Reactions of Fe_xO containing materials in Hisarna Slag and hot metal

TATA STEEL

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28th February 2023

Introduction – HIsarna Technology

- 20% without CCS
- 80% with CCS

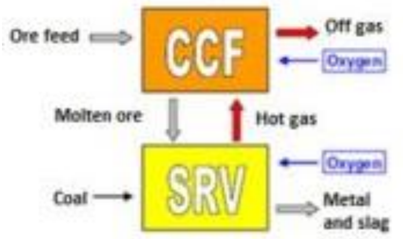
CO2 Emission

- Advance furnace technology improves the quality of steel.
- More use of scrap steel.
- Full Zinc recovery

Quality

- Reduction in cost
- Less complex
- Energy efficient
- Output = 6x

Efficiency



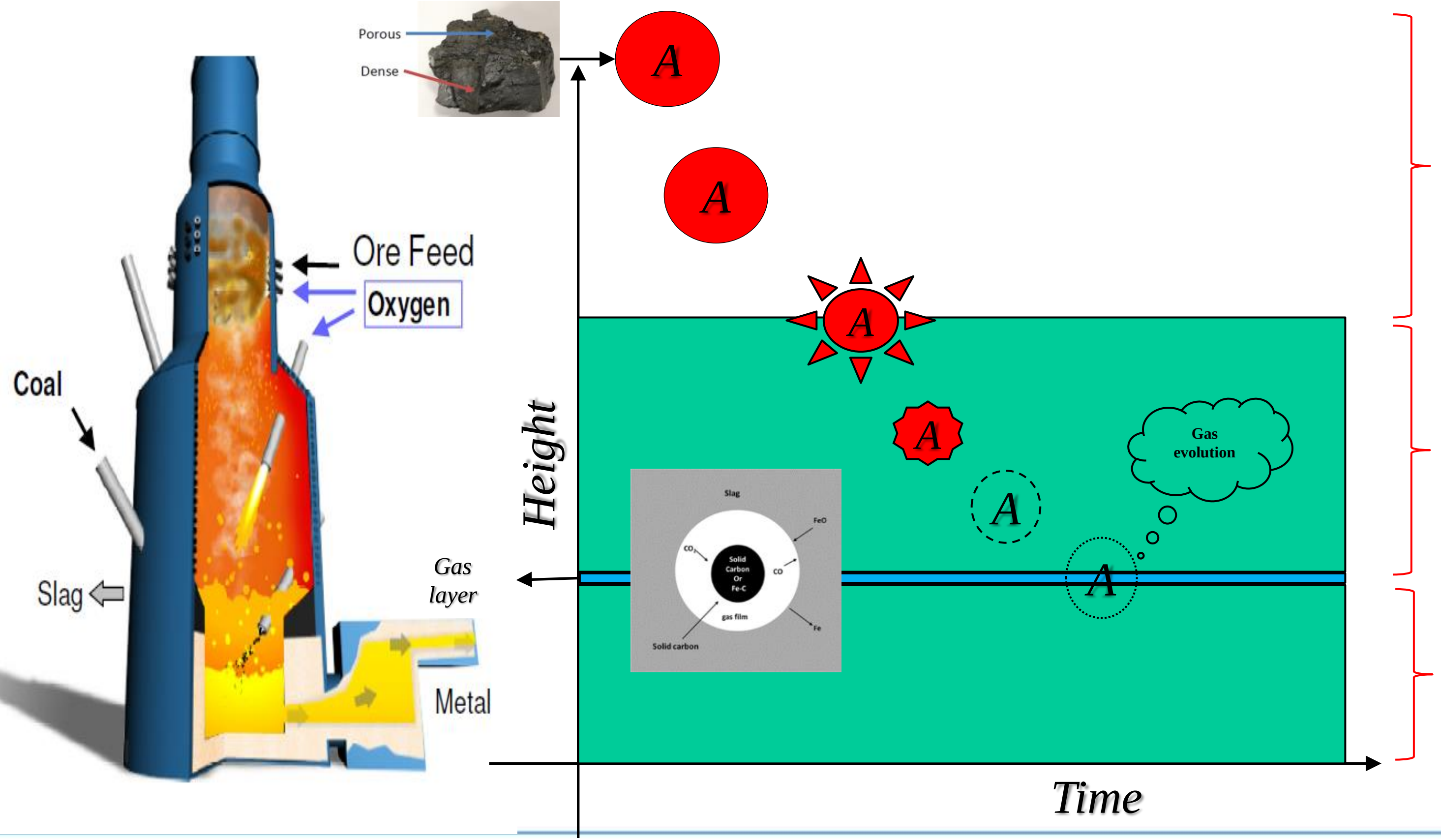
In addition to the reduction of CO_2, other gaseous emissions are also drastically reduced due to the elimination of cokemaking and sintering plants

	Emission Reduction* CO_2	NOx	SOx
HIsarna without CCS	20 %	70 %	60 %
HIsarna with CCS	80 %	90 %	85 %

* Compared to BF/BOS/HRC route

* Meijer, K., Guenther, C. & Dry, R. J. HIsarna Pilot Plant Project. *InSteelCon* 1–5 (2011)

