KMB-Roma

Eli Ringdalen

ROMA

ROMA –

Resource Optimization and energy recovery in the MAterials industry

- KMB project – Knowledge-building projects with user involvement
- 2007-2013
- Totally 57.5 mill NOK
  - 30 mill NOK paid by Norwegian Resource Council
- Participants:
  - **SINTEF** (Materials and Chemistry, Energy Research)
  - **NTNU** (Materials Science and Engineering, Energy and Process Technology)
  - **Al-consortium** (Hydro Al, Søral, Alcoa (207-2010))
  - **FFF** (Elkem, Eramet, Vale, FeSil, Wacker Finnfjord,)
  - **Ti-minerals** (Eramet Ti)
  - **Equipment producers** (Alstom)

ROMA – Project Organization

ROMA

Project manager
Eli Ringdalen

Steering committee
SINTEF (2)
NTNU (2)
FFF (1)
Al Consortium (2)
Alstom (1)
Observer Ti-industry (1)
Observer NRC (1)

Internal coordination of R&D activities

Materials flow and process integrations	Energy recovery	New raw materials	Junior programme
Task manager: **Thor A Aarhaug**	Task manager : **Petter Nekså**	Task manager: **Merete Tangstad**	Task manager: **Arne P Ratvik**

- All information from ROMA, results and reports are published on ROMA E-room.
- Technical results are presented and plans for further work discussed in resource group meetings held twice a year. Next is 14-15 February 2012
- E room and Resource group meetings are open for everybody working in companies that are member of the ROMA consortium

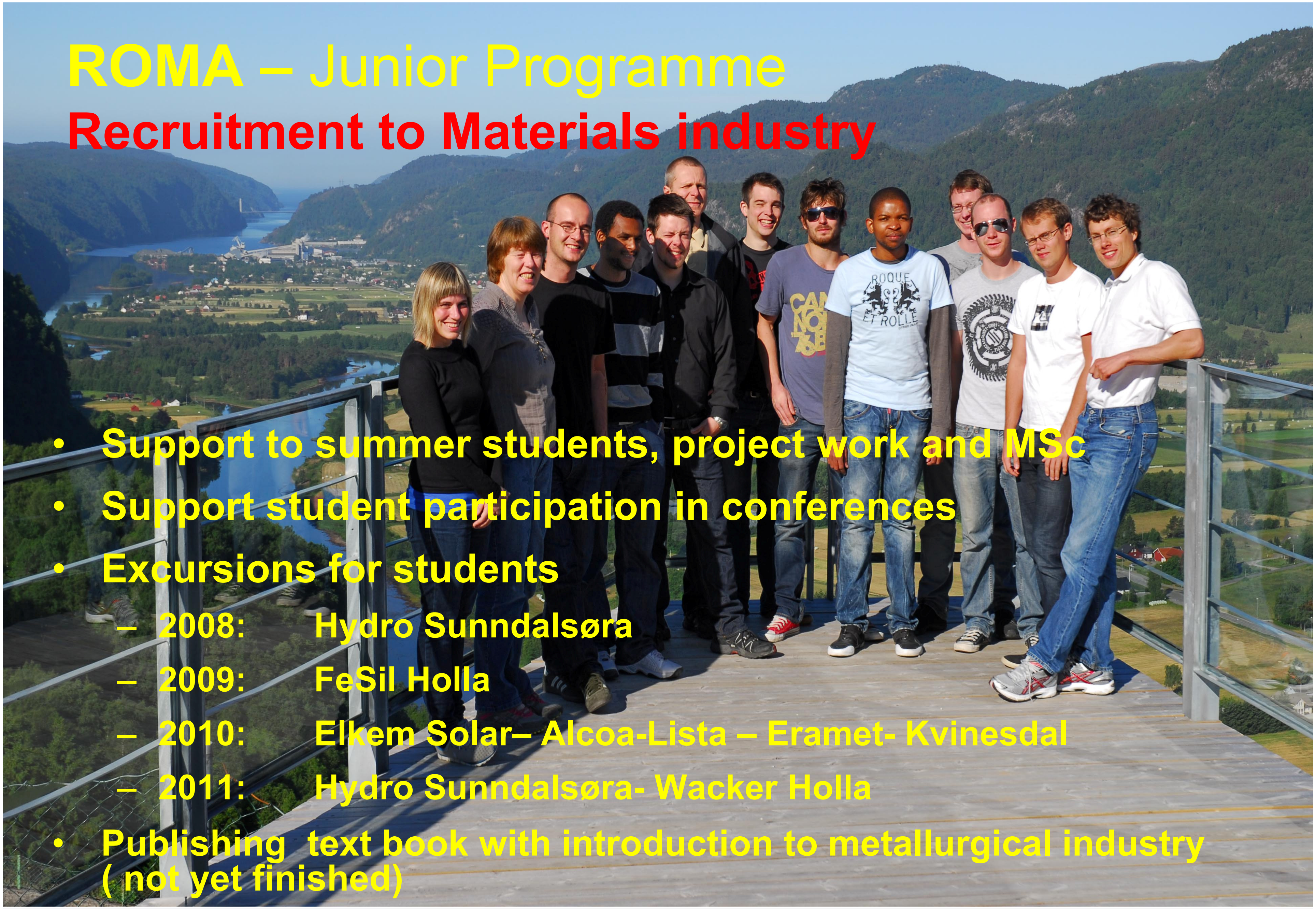
ROMA- Subprojects and Projects

ROMA

- **Materials Flow and Process Integration,**
  (Project: 10,8 mill + 2PhD: 4,2 mill)
  - Characterization of flue gas from Al-industry (Project + 1PhD)
  - HF-formation in Al-industry (Project)
  - Characteisation of secondary alumina (Project)
  - Recycling of waste from upgrading of secondary alumina (Project: + 1PhD)
  - Biocarbon materials in anode production in the Al-industry (Project)
- **Energy Recovery**
  (Project: 11,3 mill + 1PhD: 2,1 mill+ 1 Post.Doc:1.4 mill)
  - Electricity production from low temperature waste heat sources (Project + 1PhD)
  - "Fouling minimization in heat recovery from metallurgical waste gas streams (Project + 1Post.doc)
- **New Raw Materials**
  (Project: 10,6 mill + 3PhD: 6,3 mill)
  - Thermal conductivity of raw materials in the Mn-industry (Project + 1PhD)
  - Carbon reactivity of raw materials in the Ferroalloy (Mn)-industry (Project)
  - The effect of various fines and agglomerates on the furnace during Mn-production (Project + 1PhD)
  - Slag properties and phase relations in the Ti-industry (Project + 1PhD)
  - Ilmenite fines (Project)
- **Junior program**
  (Project: 3,8 mill)
- **Investments**
  (3,1 mill)
  - DTA/TGA for measurement of weight and energy changes during heating installed and in operation
  - Laser Flash for Thermal conductivity measurements installed and in operation
  - Experimental prototype for electricity production from low temperature sources installed and used in test work

ROMA – Junior Programme

Recruitment to Materials industry



- **Support to summer students, project work and MSc**
- **Support student participation in conferences**
- **Excursions for students**
  - **2008: Hydro Sunndalsøra**
  - **2009: FeSil Holla**
  - **2010: Elkem Solar– Alcoa-Lista – Eramet- Kvinesdal**
  - **2011: Hydro Sunndalsøra- Wacker Holla**
- **Publishing text book with introduction to metallurgical industry (not yet finished)**

ROMA

ROMA – Junior Program

Student Reports

- S Jørstad: Norsk Metallproduksjon fremtidens industri-2008
- S Gurrik: Norsk Metallproduksjon fremtidens industri-2010

