Preheating manganese ore in a pilot-scale rotary kiln

PROMETIA – 10 December 2020

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Overview

1. Mn production and PREMA project
2. Pre-heating of Mn ores
3. Conclusions

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Mn production and PREMA project

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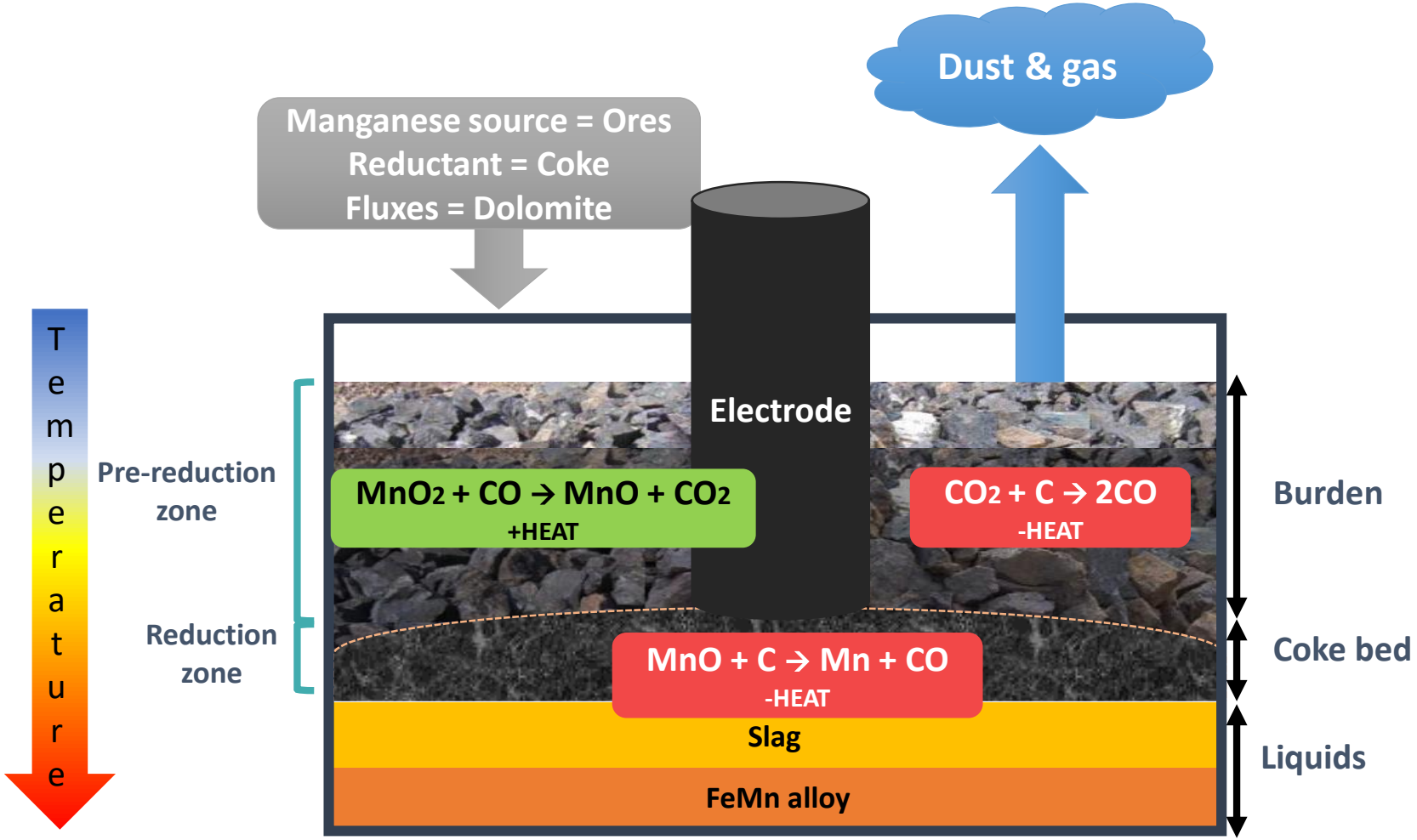
Mn process



2 options for decreasing CO_2 emissions and improve furnace efficiency:

- Make Boudouard's reaction negligible by playing on kinetics and raw materials
- Carry out the pre-reduction reactions in the absence of C ➔ outside the EAF

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PREMA : A H2020 European project

