
# Fast analysis of slag chemistry during secondary metallurgy

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# Context – why/how measuring slag chemistry ?

- Why : Impact of slag chemistry:
  - Repartition ratio of Cr, P… O usage – addition yield
  - Desulphurization of steel at ladle furnace depends on temperature, amount of oxygen and sulphur in the steel, but mainly on chemical composition and physical properties of slag.
  - The steel cleanliness is directly affected by the $\%CaO/\%Al_2O_3$ ratio, slag basicity, fluidity, and oxygen activity in the slag
  - Refractories lifetime
  - Recyclability of slags

- How : Measurement means:
  - Sampling : costs and long delay / point wise measurement
  - Direct measurement (OES, LIBS,…) : validity, accuracy, harsh working condition, lifetime

# Summary

- Terminated RFCS projects
  - AVAS (direct measurement - OES)
  - BOFDYN (sampling at converter)
  - INQUISS (sampling, direct measurement - LIBS)
- Other references
  - OES measurement at EAF
  - OES measurements at converter
  - LIBS direct measurements of slag composition
- On-going RFCS activities
  - OSCANEAF (direct measurement - OES)

# AVAS : Feasibility of a fast vacuum slag analysis by laser OES in secondary steelmaking

- Working period: 01/09/2003 – 31/08/2006
- Consortium : Dillinger Hütten (D), AMMR (F), Fraunhofer (D), Saarstahl (D)
- Objectives :
  - To prove the feasibility of a fast slag analysis at the vacuum degasser for better production control in secondary steelmaking with the emphasis on $SiO_2$, CaO and $Al_2O_3$.
  - Comparison with XRF measurements (directly on casted slags and/or after preparation).
- Main results :
  - Investigation of the feasibility of fast slag analysis for a better control during the secondary metallurgy process
  - The project was unable to produce reliable results regarding the fast slag analysis using laser OES method. Furthermore, the obtained results in some cases were also irreproducible.

# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- Working period: 01/09/2003 – 31/12/2006
- Consortium : CRM (B), Heraeus-Electronite (B), AMMR (F), SIMR (F)
- Objectives :
  - To shorten the tap to tap time in BOF plants in order to increase the productivity.
  - To use a dedicated laser methodology for a rapid discriminative determination of Mn, P, and S contained in the melt phases.
  - To develop a new process control based on the use of new in-blow samplers delivering heterogeneous samples composed of steel and slag.
  - Could be extended to AOD.

# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- New sampling development:

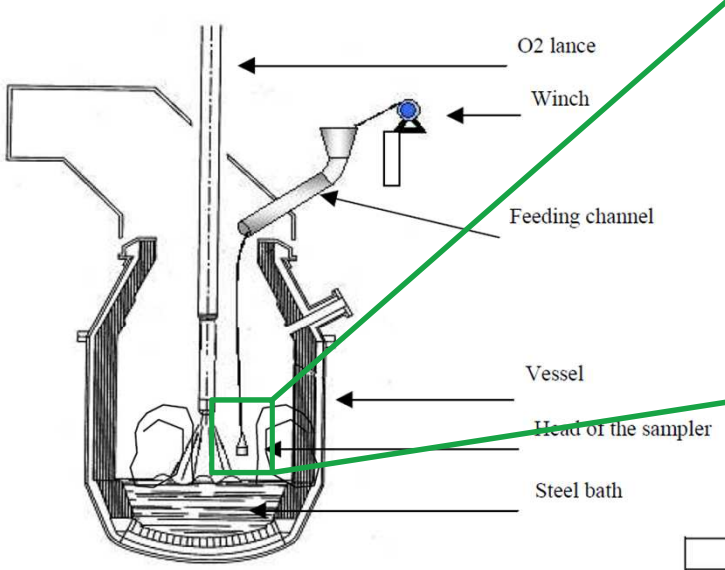



Figure 2: scheme of the sampling technique at the converter

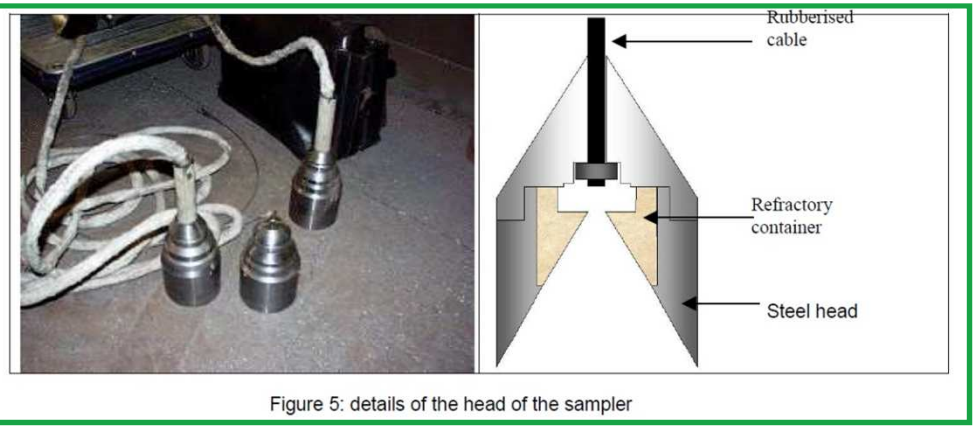
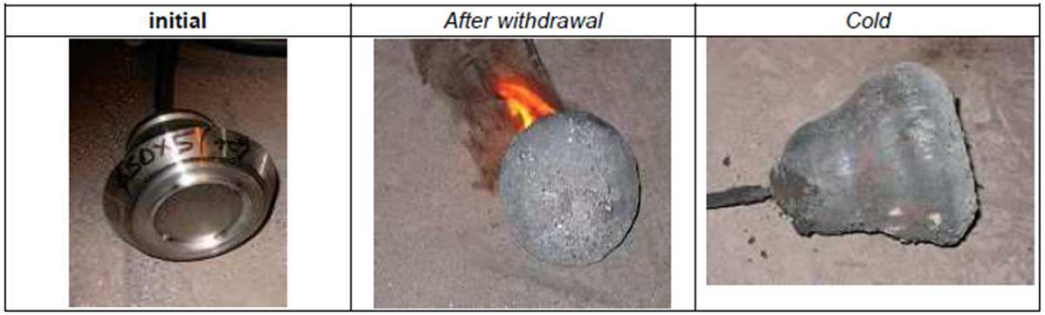



