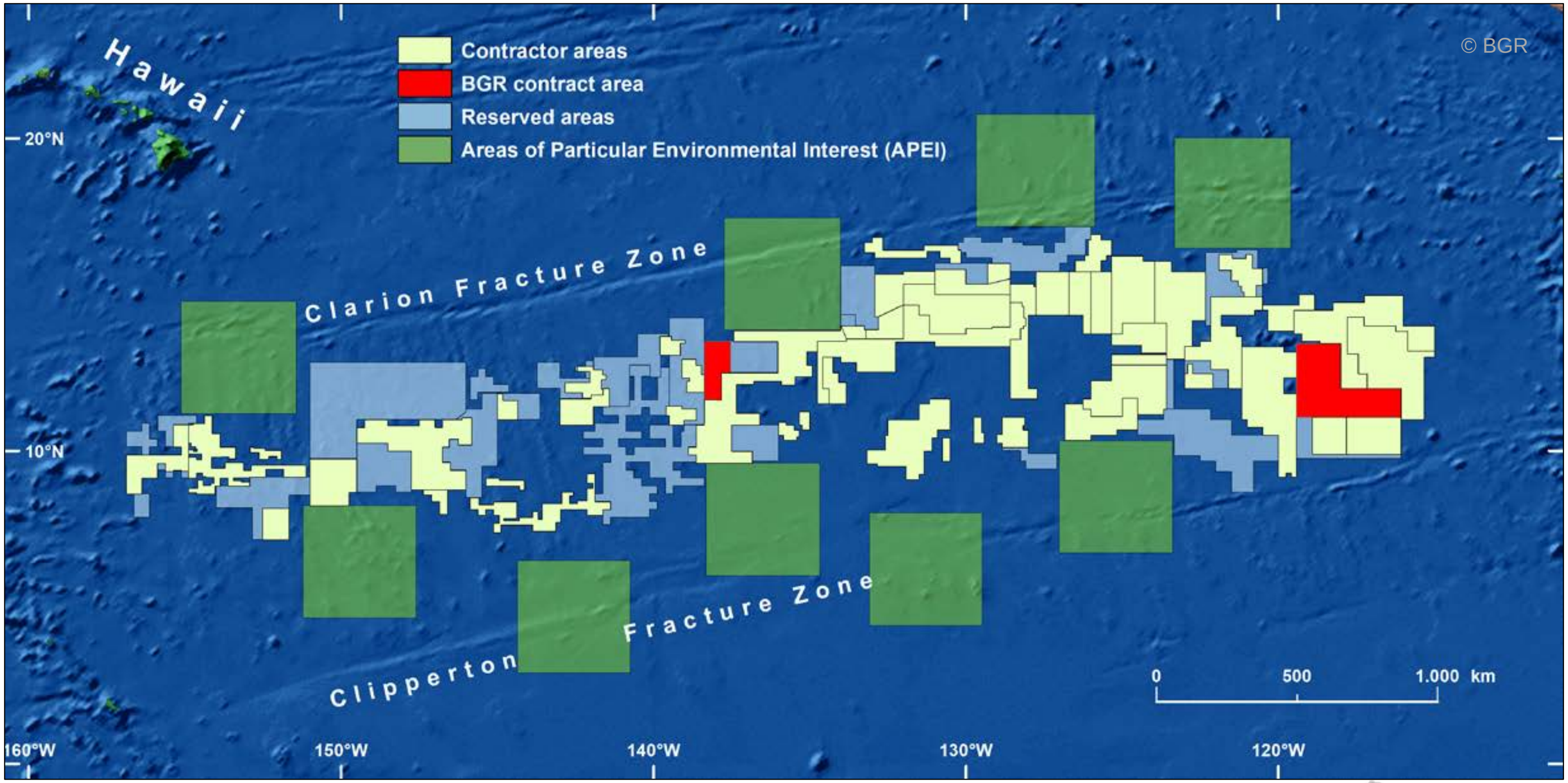
Copper

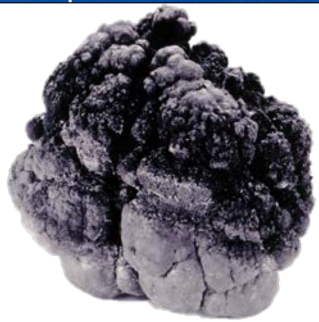


Iron

Very fine, indistinct mineral particles (<< 1 µm)
➔ Beneficiation of e.g. a NiCu-concentrate is unsuccessful

Clarion Clipperton Zone - License Areas





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Hydrometallurgical processing – bottom line

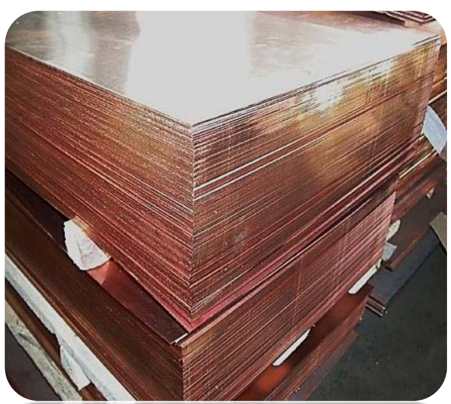
Advantages:

- → Energy intensive drying (mainly) redundant
- → Generation of „pure“ metals (Ni, Cu, Co) possible via electrolysis
- → Limited CO_2 emissions compared to pyrometallurgy

Disadvantages:

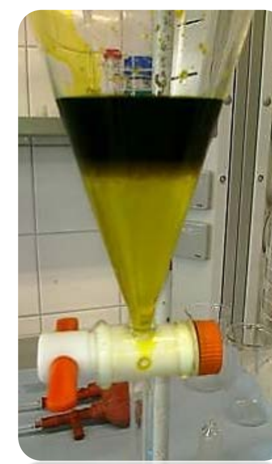
- → Large amounts of waste products and wastewater
- → Production of Manganese product uneconomical
- → Intensive consumption of chemicals
- → Costly solution treatment through precipitation, pH adjustment etc.
- → Complex multi-stage organic Solvent-Extraction (SX) necessary
- → Low throughputs