Energy efficient, primary production of manganese ferroalloys through the application of novel energy systems in the drying and pre-heating of furnace feed materials

- **PREMA objectives**
  - **Capture CO from the EAF furnace**
  - **Pre-reduce the ore in absence of C with CO gas from furnace**
  - **Transfer hot blend to the furnace**

- **4 years project: 2018-2022**

Outotec
Screening process to select pre-treatment unit technology
- Rotary kiln & Shaft furnace

Eramet Ideas
Rotary kiln pilot campaign
- Pre-heating & pre-reduction

SINTEF
- Melting & reduction

MINTEK
- Pretreatment, melting & reduction

Design, engineering and business plan

Lab scale

Pilot scale

Industrial scale

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Pilot campaigns goals

Goals

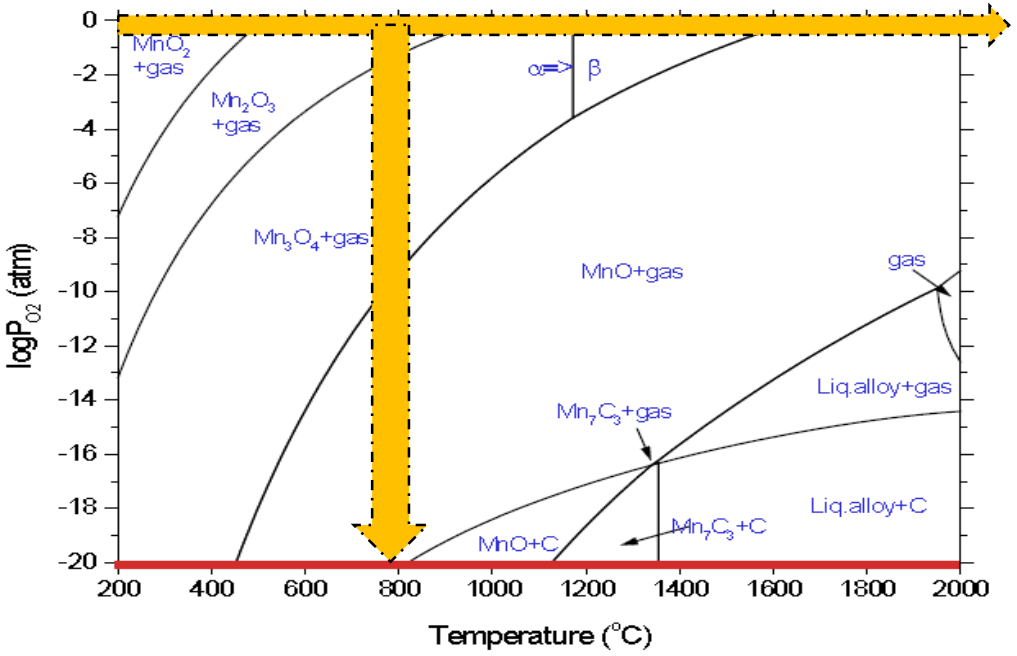
- Determine the level of pre-reduction / decomposition achievable on different ores
- Evaluate the effectiveness of the pre-reduction with different types of solid reducers
- Assess the impact of this pretreatment on the load (particle size, permeability)
- Estimate the efficiency of the operation at the thermal level
- Collect data for sizing industrial equipment

Pre-heating campaign

- Pre-heating of manganese ore alone in air
- Decomposition of Mn oxides in air in the range 700-800°C
- Comparison of Mn ores behavior to preheating

Pre-reduction campaign

- Pre-reduction of manganese ore in presence of reductant to generate CO
- Obtain calcined ore temperature similar to the first campaign: 700-800°C
- Comparison of Mn ores behavior to prereduction



