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Valorisation and Dissemination of Secondary Metallurgy Technology

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DissTec – On-line Measurement of Steel Cleanness using Rapid Inclusion Characterisation Techniques

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Background

- In general, cleanness requirements become more stringent as the final product thickness decreases
- Non-metallic inclusions are particularly important when they are responsible for producing defects during steel processing or in the final product application
- Several analytical techniques are available to indicate a measure of ‘steel cleanness’
- Traditional analytical methods are often time-consuming
- Two relatively new techniques (LIBS and PDA-OES) for rapid measurement of steel cleanness are covered in this presentation

Projects covered in this presentation

- (7210-PR-168) Improved production control through rapid characterisation of non-metallic inclusions in steel (based on LIBS- Laser Induced Breakdown Spectrometry)

- (7210-PR/300) In-line assessment of steel cleanness during the secondary steelmaking process (based on PDA-OES - Pulse Discrimination Analysis –Optical Emission Spectrometry)

Contents

(7210-PR-168) Improved production control through rapid characterisation of non-metallic inclusions in steel - Laser Induced Breakdown Spectrometry

- Objective
- The Measurement Technique
- Quantification of Inclusions
- Appropriate Equipment and Parameters
- Applications
- Summary

Objective

To develop a method for fast analysis of steel cleanness based on laser emission spectrometry

The Measurement Technique

Preliminary examination of the samples

Overview of examined steel types:

IF-Steel
Unalloyed Steels: St24; St25; St24E; St25E; ZstE340
Unalloyed Dynamostrip
Si-alloyed Dynamostrip
Pig iron samples.

- Using classical methods (such as: SEM-EDX, Optical Microscopy, ICP-OES, LECO (S) and hot carrier gas extraction (N,O)), inclusion maps were developed showing inclusion distribution, population and number for the steel samples leading to a 'Cleanness Ranking': A, C, B and D (with D being the cleanest steel) for each selected steel type

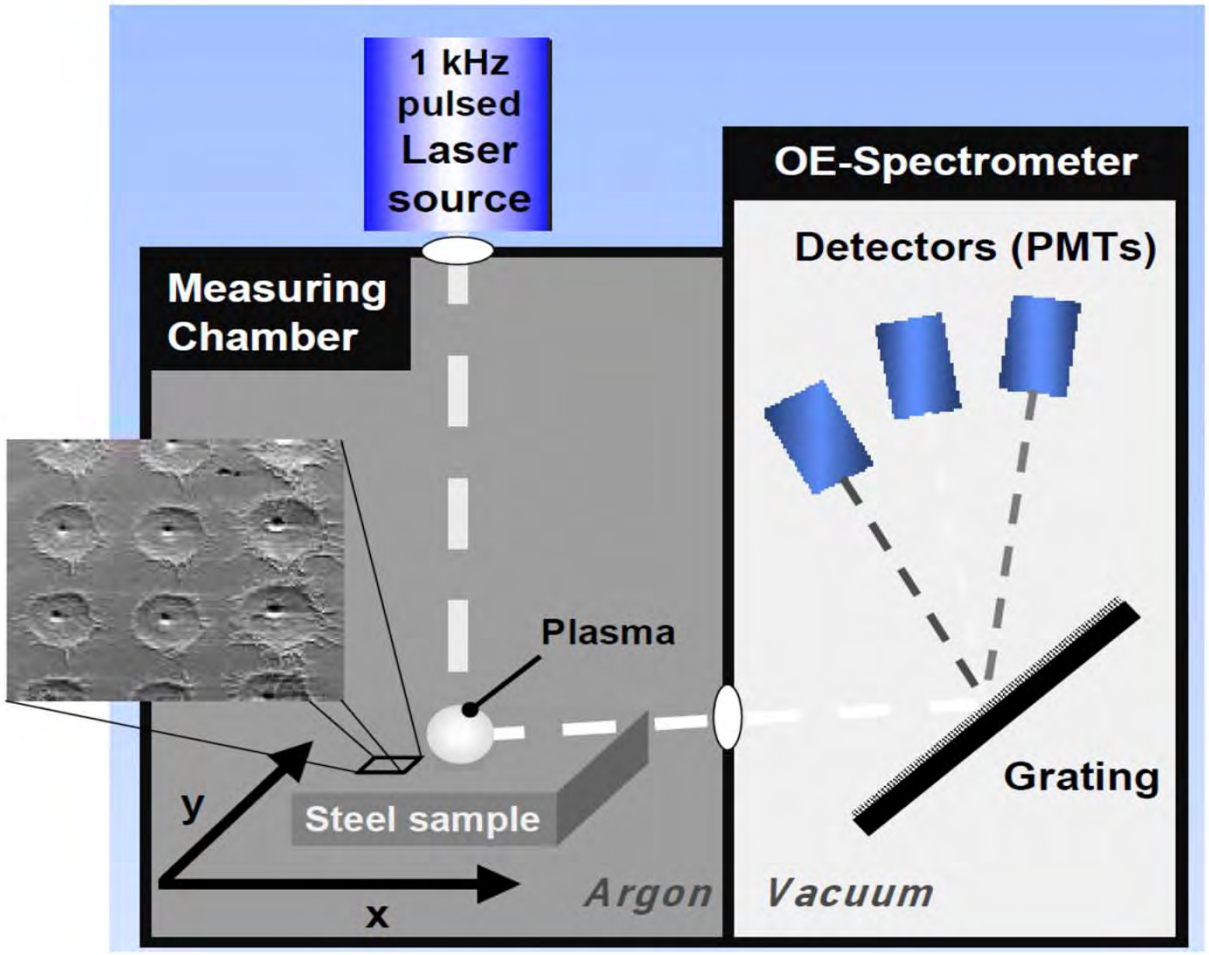
- Laser scanning and mapping was then applied to the same steel samples and the number of inclusion types (such as MnS) was determined for each sample

- Laser scanning and mapping gave the same cleanness rankings as that determined using classical methods