Nickel © Thyssen



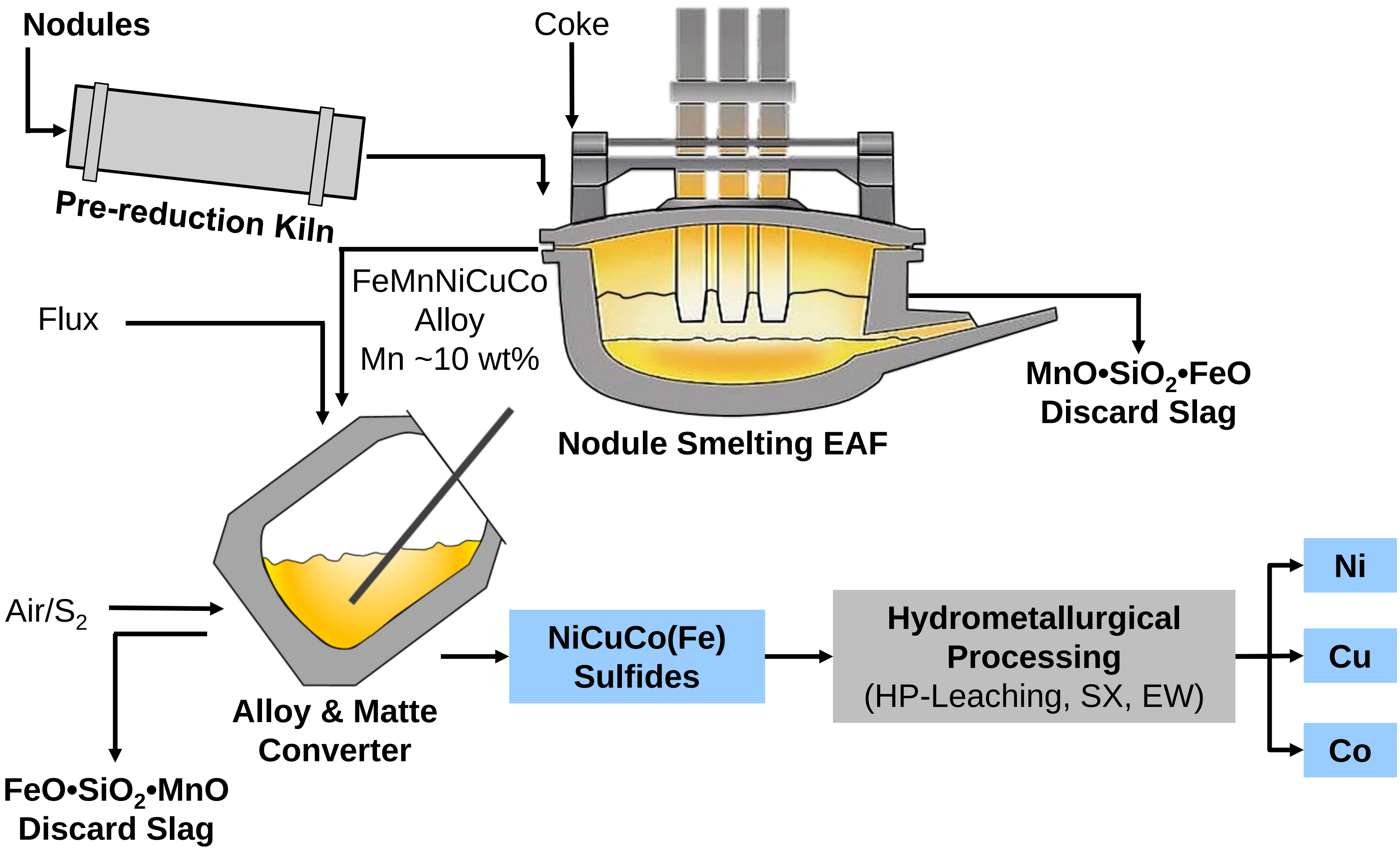
Copper © Aurubis

Red mud landfill © GreenPeace



Laboratory-SX

Simplified process developed in the 1970s by INCO



Key Aspects for a Successful Zero-Waste Concept

Main Goal:
Separation of valuable metal stream (Ni, Cu, Co, Mo; **2.5 – 3 wt%**) from Mn-stream (**> 30 wt%**) early in the process

Additional Goals:

- Complete use of Mn-bearing material stream
- Metal-recovery rates > 95%
- Recycling of flue dusts
- Slag design for high metal recovery and usable final slag