Predominance diagram for Mn-C-O system

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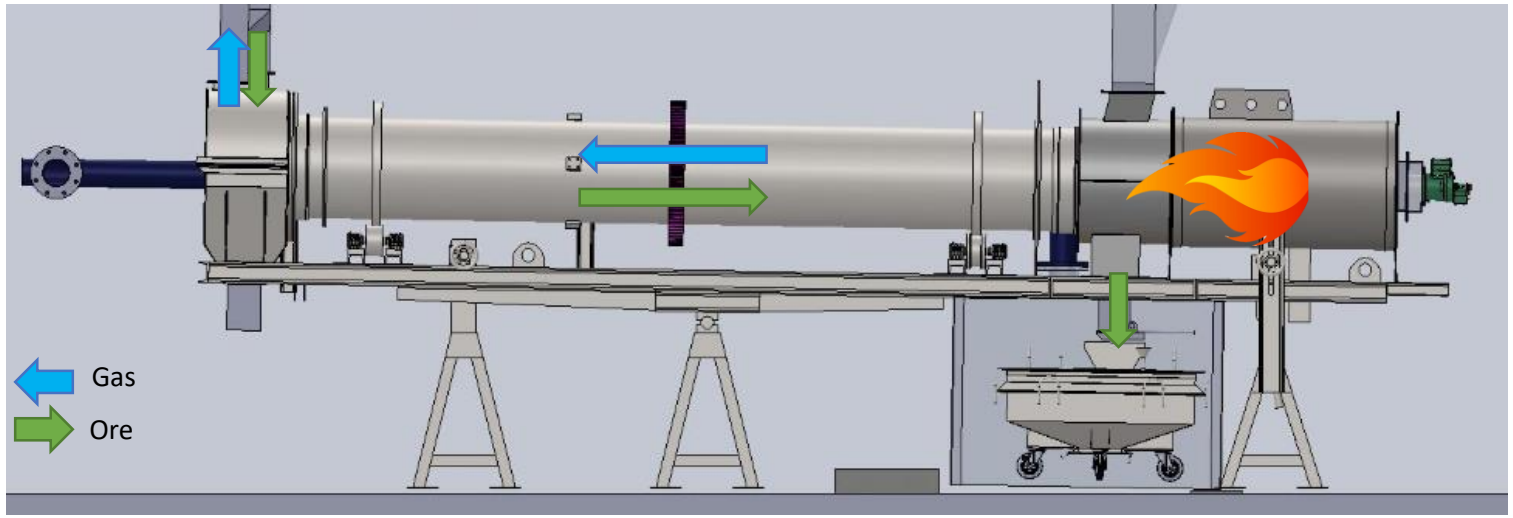
Vernon Rotary kiln

Vernon rotary kiln

- Tube length= 4m
- Tube diameter= 0.48m
- Rotation speed from 1 to 6 rpm
- Slope from 0 to 4%
- Burner (natural gas)= 220 kW



Rotary kiln principle

Calcination mode

- Counter current flow
- Gradual heating
- Insulated with refractory
- No dams or bed disturbers

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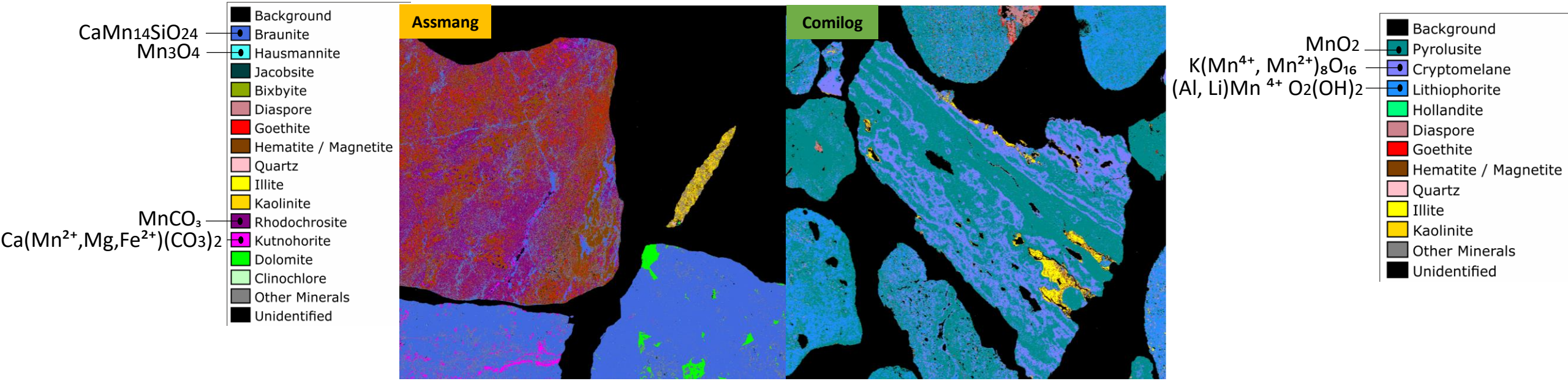
Mn ores used for the campaign