The Measurement Technique

- The selected samples were analysed with laser-OES using the following parameters: 500*500 points, point to point distance 20 µm, scanning frequency 500 Hz, scan time 16 mins, laser wavelength 1064 nm, laser pulse energy 2 mJ, ambient pressure in the measuring chamber 900 mbar Ar 4.8

The Measurement Technique

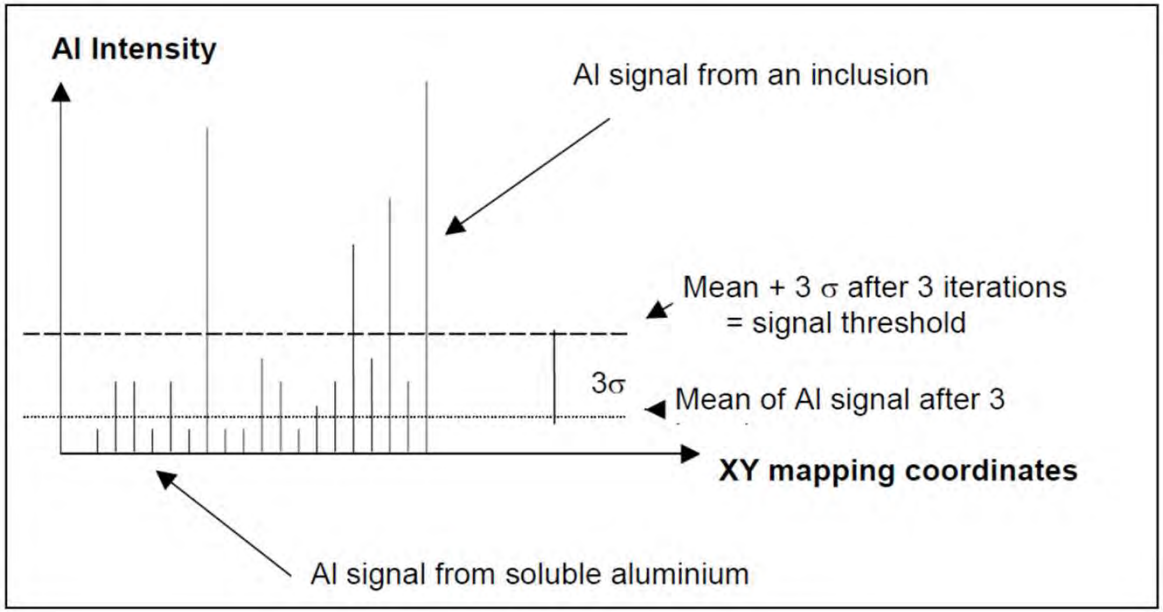


Craters after scanning measurements at 100 µm step width and 2 mJ per pulse

Experimental set-up for fast scanning laser-OES on a moving sample with 1000 Hz repetition rate

The Measurement Technique

Inclusion and matrix



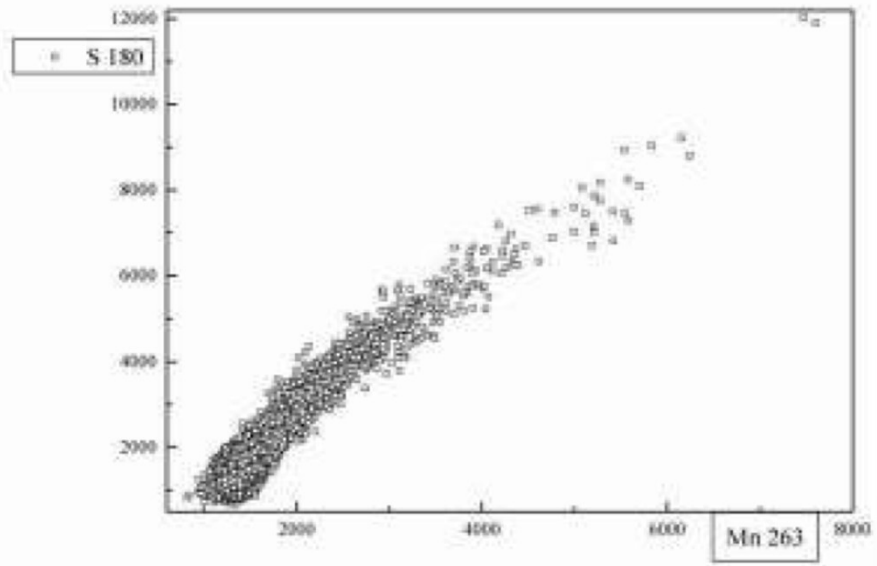
A signal intensity limit is defined under which the element is considered to be soluble in steel and above which the element is considered to belong to a non-metallic inclusion

$I_{critical} = M + nS$

M - mean of all signal intensities in one inclusion related element channel
n - factor depending on the chosen element line (= 3 to 5);
S - standard deviation of the signal

The Measurement Technique

Correlation of Signal Coincidences and Inclusion Types



Raw intensities of the S180nm and Mn263nm signals for all the 250000 measuring points

- There is a 100% correlation between Mn and S peaks.
- By counting the number of inclusions a cleanness ranking for the samples according to MnS inclusions can be made
- These kind of maps have been made for all samples (A, B, C and D).

Ranking of the detected steel cleanness in terms of manganese sulphide in different samples