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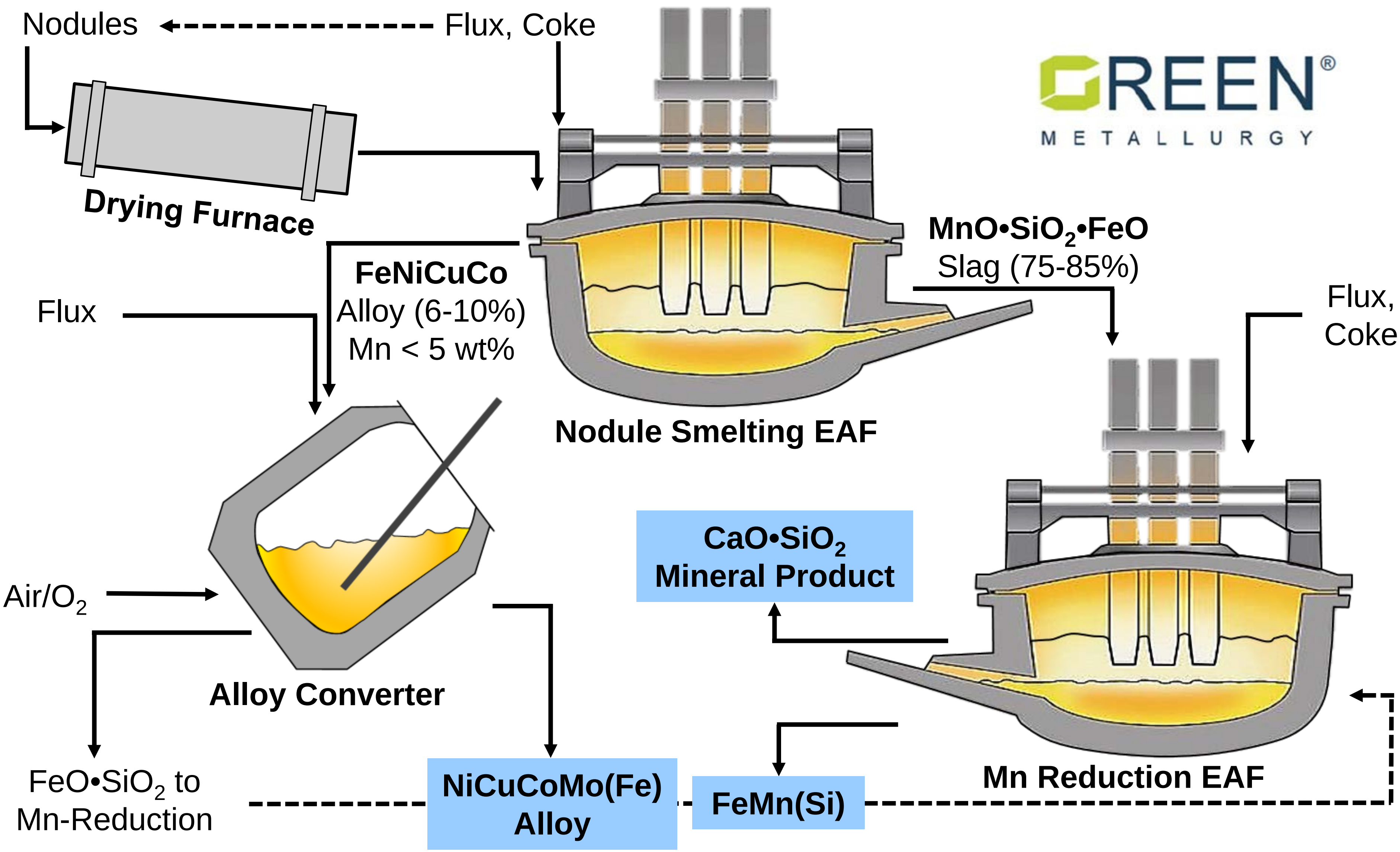
Simplified process for direct nodule smelting



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Slag Design and FactSage™ Models

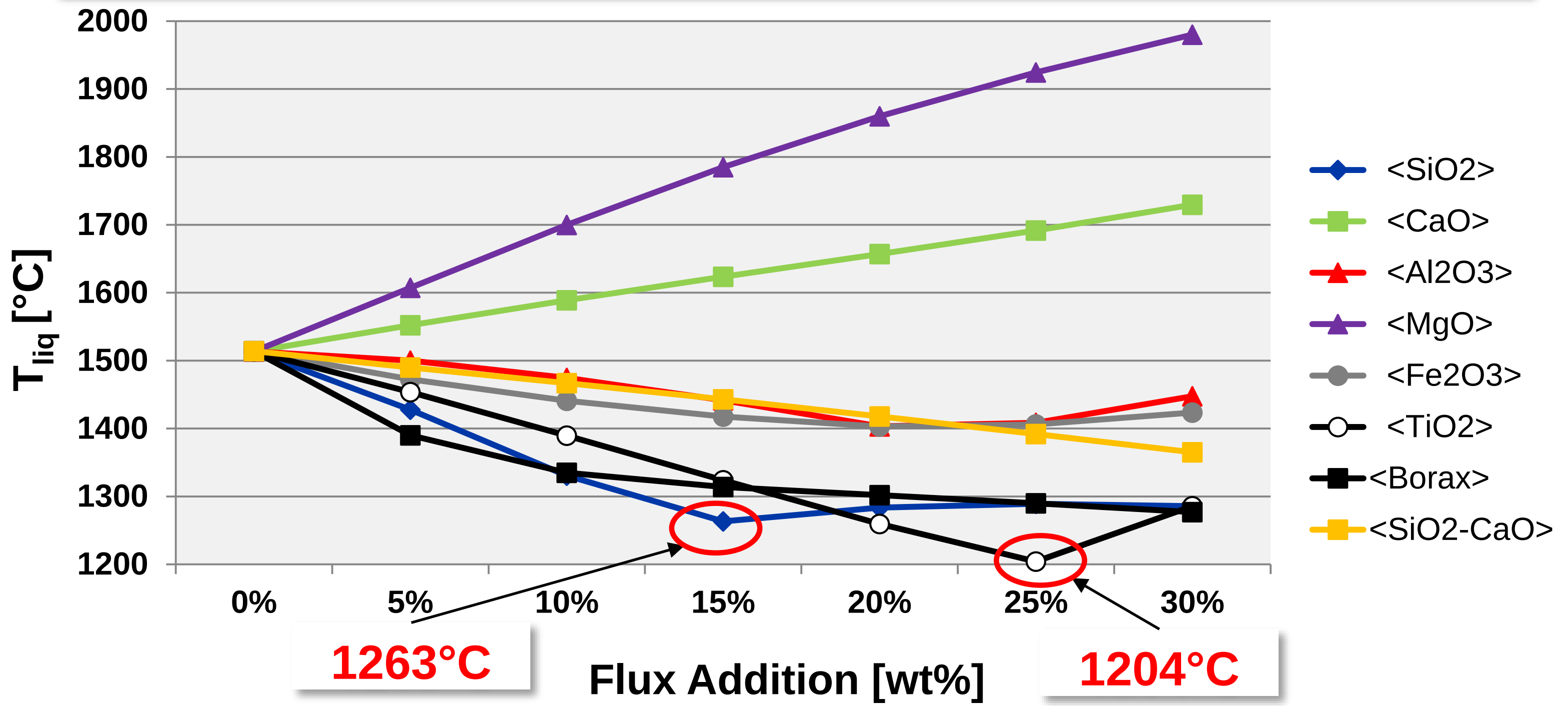
Metallurgical challenges:

Comparison MnO contents: **BGR: > 45 wt%** **INCO: 30 wt%**

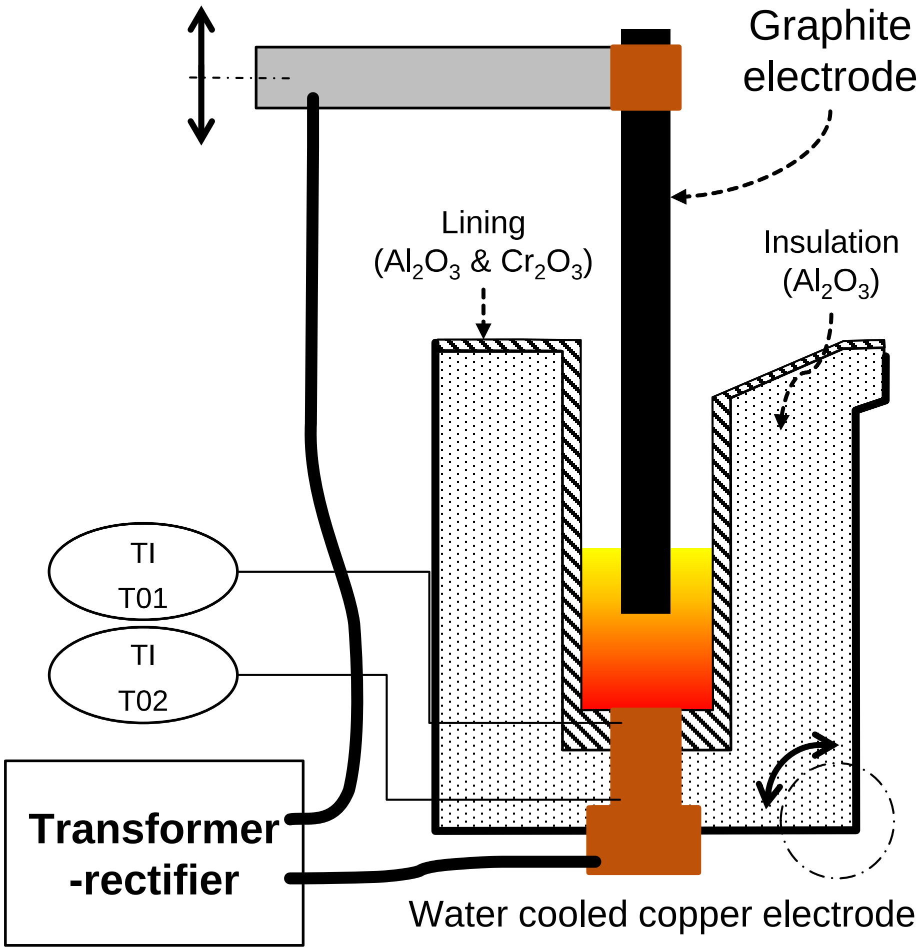
➔ **Significantly higher liquidus temperature of autogenic slag**

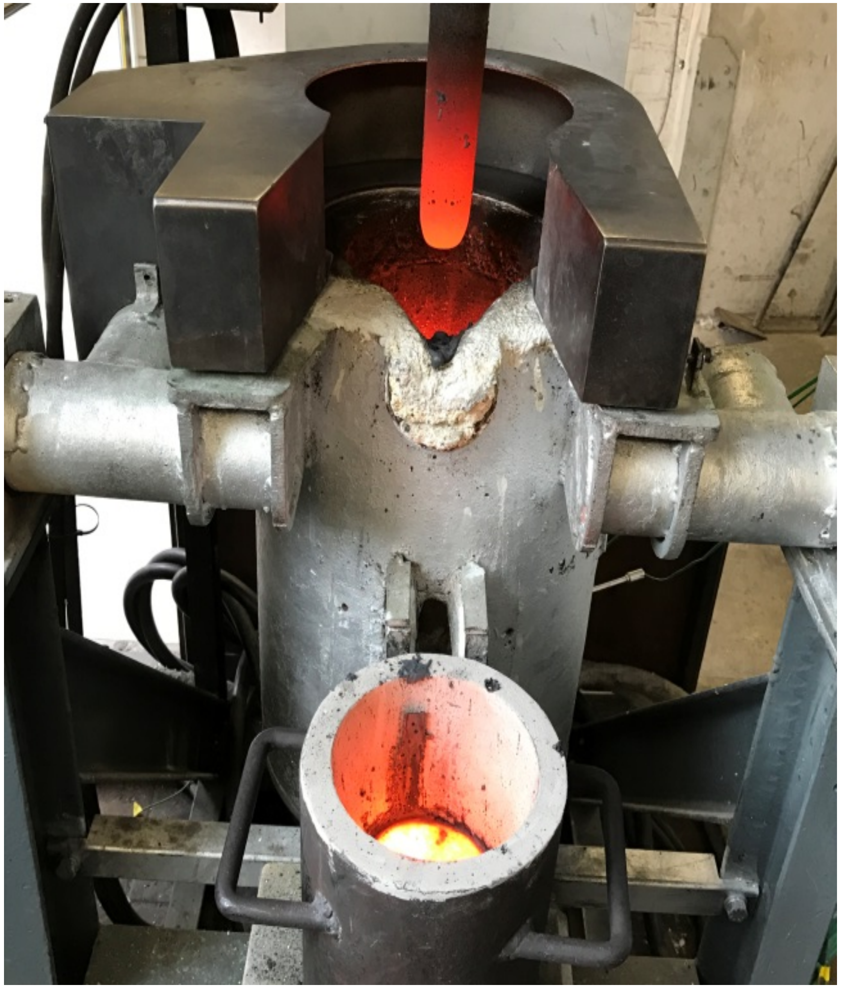
➔ **> 1500 °C: Mn reduction thermodynamically significant**

