KTH Royal Institute of Technology,
Materials Science and Engineering, Stockholm, SWEDEN

Development of Applied Process Metallurgy with Respect to Secondary Refining Processes

Andrey Karasev
Pär G. Jönsson

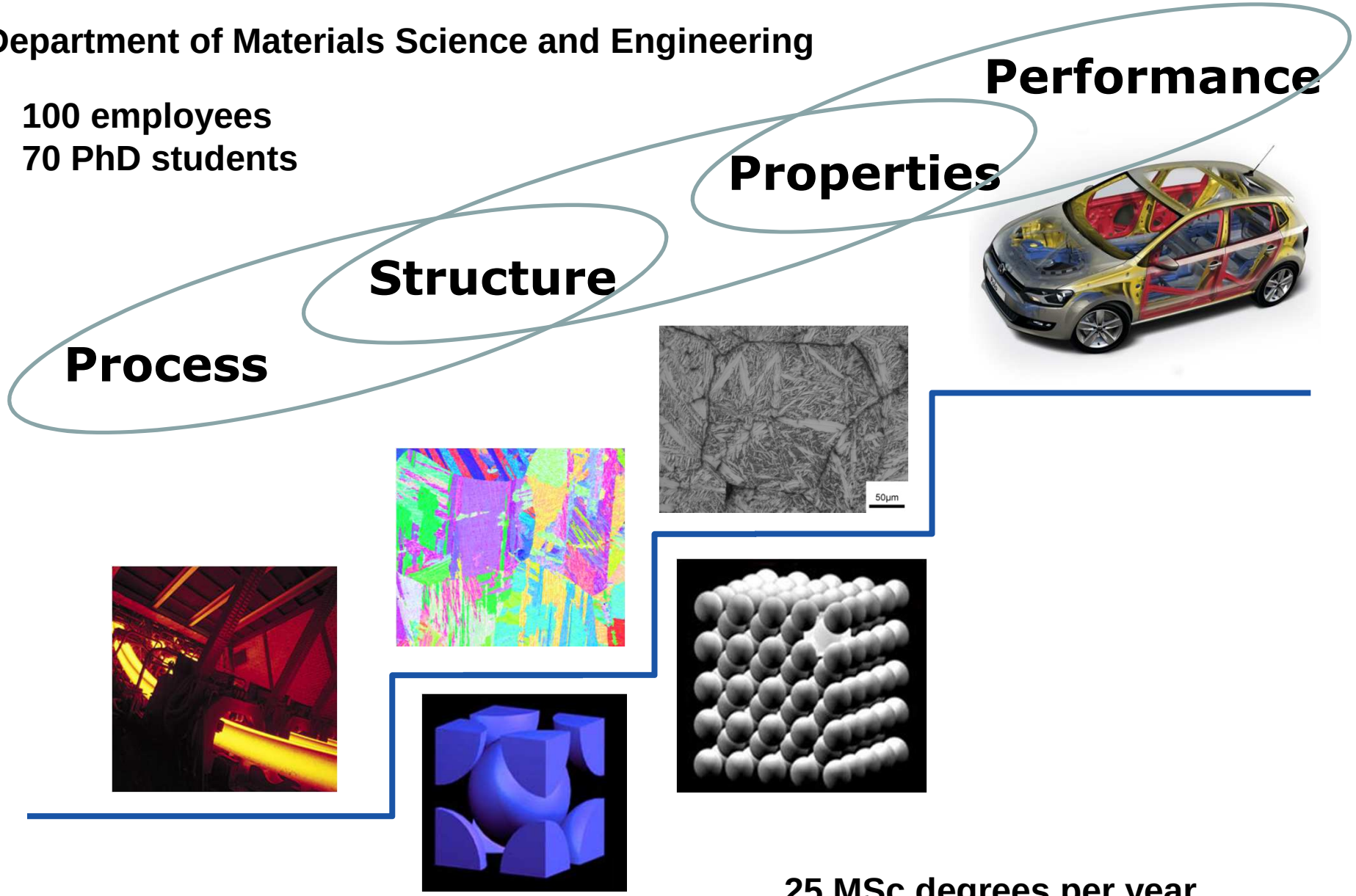
European Research of Secondary Metallurgy, Stockholm (Sweden), 22.05.2017

Content

- Dept. of Materials Science and Engineering
- Swedish Steel
- Sulfur and hydrogen
- 3D investigations of inclusions
- Recent and future projects focusing on inclusions
- New areas of Swedish Steel industry

Department of Materials Science and Engineering

100 employees
70 PhD students

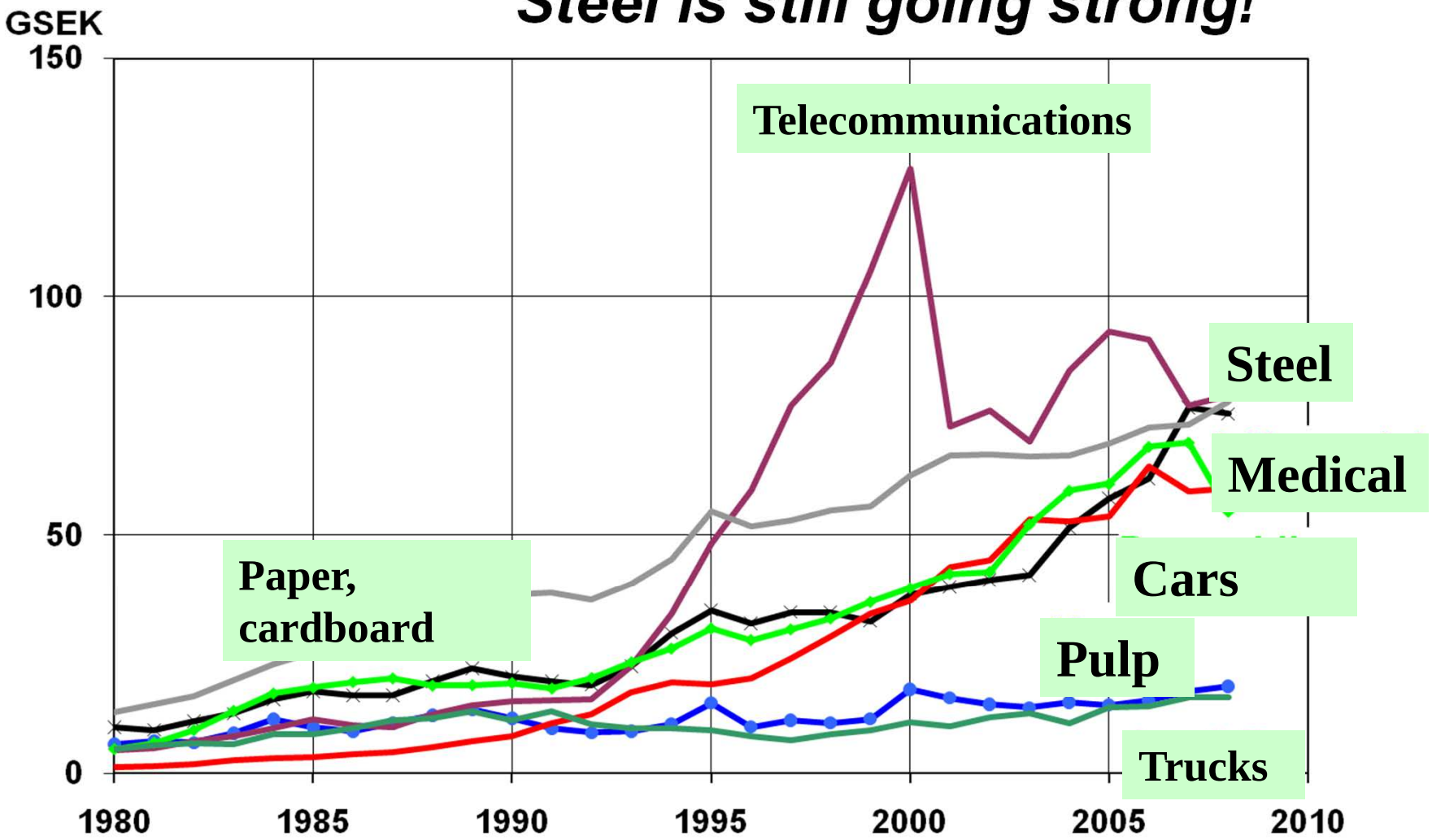


Three divisions: **Process, structure properties**

25 MSc degrees per year
20 PhD degrees per year

Value of export from Sweden =>

Steel is still going strong!



Källa: SCB

Steel companies in Sweden, with competitive niche products

Stainless	**Sandvik, seamless tubes, etc** **Outokumpu Stainless, plate, welded tubes, etc** **Fagersta Stainless, wire** **Carpenter Powder Products, powder**
Tool steel	**Uddeholm Tooling**
Speed steel	**Erasteel Kloster**
Bearing steel	**Ovako**
Low-alloy steel	**SSAB, high strengt steel, etc**
Iron powder	**Höganäs**

The majority of these grades are advanced steel grades => requires a complex ladle treatment including a stringent control of the inclusion characteristics

SQUiD – Steel QUality Design:

Need to control/determine steel quality parameters during secondary refining, casting and metal working to obtain optimum material properties to produce a specific product.:

- alloying elements (C,Si,Mn,Cr, etc)

- impurities (S,N,H,P,Cu,Zn, etc)

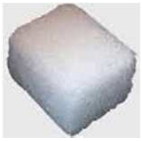
- non-metallic inclusions

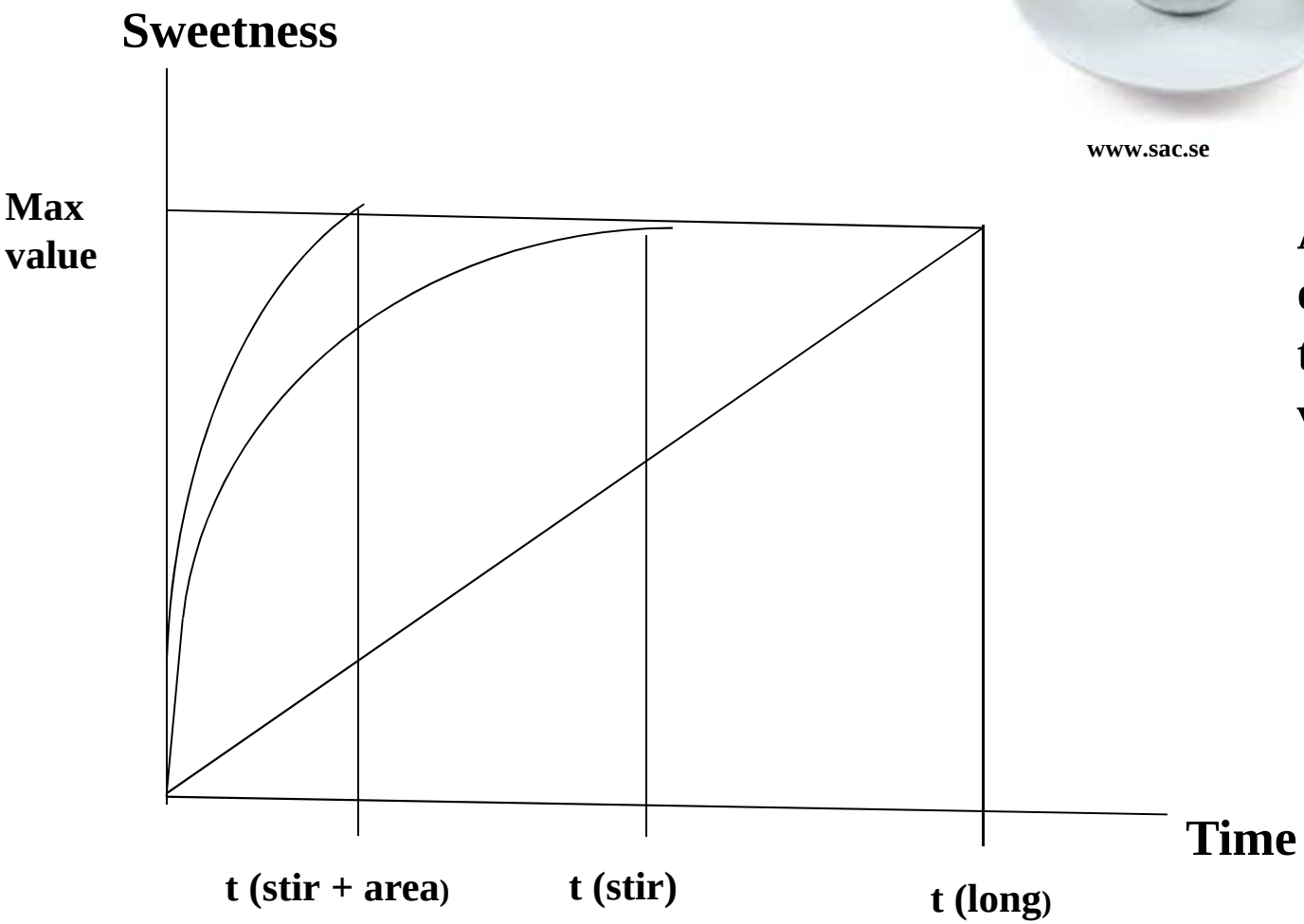
and the temperature during production

	Ladle	Tundish	Mold	Metal working mill
Alloying and impurity elements	yes	yes	yes	yes, not necessary
Temperature	yes	yes	yes	yes
Inclusion characteristics	no	no	no	yes, afterwards