Figure 5: details of the head of the sampler



# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- New sampling development:

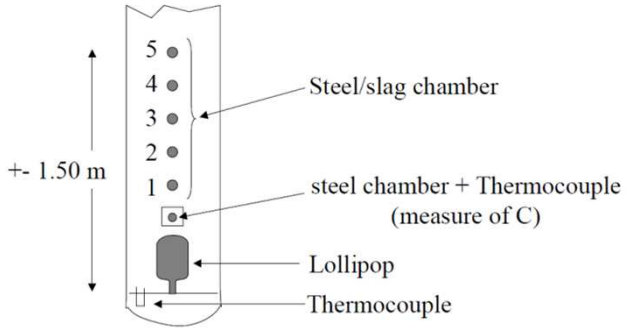


Figure 33: design of the multi-chamber probe


Figure 37: *heterogeneous sample in its chamber*

- Main results :
  - Sampling of mixed steel-slag was efficient.
  - Only part of the samples presented good characteristics for the laser analysis (good flatness, sufficient thickness, and no “crumbly” properties) → sample preparation is necessary, probably by cutting or milling the sample to get a reasonably flat, clean surface.

# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- Samples analysis:

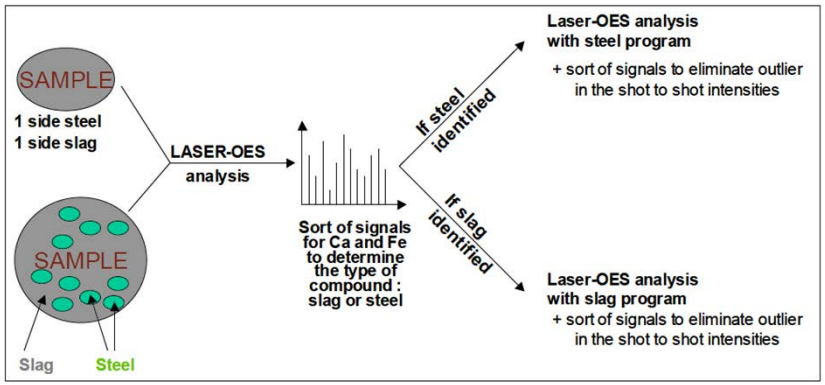
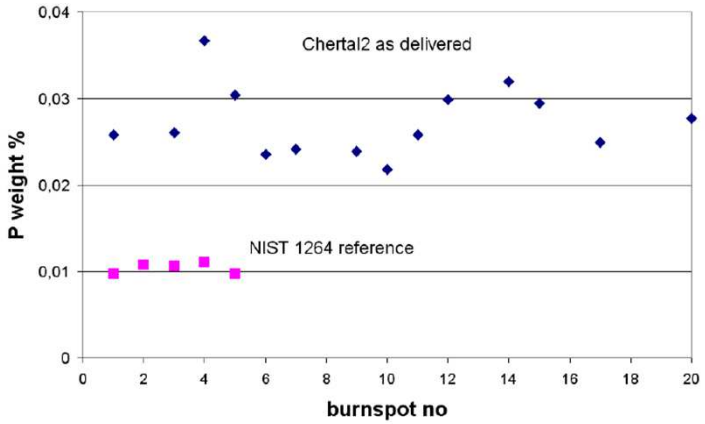



Figure 40: Arcelor Research methodology for mixed steel / slag samples analysis




- Main results :
  - While the steel samples were perfectly analysable, the mixed samples were made of steel with small slag inclusions or of slag with steel areas.
  - In order to get a good steel analysis, a “preburn” and a line- or step scan over at least 5 mm is necessary in order to identify “clean steel” areas.

# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- Slags samples analysis Main results :
  - Small steel particles included in slag part of the sample have a serious impact on the representativeness of the sample analyses.
  - Effect of the sample surface: have to surface the samples or to treat the analytical data.
  - Difficulties to analyse quantitatively slag and steel on a same program. The slag reference materials cannot be analysed with the same laser energy and focussing as the steel, and it is technically impossible to switch laser parameters in the middle of a measurement run.
  - The best chances to achieve both steel and slag analysis in one sample is for samples that are mainly steel, with relatively large (0,1 – 1 mm) slag particles embedded. The slag analysis is then possible with a “subtraction” method but a direct analysis of “pure” slag particles with LIBS is not realistic.

# BOFDYN: Dynamic end-point control in BOF through a fast and simultaneous determination of the steel/Slag composition

- Main results :
  - Analysis on industrial sample for the major “slag” elements (Ca, Si and Al) were fairly consistent with RSD. Also, the results for P are fairly consistent. For Mn, S and Ti, no real determinations can be made, but “a good indication of the level”. Obviously, carbon in the slag cannot be determined at all.