Produkt	**Syssel-satte**	**Produk-sjon** i 2009 [1000 tonn]	**Eksport-verdi** [Milliarder NOK]	**El-forbruk** [TWh]	**Utslipp av gasser** [tonn CO_2-ekv Kyoto]
Total primær Aluminium	2627	1128	14,34	17,31	2014998
Total Silisium	645	79	1,30	0,86	340414
Total ferrosilisium	526	231	2,18	2,36	828525
Total ferromangan	324	268	2,25	1,18	222021
Total Silikomangan	335	216	1,93	0,46	169701
Total TiO2-pigment	199	153	1,50	0,28	247760
Total Silisiumkarbid	410	19		0,21	51160
Resirkulering av stål	320	546		0,34	74260
Total Ni, Cu, Co	500	114	8,45	0,58	16360
Total Sink	330	140	1,59	0,63	2000
Total norsk metallproduksjon	**6516**		**33,54**	**24,21**	**3967199**

ROMA- Materials Flow and Process Integration Results

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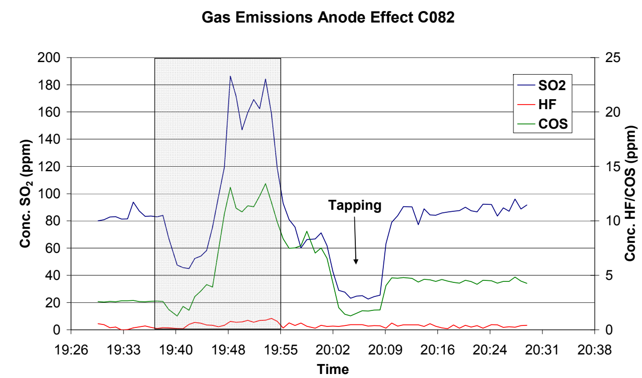
Established methodology for online monitoring of flue gas from Al-industry

- Several test campaigns performed to verify system functionality
- ELPI rig functionality documented
- Open path FTIR to be implemented for SO_3/H_2SO_4 assessment

Mapping of raw gas composition in flue gas from Al-industry (PhD 1)

- Initial results indicate interesting correlation between operational parameters and flue gas composition
- Measurements of flue gas as function of DPS parameters planned.



Recycling of waste from upgrading of secondary alumina (PhD 5)

- PhD candidate Svetlana Kalyavina started 2011-01-01
- Collaborate with PhD 1 (Heiko) on impactor measurements and chemical and physical characterization of impactor fractions by SEM, XRD, TGA/FTIR/MS
- Review of existing methodology for recovery of valuables

HF-formation in Al-industry

- Several measurement campaigns performed for simultaneous HF and H_2O assessment
- Very high HF levels recorded over feeder holes.
- Planned Laboratory Measurements
  - Alumina characterization with respect to "HF potential"
  - Develop voltammetry combined with gas analysis – correlate peak current densities with concentrations of HF and H_2O
  - Determind the "proton rate" through the melt
  - HF formation as a function of water content in inert gas in laboratory cell

Biocarbon materials in anode production in the Al-industry

- **Charcoal can not be recommended for use in anodes for aluminium production**
  - Charcoal has adverse effect on anode properties regardless of charcoal density and volatile content
- Bodil Monsen: TMS 2010 best paper award

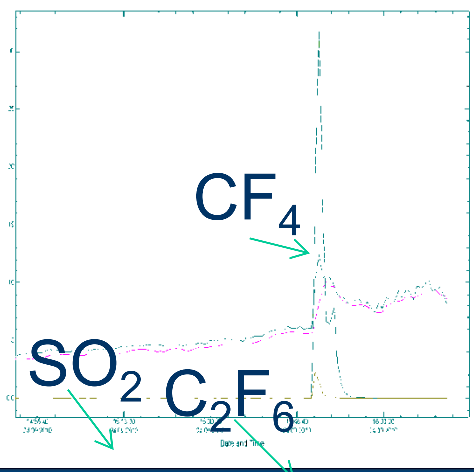
Materials Flow and Process Integration
Characterisation of flue gas from Al-industry

ROMA

Characterisation methods are developed

Equipment bought in ROMAN project used and further developed

- **Methodology for online characterization of Aluminium Primary Production gas composition developed**
  - HF removal, retaining most other gas components
  - Gas monitoring by means of FTIR + MS
  - HF and water monitoring (unfiltered) by TDLAS
  - Impactor classification of particulates 7 nm – 12 µm in 12 stages
- **PFC emission monitoring**
  - Quantification limit ~30 ppb CF_4 (FTIR)
  - Tier 3 emission quantification
- **Open Path FTIR through-cell measurements**
  - Simultaneous detection of SO_2 / SO_3 / H_2SO_4 (acid dew point assessments)
  - First to document presence of COF_2 gas in industrial scale smelters



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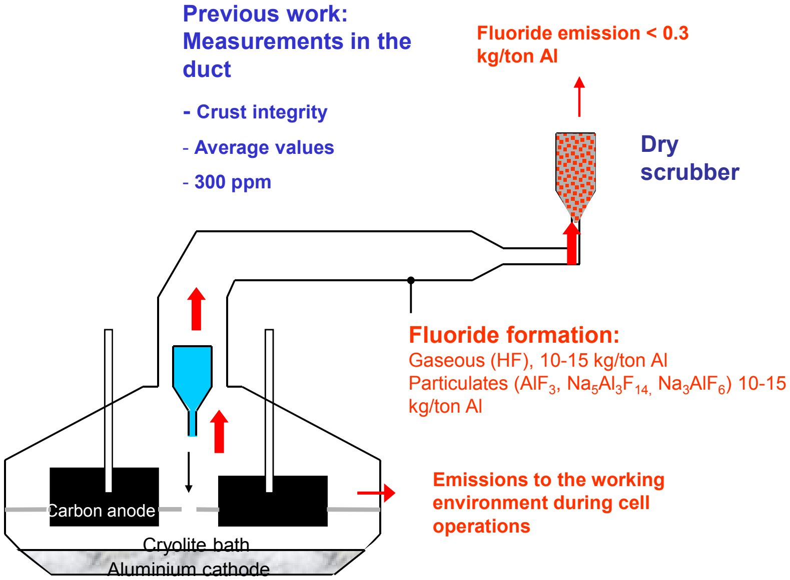
Materials Flow and Process Integration – HF formation in Al industry

- **HF mapping inside Al smelters**
  - **~3 % HF reported over feeder holes**

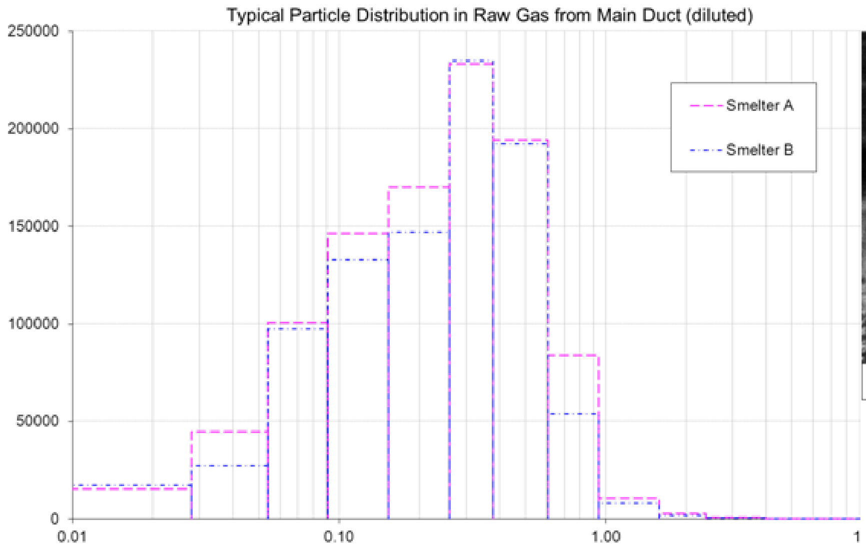
- **HF formation in aluminium primary production**
  - Laboratory instrumentation for evaluation of HF formation as function of alumina quality and water content is developed and used
    - HF formation increases with analysed LOI (Loss of ignition)
    - All water contribute to HF formation
    - HF formation potential can be reproductively evaluated for alumina type