Selected ores

- Comilog, MMA grade, highly oxidized ore
- Assmang, Nchwaning grade, semi-carbonated ore

Composition (% by mass)	Al2O3	CaO	FeO	MgO	SiO2	Mn	x in MnOx
Assmang	0,33	6,91	12,5	1,93	5,37	45,82	1,4
Comilog	6,27	0,32	4,34	0,18	4,55	49,31	2

Chemical analysis



Qemscan images

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Pre-heating Mn ore

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Tests performed: March 11-14, 2020

PRÉMA

Goals

- Decomposition of Mn oxides in air in the range 700-800°C
- Comparison of Mn ores behavior to preheating

22h

Burner start
►Obtaining thermal stability of the furnace (empty)

Optimization of parameters on Comilog
► Obtain a calcined ore between 600-700°C

12h

Production
►Preparation of a ton of Comilog with the optimized parameters

3h

Transition
► Change of ore for Assmang and stabilization

10h

Production
► Preparation of one ton of Assmang with the parameters set during the Comilog tests

3h30

Test
►Change of parameters on Assmang

12h

Transition
► Change of ore for Comilog and stabilization

Test
► Change of parameters on Comilog

Adjustment of the filling ratio and parameters of the burner

Comparison of Mn ores to preheating with production calcined ore for SINTEF

Study of the influence of parameters

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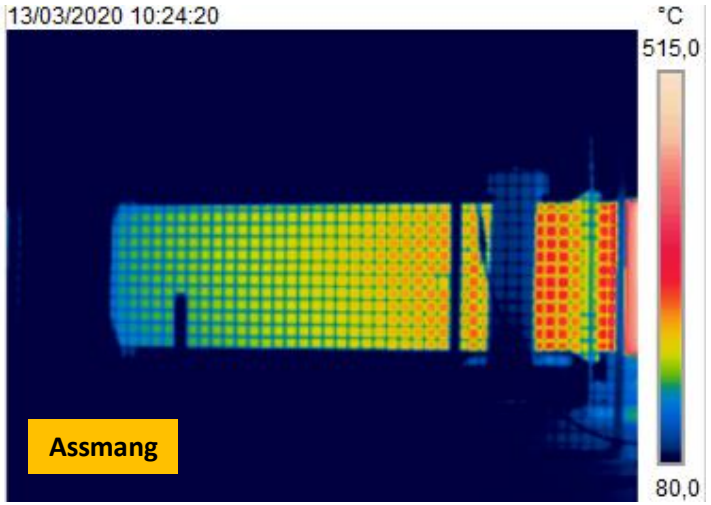
Temperatures and thermal profiles

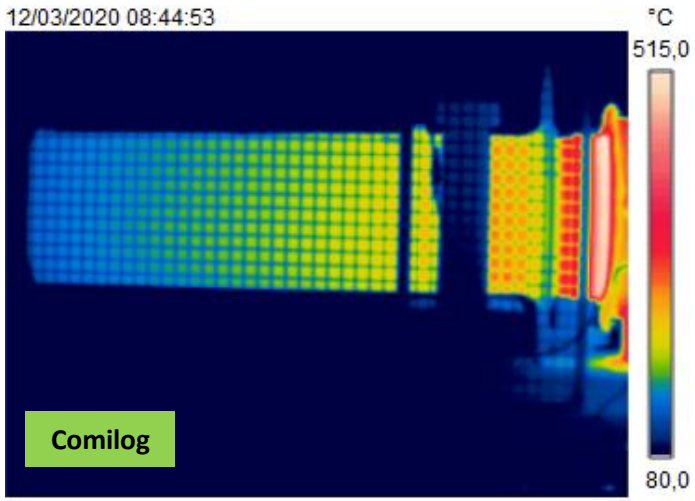
Production settings

- P_{burner} = 120 kW
- Filling ratio = 13%
- Residence time = 45 min

Thermal profile & Temperatures

- Assmang tends to heat higher than Comilog for the same set of parameters
  - Calcined Assmang = 863°C +/- 2°C
  - Calcined Comilog = 728°C +/- 15°C
- Thermal profile = Higher temperatures deeper in the furnace for Assmang