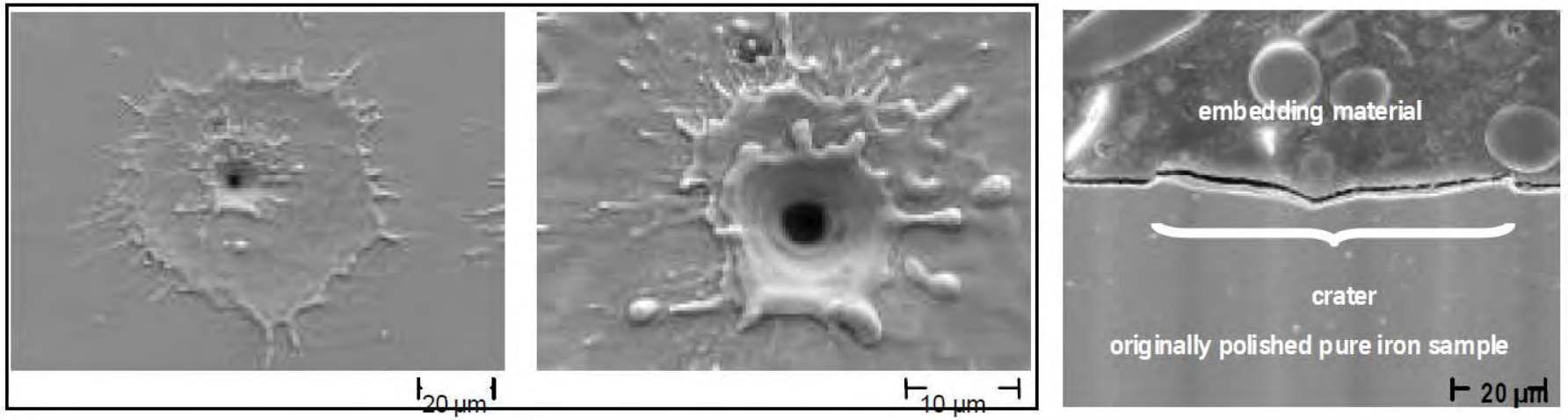
sample name	*number of signals greater than <x>+5s*
A	968
B	836
C	914
D	492

This ranking corresponds to the ranking measured by classical methods of analysing steel cleanness

The Measurement Technique

Laser induced craters

It is important to know the whether the very complex nature of the laser induced crater geometry affects the emission intensity of the plasma



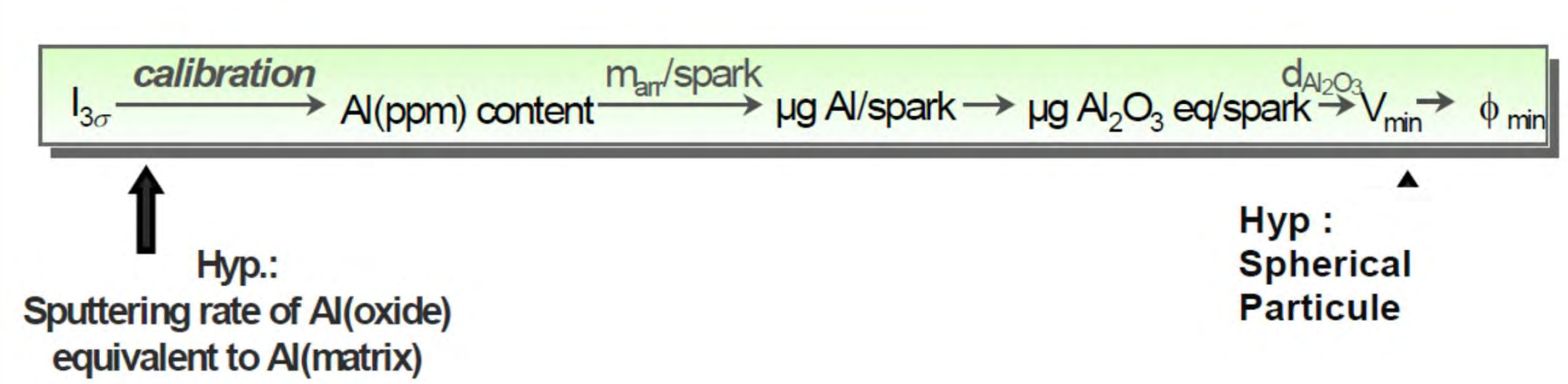
SEM micrographs: view on top and on the profile of a laser induced crater: 1 pulse, 2.0 mJ, polished sample surface

- The number of pulses affects the depth and form of the deeper hole in the middle of the shallow crater but has little effect on the diameter of the outer rim

- Application of 2D and 3D mapping shows that the associated signal collection is valid for inclusion detection and characterisation and that isolation and decomposition of inclusions in the steel matrix can be successfully observed

The Measurement Technique

Determination of minimum inclusion size limit



Methodology for determining the lowest inclusion size limit detectable with laser-OES

It is concluded that the smallest sized inclusion detectable with laser-OES is between 1 µm and 2 µm in diameter (at a level of 100-300 µg/g Al)

Quantification of inclusions

Quantification is possible:

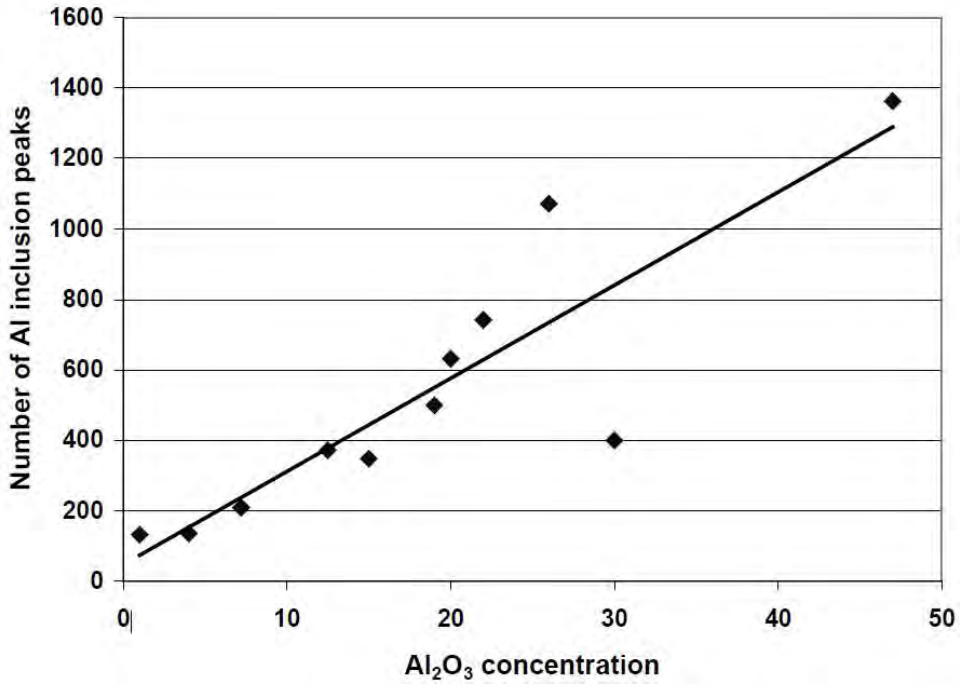
- It is assumed that the (known) volume of the laser crater is representative of the ablated and excited material