ROMA

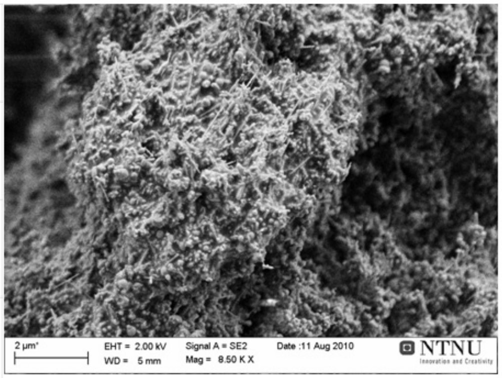
Materials Flow and Process Integration – Characterisation of secondary alumina

- **Classification of impurities on particles**
  - XRD, SEM EDS and ICP-MS characterization
  - Distribution of impurties on particles
  - Size distribution of particles



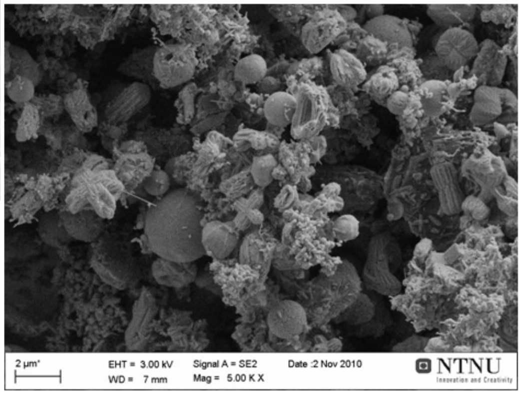
Stage 6

$D_i = 0.31 \mu m$ $D_{50} = 0.26\ \mu m$



Stage 10

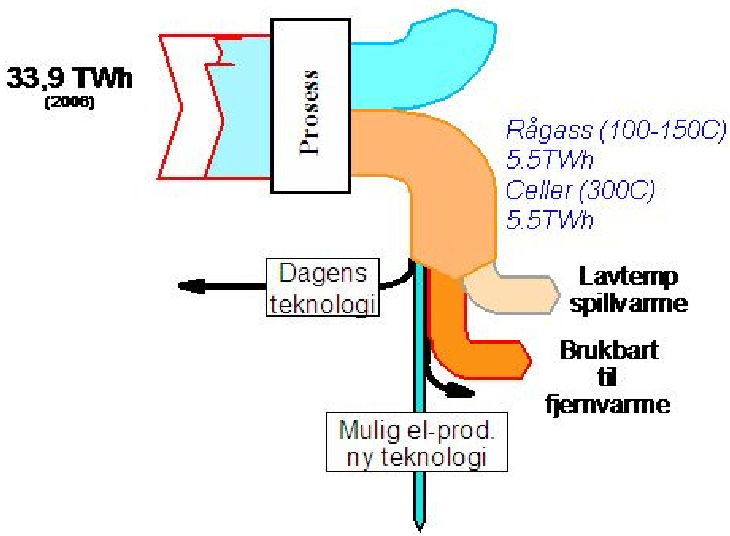
$D_i = 3.07 \mu m$ $D_{50} = 2.38\ \mu m$



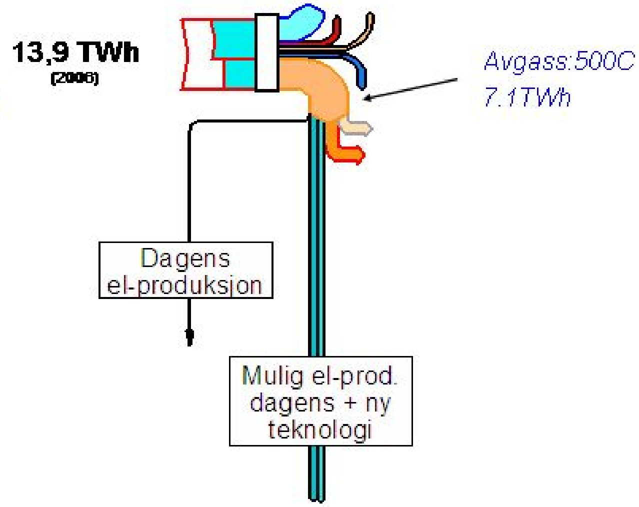
ROMA – Energy Recovery- background

Energy in the metallurgical industry

Aluminium:
Lave avgasstemperatur gir moderat el-utbytte



Ferrolegeringer:
Høyere avgasstemperatur gir større el-utbytte



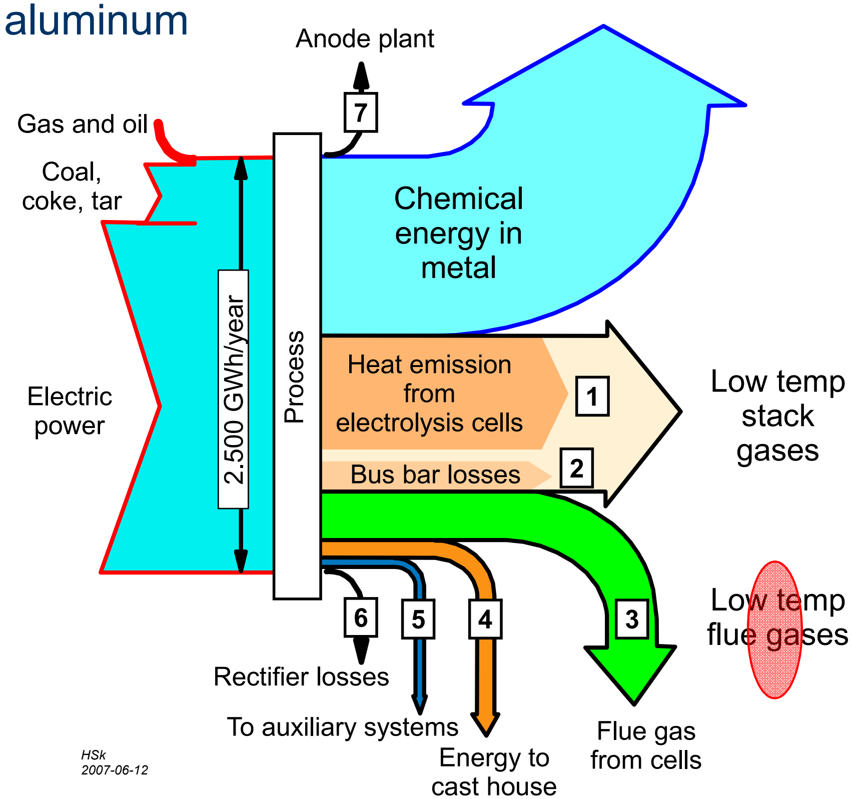
ROMA: electricity production from low temperature heat source

ROMA

- Establish performance for CO_2 based power production cycle, compare with existing technologies.
- Establish control strategy for optimum power production.
- Establish basic design for key components.
- Propose a system solution for application in aluminum production plant.