Table 23: Analytical results for the slag part in sample Chertal 2 (weight %).

| | Ca | Si | Al | Mn | P | S | C | Ti |
|---|---|---|---|---|---|---|---|---|
| **Scan 1** | 12 | 11 | 1,7 | 2,6 | 2,0 | 0,73 | 31 | 0,16 |
| **Scan 2** | 15 | 9,0 | 2,0 | 8,4 | 1,8 | 0,50 | 8,2 | 0,37 |
| **Scan 3** | 14 | 9,2 | 1,6 | 2,9 | 1,4 | 0,14 | 0,042 | 0,29 |
| **Average** | 14 | 9,7 | 1,7 | 4,6 | 1,7 | 0,46 | 13 | 0,27 |
| **SD** | 1,7 | 1,1 | 0,21 | 3,3 | 0,32 | 0,30 | 16 | 0,11 |
| **RSD %** | 13 | 11 | 12 | 71 | 18 | 64 | 123 | 40 |
| **RSDM 3** | 7,3 | 6,4 | 6,8 | 41 | 11 | 37 | 71 | 23 |

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Working period: 01/07/2001 – 30/06/2004
- Consortium : RWTH (D), Aceralia (S), Acerinox (S), Helliniki Halyvourgia (G), ISQ (P), University of Malaga (S), University of Patras (G)
- Objectives :
  - Adaptation and optimisation of laser-based sensing (LIBS) in steelmaking plant processing conditions (EAF, BOF, ladle).
  - Development of a quick/on-line, in-situ measurement system of process-critical components of molten slags.
- Main results :
  - LIBS measurements were performed off-line on sampled slag at EAF plant.
  - On-line trials at BOF plant haven't been done due to practical problems.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Lab-scale experiments

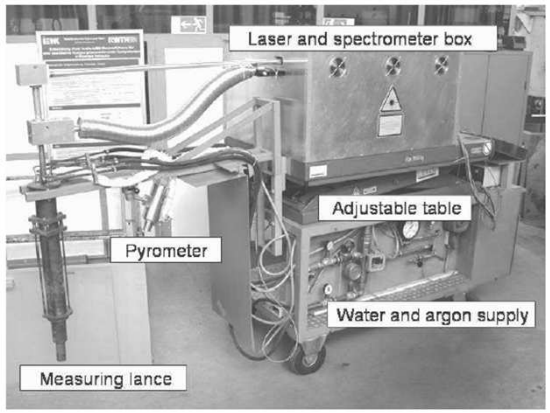
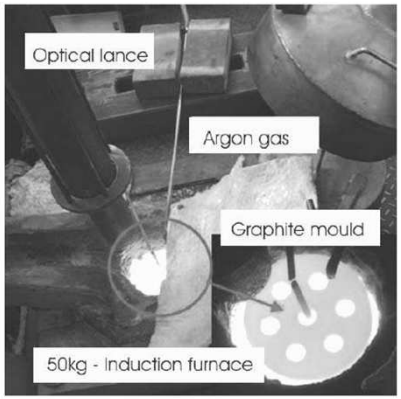



Figure 33: Complete measurement LIBS system in the laboratory at the IEHK Aachen; ready for hot tests at the 100 kg pilot facilities




View into the induction furnace at the IEHK Aachen during calibration (survey and close up)

- Main results:
  - The laser induced breakdown spectroscopy (LIBS) method has been applied to metallurgical liquid and solid slags.
  - For Ca, Al, Si, Mg, Fe and Cr calibration curves were produced; Ca is the most critical element due to strong self-absorption at the plasma location.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Lab-scale experiments – focusing issue

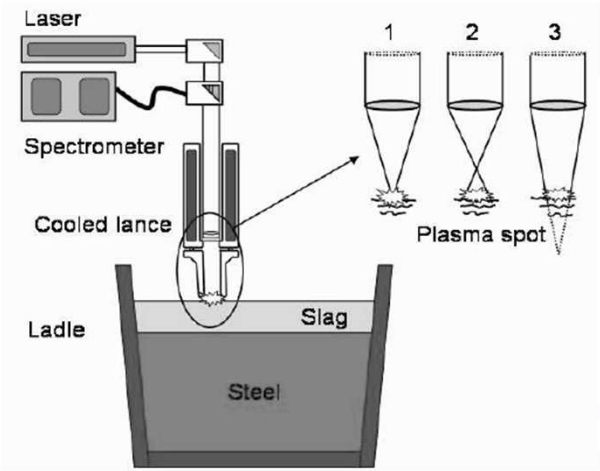



Figure 47: Three cases of plasma spot positions (Rem.: n° 1 is correct)

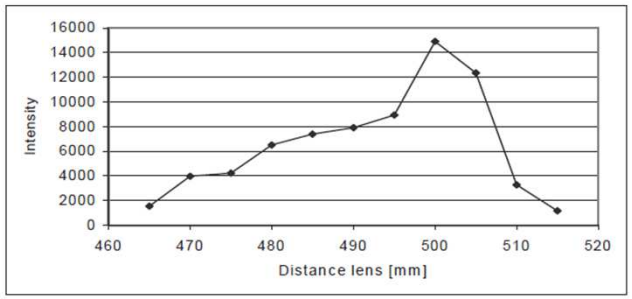
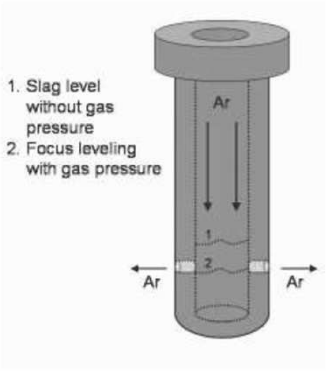



Figure 48: Development of the plasma intensity in the focus volume (Distance between lens and sample surface)