- The amount of measured inclusion material within this volume is calculated from the ratio of specific signal intensities of the pure matrix and the mixture with inclusion material:

$$\frac{V\,(\text{inclusion})}{V\,(\text{crater})} = \frac{I\,(\text{Inclusion+matrix})}{I\,(\text{pure matrix})}$$

Quantification of inclusions

A set of 13 samples with aluminium oxide contents ranging from 1 µg/g to 47 µg/g have been characterised with laser-OES

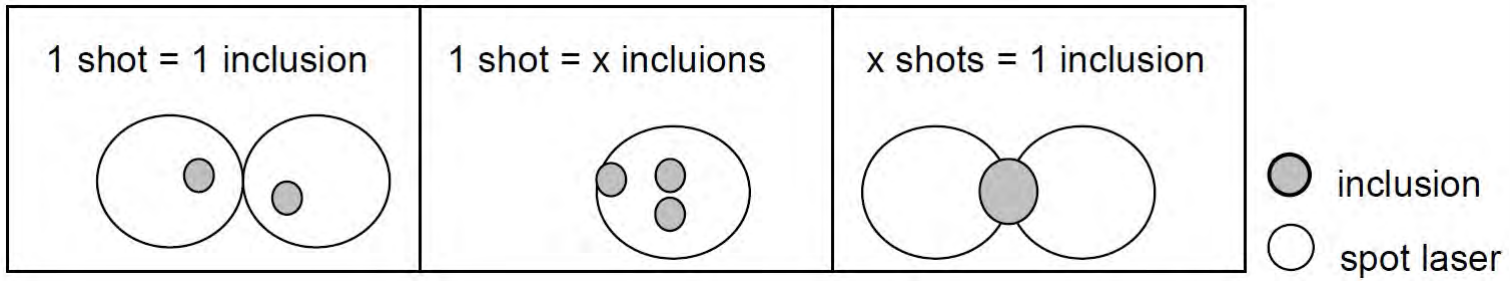


Apart from two outliers, a good (linear) correlation between alumina concentration and number of Al peaks determined by laser-OES demonstrates that it is possible to differentiate several levels of aluminium oxide cleanness by laser-OES measurements

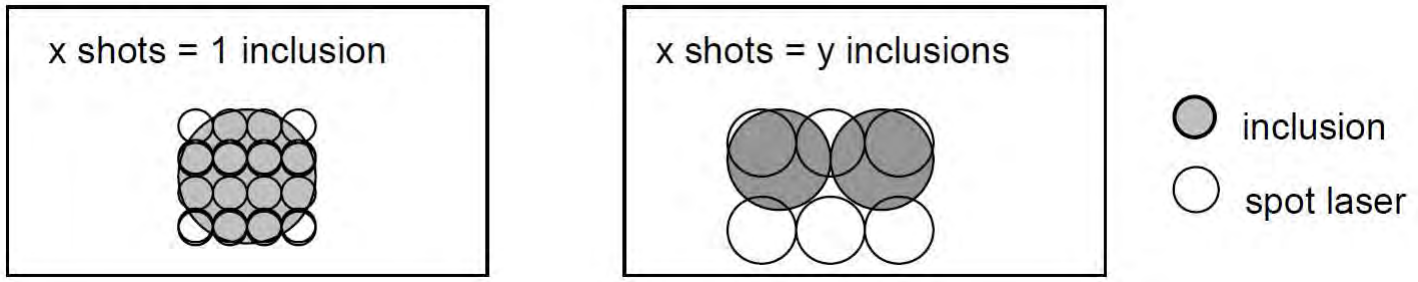
Number of aluminium containing inclusion peaks detected by laser-OES as a function of aluminium oxide concentration in the sample

Quantification of inclusions

Statistical considerations



- If the laser spot size is bigger than the inclusion size to be detected then one inclusion can be detected by one or several laser shots or one laser shot can analyse simultaneously several inclusions close to one another



- If the laser spot size is smaller than the inclusion size to be detected then several laser shots are required to describe one or several inclusions
- The inclusion description will depend on the ratio between inclusion size and laser lateral resolution
- For small inclusions, one or two laser shots are enough to describe the inclusions

Appropriate Equipment and Parameters

- For laser-OES, a well prepared sample surface is required to avoid measuring artefacts. Milling is an appropriate and quick sample preparation technique

- For the analysis, an optical emission spectrometer should be supplied with a laser source run at high pulse repetition rate (e.g. 1 KHz) to keep the analysis time as short as possible. Nd:YAG lasers at the fundamental wavelength of 1064 nm are suitable for material ablation and excitation

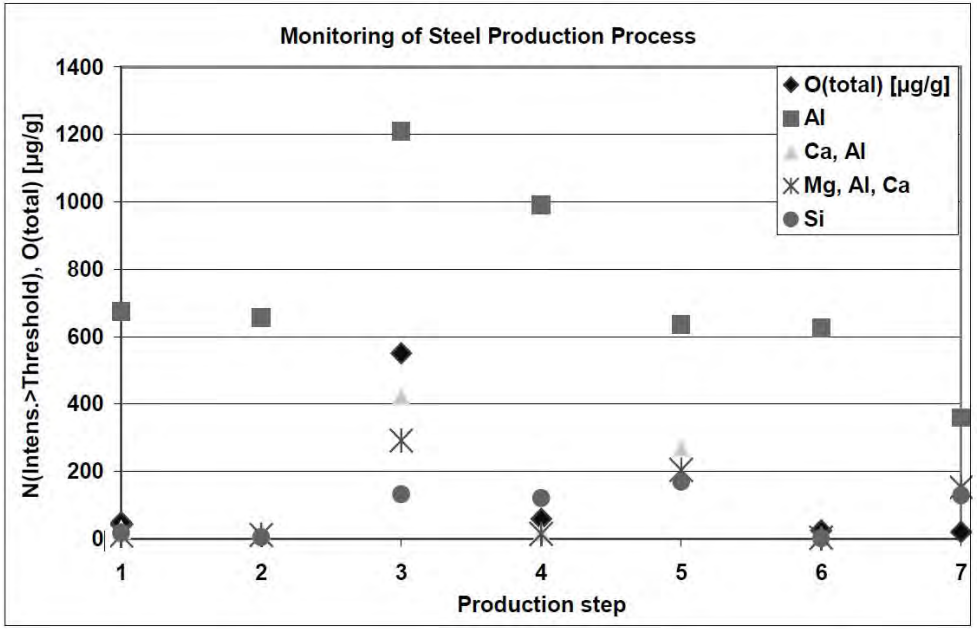
- Data evaluation can be carried out by statistics without using the spatial information. A threshold level is determined to distinguish between the two signal classes (metallic matrix vs non-metallic inclusions). Inclusion types or families are detected by coincidence of intensity peaks.