Pave the way

for a one cell industrial demonstrator



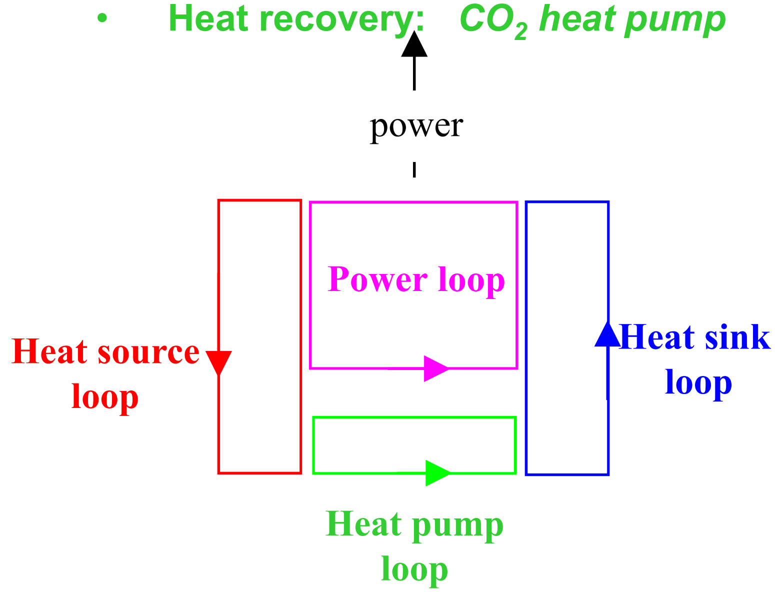
ROMA

Energy Recovery - Laboratory prototype

- Experiments performed:
- **Effect of heat source temperature (70-110C)**
- **Effect of CO_2 mass flow (1.8-3kg/s)**
- **Effect of condensation pressure (47-64bar)**

Laboratory prototype

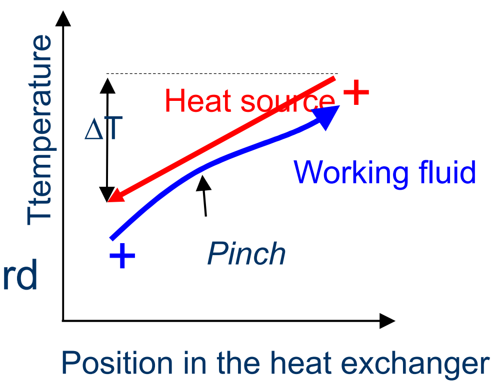
- **CO_2 power cycle: 500W** ***up to 250kg/h CO_2***
- **Heat source: air *50°C up to 160°C***
- **Heat sink: glycol *20°C down to -10°C***
- **Heat recovery: *CO_2 heat pump***



ROMA

Electricity production from low temperature off-gas

- A lab prototype has been built and basic operation and control strategies tested
  - The prototype was easy to operate
  - Optimization showed that torque control of the turbine was mandatory
- Power cycle parameters and heat exchanger design are modelled for a typical plant
- Basic design is established for the heat recovery exchanger
- Simulation showed that CO_2 transcritical cycle efficiency is dependant on large temperature glide
  - Cooling of gas is important
- Condensation of corrosive compounds is a challenge
- Pumping power is an issue
  - Thermo compression is proposed as an alternative to standard mechanical compression.



Energy recovery from " Dirty" gas streams

Primary objective

- **Enable heat recovery from particle-laden off-gases at highest possible temperature**

RESULTS

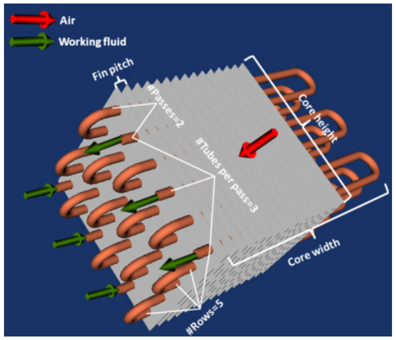
- Literature review on particle resuspension
- Mechanism of particle deposition and removal are modelled
- A lab wind tunnel test rig has been constructed
  - Design based on modelling results
  - Prelimenary tests with artificial material showed that industrial samples should be used
- Alumina particles are prepared for testing
  - Characterisation from MF-PI sub project is used as basis

ROMA

ROMA Energy Recovery

What we have learned so far

- Supercitical cycle are ”surprisingly” easy to run
  - But requires proper high pressure control for optimizaton
- Modeling acounting for heat exchanger design shows challenges for CO_2 when heat recovery is limited by dew point
  - Pump work is an important factor
- Dirty gas: challenging but crucial task (both on modelling and experimental side)



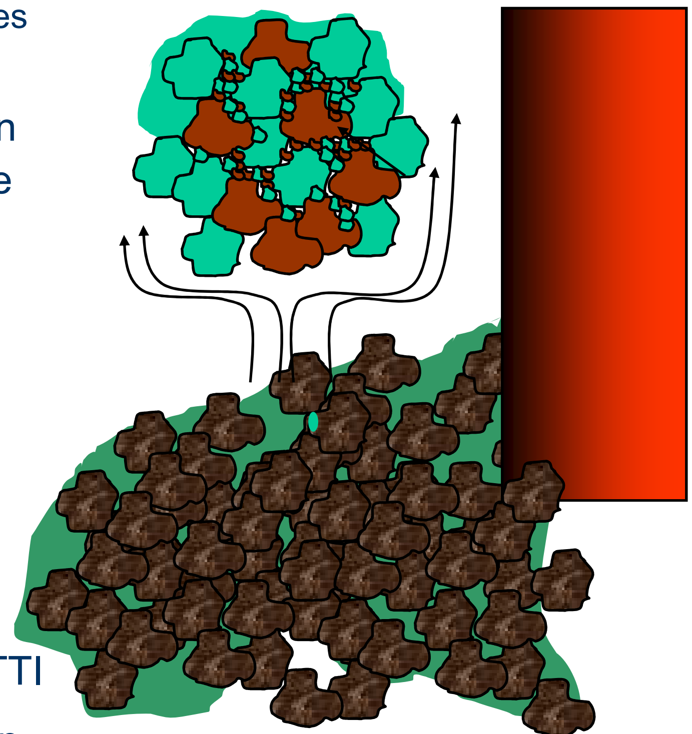
ROMA: New Raw materials-

Main objectives

ROMA

HCFeMn and SiMn production

- Know the effect of various fines on the furnace, either as fines itself or as agglomerates like sinter or briquettes
  - Determine mechanism of deteriorating furnace operation when fines are added.
- Know the thermal conductivity of the most used raw materials in the manganese processes, and be able to tell the impact on the furnace operation
- Determine quantitative effects, like CO reactivity, strength and melting, of agglomerates in comparison with lump materials



Ti-slag production

- Determine phase relations and properties in titania-slags as influenced by additions of magnesia, calcia, and silica.
- Provide overview over economic issues pertaining to slag leaching operations for beneficiation of present products from TTI
- Clarify possible opportunities to improve tramp element levels in feedstock through adjusting ore dressing parameters

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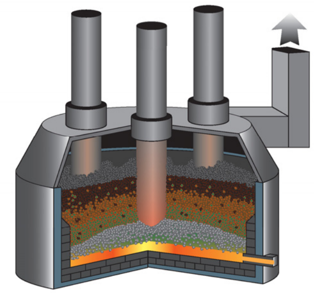
ROMA- New Raw Materials- Objectives and Results

Know differences between lump and agglomerates in Mn alloy production

- Competence and methods for determine manganese mineralogy has been developed
- Ore and sintered ore have different mineralogy
- Sinter melts at lower temperature han lump ore
- Sinter have lower CO reactivity and lower porosity than lump ore
- Sinter gives higher coke and energy consumption than lump ore
- Investigation of differences between lump ore and agglomerates continues in PhD



Determine thermal conductivity of Manganeses sources (PhD)

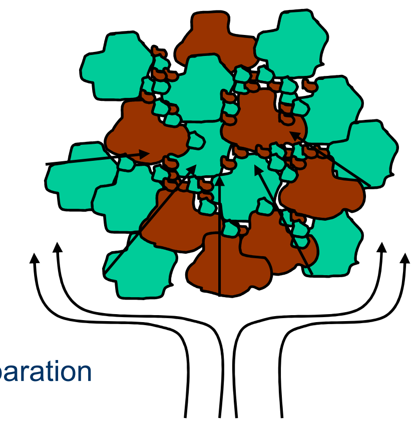
- A methode to measure thermal conductivuty of manganese ores by laser flash has been developed
- Thermal conductivity has been detrmined for selected manganese ores