Slag foaming conditions – Heat and Mass transfer Model



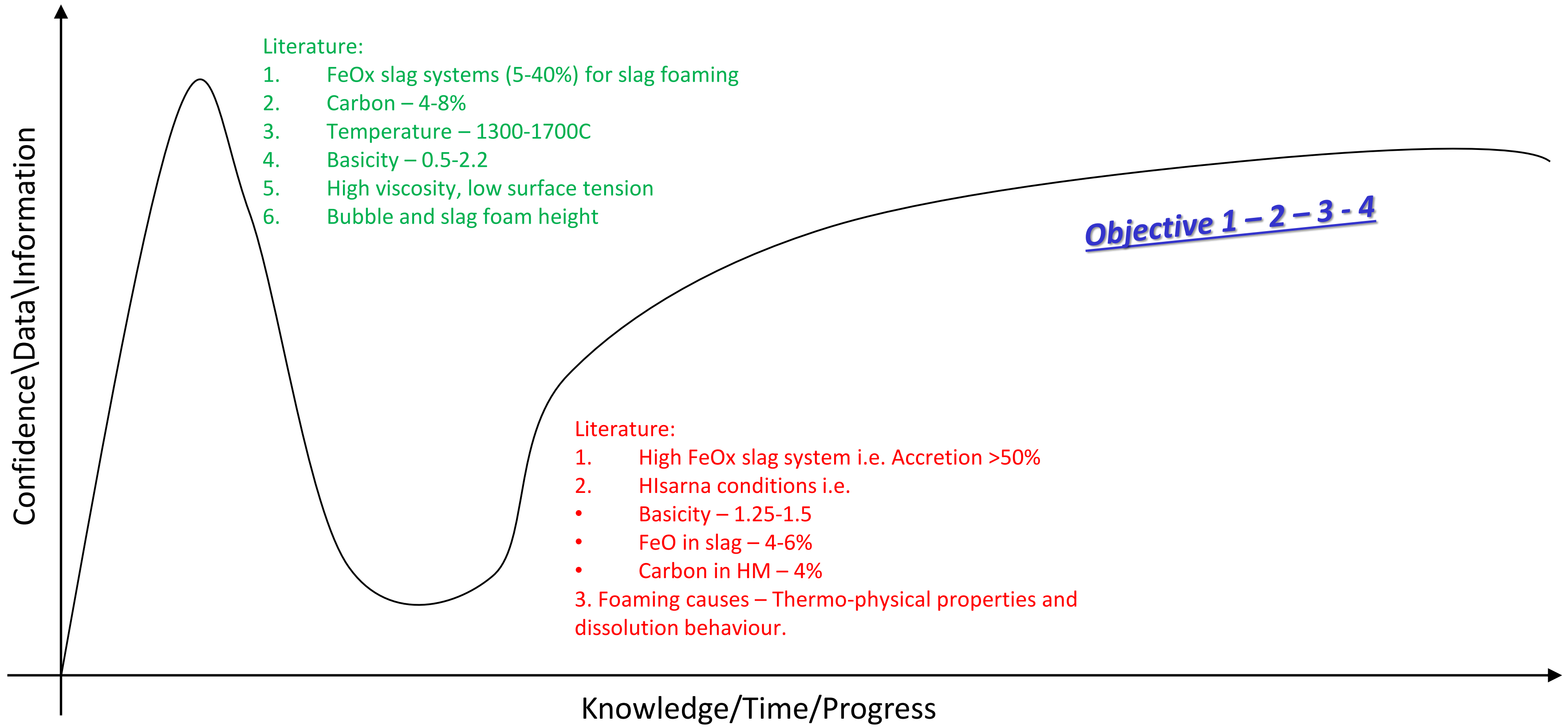
- Belly zone – 1600°C
- Accretion falling from 700°C – 1000°C zone
- PE, KE known of an assumed shape and size of accretion.
- Density, specific heat known

- Slag layer – 1450°C to 1500°C
- Viscosity, density, specific heat known
- Surface tension and buoyancy to be calculated.
- Heat transfer model (From slag into Accretion – Static model) using COMSOL

- HM layer – 1500°C to 1550°C
- Viscosity, density, specific heat known
- Surface tension and buoyancy to be calculated.
- Heat transfer model (From slag into Accretion – Static model) using COMSOL