- Considering the economics, a laser system is more expensive than a spark source. Preparation and measurement of the sample requires up to about 30 minutes. Staff are needed to handle the sample, run the spectrometer and evaluate the results

- Analysis time is longer than for bulk analysis (Spark-OE-; XRF-Spectrometry, CSNO-determination) but shorter than sample preparation for optical microscopy or EPMA analysis and therefore helpful for fast (semi-finished) product control and process optimisation that focusses on steel cleanness

Applications

- Mapping of heterogenous grain structure – Segregations – local distribution of elements typical for segregations like Si, Cu, Mn, S P, C etc
- Detection of heterogeneously distributed metallic and light elements
- Mapping of inclusions in high alloy steel – Inclusions such as MnS and Al_2O_3
- Detection of “light elements” nitrogen and oxygen
- Monitoring the steel production process:



Inclusion monitoring of steel production process by scanning laser-OES on production control samples: 1,2 –vacuum degassing; 3 –Ar stirring (1st step); 4,5 –Ar stirring (2nd step); 6,7 –mould of continuous casting machine

Summary- LIBS

- Scanning laser-OES is a powerful tool for rapid steel cleanness measurement and is able to provide both qualitative and quantitative information on the amounts of non-metallic inclusions in steel within a short time frame
- Qualitative and quantitative results have been successfully verified by conventional techniques such as optical microscopy, electron microprobe and chemical isolation methods
- Milling is the most appropriate technique for sample preparation. Grinding is appropriate for segregation analysis
- Typical analysis time is less than 30 minutes for scanning an area of 1 cm^2 with 250 000 single measurements (20 micron step width).

Laser-OES is a quick and powerful micro-analytical technique for mapping of local element distributions requiring only easy sample preparation

Contents

(7210-PR/300) In-line assessment of steel cleanness during the secondary steelmaking process - Pulse Discrimination Analysis –Optical Emission Spectrometer

- Objectives
- Background and Importance
- Sampling Methodology
- Statistic and Modelling Developments
- Cleanness Indexes
- Assessment of Process Indexes
- Summary

Objectives

(1) To develop an index for in-line assessment of steel cleanness during secondary steelmaking

(2) To develop statistical model of inclusion distribution based on PDA-OES measurement of samples taken in liquid steel and on solid samples

Background and Importance

Equipment used for pre-industrial test – 2 burns for steel composition (3 min); after 3 additional burns, determination of cleanness index (+3 min)

During this project, the following methodologies have been used:

- Set of reference materials fully characterized by SEM have been compared with the PDA-OES method
- Set of reference materials with Al_2O_3 fully characterised by chemical methods have been analysed by PDA-OES
- All the deconvolution methods used in PDA-OES have been compared and validated

- Comparison of instrument performances have been presented
- Calibration curve available for Al_2O_3, CaO, MgO
- Possibility to check oxides content by PDA-OES and by SEM has been demonstrated

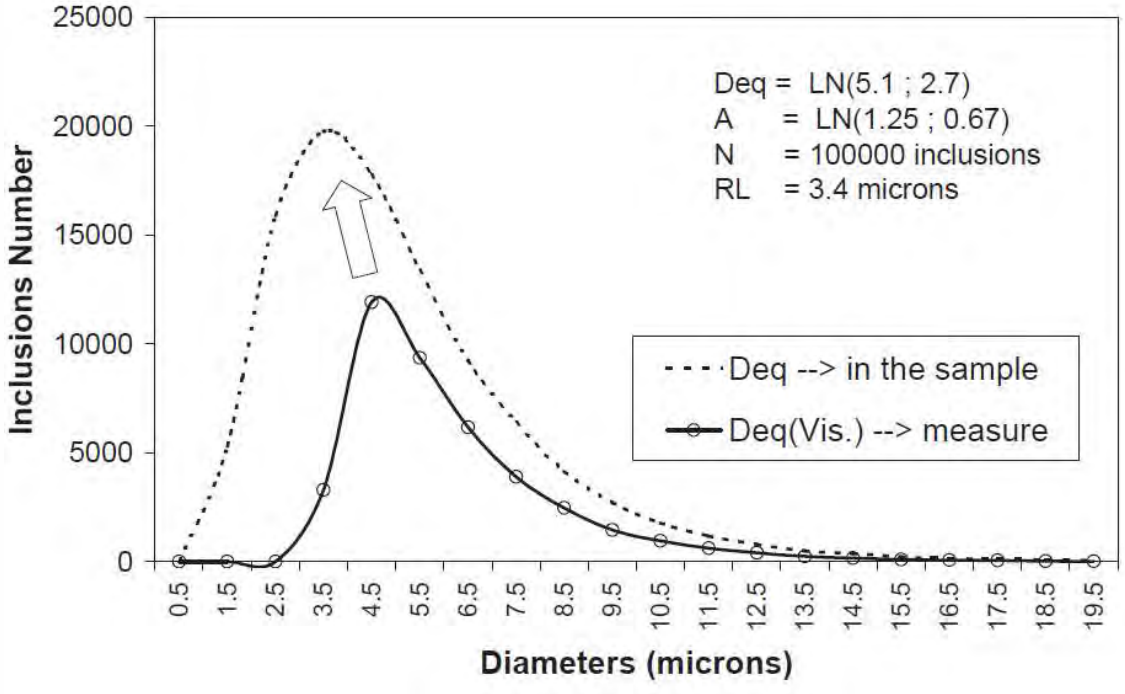
Background and Importance

- The state of the art in ‘Image Analysis’ was assessed
- It was important to have a good method of inclusion population characterisation in order to be able to assess the correlation with the PDA-OES results
- Three different samples were characterised by different partners to verify the coherence between different methods used (automatic vs manual method for Image Analysis)