Know the effect of fines on furnaces in Mn alloy production

- Sintering of charge requires temperatures above 1250 ^{o}C and the top of the charge is not sintered by itself
- A method for measuring pressure drop through charge mixtures with different fines contents, is being devloped

Slag-carbon reactiviy

- Slag –carbon reactiviy measured with sessile drop apparatus gives consistent results
- Coke reduces the slag faster than charcoal



Determine phase relations in titania slags (PhD)

- Slag/metal equilibrium line experimentally established
- Liquidus temperature decrease with increasing FeO

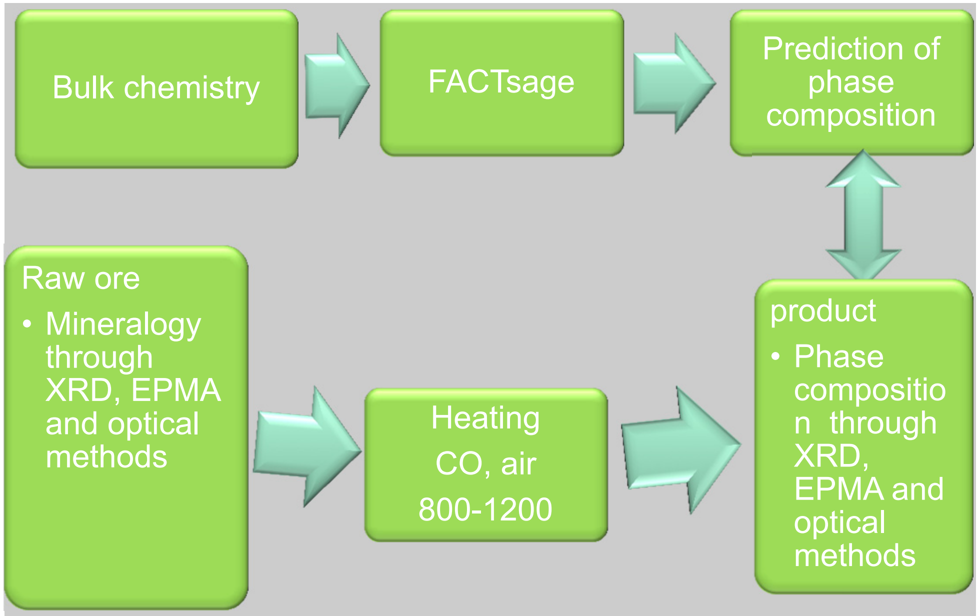
Removing tramp elemts in ilmenite

- A substantial amount of impurities can be removed by milling followed by magnetic and electrostatic separation

Reactions in Si furnaces

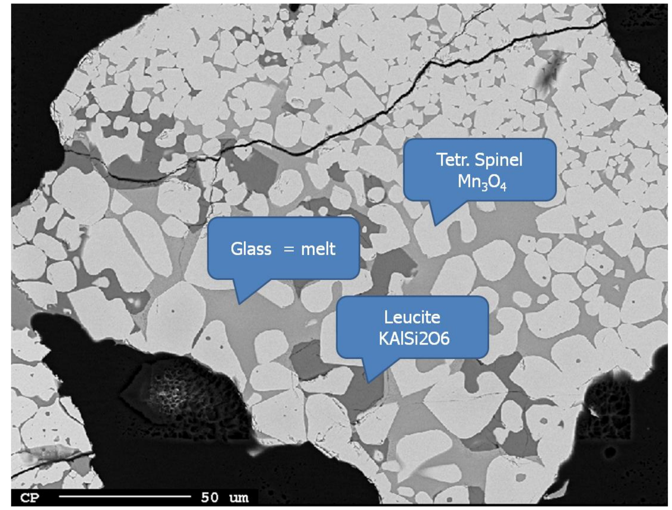
- Si is not included in ROMA, but some studies based on method developed in ROMAM,

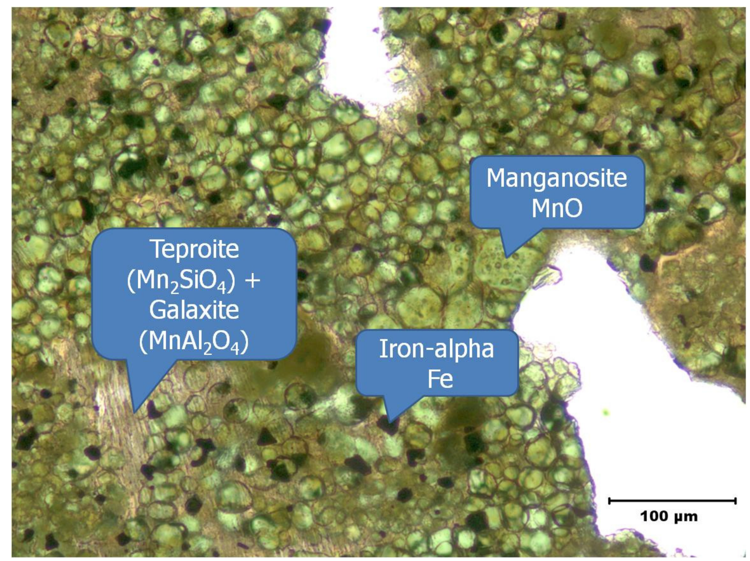
Mineralogical changes during heating



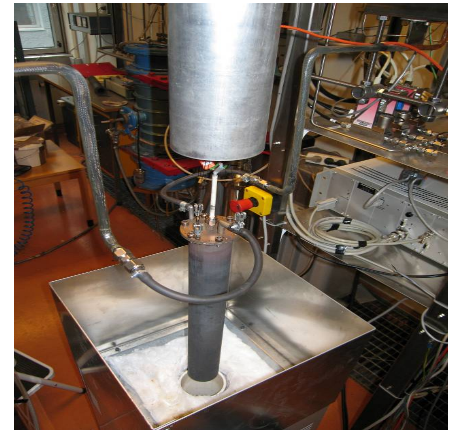
Conditions	Mineral	Formula	Wt%
800°C, CO	Manganosite	(Mn, Fe)O	76.2
	Galaxite	$(Mn^{2+}, Fe^{2+}, Mg^{2+})(Al, Fe^{3+})_2O_4$	14.4
	Iron alpha	Fe	<1
	Quartz	SiO_2	8.7
	Graphite-3R	C	<1
1200°C, CO	Tephroite	$(Mn, Mg, Fe)_2SiO_4$	24.3
	Manganosite	(Mn, Fe)O	56.3
	Iron alpha	Fe	1.4
	Spinel	$(Mn, Mg, Fe)Al_2O_4$	8.6
	Unidentified		9.4

Gabonese ore





ROMA New Raw Materials- CO reactivity



$^1/_3 Mn_3O_4 + ^1/_3 CO = MnO + ^1/_3 CO_2$ $\Delta H^\circ_{298} = -16.9 kJ$

$^1/_3 CO_2 + ^1/_3 C = ^2/_3 CO$ $\Delta H^\circ_{298} = 57.5 kJ$ (> 800°C)

$^1/_3 Mn_3O_4 + ^1/_3 C = MnO + ^1/_3 CO$ $\Delta H^\circ_{298} = 40.5 kJ$

	Start MnO_x before experiment	MnO_x at 800°C Calculations based on CO in off-gas / weight loss	MnO_x at 1100°C	Theo. C consumtion (kg) per tonn of FeMn	Theo. power consumption kWh per tonn of FeMn
Ore A	1.94	1.00 / 1.00	1.0	0	0
Sinter	1.22	1.14 / 1.10	1.0	18 – 25	72 – 100
Pellet	1.34	1.15 / 1.10	1.0	18 – 26	72 – 104
Briquettes	1.93	1.00 / 1.01	1.0	0 – 2	0 – 8
Ore B	1.94	1.04 / 1.00	1.02	0 – 7	0 – 28
Pellets	1.31	1.22 / 1.10	1.03	18 – 38	72 – 152
Briquettes	1.95	1.00 / 1.01	1.0	0 – 2	0 – 8
Sinter	1,27	1,11	1,03	19	76