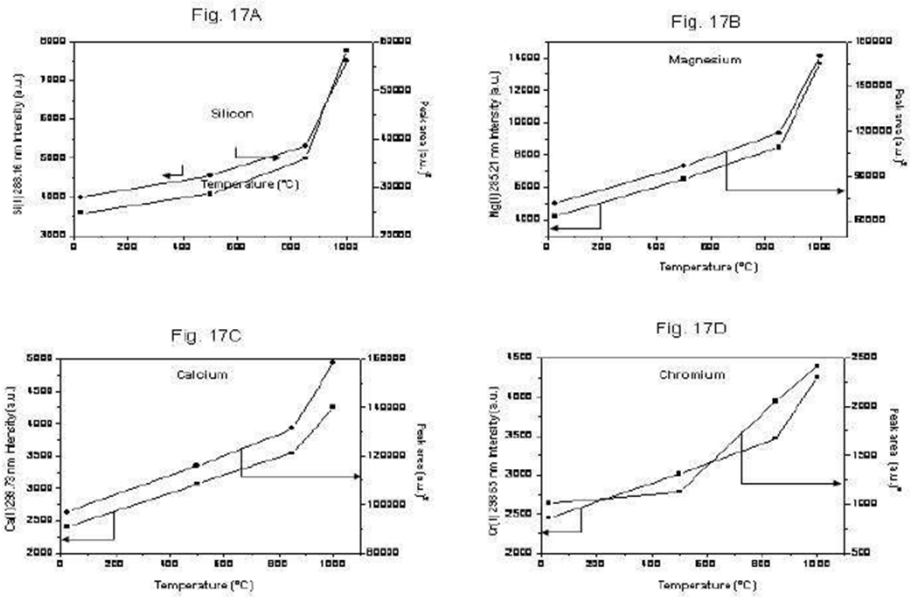



Special graphite nozzle for auto-focus action

- Main results:
  - Problems of focussing the laser beam to a wavy slag surface have been overcome by new submerged graphite nozzle into the liquid slag.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Lab-scale experiments – impact of T




- Main results:
  - Strong influence of temperature: the exact knowledge of slag temperature and of roughly defined flow behaviour of the slag (viscosity) are necessary.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Off-line trials at EAF plant

Pic. 5. Front view of EAF

Pic. 6. Slag samples - Step 1

Pic. 7. Slag samples - Step 2

Pic. 8. Slag samples - Step 3

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Off-line trials at EAF plant:
  - It was possible to measure main chemical elements of steel plant slags like Ca, Si, Fe, Mg, and Cr in the rough environment of an EAF production facilities.
  - Slag samples were solidified in special Cu crucibles and subsequently analysed by LIBS beneath the furnace. The inhomogeneous concentration from solidification path ways and the uneven surface of the solidified slags led to strong problems of LIBS application so that only qualitative results can be given.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Preparation of on-line trials at BOF plant

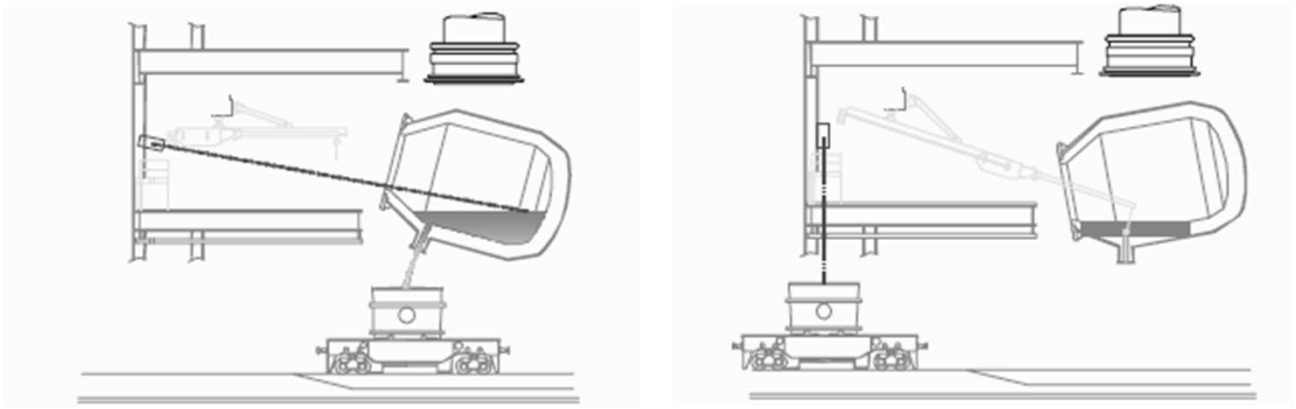


**Figure 91:** Arrangement of equipment at the converter area:
left side: slag detection in converter, right side: slag detection in the ladle

- Main results:
  - Main problem for the time being is the dusty atmosphere in the converter vessel during blowing and the long distance between lens and slag surface where dust disturbs the beams heavily.
  - Second problem which has to be overcome is the protection of employees against main laser beams and unwanted reflexions in the plant.

# INQUISSS: In situ, quick sensing system for measurements of process-critical components in steelmaking slags

- Main results:
  - The LIBS-method can be used in steelmaking plants to control the slag composition online in spite of the rough environment.
  - The system could be used in process steps like continuously melting of DRI, control of foaming slag in an EAF, metallurgical work in a vacuum tank, where a homogeneous liquid slag of low viscosity exists.
  - Investigation of discrete taken slag samples directly near by the furnace in terms of rapid process control is also possible.