Kinetics and thermodynamics are important in steelmaking and during short coffee breaks

www.sac.se



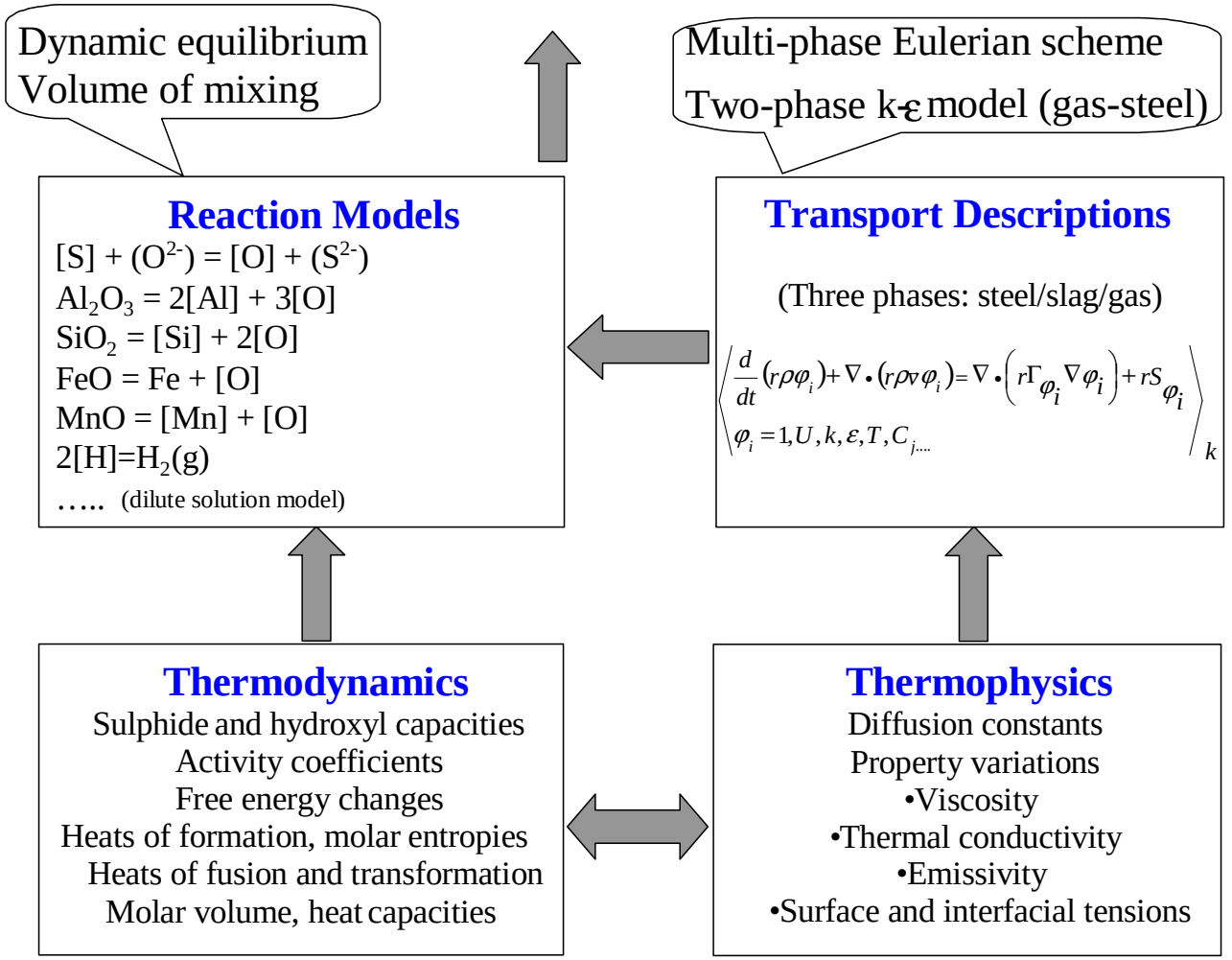


A fixed volume of sugar added to a fixed volume of coffee

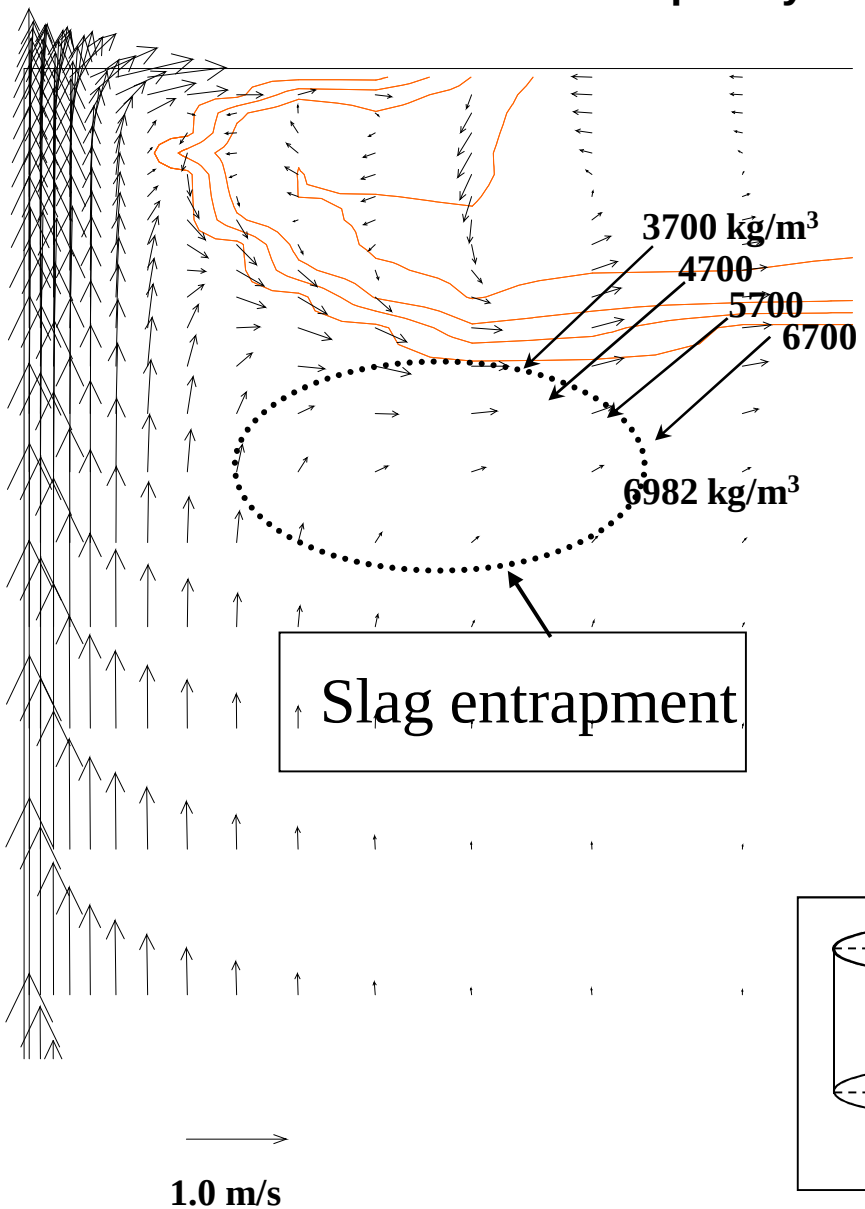
*The same "**coupled thermodynamic and kinetic approach**" is useful when studying refining of sulfur and hydrogen in metals*

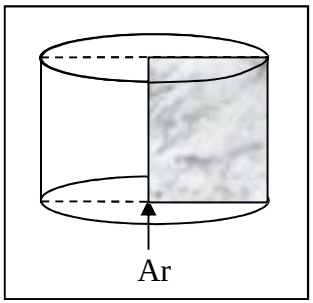
How to model coupled kinetic and thermodynamic reactions in steelmaking?

Modeling Ladle Refining
- A Fundamental Approach

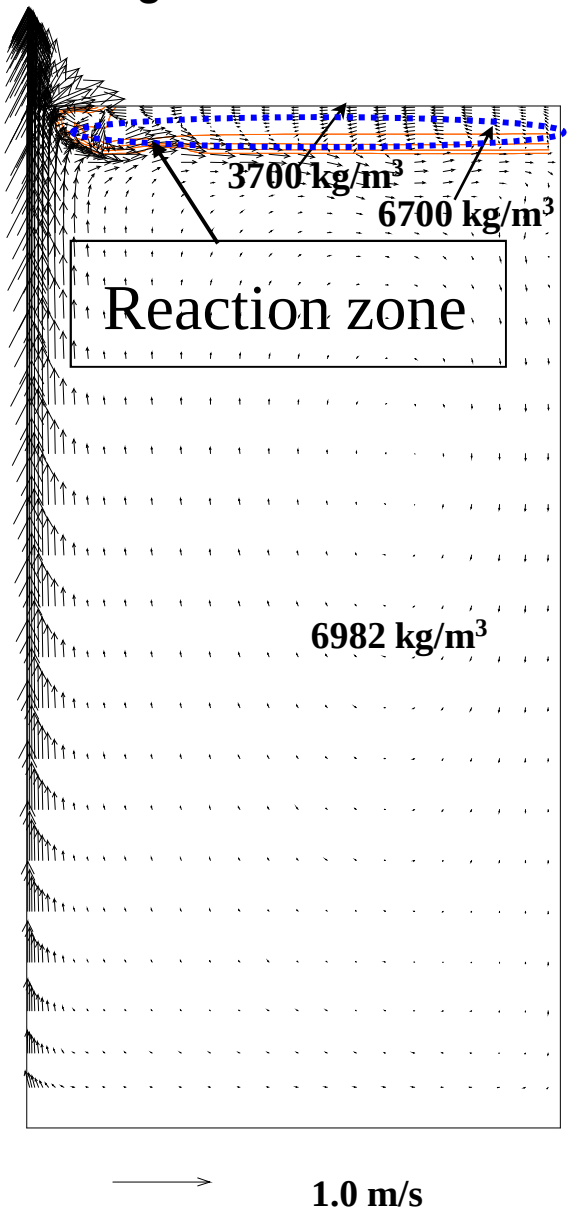


Area close to the open eye

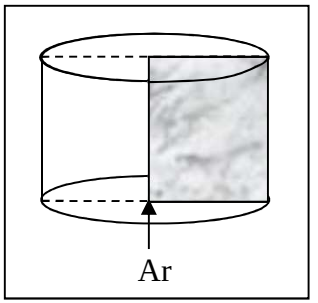




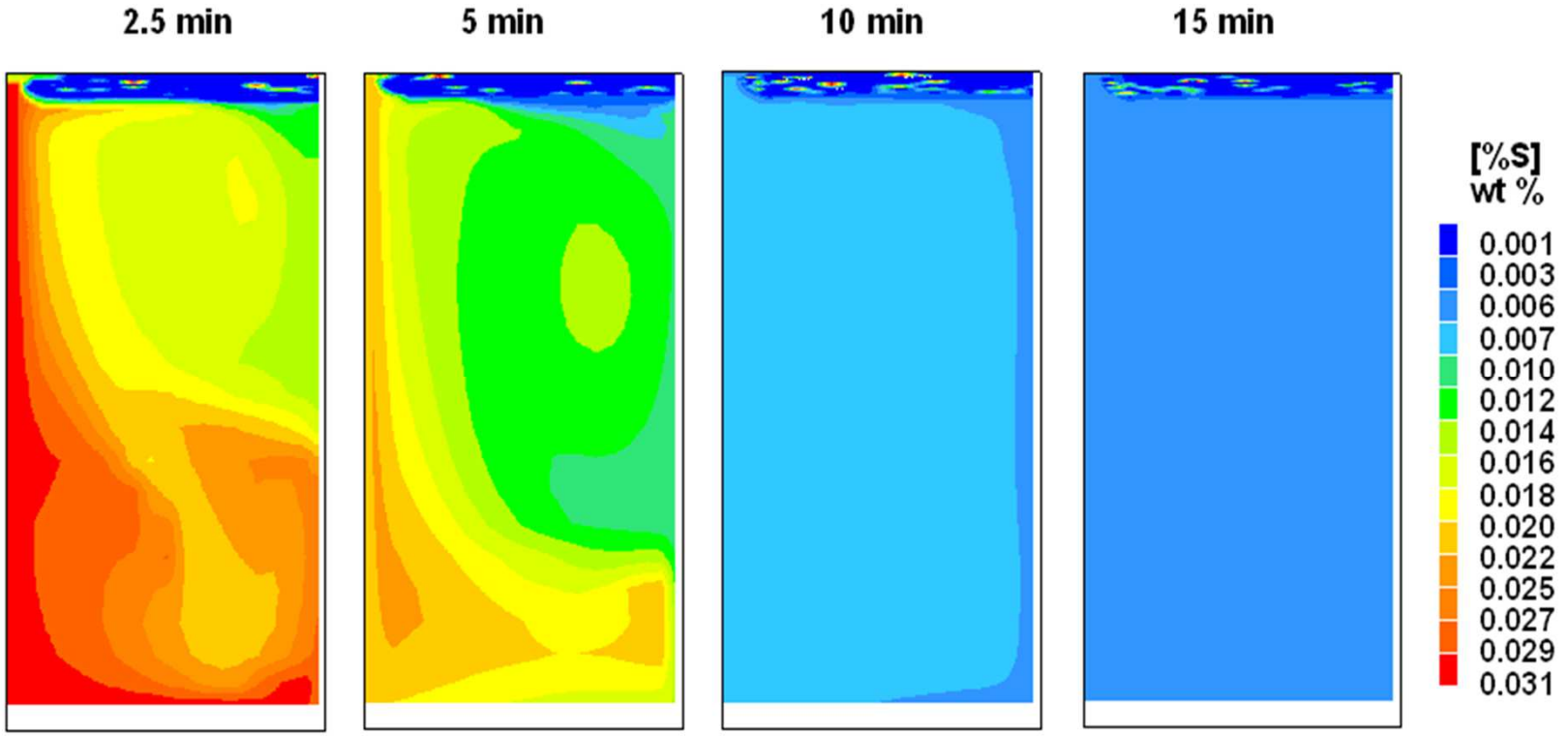
2D view showing a vertical plane through one half of the ladle