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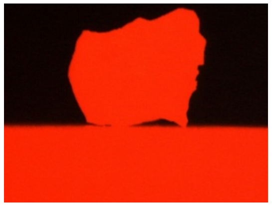
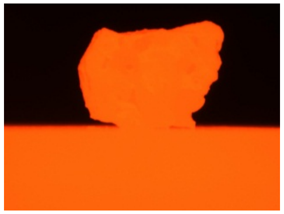
Melting behavior

Material	Start melting
Ore B	Ref
briquette	-44
sinter	-81
pellet	-4
Ore A	Ref.
briquette	-203
sinter	-94
pellet	-159

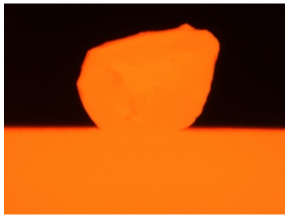
Cold



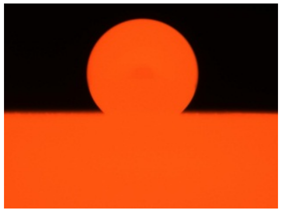
Start melting



Start reduction



Liquid



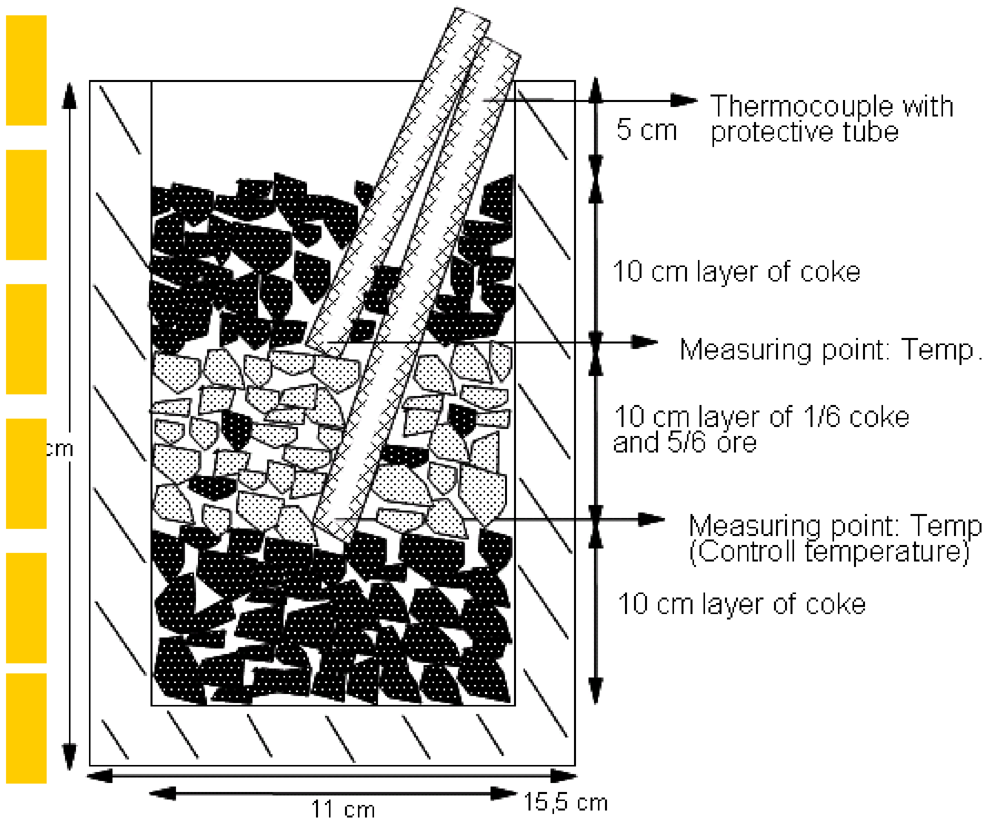
Sessile drop

Melting properties of Manganese ores

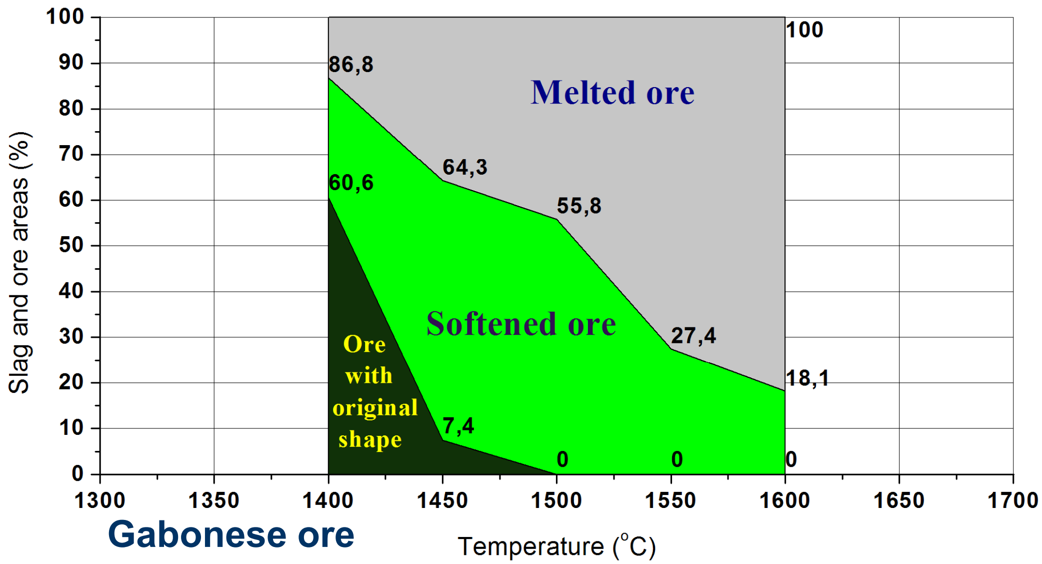
Induction furnace

Maximum power	50 kVA
Frequency	3830 Hz
Max temperature	2200 ^{o}C

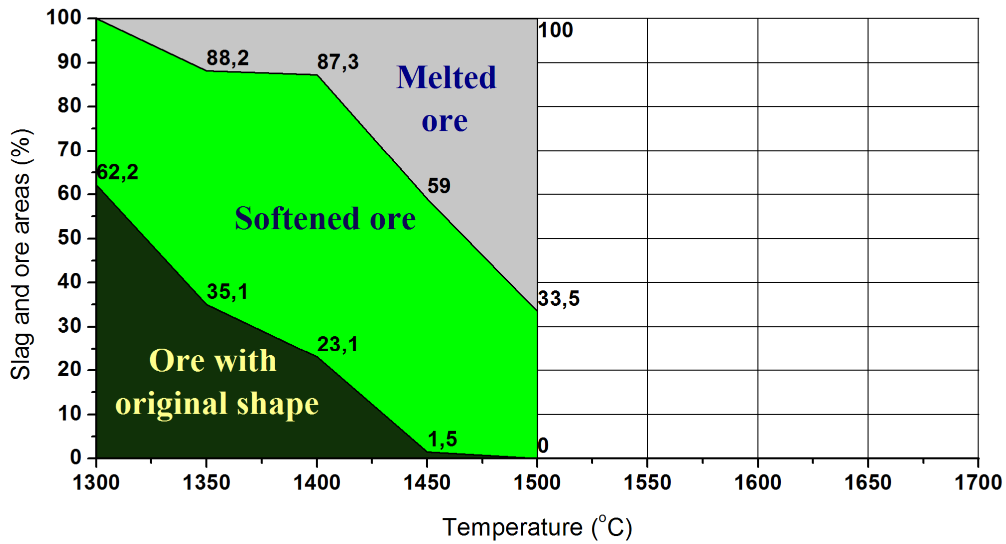
Experiment → Cooling → Filling of the crucible with epoxy → Cutting