➡ Lowest reachable liquidus with a maximum of 30 wt% flux addition



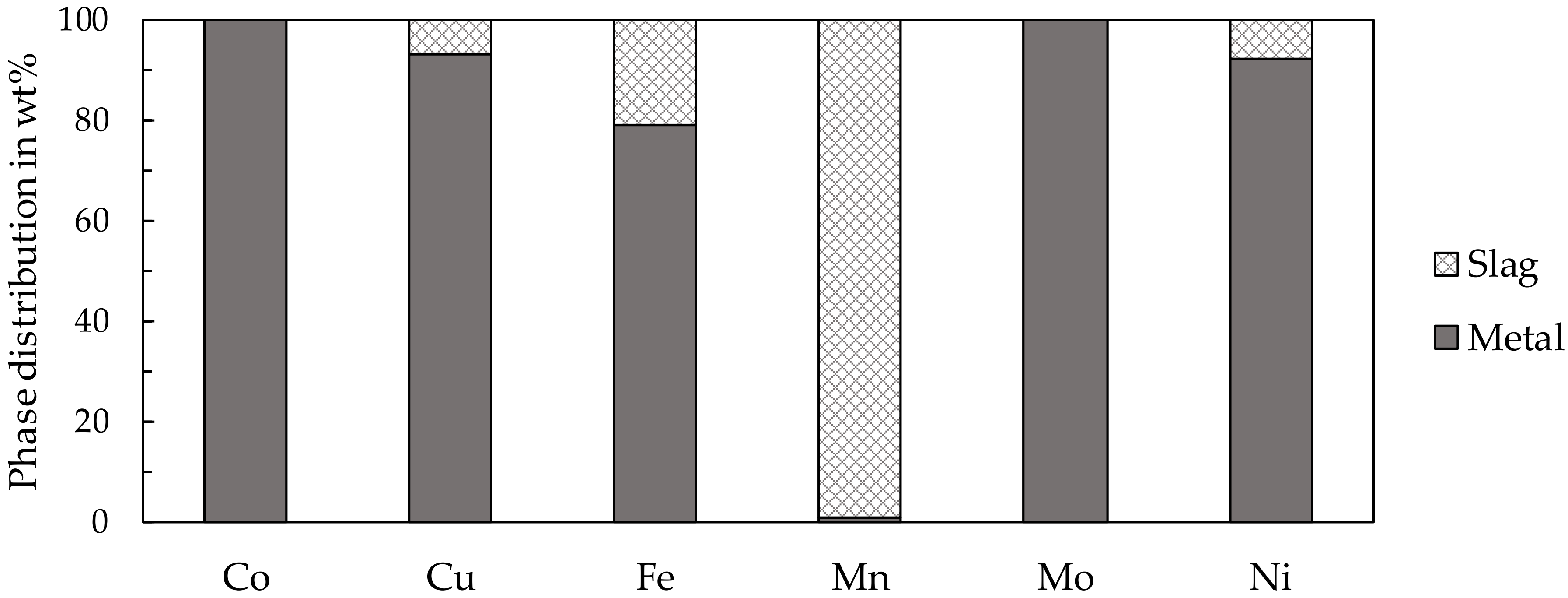
Experimental Setup – Lab-scale SAF at IME