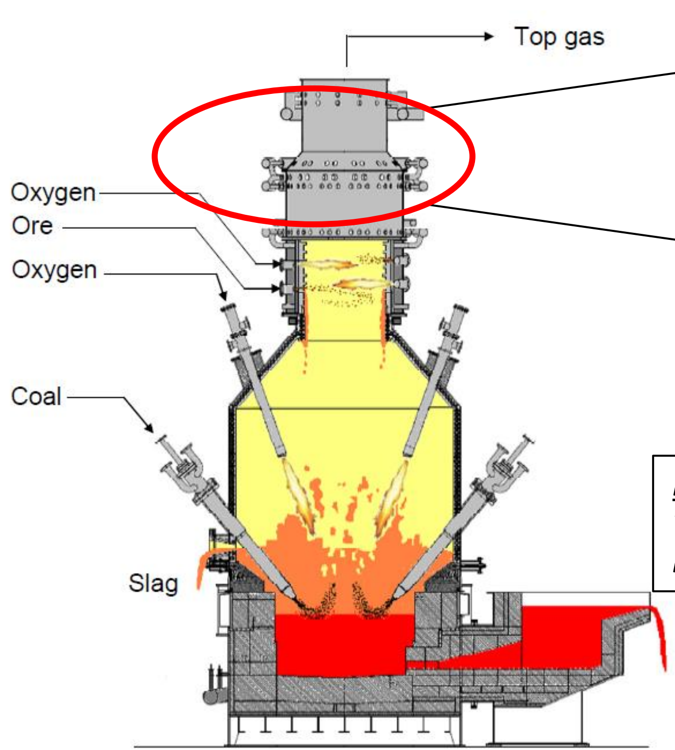
* Ab, L. *HIsarna Experimental Campaigns B and C*. vol. 9424 (2013).
* Khasraw, D., Yan, Z., Hage, J.L.T. *et al.* Reduction of FeO in Molten Slag by Solid Carbonaceous Materials for HIsarna Alternative Ironmaking Process. *Metall Mater Trans B* **53**, 3246–3261 (2022).

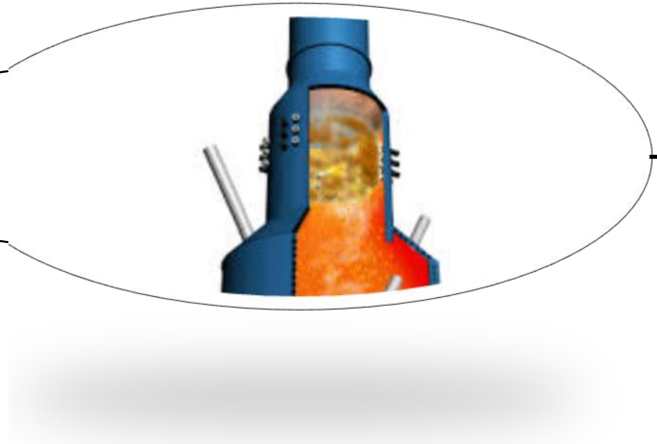
Dunning Kruger Effect – Knowledge gap



* Jouhari, A. K., Galgali, R. K., Chattopadhyay, P., Gupta, R. C. & Ray, H. S. Kinetics of iron oxide reduction in molten slag. *Scand. J. Metall.* **30**, 14–20 (2001).
* Zhu, T. X., Coley, K. S. & Irons, G. A. Progress in slag foaming in metallurgical processes. *Metall. Mater. Trans. B Process Metall. Mater. Process. Sci.* **43**, 751–757 (2012).
* Yi, S. H. & Rhee, C. H. Effects of additives on the foaming behavior of the FeO-SiO2 based slag. *Steel Res.* **68**, 429–433 (1997).

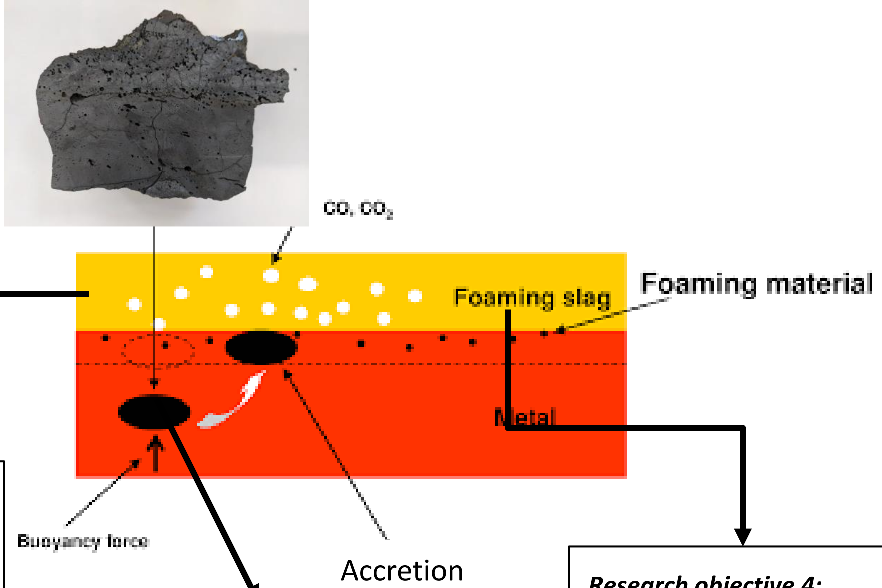
HIsarna challenges and research idea





Research Objective 1:
To study the properties of Accretion (metal oxide compound) formed during HIsarna Fe reduction process

Project aim and HIsarna conditions



Research Objective 2:

To study the Fe_xO containing material dissolution mechanism and reaction rate in HIsarna slag

Research Objective 3:

To study the Fe_xO containing material reaction mechanism in Fe-C melt

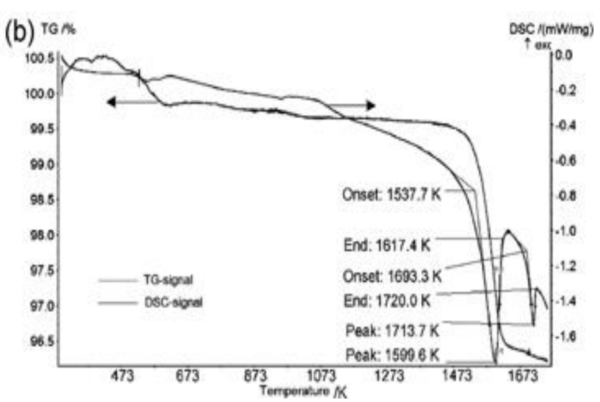
Research objective 4:

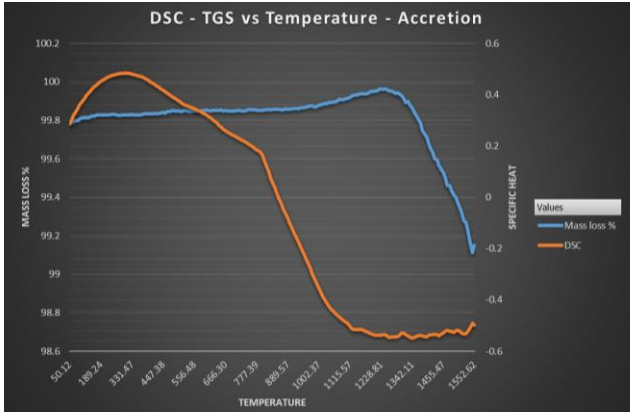
Study the factors affecting and reaction mechanisms for sudden foaming in HIsarna slag

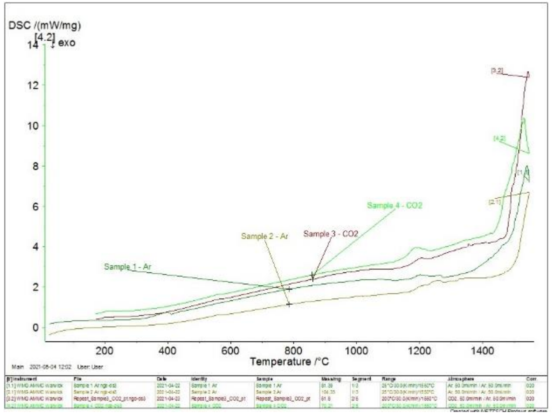
HIsarna conditions:

- Slag composition – CaO+SiO2+Al2O3+MnO+MgO+FeO
- FeO – 4-6% (initial high and accretions falling into the SRV)
- Carbon in melt – 4-5%
- CO2+H2O+N2+CO – Gases evolved
- Presence of Zn, Ti, P in the slag
- Temperature range – 1500°C
- Accretions build-up and sudden/uncontrolled slag foaming

Analysis of TGA\DSC Curves – Iron ore vs Accretion





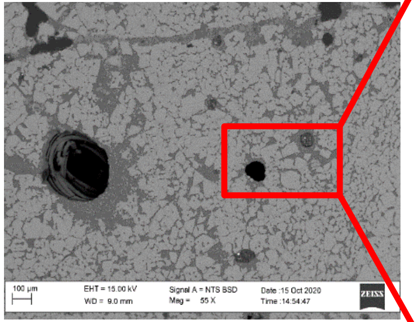


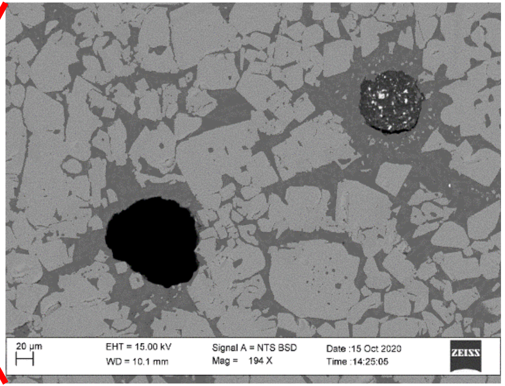
Temperature	Element	Observation	Reason
200-400	Goethite	Endothermic peaks(flat and double peaks)	Dehydration – Mass lass. Size distribution of Goethite crystals and rearrangements.
>700<850-950	Hematite	Sharp endothermic peak	Phase transformation to Magnetite – Thermal reduction of hematite
>950<1350-1500~	Magnetite	Sharp exothermic curve	Phase transformation from Magnetite to ferric iron – Melting/reduction

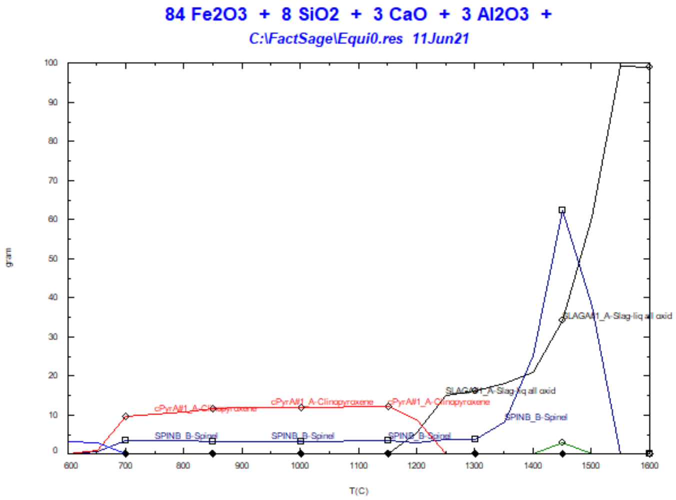
- Limiting oxygen index – higher the value, better the flaming combustion of the material.
- Due to decomposition of certain elements (endothermic) larger surface area is exposed for adsorption
- In exothermic curve, adsorption capability will be higher along the pores and increased surface area.