Background and Importance

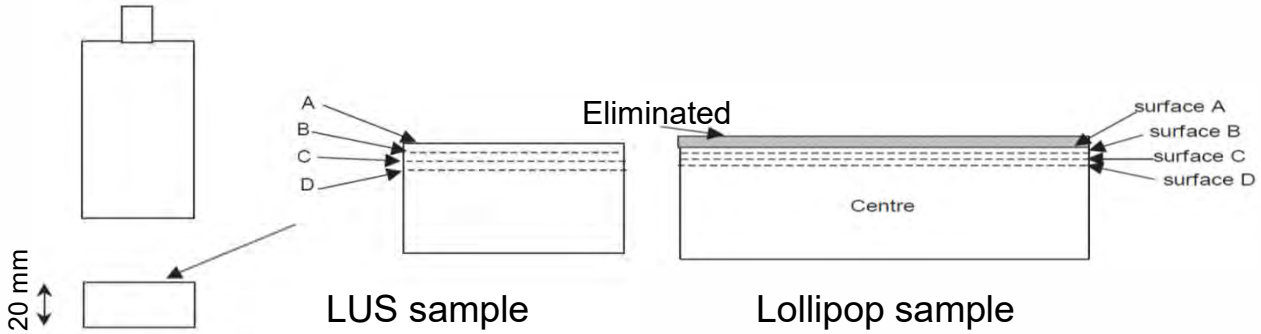
- During preparation of the sample surface (grinding, milling or polishing) the inclusions are cut in the remaining surface plane. Therefore the size distribution of all inclusions in the surface is shifted to smaller particle sizes related to those embedded in the bulk

- A model was developed to determine the real size of inclusion population according to the resolution limit and cutting factor:



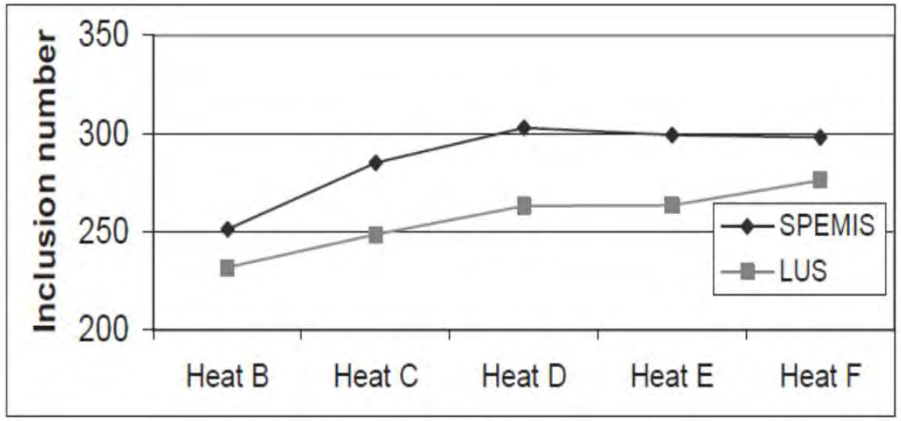
Histograms of visible and real equivalent diameters of inclusions

Sampling Methodology



Location of analysed surface by PDA-OES (after milling)

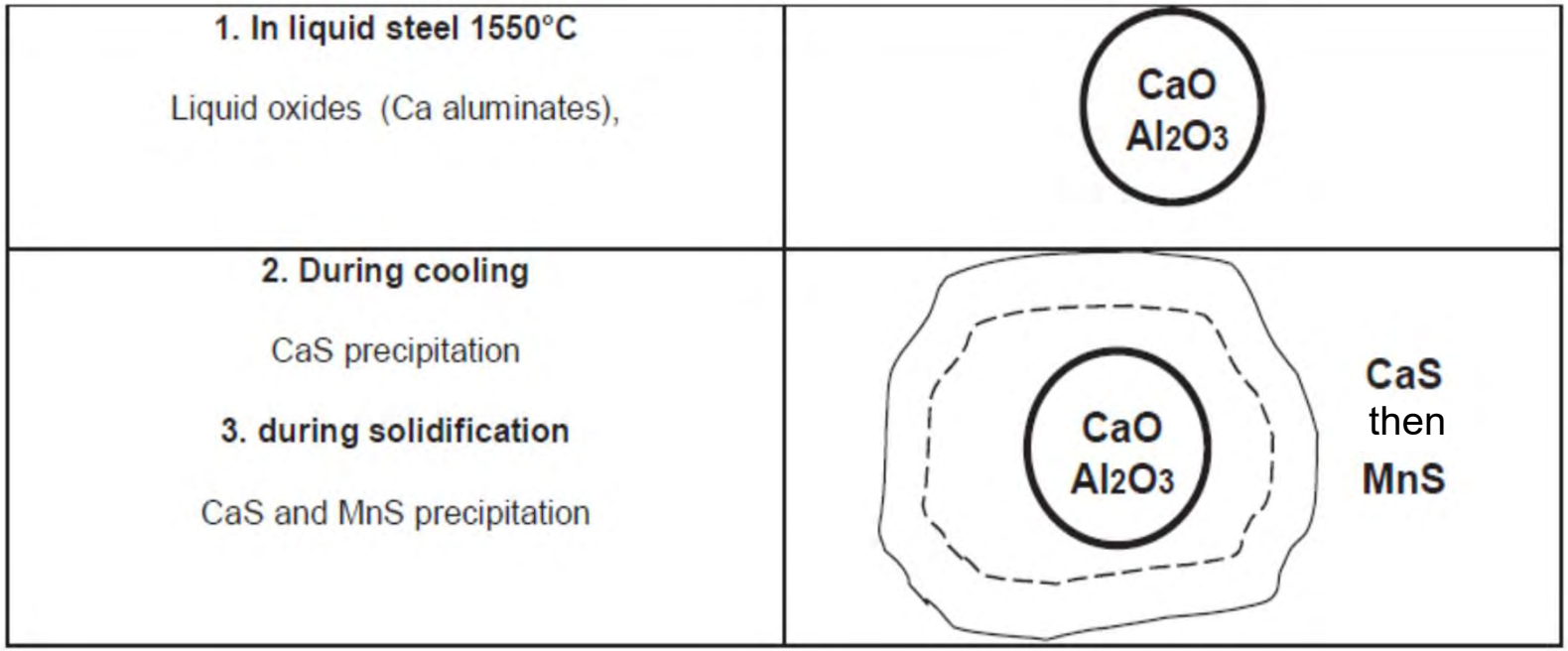
- PDA-OES analysis is able to detect the number and nature of inclusions such as alumina, Al-Mg, Al-Ca, Al-Mg-Ca etc
  .
- The classification of heats by cleanness order for both LUS and lollipop samples shows an equivalent classification
- The number of detected inclusions on LUS samples is systematically less than measured on lollipop samples
- Lollipop samples can be used to characterise cleanness by PDA-OES