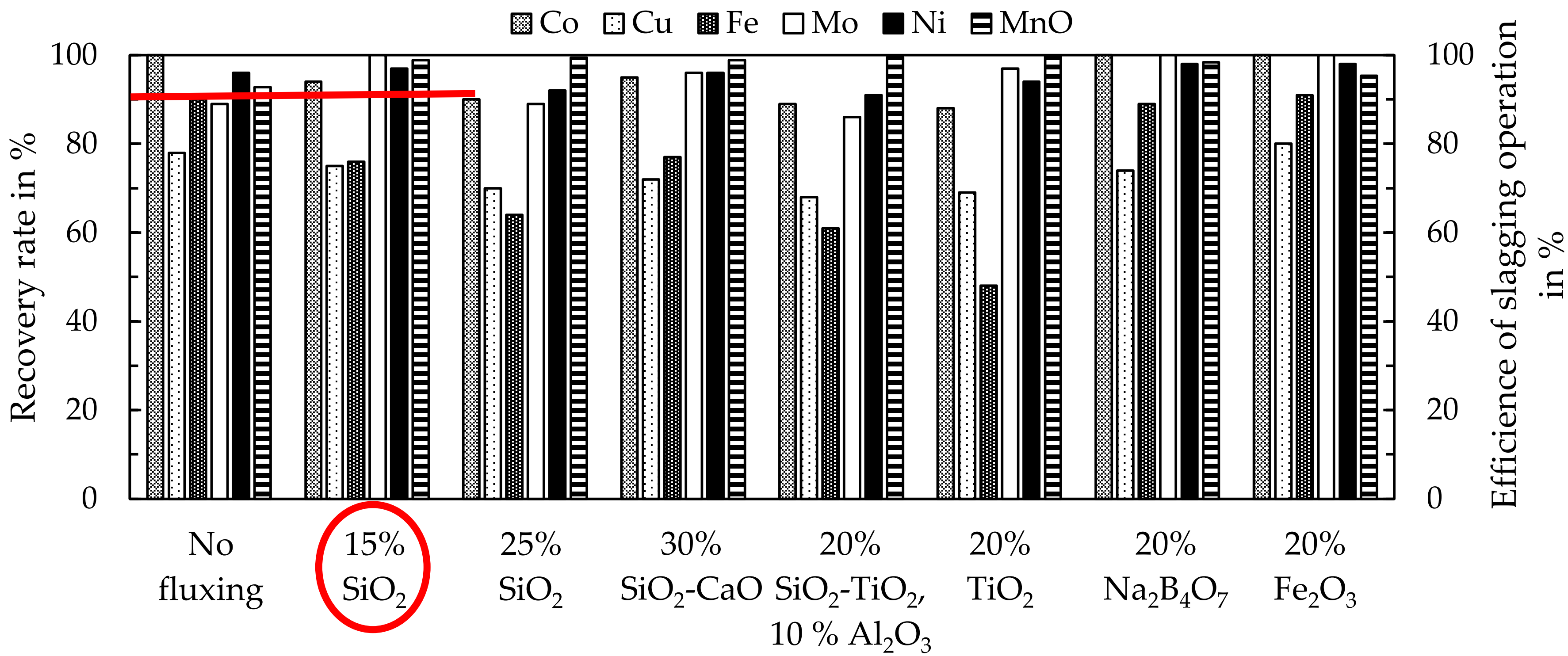


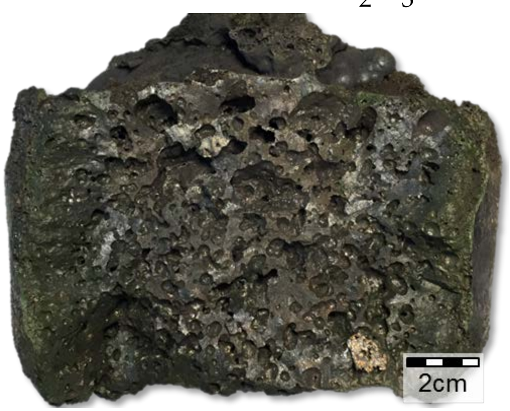
- Power supply: 3 - 100 kW DC
- Up to 6 L melt volume
- Optionally with graphite crucible insert

Experimental Results – 1. Smelting Step

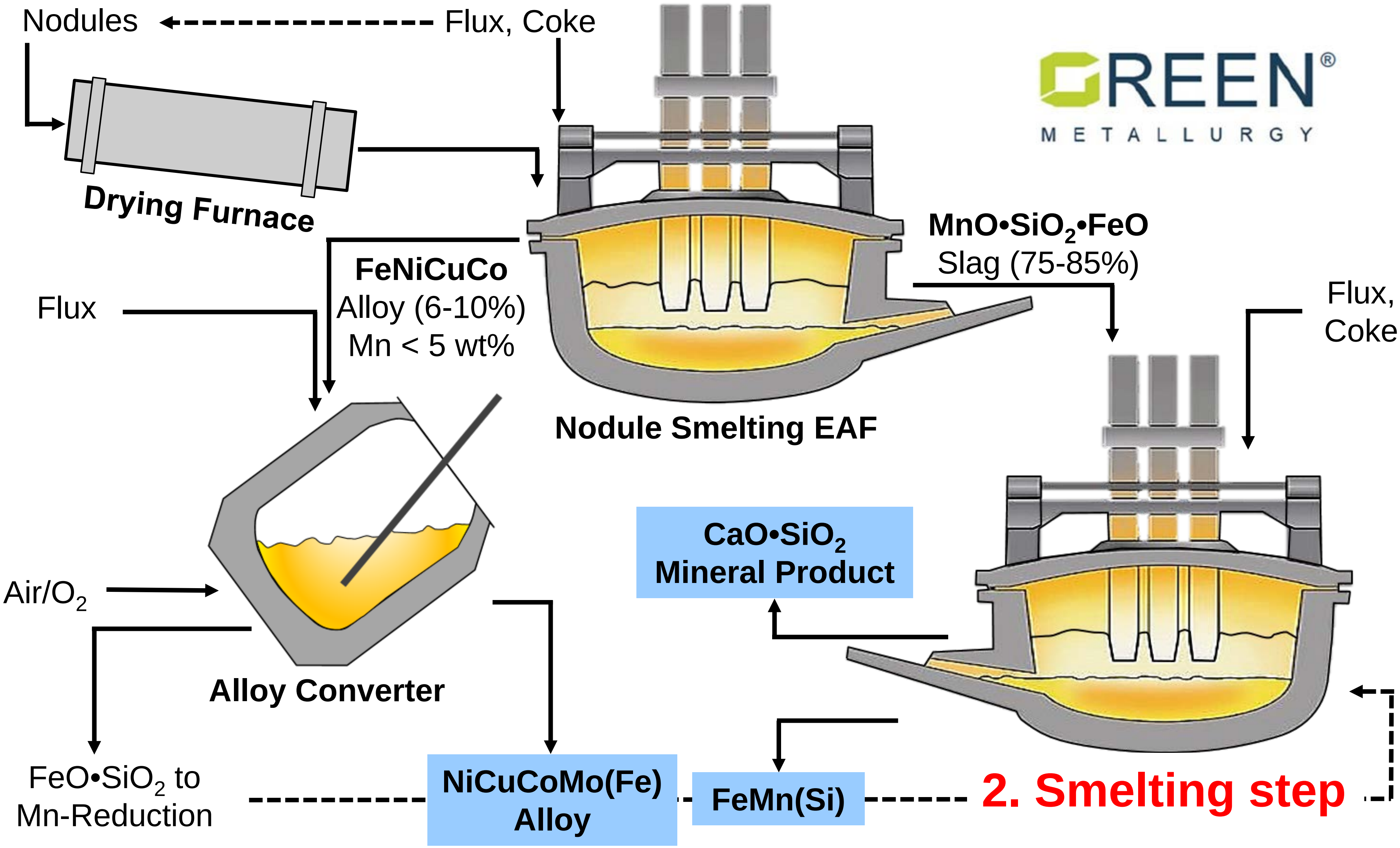


Experimental Results – 1. Nodule Smelting Step





Simplified process for direct nodule smelting



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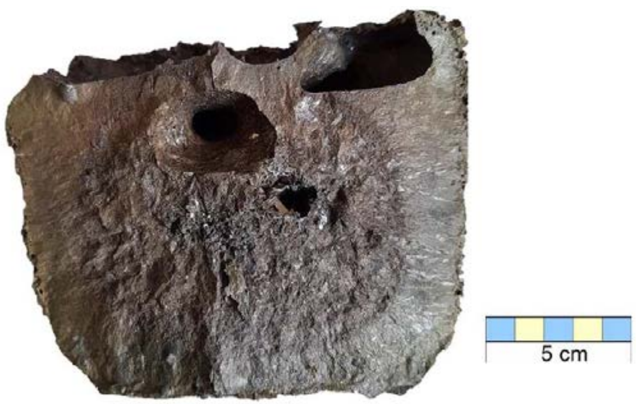
Addition of flux and resulting liquidus temperature