* Jouhari, A. K., Galgali, R. K., Chattopadhyay, P., Gupta, R. C. & Ray, H. S. Kinetics of iron oxide reduction in molten slag. *Scand. J. Metall.* **30**, 14–20 (2001).
* Qu, Yingxia & Yang, Yongxiang & Zou, Zongshu & Zeilstra, Christiaan & Meijer, Koen & Boom, Rob. (2014). Thermal Decomposition Behaviour of Fine Iron Ore Particles. ISIJ International. 54. 2196-2205. 10.2355/isijinternational.54.2196.

Characteristics of Accretion



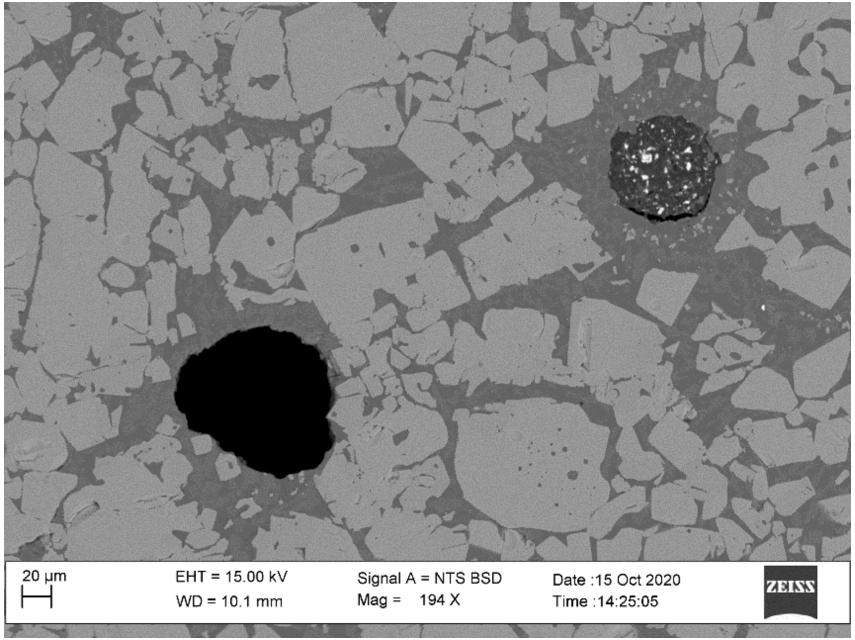


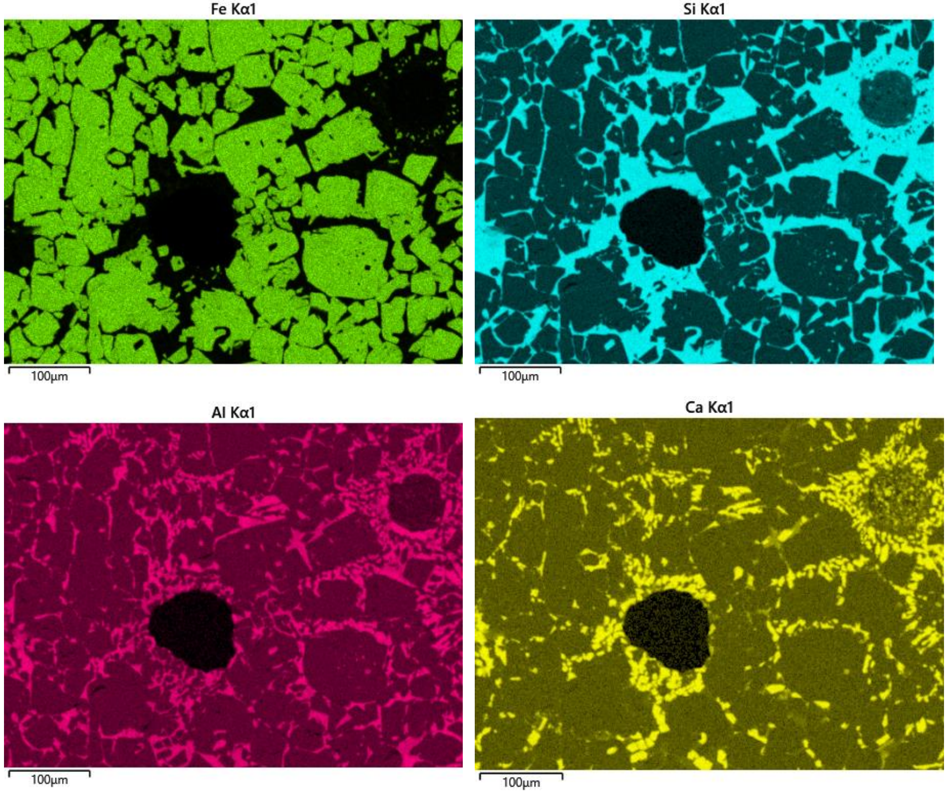


Elements	FeOx	SiO_2	Al_2O_3	CaO	MgO	MnO	TiO_2
Quantity	84.5%	8%	2.5%	3%	1%	0.5%	0.5%

- The Factsage model for Accretion shows the formation of slag(l) phases after 1150°C and complete liquid phases post 1500°C.