Change of sulfur concentration with treatment time Due to the reaction: CaO + S = CaS + O

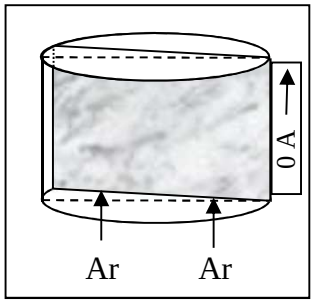


2D view showing a vertical plane through one half of the ladle



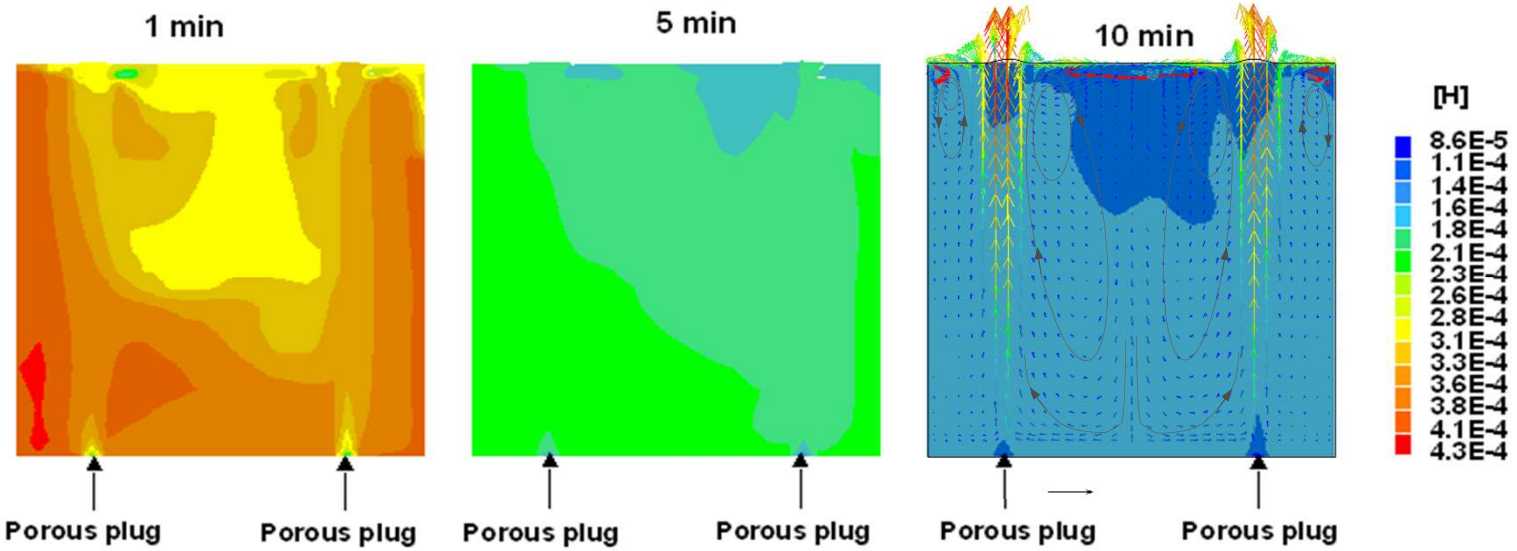
Assumptions: Homogeneous distribution of S initially, gas flow= 80 l/min, size = 100t, radius = 1.4m, slag thickness = 9 cm.

Hydrogen concentration in steel during vacuum degassing



H => 1/2 H_2 (g)

$$P_{H_2} = \frac{Q_{H_2}}{Q_{H_2} + Q_{Ar}} P_{tot}$$



Gas stirring only. Q_1=100 l/min, Q_2=117 l/min, T_0=1595 °C, H_0=5.4 ppm.
Slag depth at start of treatment 9 cm

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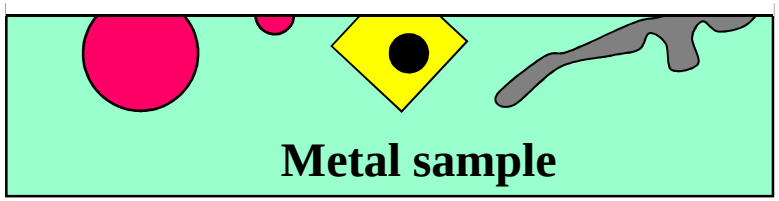
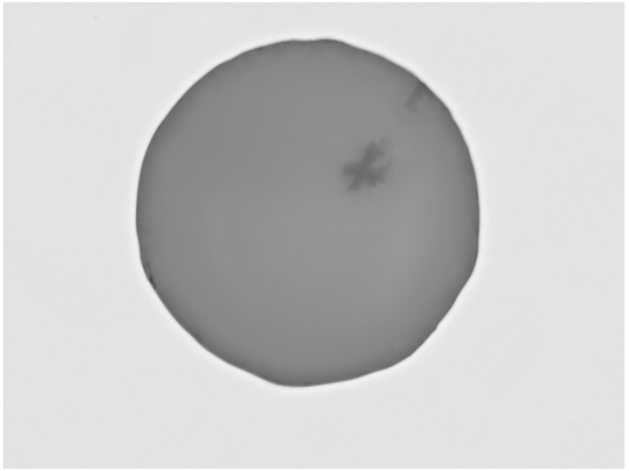
Three-dimensional investigations of non-metallic inclusions in different industrial steels during secondary metallurgy processes

European Research of Secondary Metallurgy, Stockholm (Sweden), 22.05.2017

1. Introduction. 2-D and 3-D analysis of inclusion characteristics

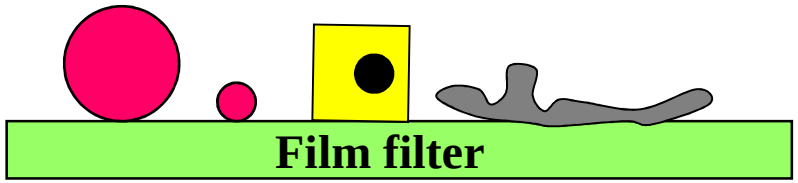
2-D analysis of inclusions on polished cross section of steel sample

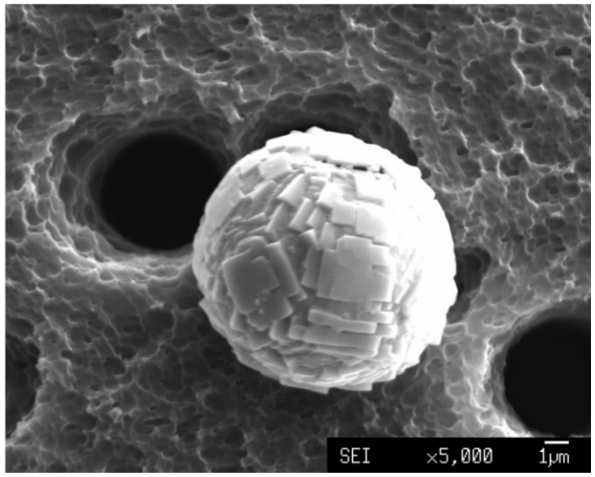




Electron Image 1

3-D analysis of inclusions on film filter after extraction of steel sample





J. Janis et al. (*Steel Res. Int.*, 80 (2009), 450-456).

Comparison of inclusion characteristics obtained by 2-D and 3-D analysis.

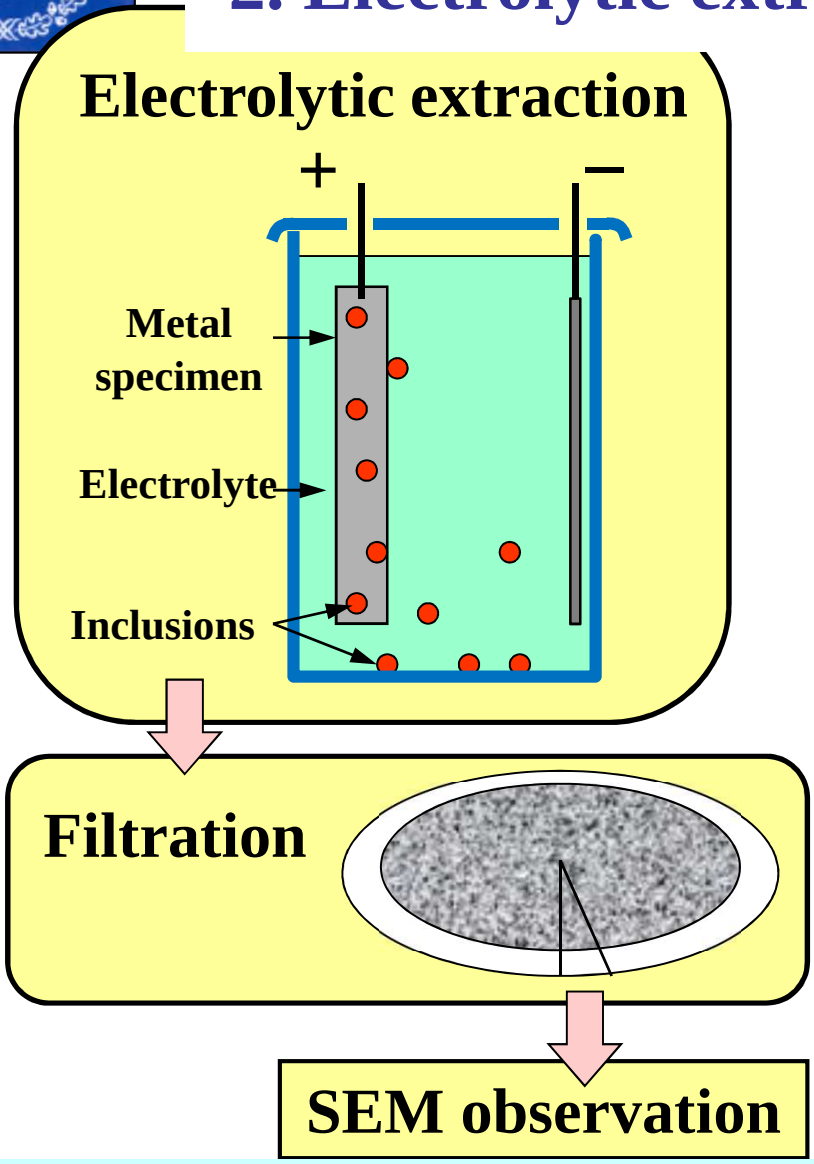
	2-D	3-D
Particle characteristics	On cross section of metal sample	On film filter after extraction
Number of particles: - d_v > 0.5 μm - d_v < 0.5 μm	**+ (-)** -	++ ++
Size of particles, μm	> 0.5	> 0.05
Location of particles in metal	+	**- (+)**
Composition of particles:	+ and -	+ and -
Morphology of particles	**- (+)**	+
Observation of clusters	**- (+)**	**+ (-)**

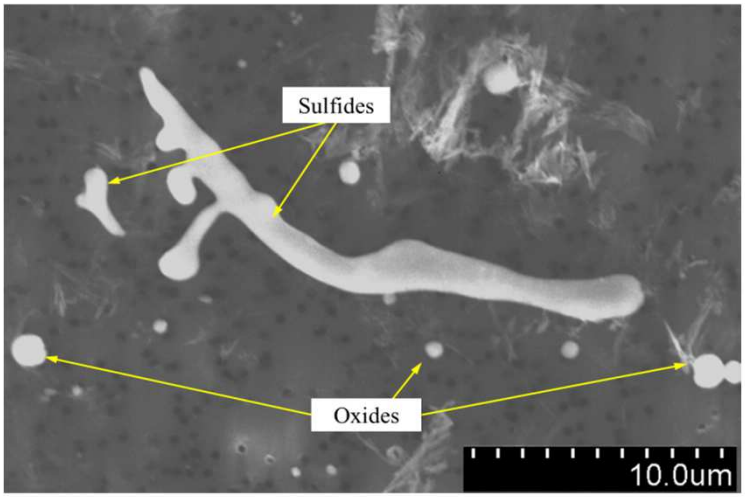
Wide range of problems in steelmaking related to NMI:

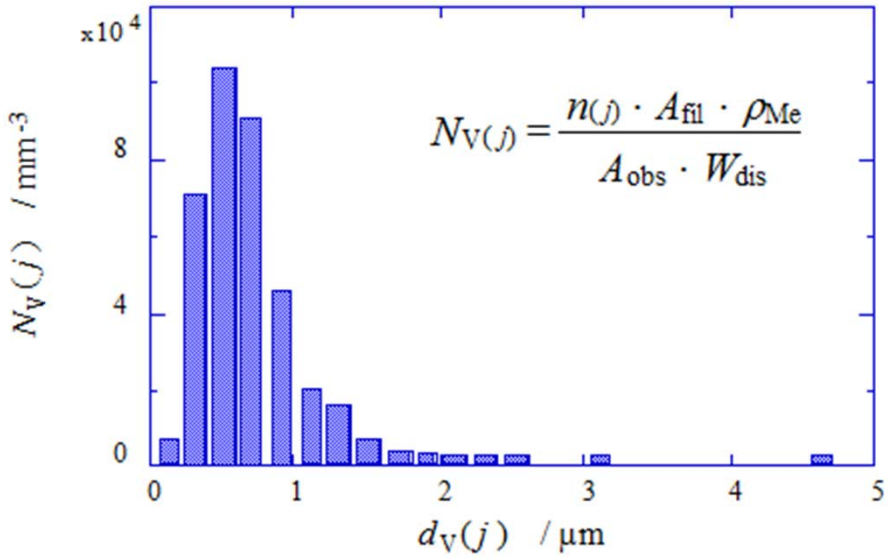
- the formation and growth of clusters,
- clogging problems during casting,
- effect of NMI and clusters on the microstructure, quality, surface defects, mechanical properties and machinability of finished steel products.

Purpose: summarize experience of application of the EE+SEM method at the KTH Royal Institute of Technology for evaluation of different NMI and clusters in various industrial steels and alloys.

2. Electrolytic extraction method (EE+SEM)

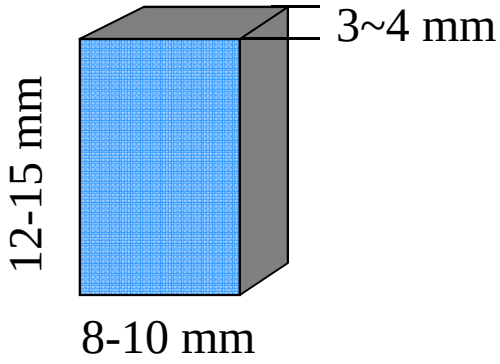






Typical parameters for electrolytic extraction

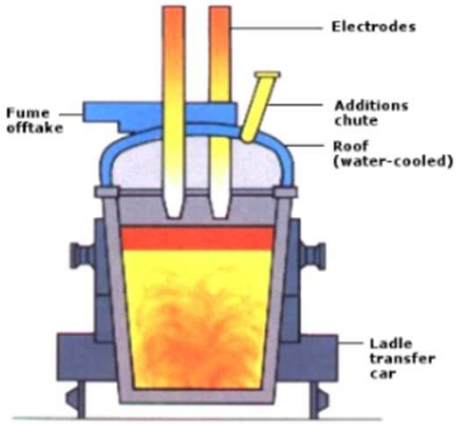
Metal specimen for electrolytic extraction

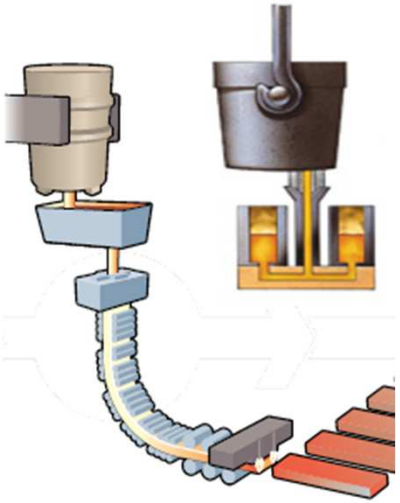


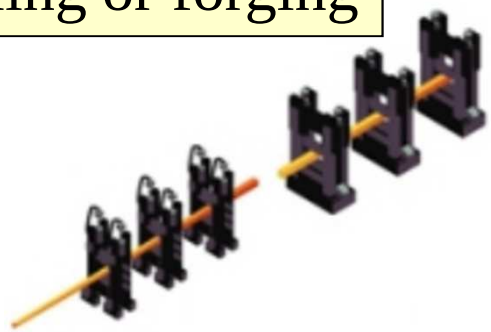
- Electrolytes: 10%AA, 2% TEA, 4% MS.
- Weight of dissolved metal: 0.05-0.35 g.
- Dissolved layer: 20~500 µm.
- Time of extraction: 1~15 h.
- Polycarbonate film filter with open pore size (µm): 0.05, 0.4, 1.0, 5.0.
- Size range of investigated Inclusions (µm): 0.05 – 500.

Application of EE+SEM for various industrial steels

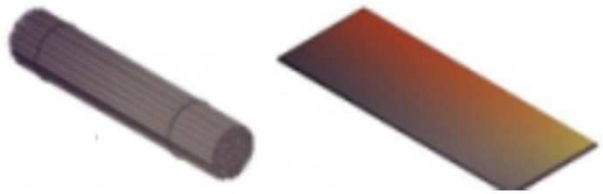
Ladle treatment → Casting → Heat treatment, rolling or forging







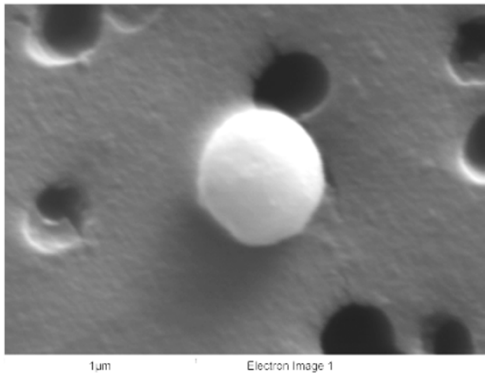
Steel products



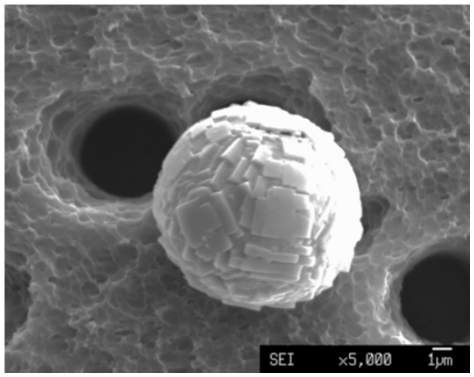
Mashining → Welding

Typical inclusions and clusters on surface of film filter after electrolytic extraction.

(Ti,Mn,Si,Mg)O

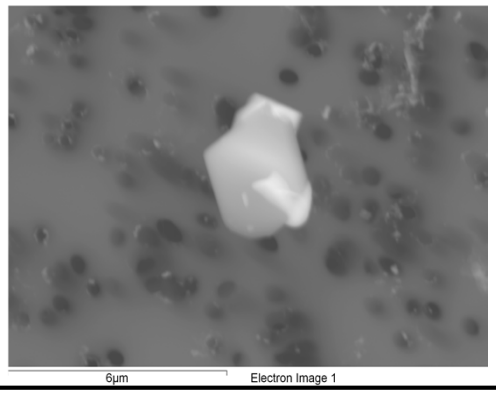


$(Ce,Ti)O_x$ and TiN

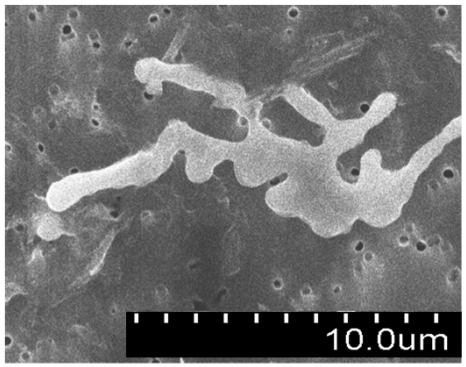


Al_2O_3 cluster

(Al,Mg)O + (Ti,Nb)C +MnS



MnS in "as cast" steel



MnS in rolled steel

A. KARASEV, A. TILLIANDER and P. G. JÖNSSON, 30th Journees Siderurgiques Internationales (JSI) Inter. Conf., Paris, France, 18-19 December 2012, pp. 1-2.

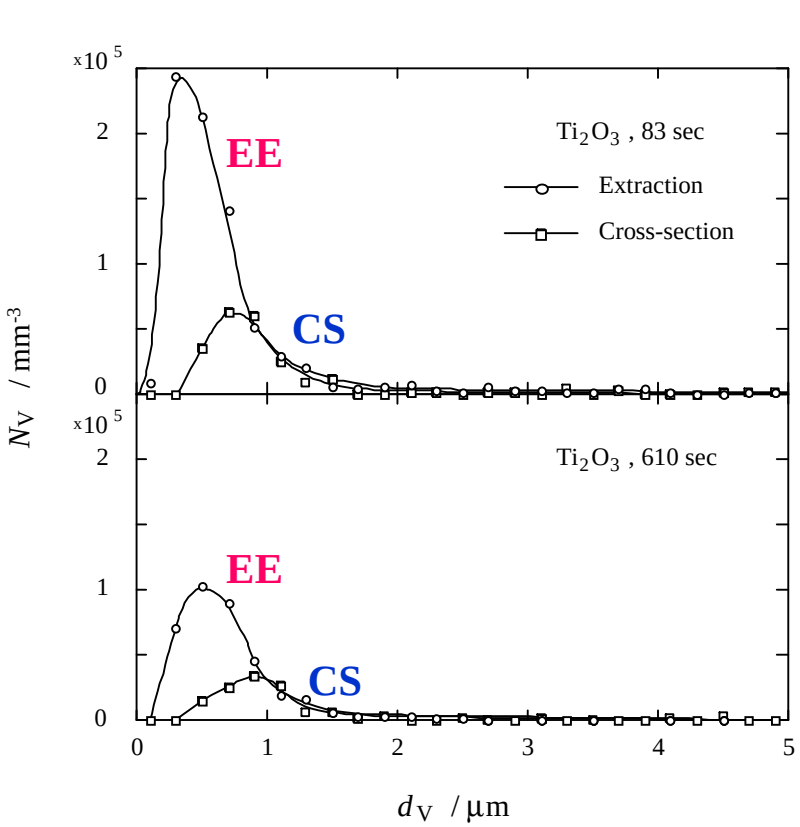
Application of EE+SEM for various industrial steels

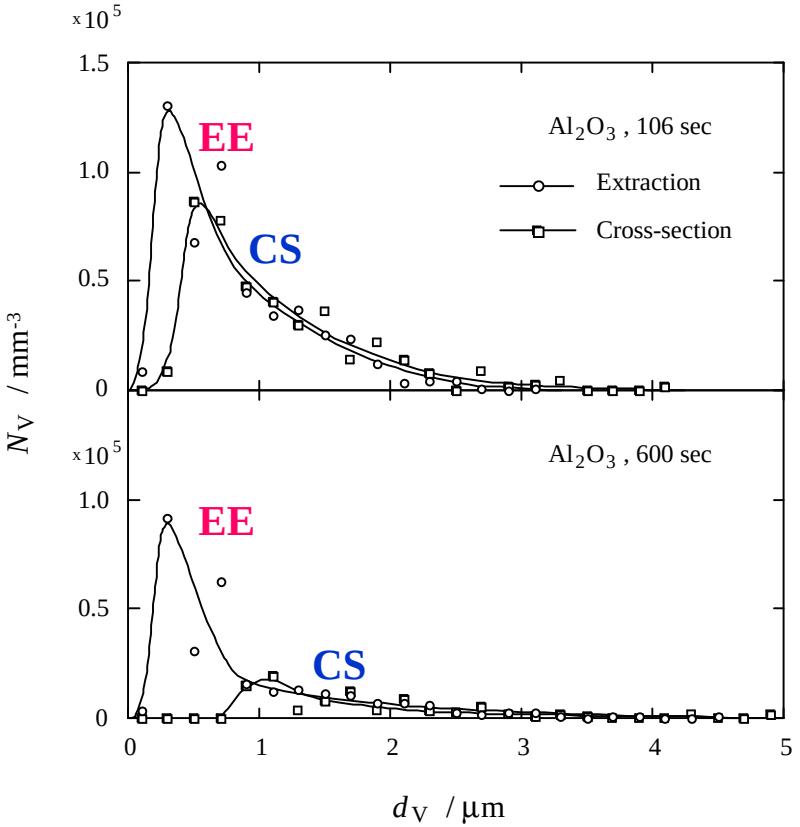
Steel grade	Steel samples	Contents of elements (%)	Inclusions and clusters	Main components in inclusions	Size range (μm)
Various low carbon low alloyed steels	- Liquid steel (ladle, tundish, mould). - "As cast" steel (ingot, slab). - Rolled steel. - Final product.	0.01-0.2%C, < 1.5%Cr	- Oxides (NMI and clusters). - Sulfides. - Nitrides. - Complex.	CaO, MgO, Al_2O_3, SiO_2, TiO_x. MnS, CaS. TiN, NbN.	**0.05-20** **2-500** **0.05-5**
Various stainless steels (316L, 253MA and other)	- Liquid steel (ladle, tundish, mould). - Solidified steel (nozzle zone). - "As cast" steel (ingot).	0.02-0.2%C, 17-21%Cr, 9-11%Ni	- Oxides (NMI and clusters). - Sulfides. - Complex.	Al_2O_3, MgO, CaO, SiO_2, REM_xO_y. MnS, CaS, REM-S. Oxysulfides.	**0.05-30** 3-25