ROMA- New Raw Materials- Melting propeties

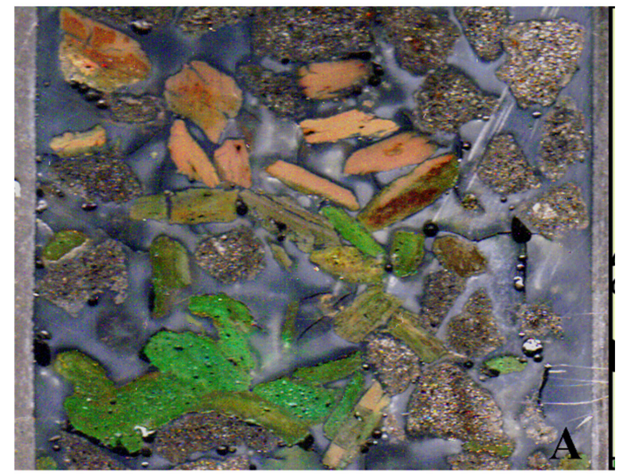


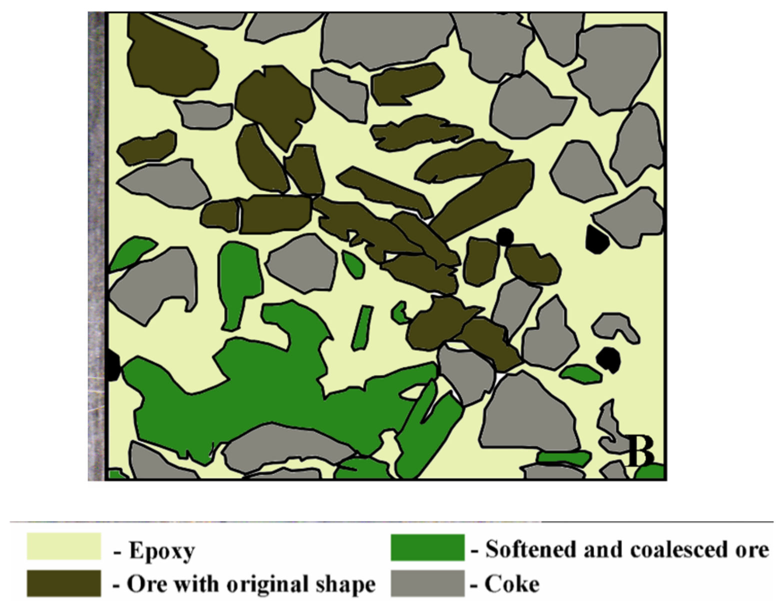
Gabonese ore



Gabonese sinter

Cross sections from crucible





ROMA

Removing tramp elements in ilmenite

- The amount of gangue minerals increases towards the finer fractions.
- Around 82 % of ilmenite liberated in the finest fractions .
- The unliberated silicates are almost entirely associated with ilmenite.

Milling and screening

A substantial amount of impurities can be liberated by milling the 0-300 μm material

Magnetic separation

Up to 50% reduction of Al_2O_3, SiO_2 and CaO
Up to 10% red. of MgO
High yield

Electrostatic separation

More than 50% red. of SiO_2 and 40% red. of CaO on magsep concentrate
Good reduction of MgO, CaO, Cr_2O_3 and P_2O_5 on magsep concentrate
High yield

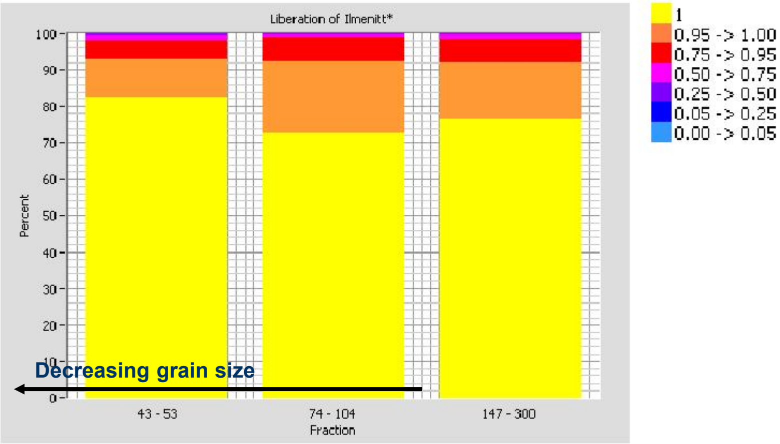
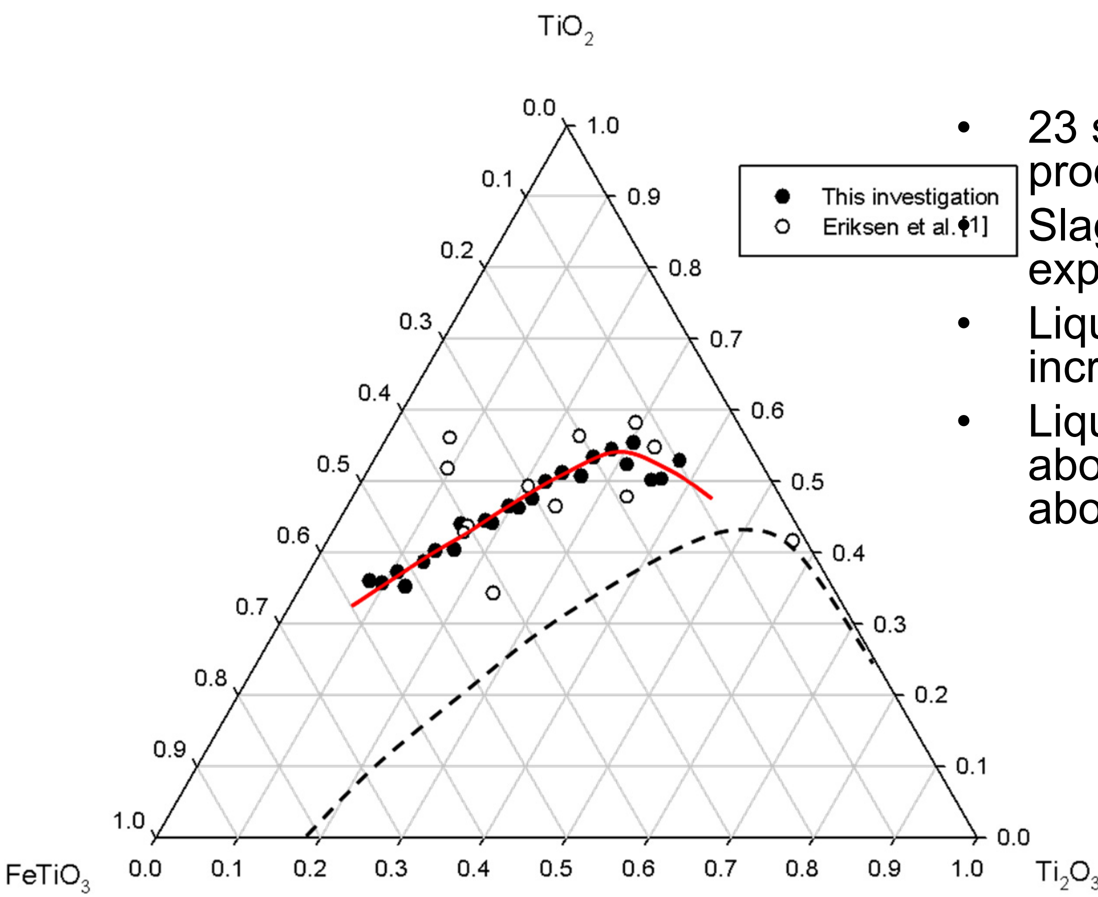


Fig. Liberation of ilmenite (Kari Moens report)