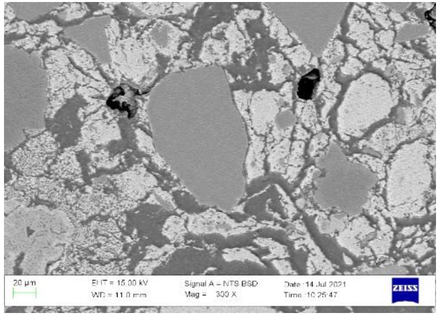
SEM EDS Analysis – Original Accretion



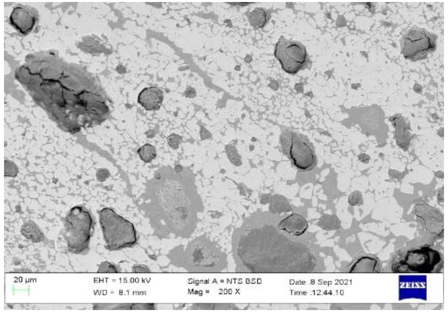


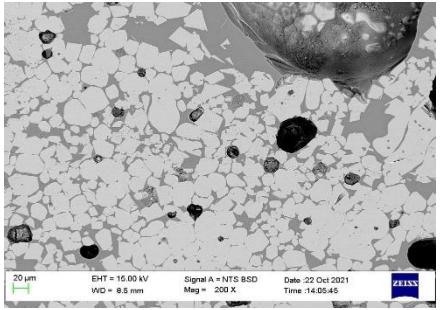
SEM EDS Analysis – Synthetic Accretion

3 hours

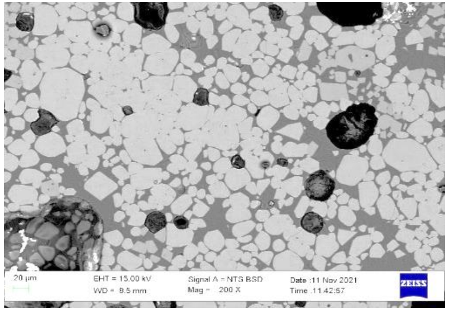


6 hours



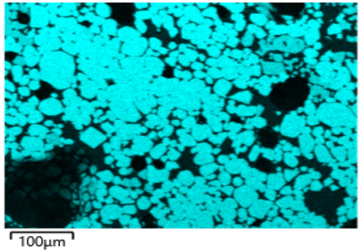


12 hours

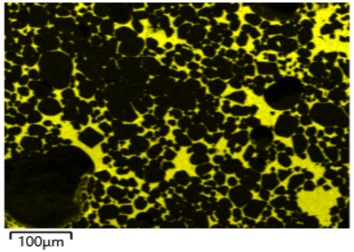


24 hours

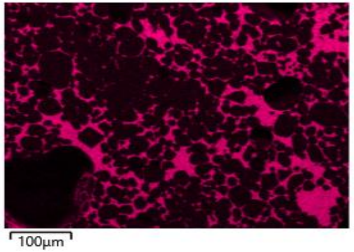
Fe Kα1



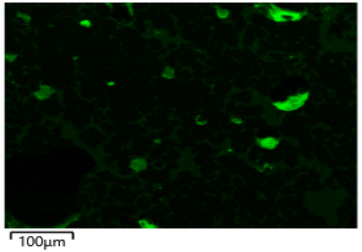
Si Kα1



Ca Kα1



Al Kα1



Equipment:
Muffle Furnace
Pelleting die and press

Parameter:
Temperature – 1150/1200/1250°C
Time – 3/6/12/24 hours
Heating rate – 5°C/min
Cooling rate – 3°C/min
Atmosphere - Air

Slag-Accretion dissolution – Experimental method

Slag+Crucible

- Measure 20g of HIsarna slag.
- Add the slag powders into the crucible and mix/stir it well.

Melting of slag

- Place the crucible in the Muffle furnace.
- Heat the slag to 1500°C at 50°C/min.
- Isothermal for 30minutes to attain homogeneity.

Accretion

- Prepare synthetic accretion using the proven sintering method. (24 hours)
- Measure and prepare a 10g/5g/2.5g accretion sample for dissolution.