Application of EE+SEM for various industrial steels

Steel grade	Steel samples	Contents of elements (%)	Inclusions and clusters	Main components in inclusions	Size range (μm)
INCOLOY	- Liquid steel (ladle, tundish, mould). - Solidified steel	<0.05%C, 19-24%Cr, 38-46%Ni	- Oxides (NMI and clusters). - Nitrides	Al_2O_3, MgO, CaO, TiO_x. TiN	**0.5-40**
High silicon stainless steel	- Liquid steel (ladle, tundish).	0.2-0.5%C, 19-24%Cr, 11-20%Ni	- Oxides (NMI and clusters). - Sulfides. - Complex.	Al_2O_3, MgO, SiO_2, CaO. MnS, CaS. Oxysulfides.	**1-25**
Tool steel (AISI H13)	- Liquid steel (ladle, tundish). - “As cast” steel (ingot).	0.3-0.4%C, 4-6%Cr, 1-2%Mo	- Oxides. - Sulfides. - Complex.	CaO, MgO, Al_2O_3, SiO_2, CaS, MnS. Oxysulfides.	**2-30**

Size distribution of inclusions in metal samples obtained by 2-D (CS) and 3-D (EE) analysis.

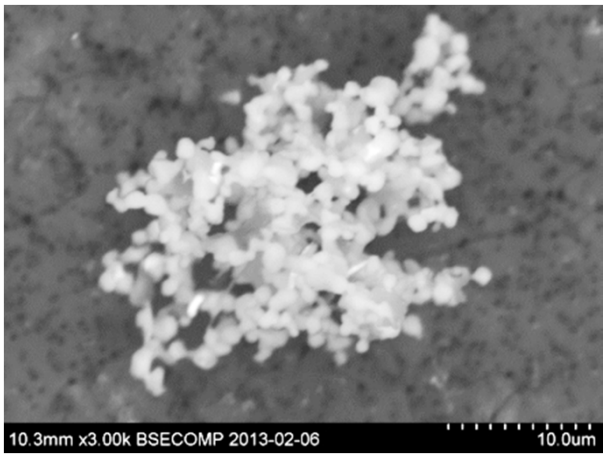


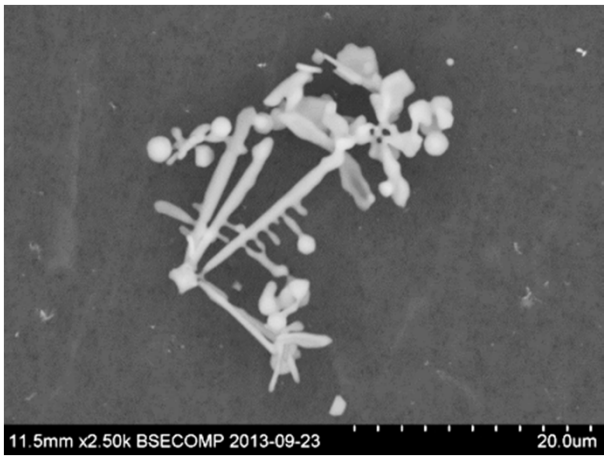


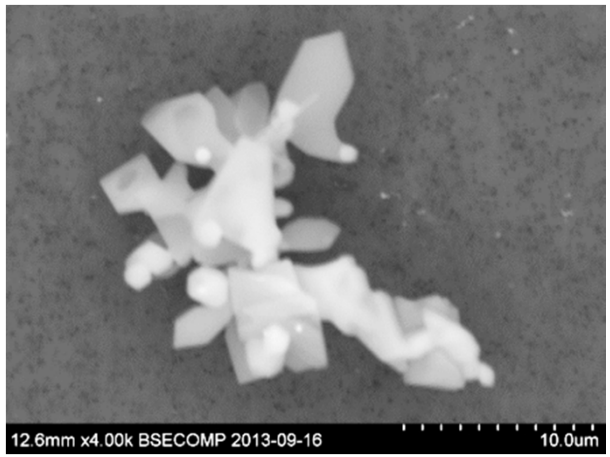
A.V. Karasev and H. Suito: *Metall. Mater. Trans. B*, 1999, 30B, 259-270.

3D investigations of clusters in different steel samples.

- Characteristics of clusters in steel (number, size and morphology).
- Characteristics of clustered inclusions (number, size, morphology and composition).

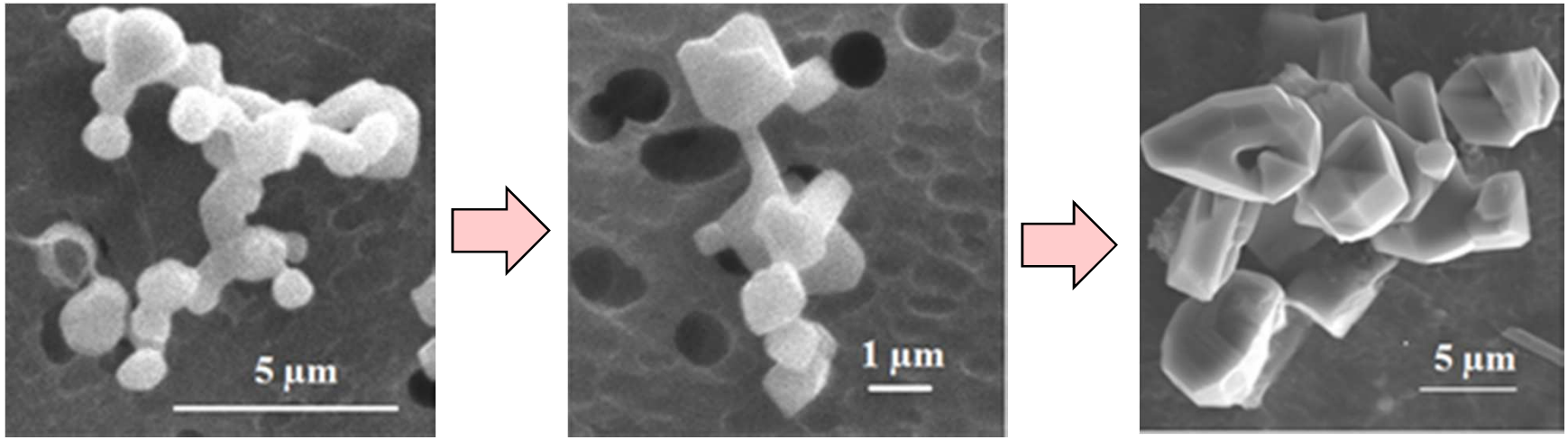






- Mechanisms of agglomeration of different inclusions.
- Cluster growth and their behaviour in the different steels and alloys during ladle treatment and casting.
- Effect of clusters on clogging process and mechanical properties of steels.

Al_2O_3 clusters. Size and morphology of clusters and inclusions in liquid steel



Time after Al addition [min]	1 - 2	3 - 4	5 - 12
Type of NMI in cluster	Spherical	Irregular	Regular
Size of inclusions [µm]	1-3	2-4	2-8
Size of clusters [µm]	3-62	3-38	4-25

D. Janis, A. Karasev, R. Inoue, and Pär G. Jönsson: *Steel Res. Int.*, 85 (2015)

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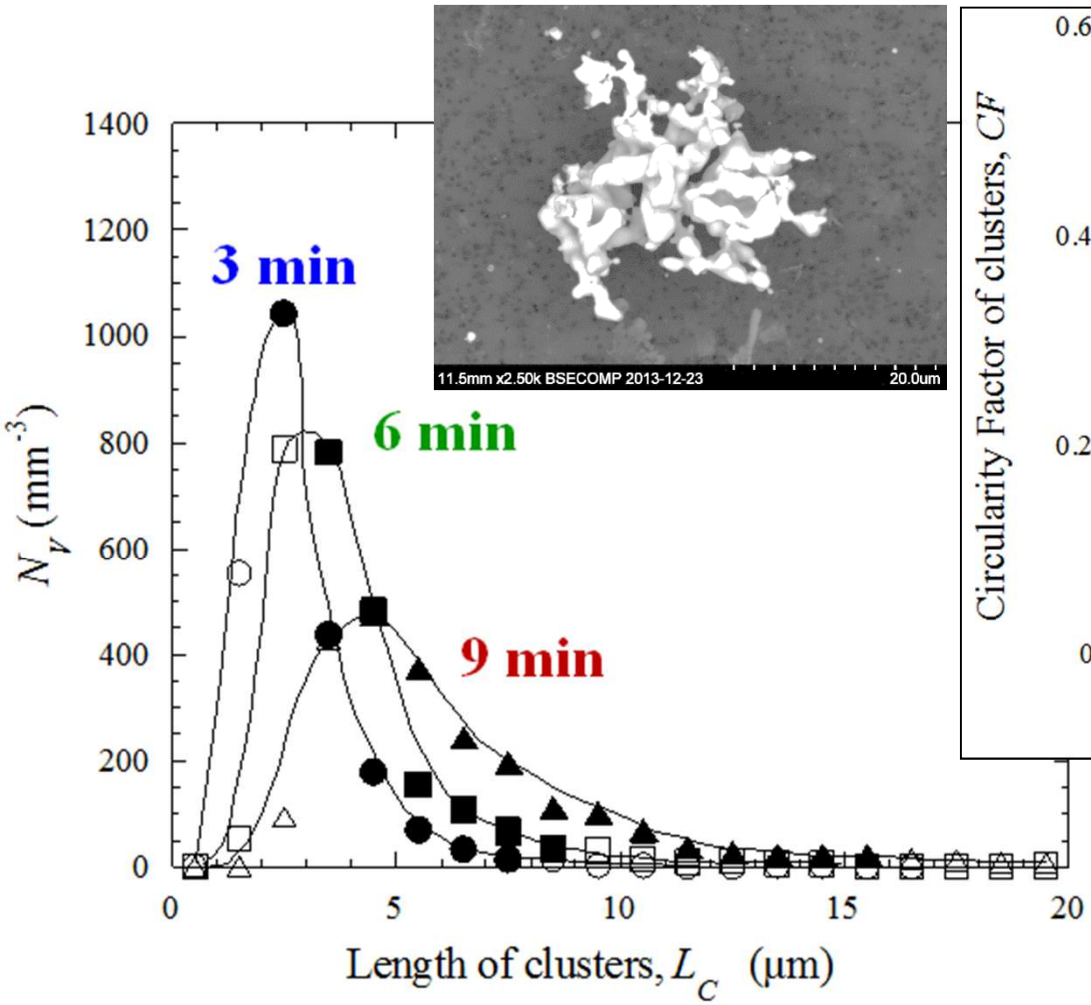
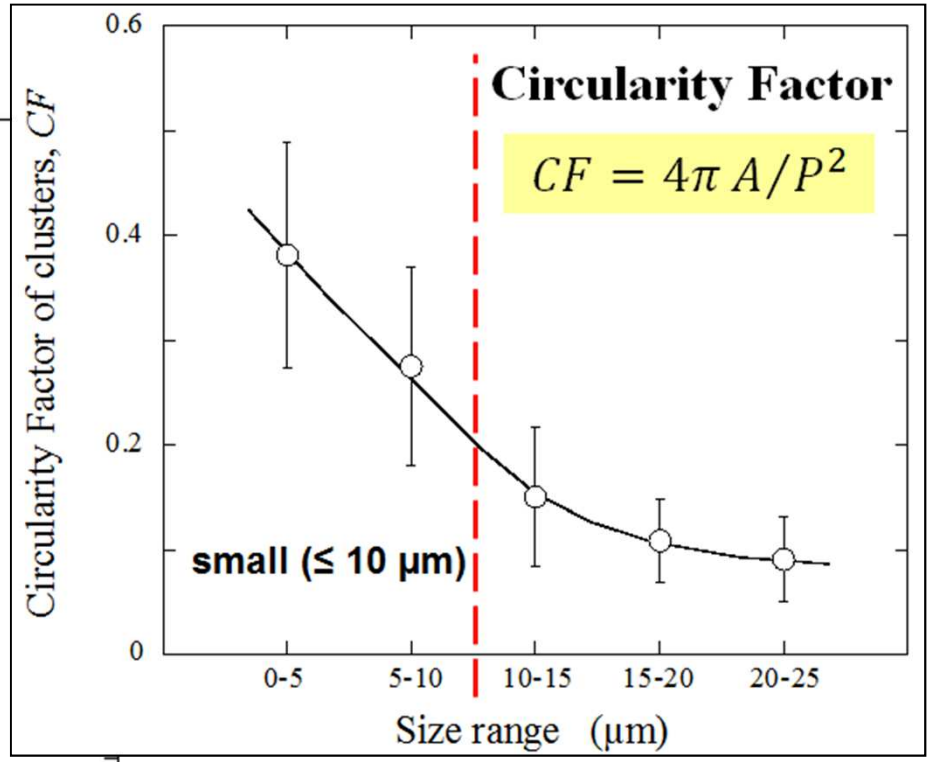
REM-oxide clusters. Size distributions and morphology in liquid steel