Thermal pictures

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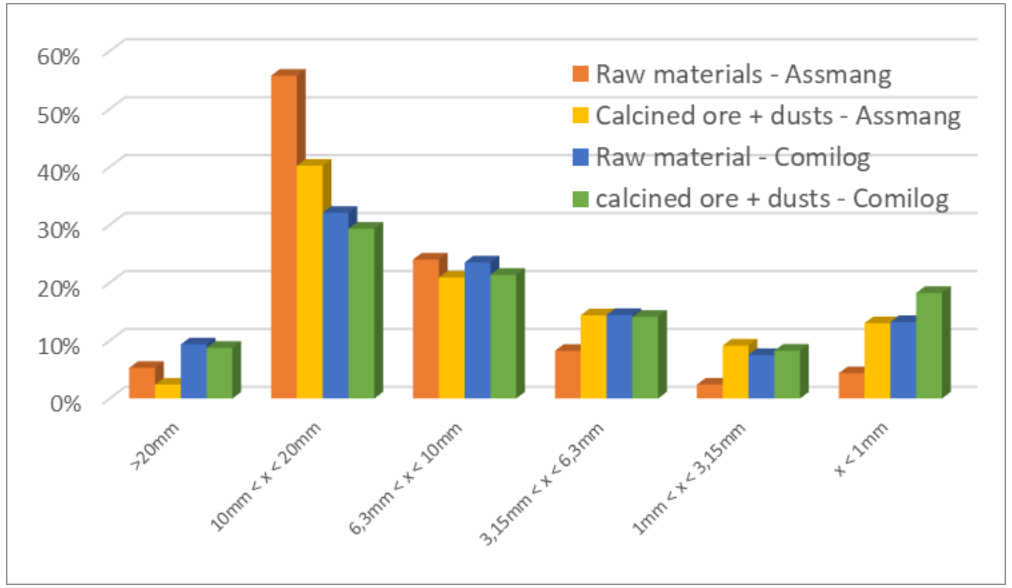
Physical properties

Particule size distribution: Calcined ore + dusts

- **Assmang ore:** Raw material with coarse particles: 50% of 10-20 mm compared to 41% of 10-40 mm for Comilog
- **Comilog ore:** Raw material with more fines: 33% < 6.3mm compared to 15% for Assmang
- Decrepitation of both ores with more impact on Assmang



Particule size measurement before and after calcination

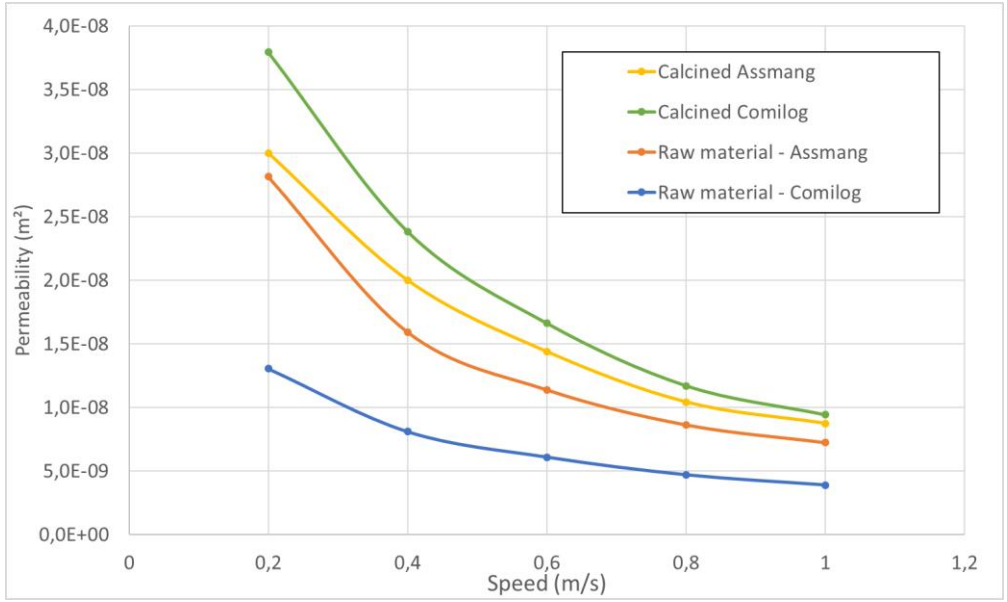
Dust take-off

- More important on MMA than Assmang

Ore	Loading (kg)	Calcined (kg)	fine dust (kg)	Take-off rate (%)
Comilog	1847	1431	148	8%
Assmang	2085	1648	90	4%

Permeabilities

- Comilog : Lowest permeability at first but best results after calcination
- Assmang: Slight improvement of permeability