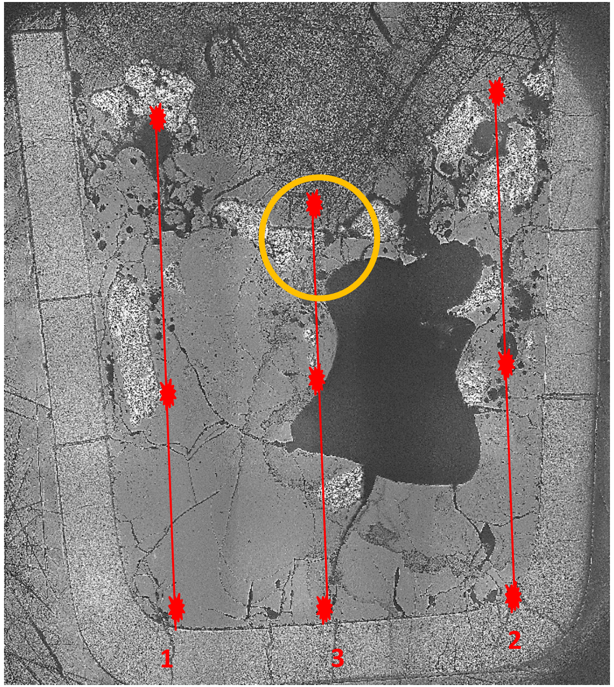
Dissolution

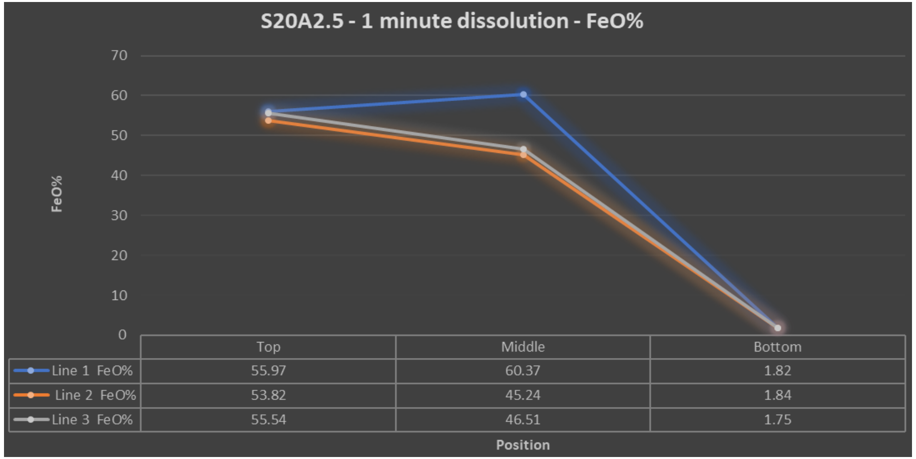
- Open the furnace and drop the accretion into the molten slag.
- After 1/3/5 minute take the crucible out and quench in water.
- Iterate

Characterization

- Cut the crucible in half to assess the dept of fall/dissolution.
- Sample preparation for SEM.
- Characterize.
- Repeat the same for different accretion samples.

<u>20g Slag – 2.5g Accretion – 1 minute dissolution</u>

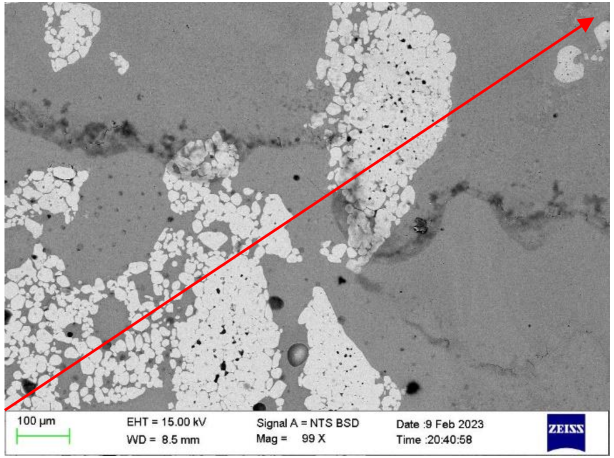




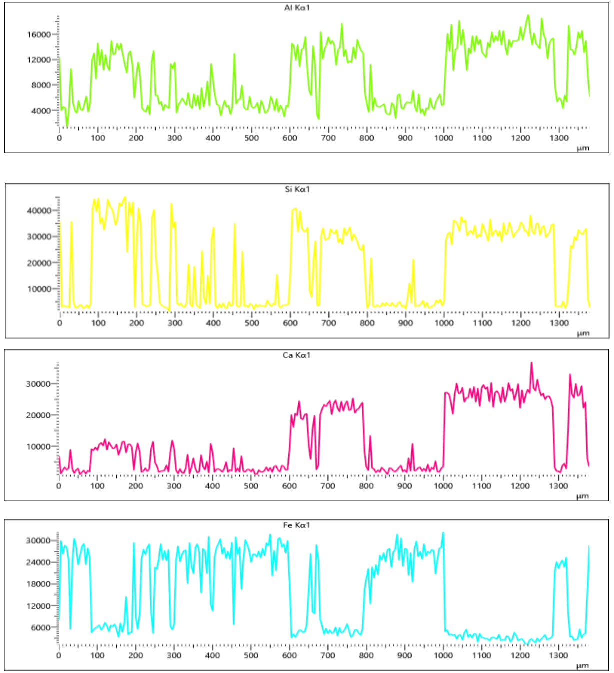
	Top	Middle	Bottom
Line 1 FeO%	55.97	60.37	1.82
Line 2 FeO%	53.82	45.24	1.84
Line 3 FeO%	55.54	46.51	1.75

- ❖ Accretion disintegrated into fragments i.e. onset of decomposition.
- ❖ FeO% measured on the Accretion-slag boundary layer.
- ❖ No increase in slag FeO% without accretion presence. (See bottom slag composition)