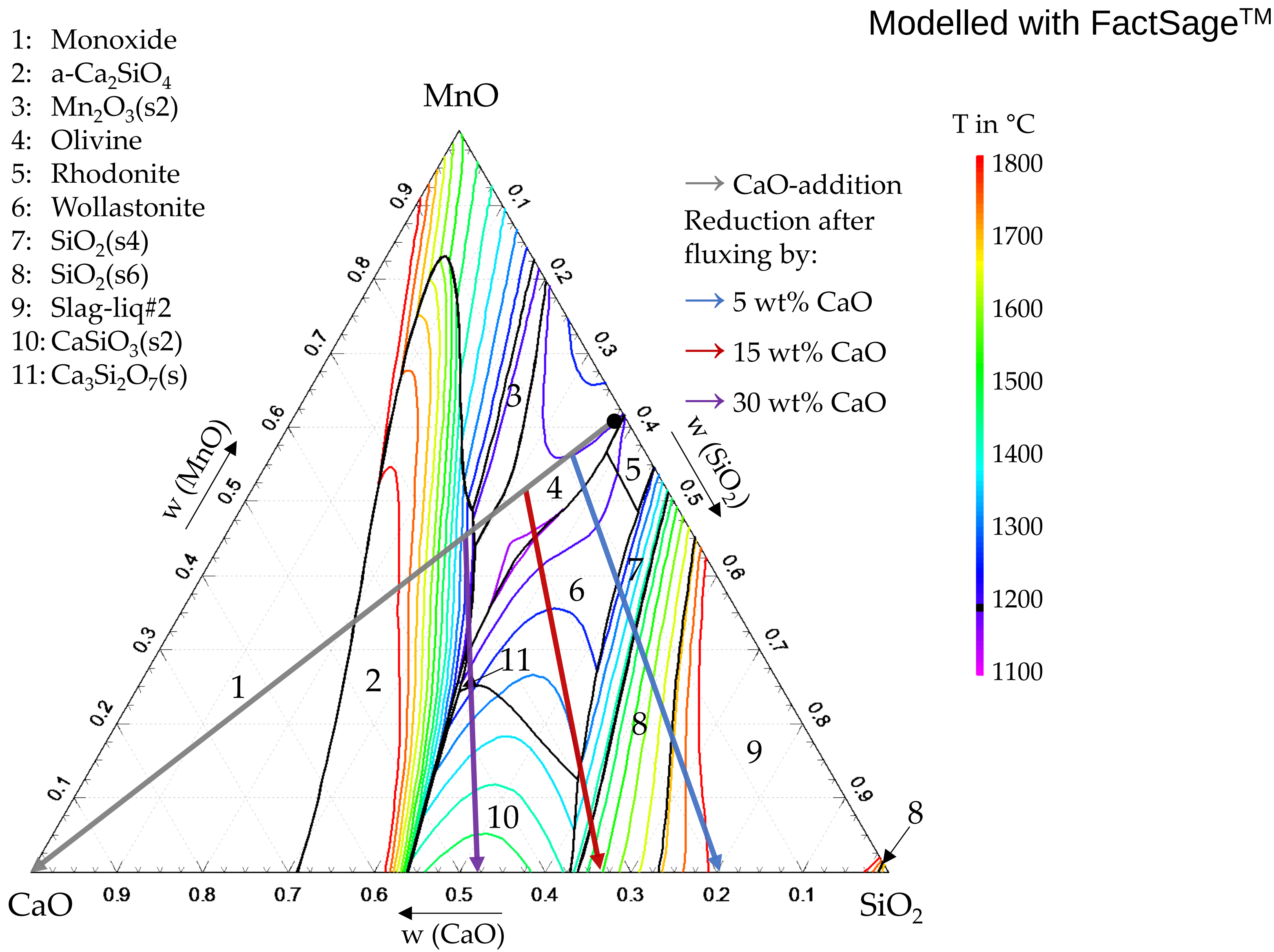
Fluxing	5% CaO	15% MgO	15% CaO-MgO	15% CaO	30% CaO
T_{Liq} in °C	1308	1409	1335	1351	1401
B	0.48	0.91	0.91	0.91	1.55



Slag

Metal

Experimental Results – 2. Smelting Step



Experimental Results – 2. Smelting Step

Element content of ferromanganese (wt. -%)

Werte in Gew.-%	15 % CaO		
	15.11/1	15.11/2	Fact-Sage
C	6,73	6,77	6,54
Cu	0,39	0,55	0,90
Fe	3,34	4,45	7,65
Mn	86,1	85,9	82,64
Ni	0,30	0,43	0,33
P	0,19	0,40	0,03
Si	2,63	1,25	1,76
Ti	0,17	0,05	0,00
V	0,21	0,17	0,13
m in g	974,6	800,4	1063,3