Permeability measurement before and after calcination

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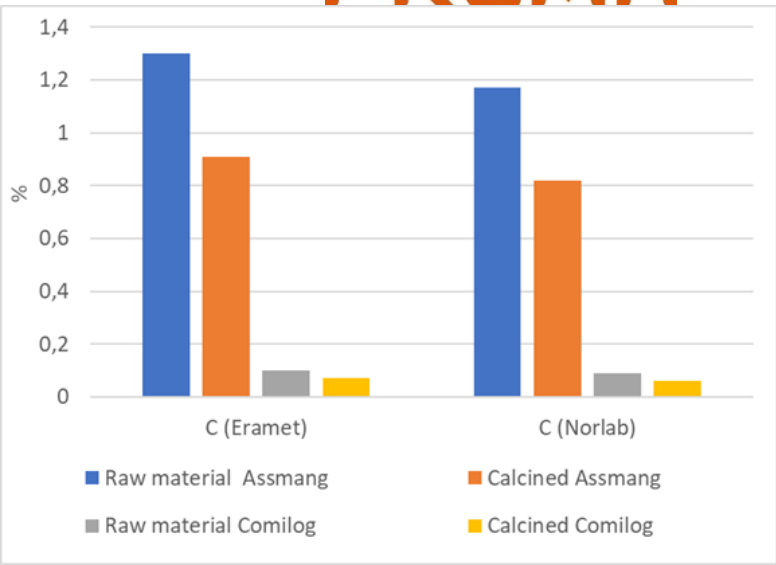
Chemical properties

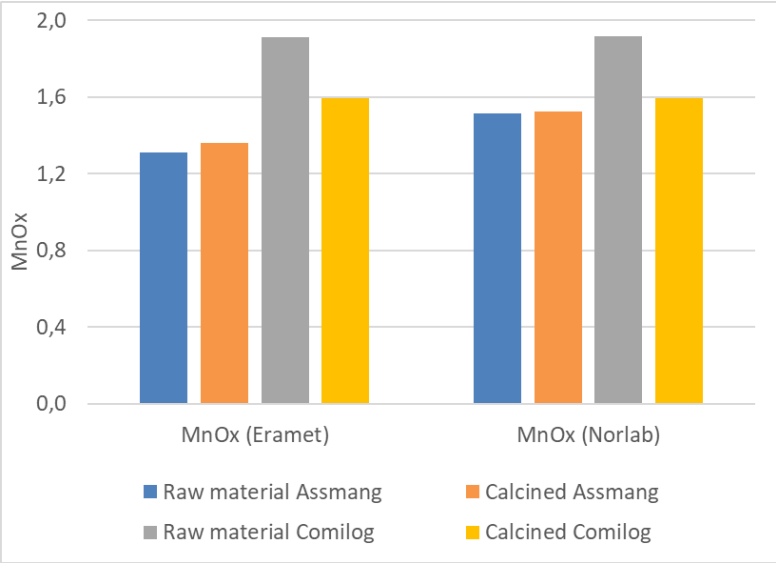
- **Analyzes carried out at Eramet and Norlab**

- **Elementary analysis**
  - > Close results for both lab
  - > No major differences before and after calcination : little chemical degradation
  - > Incomplete decarbonation for Assmang

- **Determination of Mn valence**
  - > Reducing potential of the ore expressed as MnOx
  - > Same method for both laboratories but differences for Assmang
  - > Comilog: Decomposition of Mn oxides
  - > Assmang: No impact of calcination