M. Nabeel, A. Karasev and P. Jönsson: ISIJ Int., 55 (2015), No. 11.

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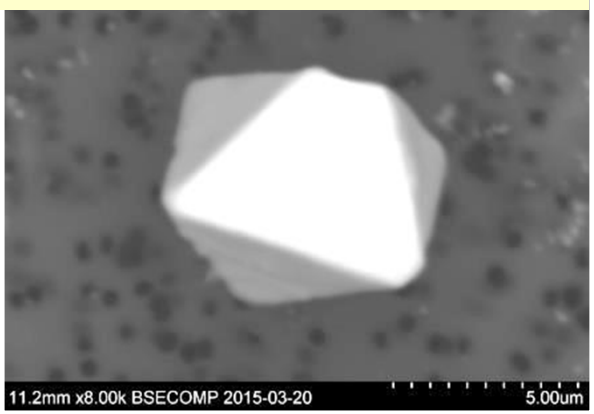
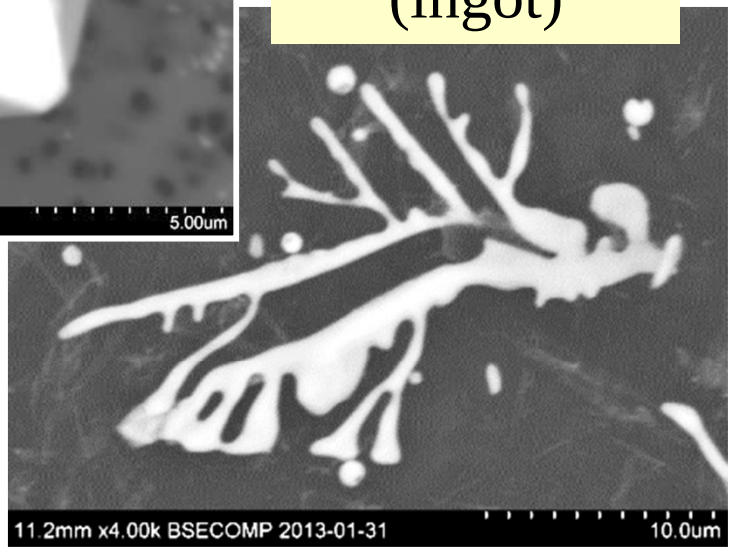
Materials Science and Engineering, Stockholm, SWEDEN

Investigation of sulphides in "as-cast" and deformed steel.

Regular MnS (ingot)

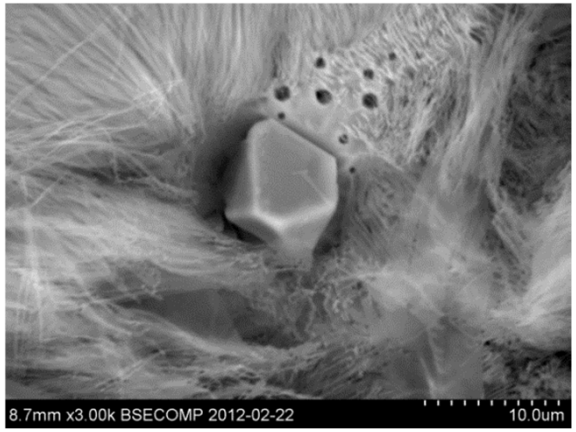
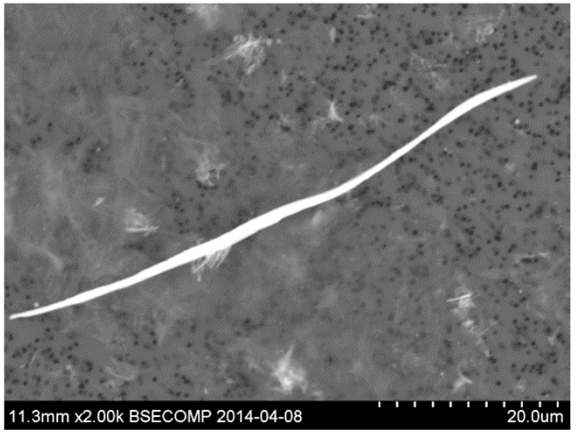
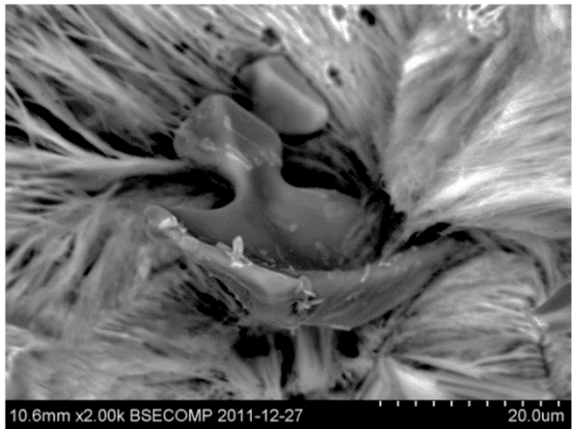
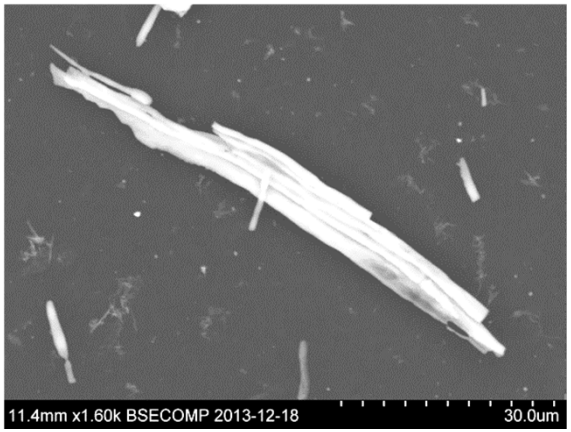


Eutectic MnS (ingot)



Elongated MnS (rolled steel)

Formation of different sulfides during steel deformation

	Sulfides before deformation	Sulfides after deformation
Elongated Rod-like Sulphides (ERS)		
Elongated Plate-like Sulphides (EPS)		

Application of electrolytic extraction for different projects, publications and conference presentations (KTH, 2008-2017)

Projects (3 RFCS + 9 JK)

- SOPLIQS (RFCS)
- RAMSCI (RFCS)
- NAMOS (RFCS)
- INNESTIR, MACHINOPT and other (9 JK)

Journal Publications (26)

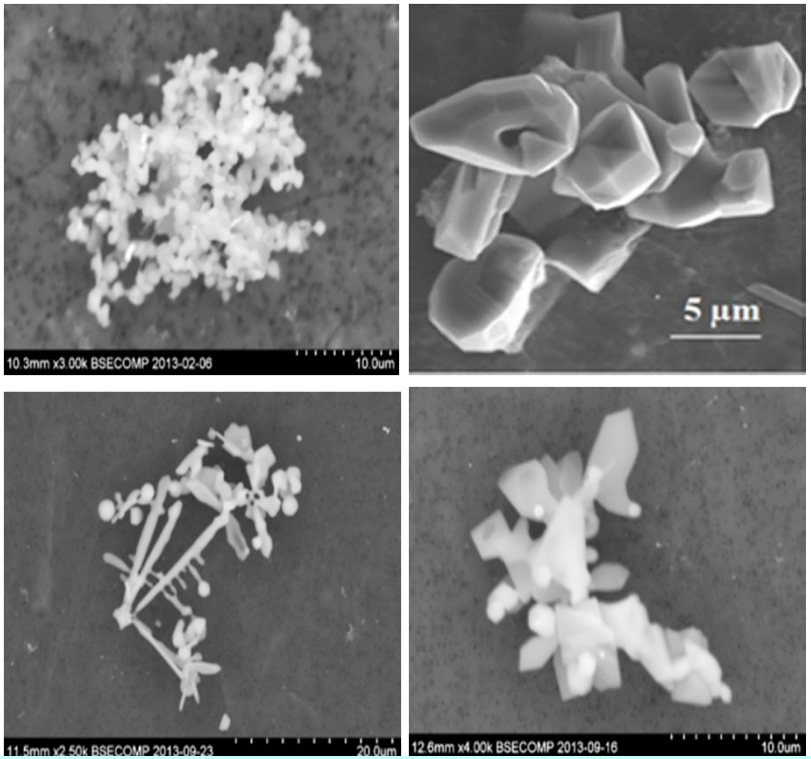
Materials, Wear, Steel Res. Int., ISIJ Int., Ironmaking and Steelmaking, J. Mater. Sci., Advances in Materials Science and Engineering

Conference Presentations (29)

- SCANMET (Sweden, 2008, 2012, 2016),
- 17th Steelmaking conf. (Argentina, 2009),
- ISIJ conf. (Japan, 2009-2017),
- CETAS-2011 (Luxembourg, 2011),
- 6th EOSC (Sweden, 2011),
- CLEAN STEEL (Hungary, 2012, 2015),
- MOLTEN 12 (China, 2012),
- RATEC2012 (Japan, 2012),
- 30th JSI (France, 2012), ...

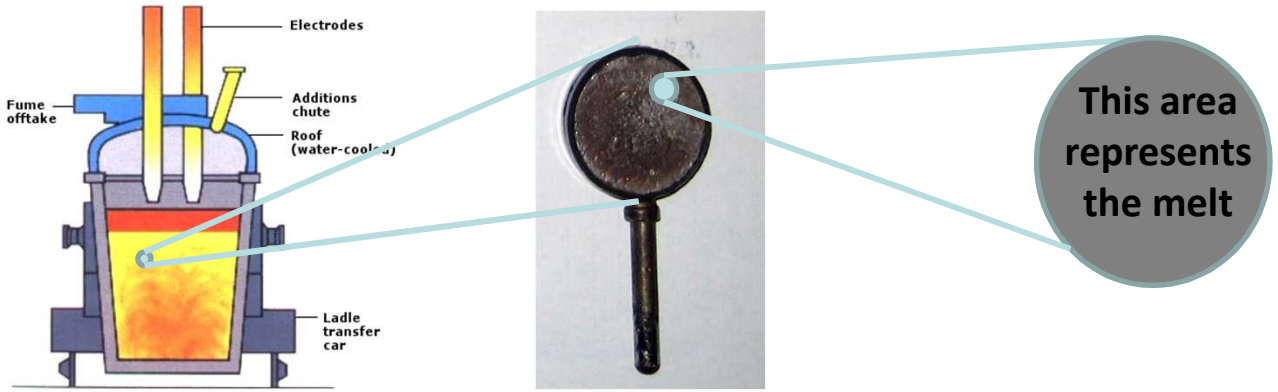
Secondary refining

- Focus on inclusions



Reliable samples

This small sample amount will be analysed and should represent the whole melt

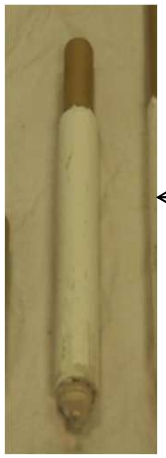


100 t **40~160 g** **<1 g**

The sample should enavle us to get a snap shot of the inclusion characteristics that exist at steelmaking temperatures!