XRF analyses, RWTH Achen, Sommmerfeld, 2018

Ferromangan (carburé, high-C): DIN 17564

Wt.-%

Mn: 75 – 80 —

C: 6.0 – 8.0 ✓

P: 0 – 0.25 ✓

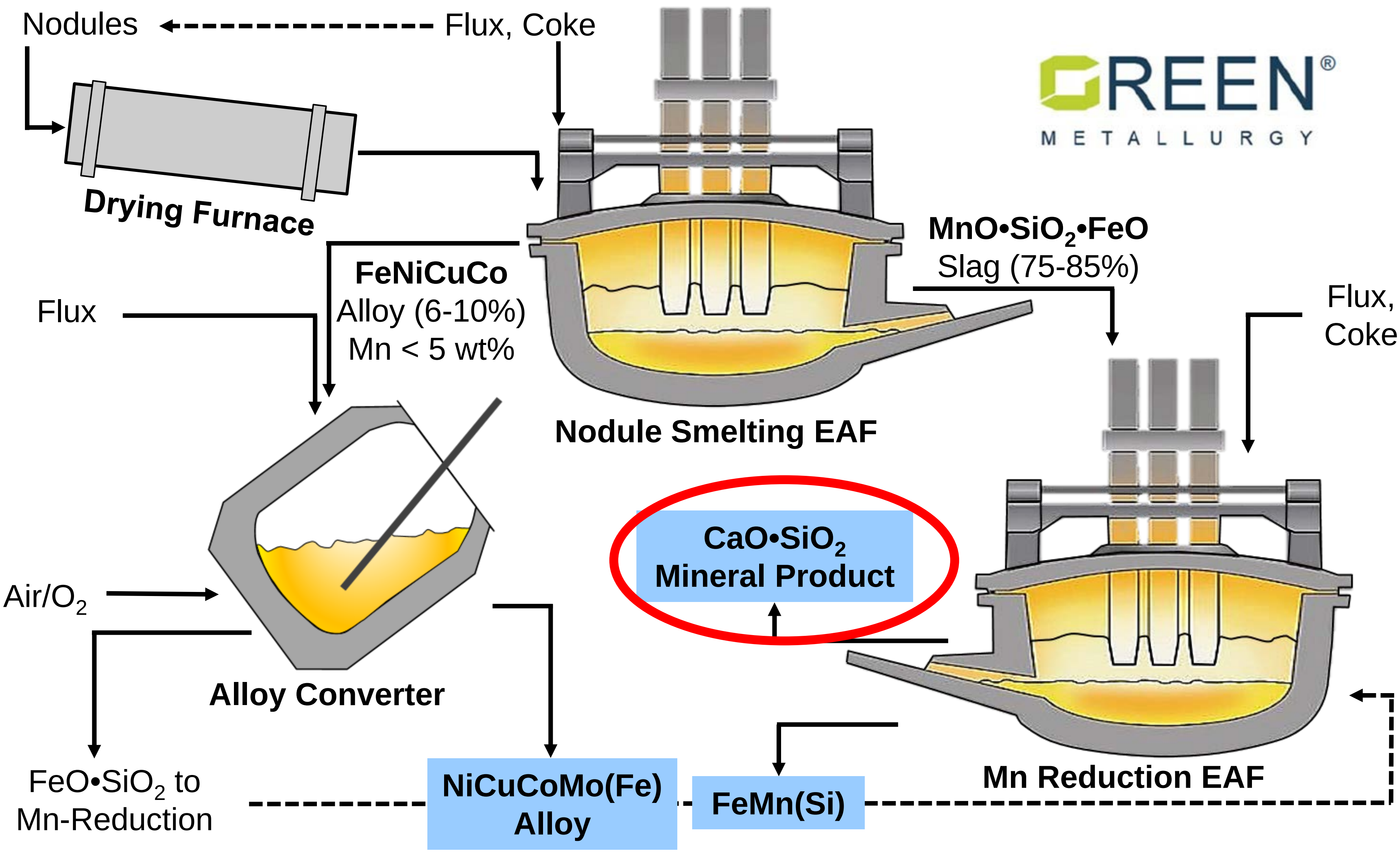
Si: 0 – 1.0 —

Ti: 0 – 0.20 ✓

V: 0 – 0.20 ✓

Cu: 0 – 0,013 —

Simplified process for direct nodule smelting



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Experimental Results – Final Mineral Product

Heavy metal content of the final mineral product (wt. -%)

Zusatz der zweiten Reduktionsstufe	15% CaO	15% CaO+MgO	30% CaO	5% CaO	15% MgO
Werte in Gew.-%	21.11/2	22.11/1	22.11/2	23.11/1	23.11/2
Cr_2O_3	<0,01	<0,01	0,01	<0,01	<0,01
CuO	<0,01	<0,01	<0,01	<0,01	<0,01
NiO	<0,01	<0,01	<0,01	<0,01	<0,01
PbO	0,03	0,03	0,03	0,04	0,03
V_2O_5	<0,01	0,01	<0,01	<0,01	0,01

XRF analyses, RWTH Achen, Sommmerfeld, 2018

Summary

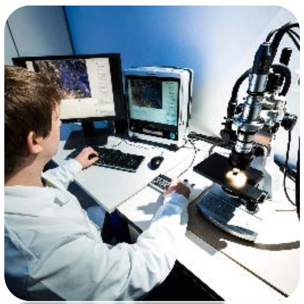
Summary

- SiO_2 flux of 10-15 wt% is sufficient to reach < 5 wt% Mn in Fe Metal
- SiO_2-CaO and $Na_2B_4O_7$ also show good results
- Metal-recovery rates > 95% for Ni, Co, Mo
- Mn-slag is suitable for FeMn production (Basicity adjustment required)
- >75 wt% Mn in metal, Si, Ti, Cu in some cases too high
- Final calcium-silicate slag is almost heavy metal free

Outlook

- Further look at Cu-reduction in first melting step → Kinetics
- Scale-up of entire process necessary

Thank you for your attention!





Federal Institute for Geosciences and Natural Resources (BGR)
Dr. Thomas Kuhn
www.bgr.bund.de

IME Process Metallurgy and Metal Recycling
RWTH Aachen University
Prof. Dr.-Ing. Dr. h.c. Bernd Friedrich
www.ime-aachen.de