Comparison of the detected inclusion number by PDA-OES on LUS and lollipop samples

Sampling Methodology

Influence of sample cooling



Schematic of inclusion solidification

- **Fast Cooling** highlights the inclusion composition at liquid steel temperature
- On the other hand, **Slow Cooling** provides a better indication of the inclusion types that evolve in the final steel product and therefore the final product cleanness

Statistic and Modelling Developments

PDA-OES measurement

- Three different steel grades were characterised by PDA-OES (five impacts by samples).
- The possible chemical inclusion compositions were taken into account.
- A peak with an intensity greater than the limit level corresponding to the matrix peak intensity is considered to be an inclusion.

Early results obtained by PDA-OES were compared with image analysis results for the same samples. Significant differences (not always great) were found. These differences could be explained by:

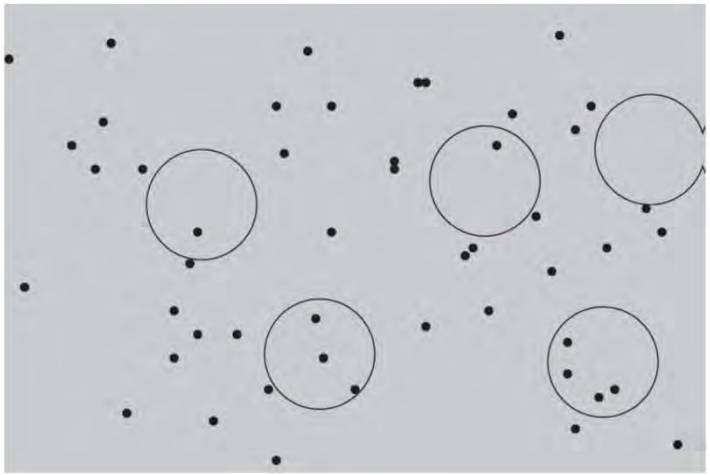
- The size of the analysed volume
- Diameter and density measurement errors
- Inclusion dispersion in the sample is not homogeneous
- The detection limit might be incorrect
- One peak is not always one inclusion and one inclusion on the analysed area is not always one peak
- The number of sparks (5) is insufficient
- The spark conditions on the spectrometer

Statistic and Modelling Developments

PDA-OES measurement

Calculation of the analysed inclusion number according to the inclusion density

To validate the PDA-OES method, it is important to know the mean and the standard deviation of inclusion number analysed by PDA-OES according to inclusion density, impacted area and the impact number