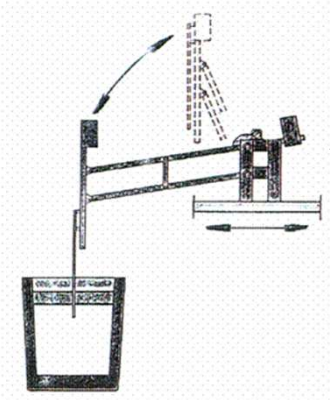
Optimization of sampling procedure

Min slag,
Anti splash

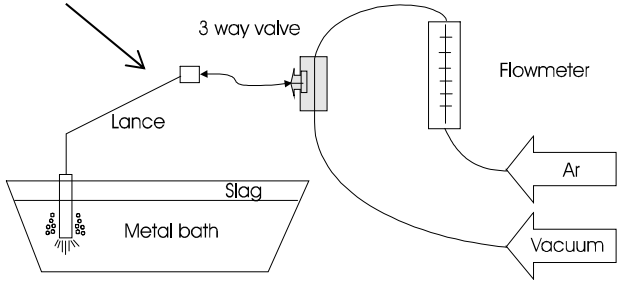


Good sample

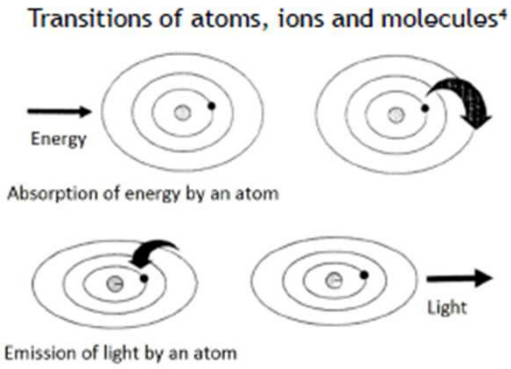
Dry samplers,
heating box



Repeatability,
automatic
samåling



Min reoxidation,
Argon flushing

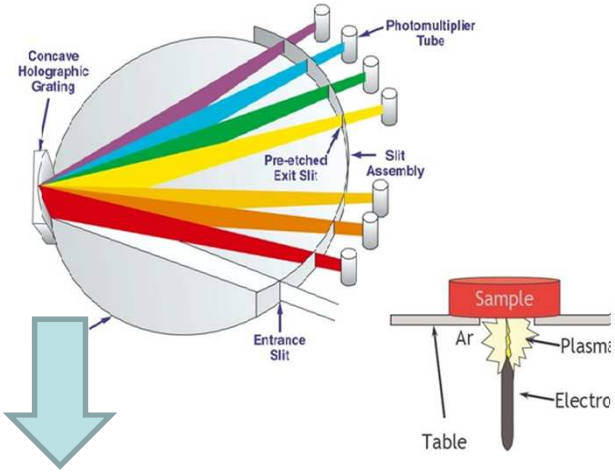


Sparks at 200 – 800 Hz emit element – specific light analysed by the spectrometer in a few seconds

ONLINE METHODS

Optical emission spectroscopy/PDA to determine inclusions in steels

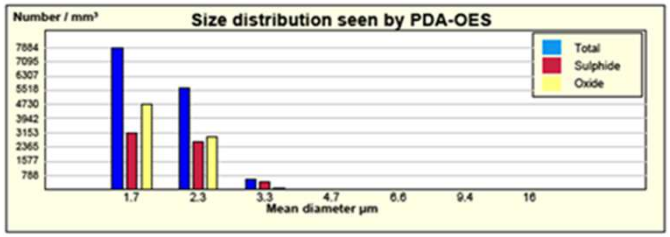
Thomsen, V. B. E. (1996). ***Modern spectrochemical analysis of metals*****. Materials Park, OH: ASM International**



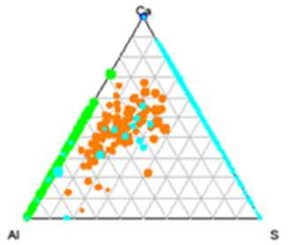
Quantitative inclusion data

Bulk elemental composition

C	Si	Mn	P	S
As	Sn	Ti	B	W
.226	.383	1.58	.009	.040
.012	.012	14	0.0	.01



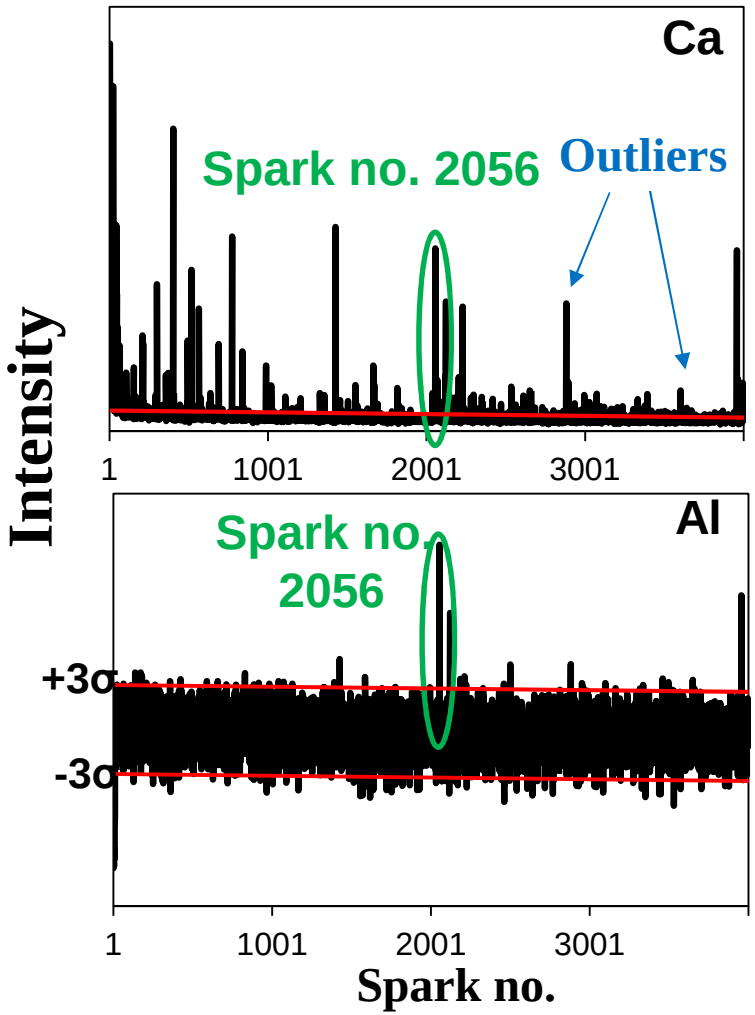
	>0	>1.4	>2	>2.8	>4	>5.7	>8	>13
Oxid	42637	7827	3068	113	9	0	0	0
Sulfid	7204	6297	3172	500	57	9	0	0
Total	49841	14124	6240	613	66	9	0	0



Composition
weight % deviation %

SiO_2	0,00003		Si	0,00001	
MnS	0,00005	0,00002	Mn	0,00003	0,00001
CaS	0,00252	0,00010	S	0,00052	0,00003
CaO	0,00121	0,00016	Ca	0,00206	0,00019
Al_2O_3	0,00142	0,00029	Al	0,00075	0,00015
MgO	0,00000	0,00000	Mg	0,00000	0,00000
TiO_2	0,00003	0,00000	Ti	0,00002	0,00000
TiN			calc O	0,00136	

The use of the PDA/OES method to study complex inclusions

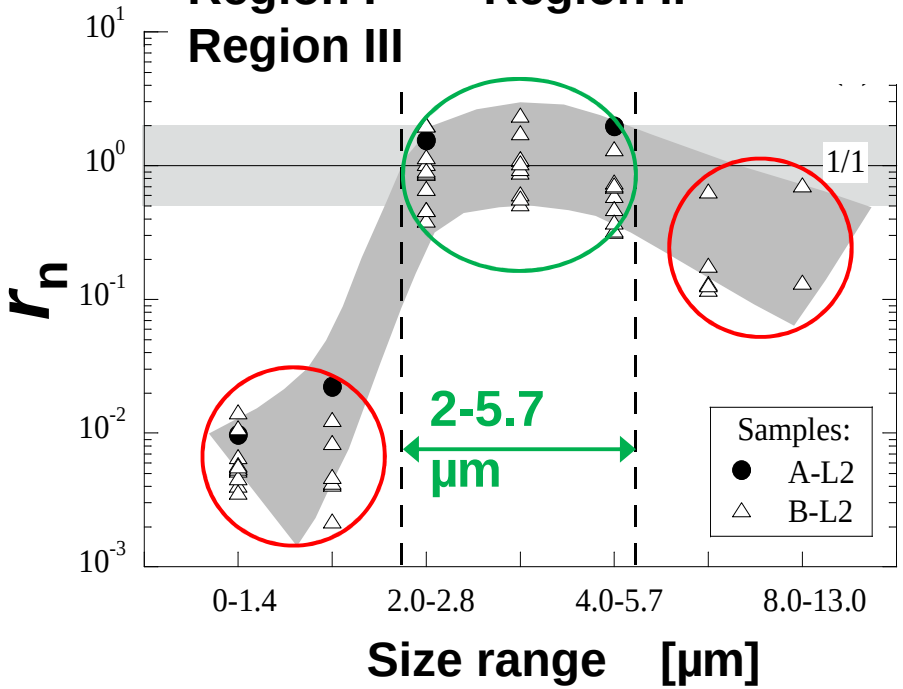


- **Pulsograms from one measurement for Ca and Al**
- **Intensities above a certain level are outliers (inclusions)**
- **Masses (composition) and sizes are calculated based on intensity values and calibration functions**
- **Complex inclusions are identified based on coincidences between two or several elements**

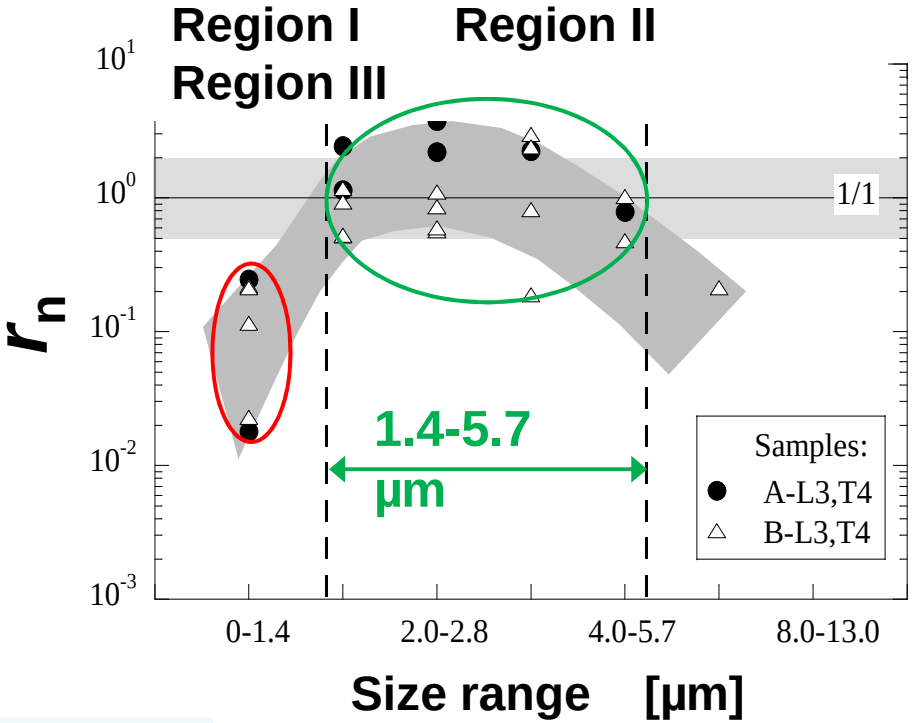
”Ca-Al” match!

Range where the PDA/OES method can be used

Before Ca-addition



After Ca-addition



$$r_n = \frac{N_{V(PDA/OES)}}{N_{V(EE)}}$$

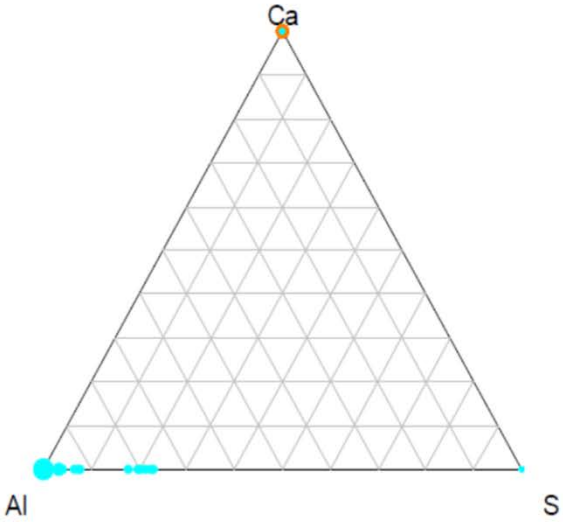
Region II: good agreement

Regions I and III: lower values

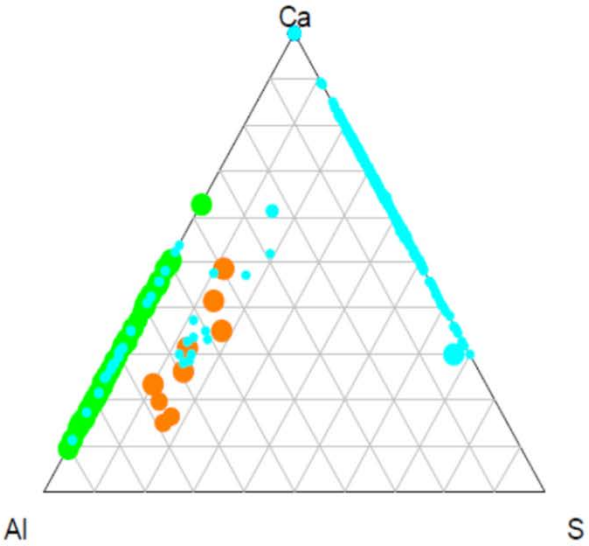
The size range in which a reliable number is detected depends on type of inclusions