TiO_2 slags

ROMA



- 23 synthetic slags successfully produced
- Slag/metal equilibrium line experimentally established
- Liquidus temperature decrease with increasing FeO
- Liquidus temperatures range from above 1700 ºC at 6-9 wt% FeO to above 1500 ºC at 31-33 wt% FeO

ROMA

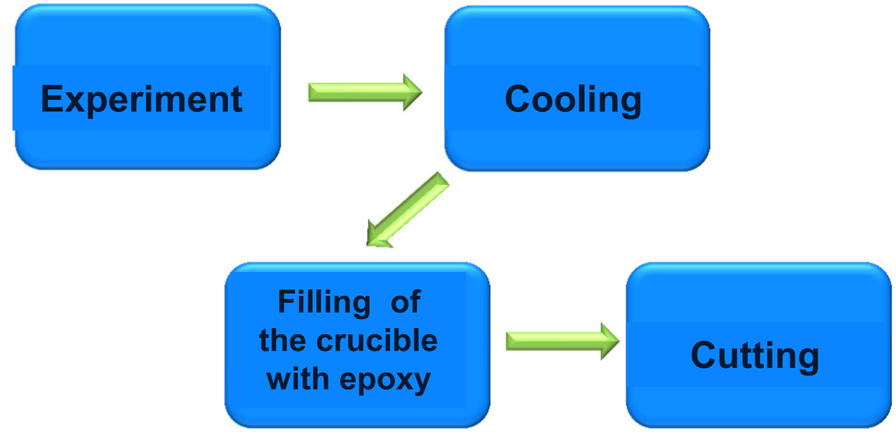
ROMAM- Extension of ROMA in 2008

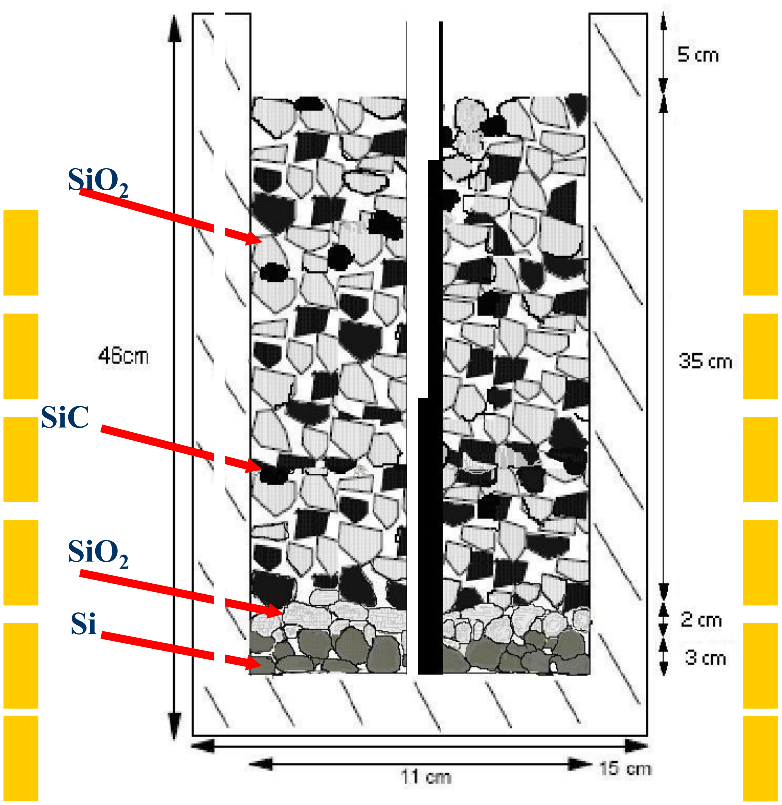
- Equipment (7,3 mill. kr)
  - Portable gas measurement equipment (3,3 mill)
  - Upgrading of submerged arc pilot scale furnace (4 mill kr + 0,5 mill from FFF+ 0,5 mill from SINTEF)
- Research work (1,375 mill)
  - Reactions in FeSi/Si production
    - New investigation method developed
  - Industrial measurements of off-gas analysis,
  - Energy analysis and CO_2 footprint in ferroalloy production including initial energy analysis at Sauda
- Funding
  - From NRC as part of "Miljøpakke"where selected existing project where invited to apply
  - 8,36 mill from NRC. Remaining 0,315 mill is contribution from Elkem and Eramet

New method for studing reactions in Si/FeSi production

Induction furnace

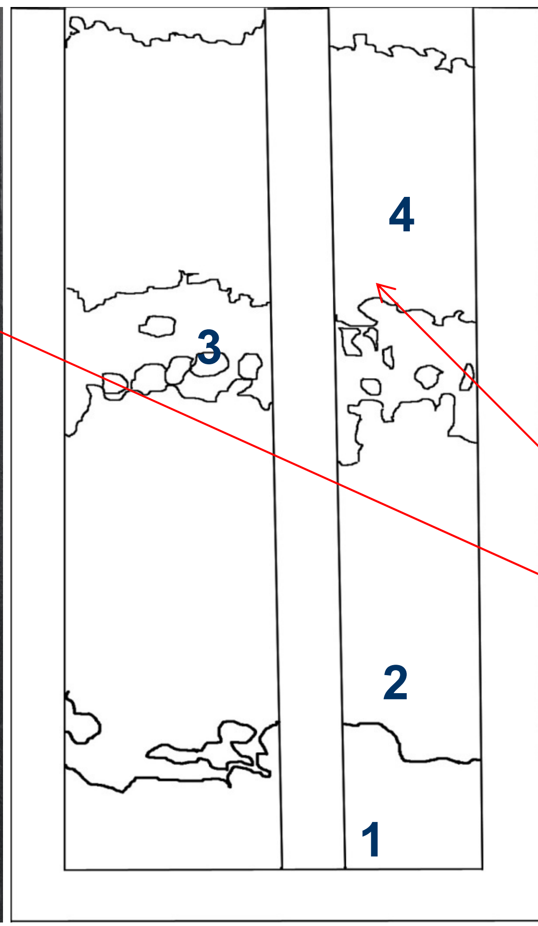
Maximum power	50 kVA
Frequency	3830 Hz
Max temperature	2200 °C



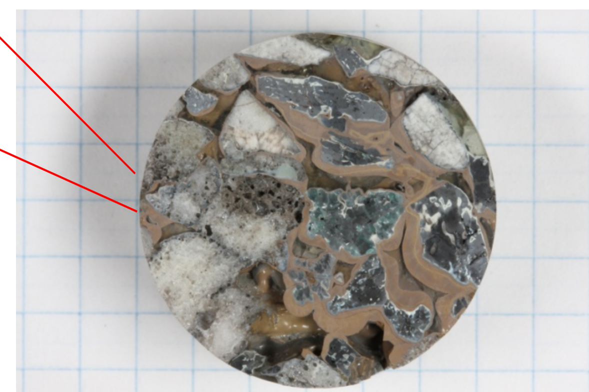


Formation of cavity in Si-process

- Formation of cavity is simulated
  - The condensates that forms the cavity are investigated



1. Si metal
2. Softened quartz, SiC, condensate
3. Cavity
4. Solid SiO_2, SiC, condensate



ROMA

ROMA - Dissemination and results

- **Publications and reports** (ROMA + ROMAM)
  - Ca. 30 SINTEF reports
  - 4 other reports
  - 1 PhD (Stian Seim, 2011)
  - 8 MSc
  - 7 Journal Publications
  - 17 Student memos
  - 16 Publications from conferences
  - 3 Presentations from conferences and meetings

All reports and memos can be found in E-room

https://project.sintef.no/eRoom/materials/805240ROMA

- **Other Research results**
  - 7 industrial measurements campaigns
  - Experimental prototype for electricity production from low temperature sources installed and used in test work
  - Designed and constructed experimental prototype for heat recovery from dirty gas streams


Thanks for your attention