# Summary

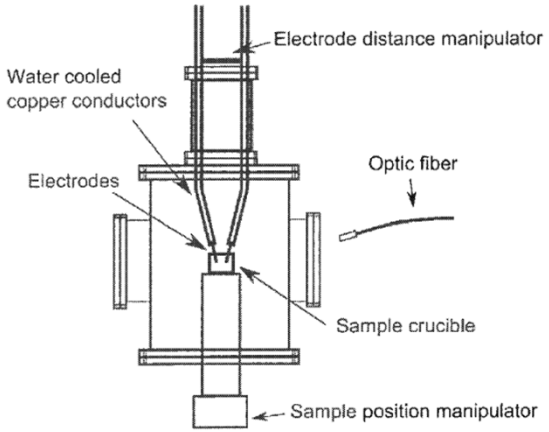
- Terminated RFCS projects
  - AVAS (direct measurement - OES)
  - BOFDYN (sampling at converter)
  - INQUISS (direct measurement - LIBS)

- Other references
  - OES measurement at EAF
  - OES measurements at converter
  - LIBS direct measurements of slag composition

- On-going RFCS activities
  - OSCANEAF (direct measurement - OES)

# EAF spectra analysis – lab trials

- Lot of work from Finland team (Univ of Oulu and Helsinki)

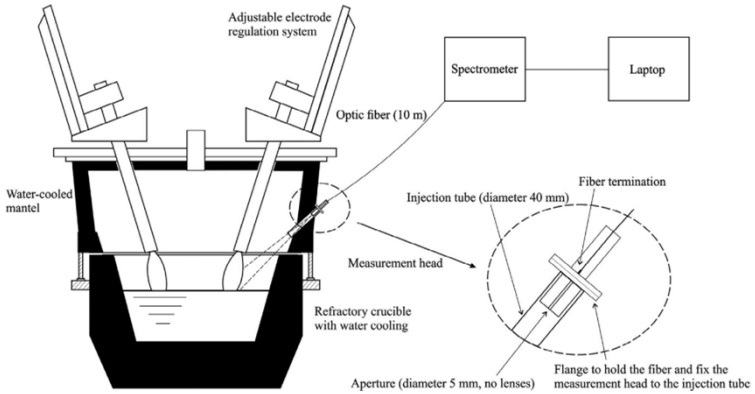


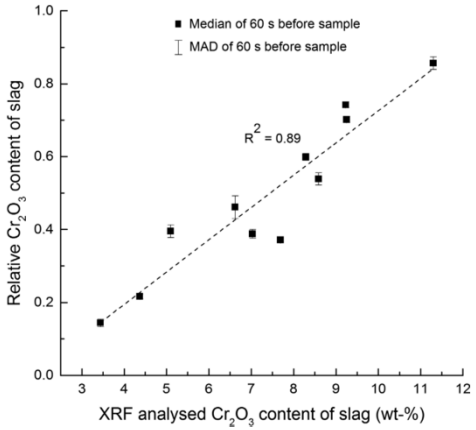

- Laboratory scale DC electric arc furnace to study the usability of optical emission spectroscopy in real electric arc furnaces.
- Topic is EAF stainless steelmaking (→ fewer slag foaming).
- Optical emission spectra of Fe, Cr, $Cr_2O_3$, Ni, $SiO_2$, $Al_2O_3$, CaO, and MgO were recorded in the wavelength range 250–600 nm and the results were analysed with the help of reference data.
- Benefit of using arc emission is that no additional radiation sources are needed and emission comes directly from the core of the furnace without separate sample handling.
- Good correlation of emission peaks with CrO/FeO and $MnO/SiO_2$ ratios → Cr and Mn yield.


- M. Aula, A. Mäkinen, T. Fabritius: "Analysis of Arc Emission Spectra of Stainless Steel Electric Arc Furnace Slag Affected by Fluctuating Arc Voltage". Applied Spectroscopy. 2013. 68: 26–32.
- A. Mäkinen, J. Niskanen, H. Tikkala, H. Aksela: "Optical Emission from a Small Scale Model Electric Arc Furnace in 250-600 nm Region." Review of Scientific Instruments. 2013. 84: 043111

# EAF spectra analysis – lab trials

- Collaboration of Univ of Oulu and RWTH



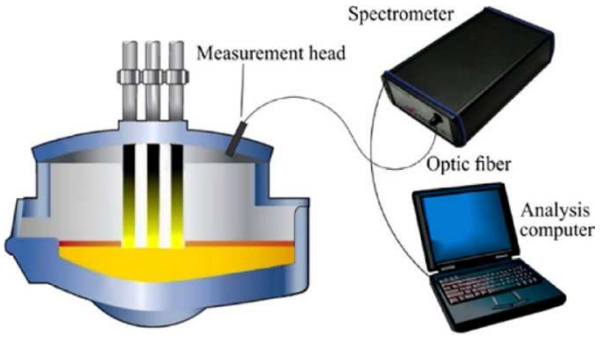

- Trials performed on RWTH's pilot EAF in AC mode.
- Topic is EAF stainless steelmaking.
- $Cr_2O_3$ content of slag was analysed by measuring the optical emission spectrum of the electric arc and compared with XRF analysis of samples.
- The results indicate that best accuracy in a pilot scale can be obtained by using combination of Ca I, Fe I or Mn I lines as reference for Cr I lines.
- Average absolute error of 0.62%-points and a standard deviation of 0.49%-points
- Accuracy of measurement limited by variation of reference material amount, vaporization and thermal stability of slag component and slag homogeneity.