Application of the OES method for Ca treatment

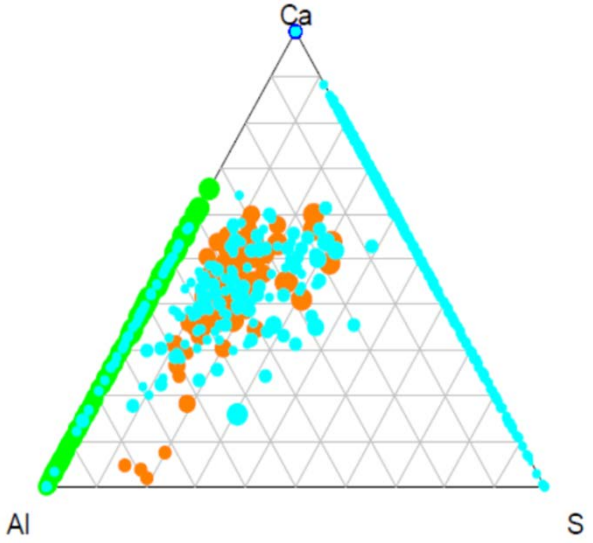
Before Ca addition



After Ca addition



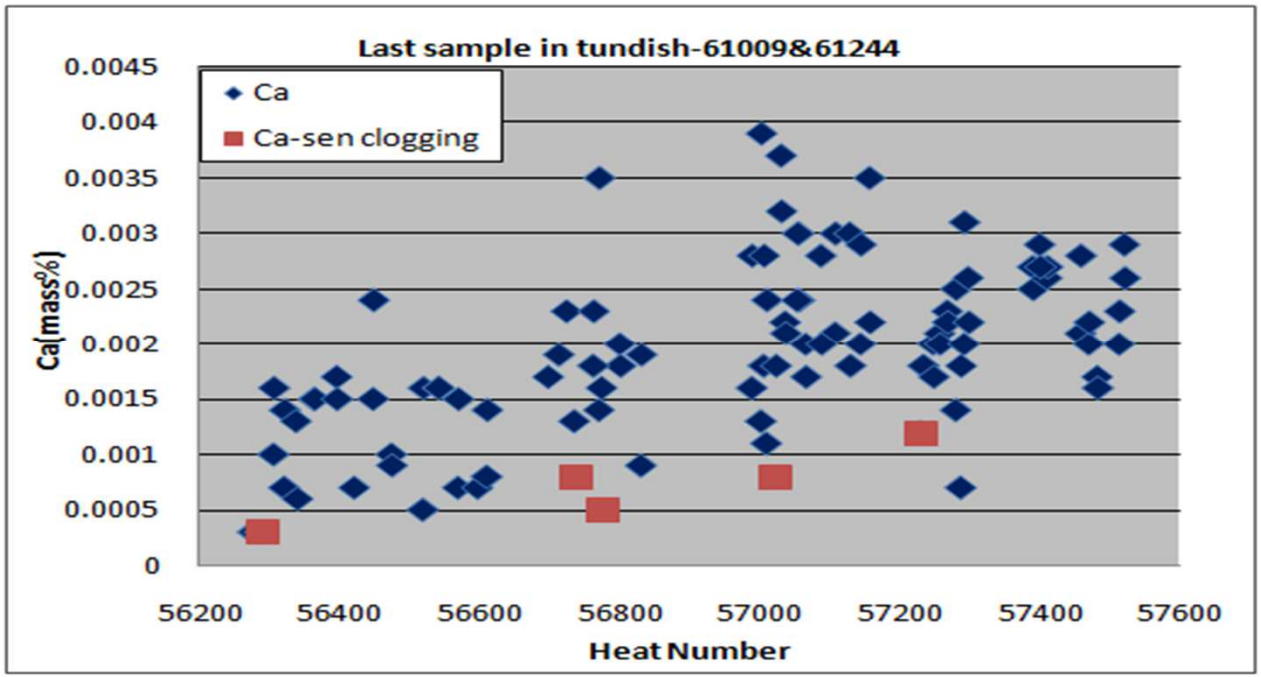
Tundish

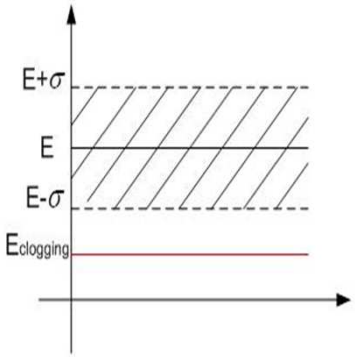


Can be used to detect changes in inclusion composition throughout the process

D. Janis

Example of use of the PDA/OES method to provide process feedback on clogging potential

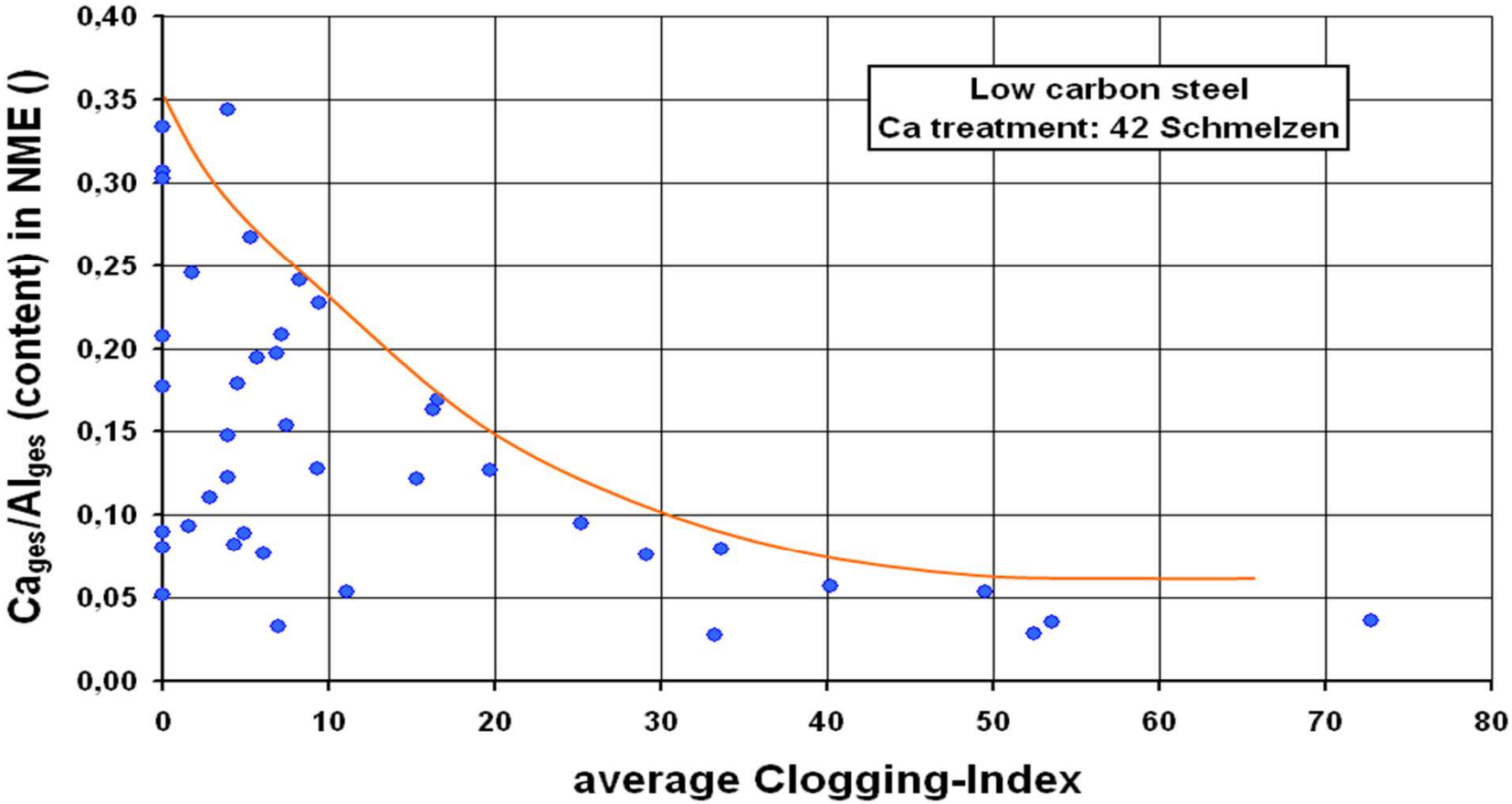




	MeanValue(E)	Standard Deviation(б)	E-б	E+б
Heats without clogging	0.001919	0.000795	0.001124	0.002714
Heat with clogging	0.000720	0.000342	0.000378	0.001062

Rolf Didriksson, SSAB

Example of use of the PDA/OES method to provide process feedback (Ca/Al) on the clogging potential



Andreas Pissenberger, VOEST-ALPINE

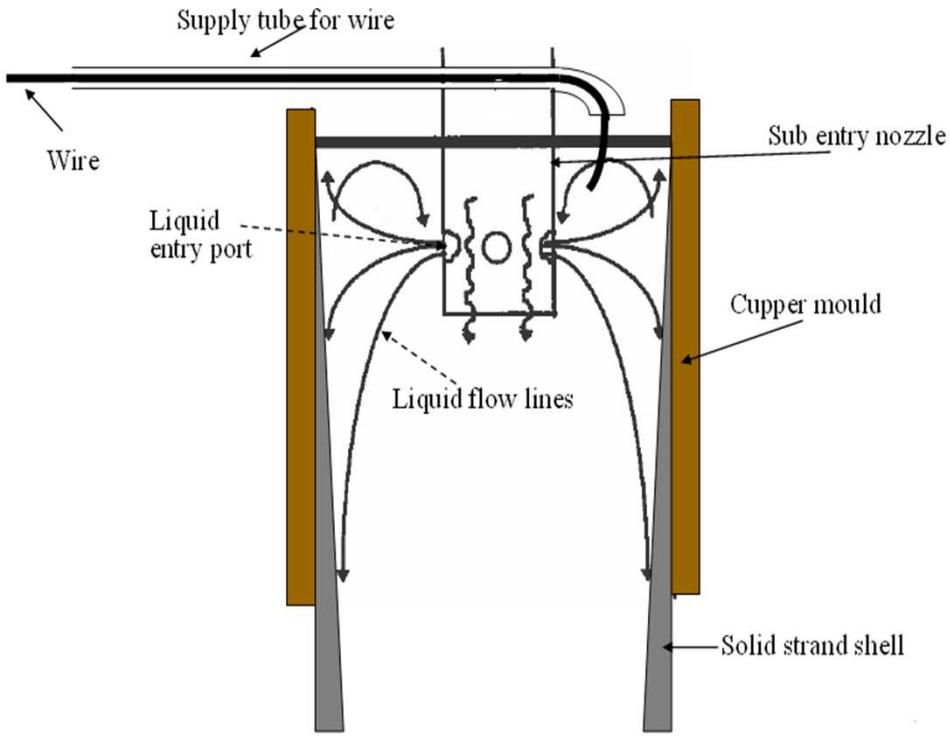
Mold metallurgy

- **Move late additions from ladle to mold**

- Purposes:
  Decrease clogging when adding REM, etc
  Adding elements for grain refining (*J. Janis presentation*)

- Important factors
  Dissolution rate of wire
  Inclusion formation over time

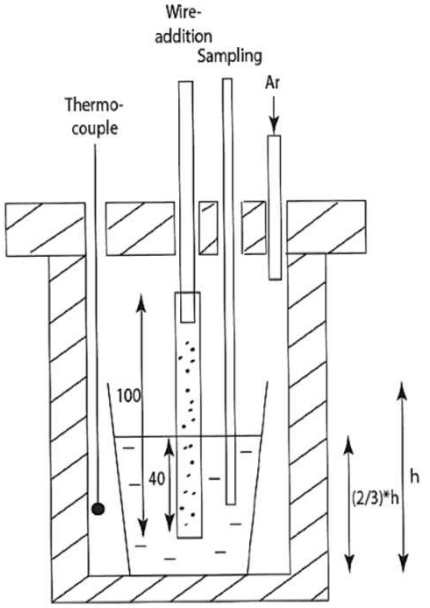
- Collaboration with Sandvik Materials Technology



Example of laboratory tests to determine the dissolution rate of different wire materials to be used for late additions

Wire feeding has the potential to be used both in contiunuous casting and ingot casting

Type of wire-casing	T(℃)	Dissolution rate	
		Without powder (s)	With powder (s)
Steel	1530	8 < t < 17	5 < t < 15
	1500		18 < t < 20
Cu	1530	t ≤ 2	t < 10
	1500		t ≤ 10
Al	1530	t < 1	t < 2
	1510		t < 1
	1500		0.5 < t < 1



Example copper casting

Future of the Swedish steel industry

- Today the Swedish steel production is small (6 Mton/year) but it consists of mainly niche products that primarily are exported due to a small home market

- How will the industry survive in the future? Surely by continuing to focus on niche products!

- What are the new markets where the steel can be used?

Is the future of Swedish steel the fashion industry???????????

Photos from fashionweek.se

Dresses made of strip steel from Böhler Munkfors shown on the cat walk. Design Naim Josefi.

Thank you for listening!

<u>3D printed shoes:</u>
Large shoe printed with stainless steel powder from Sandvik. Designed by Naim Josefi for Lady Gaga.
Small Shoe printed with iron powder from Höganäs.

***Any* process feedback with respect to inclusions is of use for this person!**

Thank you for your attention!