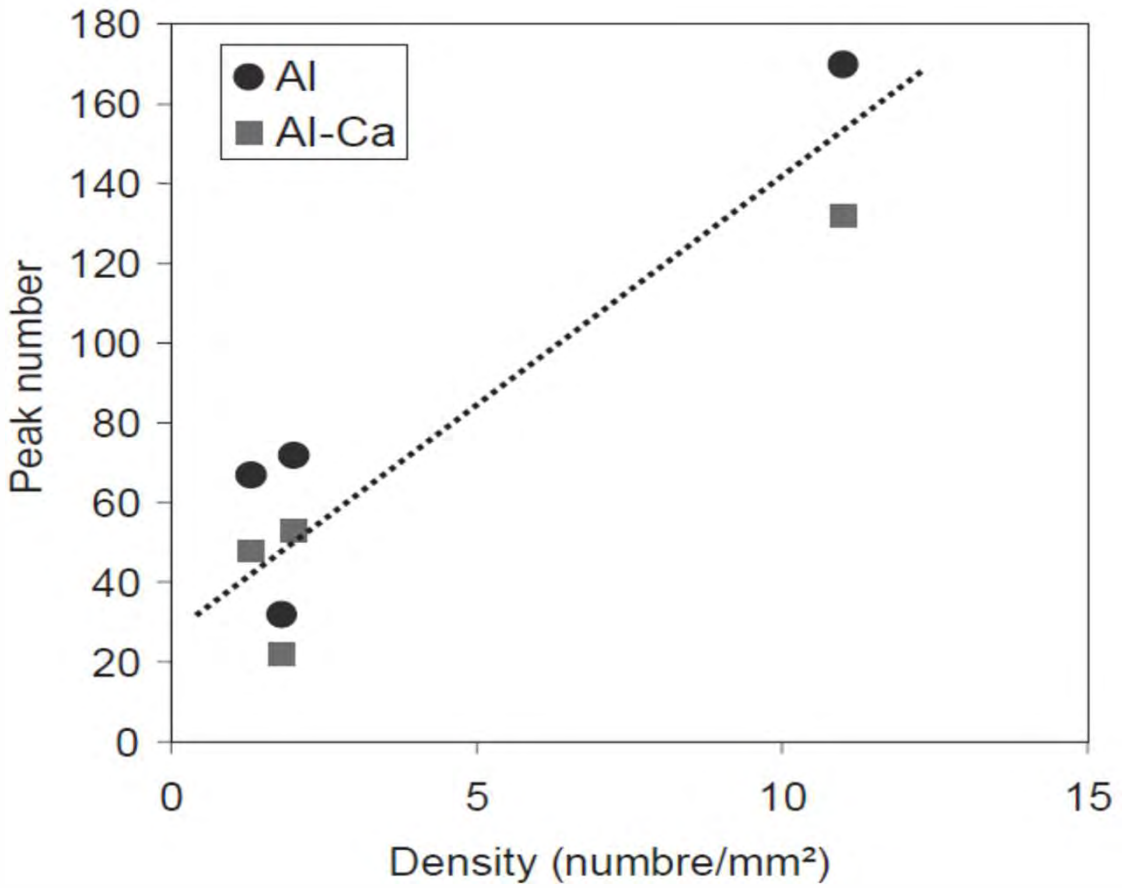


Inclusion repartition on the polished surface

PDA-OES can be effective when the inclusion density ranges from 0.5 to 5 /mm^2 and there are a high number of impacts (e.g. 5). Higher impact numbers are particularly important at low inclusion densities

Assessment of Process Indexes

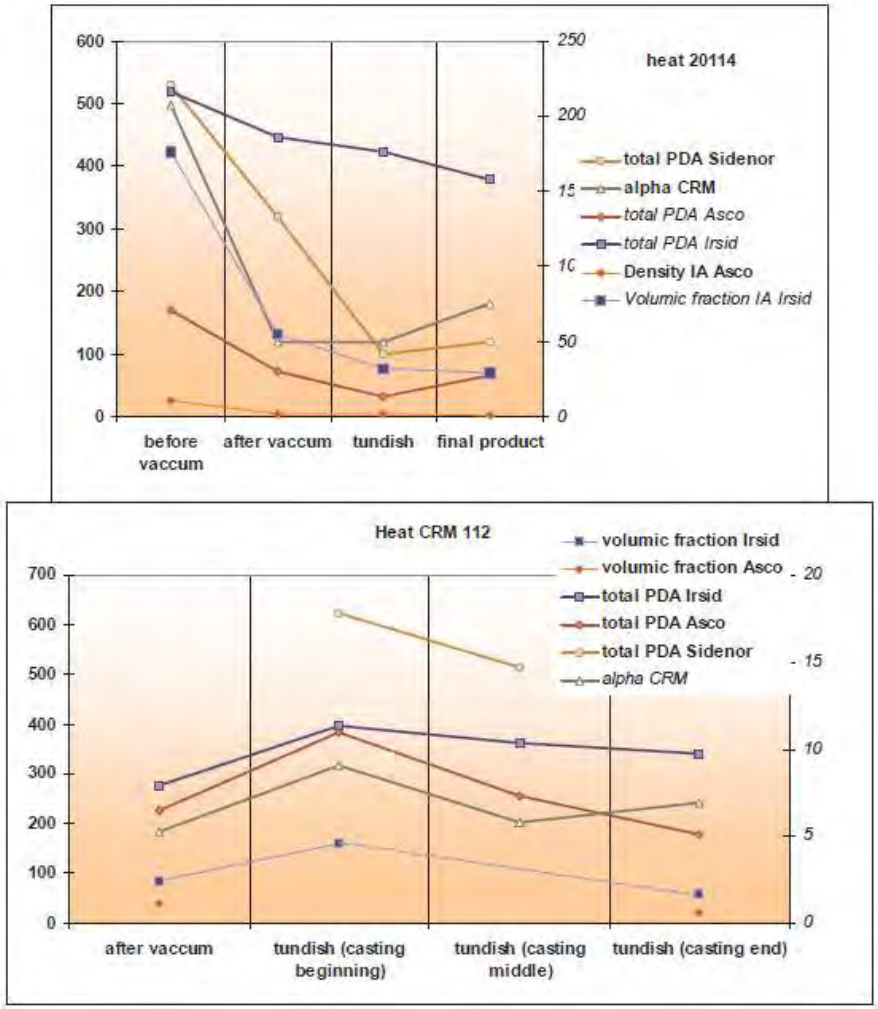
Correlation between image analysis (IA) and PDA-OES results



This shows a fairly good correlation between image analysis data (inclusion density) and PDA-OES (number of peaks for Al and Al-Ca)

Correlation between image analysis and PDA-OES

Assessment of Process Indexes



- Indexes which are able to qualify the cleanness along the process have been developed
- Two PDA based cleanness indexes (total inclusion peaks and alpha factor) have the same evolution and are in agreement with the expected cleanness along the process
- Indexes have similar variations as the density or volume fraction measured by image analysis
- These indexes allow some control of the process but do not predict the final product cleanness

Comparison between evolution of image analysis parameters and PDA-OES indexes

Summary- PDA-OES

- A control tool for in-line steel cleanness during secondary steelmaking and based mainly on PDA-OES measurements has been validated by the development of a statistical model of inclusion distribution
- Use of specific cleanness indexes allows inline follow up of the process with respect to inclusion content
- PDA-OES, that does not require any additional analytical hardware, can lead to improvement in the quality and homogeneity of steel products

Further Projects: Use of PDA-OES

(7210-PR-332) Optimisation and evaluation of different secondary metallurgy routes to achieve high-quality strip steel

(RFSR-CT-2005-06) Prediction of inclusions in the slabs from the process characteristics (PREDINC)

PDA-OES technique has been used as a method of on-line steel cleanness in the above projects by different partners

Summary- Rapid Cleanness Measurement Techniques

- Present status of rapid steel cleanness measurement is that both LIBS and PDA-OES have potential to provide rapid feedback on steel quality
- It appears that PDA-OES is applied more than LIBS because no extra cost, equipment or resource is required and it can be used to selectively help control steel quality on-line
- PDA-OES has been continuously developing for online assessment of steel cleanness
- Both techniques are applied extensively across European steelplants