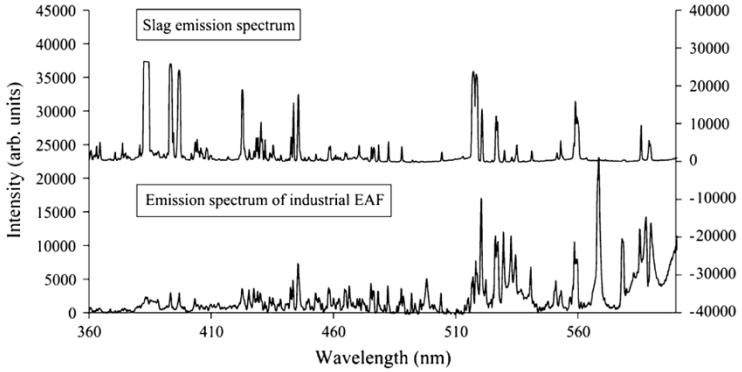


- M. Aula, T. Demus, H. Pfeifer, T. Fabritius: "Analysis of Cr2O3 content of the slag in pilot scale EAF by measuring the optical emission spectrum of the electric arc." ISIJ International. 2017. 57(3): 478-486.

# EAF spectra analysis – plant trials

- Still Finland team with industrial application at Outokumpu Stainless steel plant

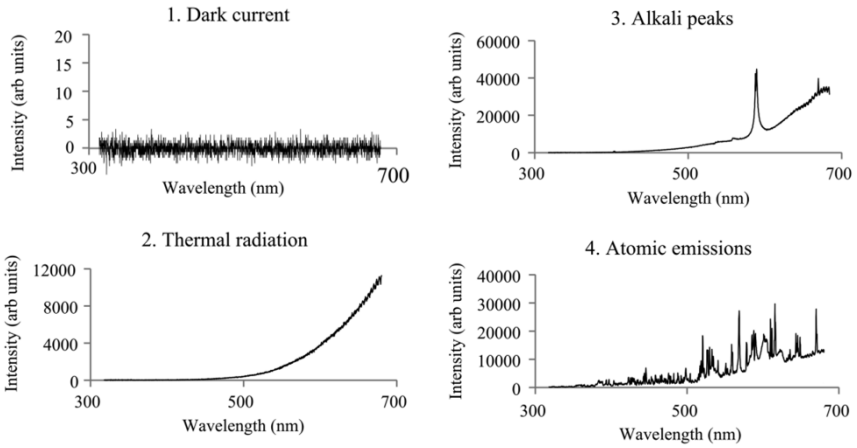



- 140t AC stainless steelmaking EAF.
- High intensity peaks of Ca I, Ca II, Cr I, Mg I, Mn I, Na I, Li I were observed in the spectrum.
- The comparison shows that the optic emission of an arc is dominated by slag components.
- Results differ from lab trials due to different atmosphere.

# EAF spectra analysis – plant trials

- Still Finland team with industrial application at Outokumpu Stainless steel plant

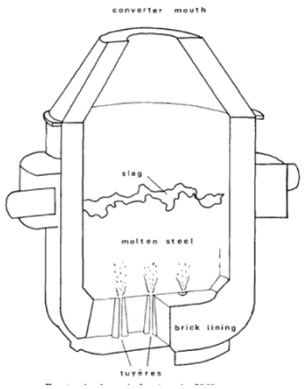


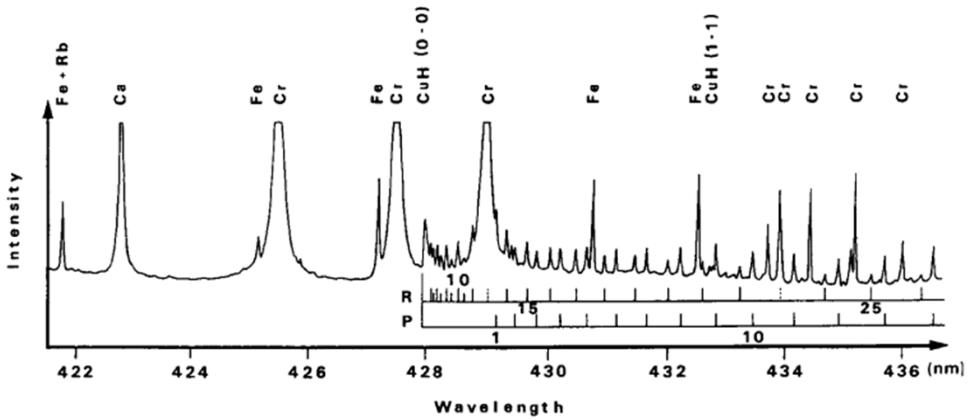

- 140t AC stainless steelmaking EAF.
- Four basic types of emission spectra were obtained during the EAF process cycle.
  - The first one is obscured by scrap steel
  - The second is dominated by thermal radiation of the slag (too low T to excite atomic/ionic transition)
  - the third is dominated by alkali peaks and sodium D-lines
  - the fourth is characterized by multiple atomic emission peaks.
- Study focus on spectrum types related to the thermal radiation of hot slag or gas and excitation of alkali metals by the exothermic reactions inside the EAF.


- M. Aula, A. Mäkinen, T. Fabritius: "Analysis of Arc Emission Spectra of Stainless Steel Electric Arc Furnace Slag Affected by Fluctuating Arc Voltage". Applied Spectroscopy. 2013. 68: 26–32.
- A. Mäkinen, J. Niskanen, H. Tikkala, H. Aksela: "Optical Emission from a Small Scale Model Electric Arc Furnace in 250-600 nm Region." Review of Scientific Instruments. 2013. 84: 043111
- O. Block: Dissertation, University of the Federal Armed Forces Hamburg, Hamburg, 1995.