Carbon analysis before and after calcination for both ores



Reducing potential expressed as MnOx

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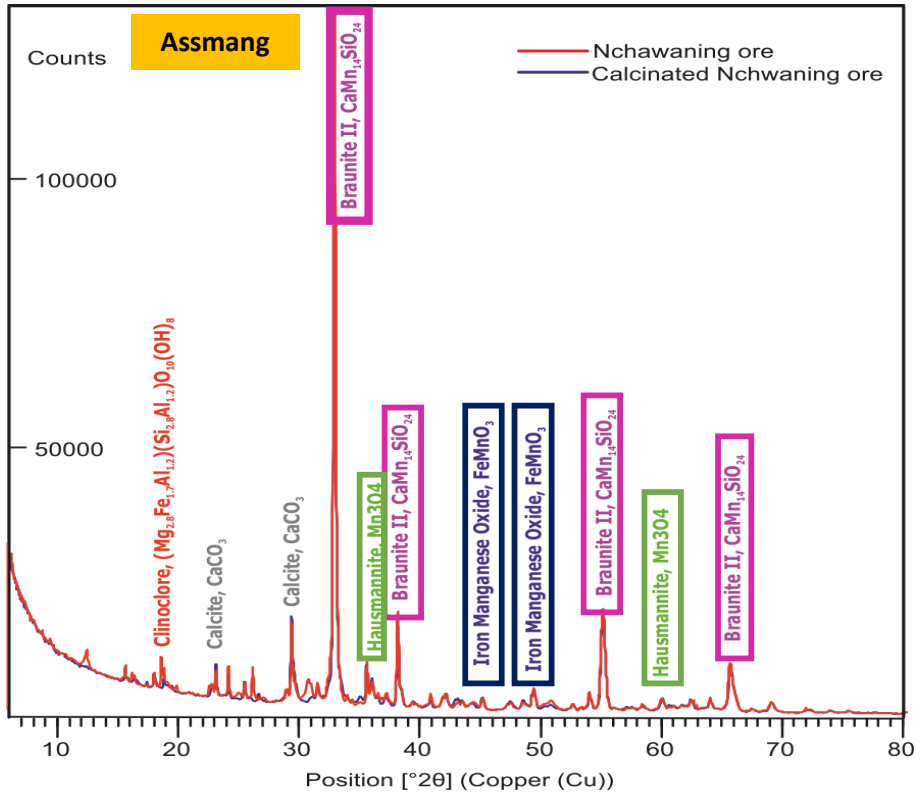
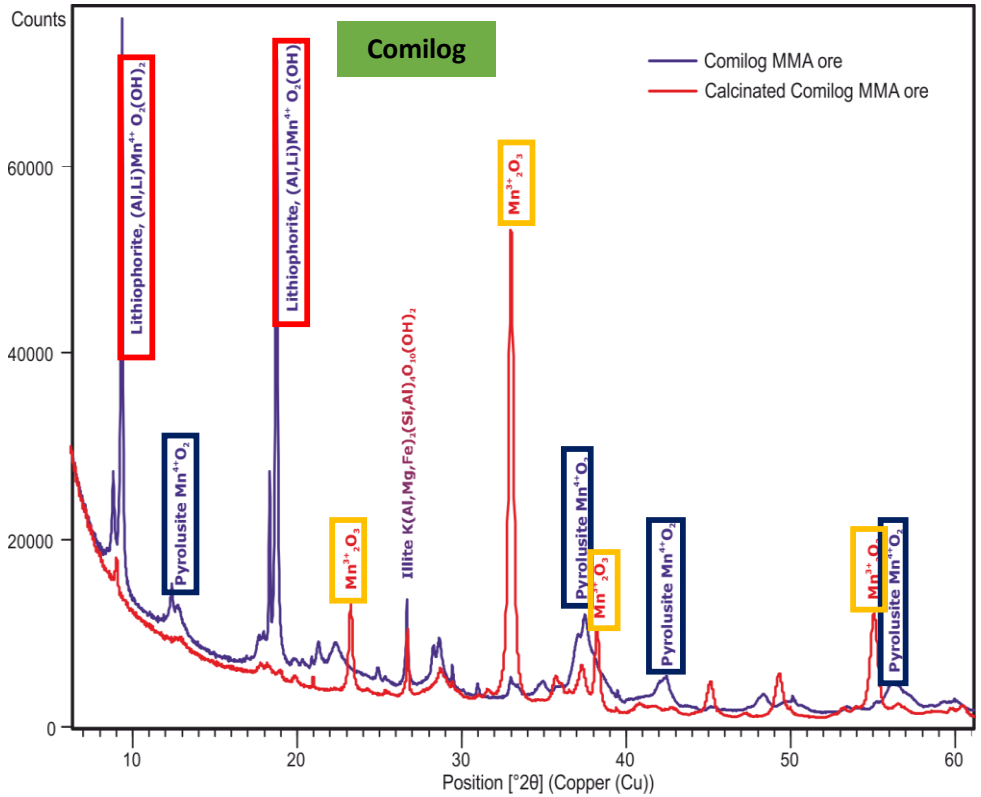
Chemical properties - XRD





- **Before and after pre-heating**
  - Braunite = Mn^{3+}
  - Haussmannite = Mn^{2+} /Mn^{3+}
  - Iron manganese oxide = Mn^{3+}