# Optical spectroscopy at converter – plant trials

- Work from Swedish and Japanese teams
  - Topic is converter (CLU) but largely extendable to AOD.
  - Study of the spectrum emitted from the flame above the mouth of converter.
  - Possible to identify spectral features of interest for process control (MnO)



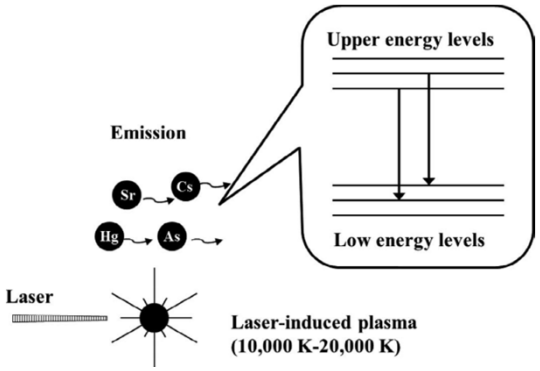



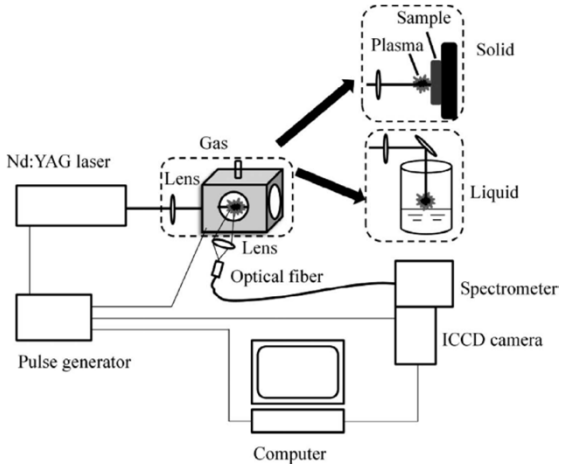


- W. Wendt, W. Persson: ‘‘Optical Spectroscopy for the Characterization of an Alloy Steel Converting Process’’. Appl. Spectrosc.1990. 44(6): 987-991 .
- K. Chiba, A. Ono, M. Saeki, M. Yamauchi, M. Kanamoto, T. Ohno: ‘‘Development of Direct Analysis Method for Molten Iron in Converter: Hotspot Radiation Spectrometry’’. Ironmaking and Steelmaking 1993. 20(3): 215-220.

# Slags analysis with LIBS

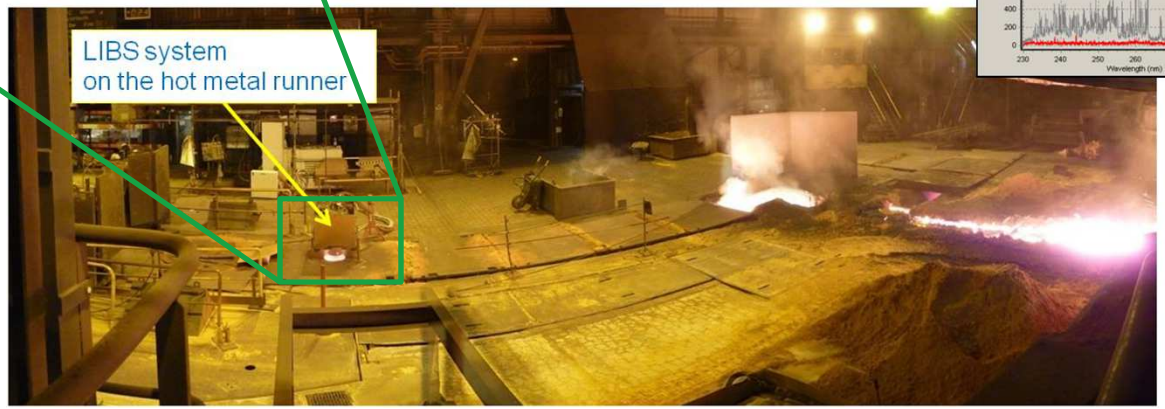
- LIBS principle:
  - laser beam is focused into a small area, producing the hot plasma. The material contained in the plasma is atomized and the light corresponding to a unique wavelength of each element is emitted from the excited atoms.
  - A calibration of the LIBS signal is necessary for quantitative analysis.
  - Emission signals are detected by the combination of a spectrometer, an ICCD camera and auxiliary equipment. According to the measured materials of solid, liquid and gas phases, different measurement chambers or platforms can be employed.
  - Multi-elemental capability with very short response time.

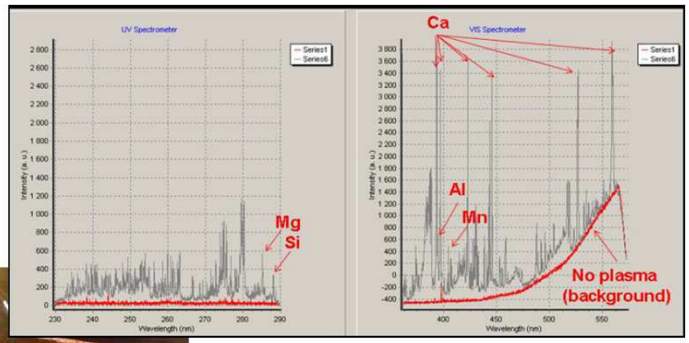


# Slags analysis with LIBS

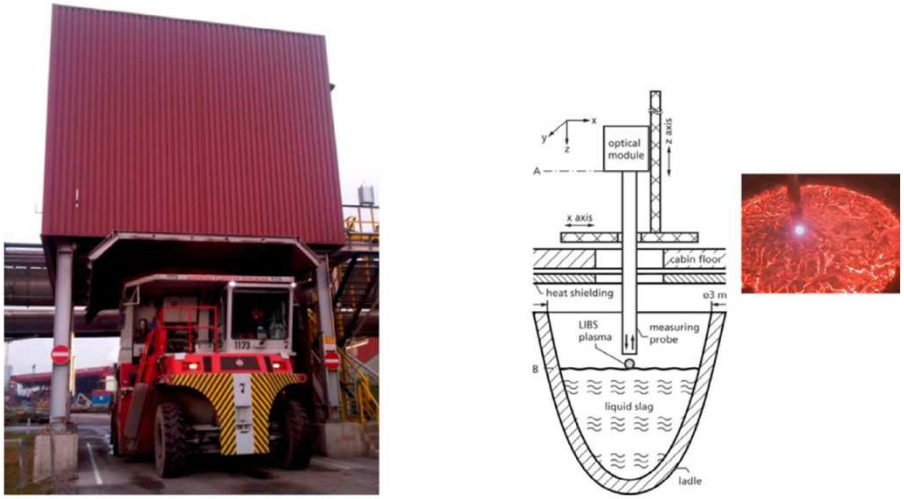
- Online slag analysis on BF runner
  - The results have proved the possibilities of the LIBS method to allow accurate measurements in harsh environment.
  - Elements important for the process, like Ca, Si, Al, Mg, Fe, could be identified on-line in the slag runner.
    - G. Monfort, L. Bellavia, M. Tonteling, C. Ojeda, O. Ansseau, On-line measurement of the hot metal temperature and composition in the blast furnace runners by LIBS, JALS vol. 1, Num. 1, 2014

# Slags analysis with LIBS

- Analysis of solidified samples taken from the liquid slag layer in a vacuum degasser station of a steel plant
  - V. Sturm, H.-U. Schmitz, T. Reuter, R. Fleige and R. Noll: *Spectrochim. Acta, Part B*, **63** (2008), 1167.
- On-line analysis of liquid slag at VA steel plant. The slag in the ladle of a slag transporter was measured automatically at a distance of several meters during a short stop of the transporter within 2 min. The major components, such as CaO, Fe, $SiO_2$, MgO, Mn and $Al_2O_3$, were analysed and compared with reference values from the laboratory for solid pressed slag samples as well as for samples from the liquid slag. Stable 24/7 operation during the first three-month test run has been demonstrated successfully under these conditions.
  - V. Sturm, R. Fleige, M. de Kanter, R. Leitner, K. Pilz, D. Fischer, G. Hubmer and R. Noll: *Anal. Chem.*, **86** (2014), 9687.




(a) Slag transporter with ladle during analysis underneath the measuring cabin.
(b) Schematic diagram of the LIBS analyzer setup.

# Slags analysis with LIBS

- Analysis of solidified samples taken from the liquid slag layer in a vacuum degasser station of a steel plant
  - V. Sturm, H.-U. Schmitz, T. Reuter, R. Fleige and R. Noll: *Spectrochim. Acta, Part B,* **63** (2008), 1167.
- On-line analysis of liquid slag at VA steel plant. The slag in the ladle of a slag transporter was measured automatically at a distance of several meters during a short stop of the transporter within 2 min. The major components, such as CaO, Fe, $SiO_2$, MgO, Mn and $Al_2O_3$, were analysed and compared with reference values from the laboratory for solid pressed slag samples as well as for samples from the liquid slag. Stable 24/7 operation during the first three-month test run has been demonstrated successfully under these conditions.
  - V. Sturm, R. Fleige, M. de Kanter, R. Leitner, K. Pilz, D. Fischer, G. Hubmer and R. Noll: *Anal. Chem.*, **86** (2014), 9687.
- Qualitative and quantitative measurement of elemental concentration in iron slag and open pit ore samples. Various elements of Cd, Ca, Mg, Cr, Mn, Ti, Ba, P, Cu, Fe, Zn, *etc.* in these samples were determined. The concentrations of trace metals estimated with the LIBS setup were in close agreement with the results achieved with ICPAES. The LIBS detection limits were estimated for these mentioned elements under the optimal experimental conditions.
  - T. Hussain and M. A. Gondal: *J. Phys.: Conf. Ser.*, **439** (2013), 012050-1.

- Z. WanG, y. Deguchi, F. Shiou, J. Yan, J. Liu: “Application of Laser-Induced Breakdown Spectroscopy to Real-Time Elemental Monitoring of Iron and Steel Making Processes”. ISIJ International. 2016. 56(5): 723-735.

# Summary

- Terminated RFCS projects
  - AVAS (direct measurement - OES)
  - BOFDYN (sampling at converter)
  - INQUISS (direct measurement - LIBS)

- Other references
  - OES measurement at EAF
  - OES measurements at converter
  - LIBS direct measurements of slag composition

- On-going RFCS activities
  - OSCANEAF (direct measurement - OES)

# OSCANEAF: On-line slag composition analysis for electric arc furnaces

- Working period: 01/09/2016 – 31/08/2019
- Consortium : RWTH, Oulu, KTH, Lux Met, Osoy, Dew
- Objectives : The objective of the project is the development of a continuous measurement system for EAF/LF slag component analysis based on optical emission spectroscopy. The aim is the analysis of $Cr_2O_3$, MnO, FexOy, CaO, $SiO_2$, $Al_2O_3$, MgO and CaF content of the slag for stainless and carbon steel grades in the EAF and LF. Project activities aim at:
  - remote and continuous measurement system for online slag analysis,
  - low maintenance system design,
  - optimised operating practices based on continuous slag composition data increasing resource and energy efficiency.

# Fast analysis of slag chemistry during secondary metallurgy