- **Before pre-heating**
  - Pyrolusite = Mn^{4+}
  - Lithiophorite = Mn^{4+}
- **After pre-heating**
  - Manganese oxide = Mn^{3+}

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Conclusions

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Conclusions (1/2) – First campaign

PREMA

Comparison of Mn ores behavior to pre-heating in the same conditions

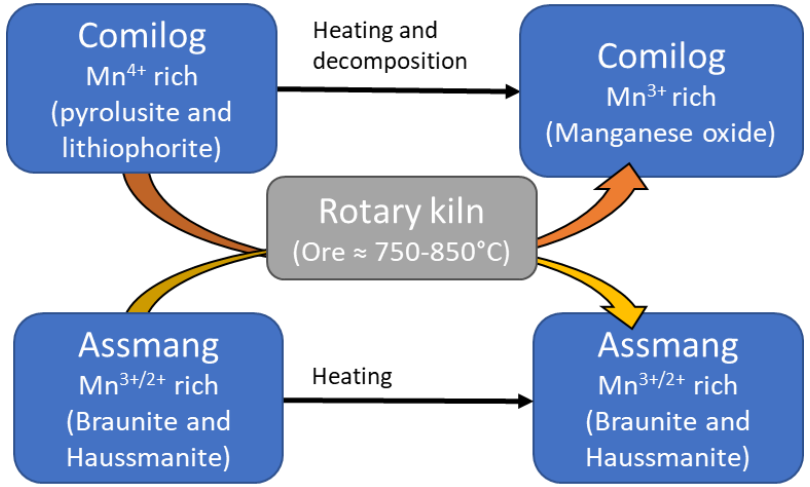
Comilog

- Calcined ore temperature = 728°C +/- 15°C
- Slight decrepitation and blow off ultrafines
- Improved permeability
- Decomposition of MnO_2 into Mn_2O_3

Assmang

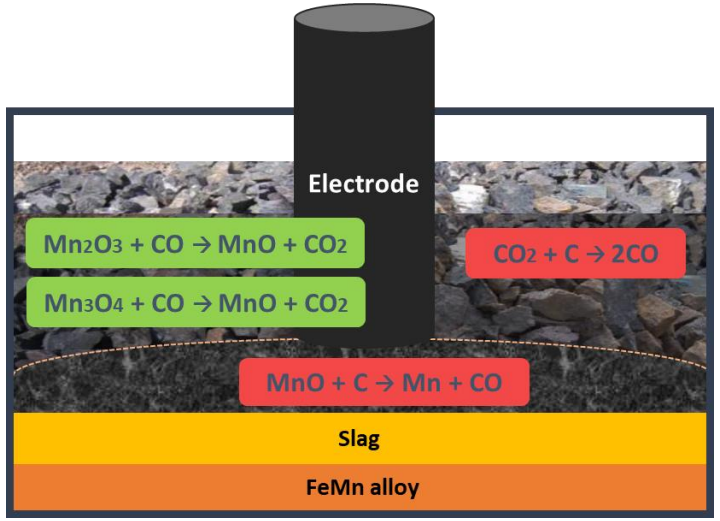
- Calcined ore temperature = 863°C +/- 2°C with higher temperatures inside the kiln and thus different thermal profile
- Important decrepitation
- Slight improvement of permeability
- No decomposition of Mn_2O_3 into Mn_3O_4

Thermal decomposition in air



No further decomposition available at this temperature range

Not hot enough to decompose it



- More potential for Comilog than Assmang
- Boudouard reaction still present

Goal achieved: Data collection to size a rotary kiln and study of parameters influence

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Conclusions (2/2) -Second pilot campaign

Aim of the campaign

- Evaluate the extent of the pre-reduction reachable in a rotary kiln
- Provide data for design and dimensioning

Experimental set-up

- Addition of reductant to generate reducing atmosphere
- Higher constraints on the inerting of the calcined ore because of CO generation and potentially re-oxidation of MnO

Reductant used

- **Coal**: Silero 1-7mm from Enerco

Typical use: reducing agent in the production of elemental metallic silicon from silicon dioxide by application of extreme temperatures

- **Charcoal**: 5-20 mm briquettes from Valbois

Typical use: Barbecue

Tests performed in November

- Date processing in progress

Reductant pictures: Coal (above) and Charcoal (below)

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Thank you for your attention

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