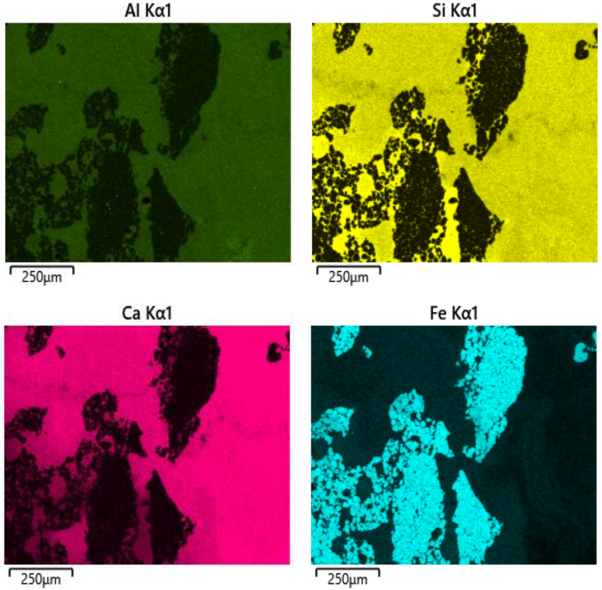
20g Slag – 2.5g Accretion – 1 minute dissolution



SEM Image – 3 - Top

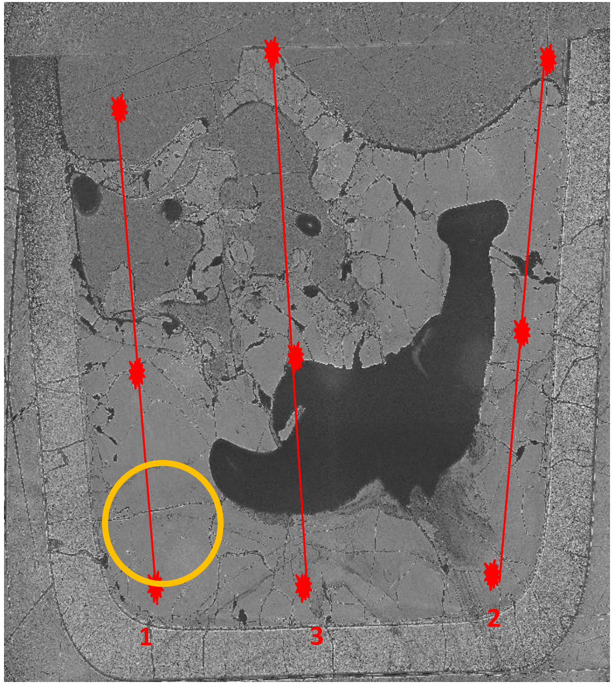


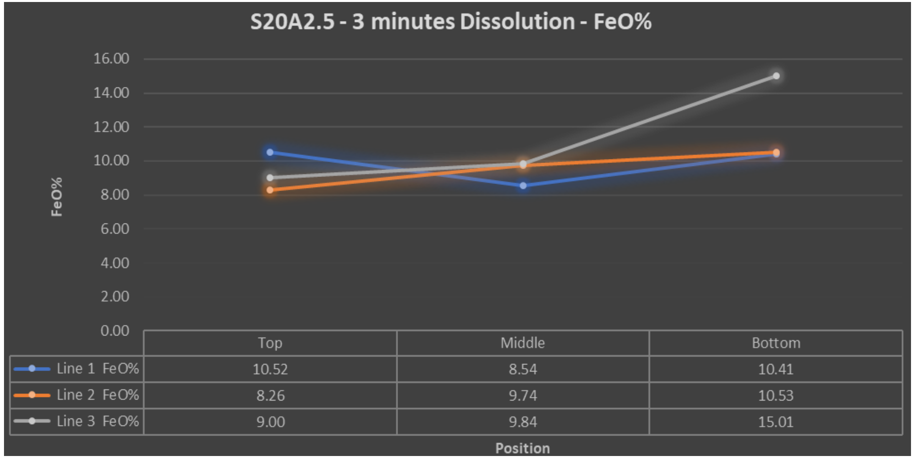
Line scan



EDS Map scan

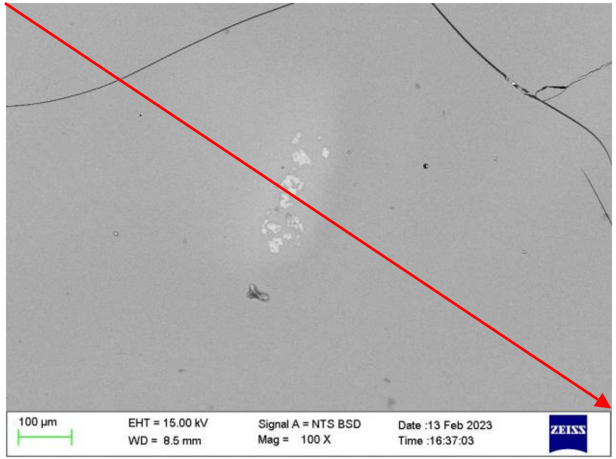
20g Slag – 2.5g Accretion – 3 minute dissolution



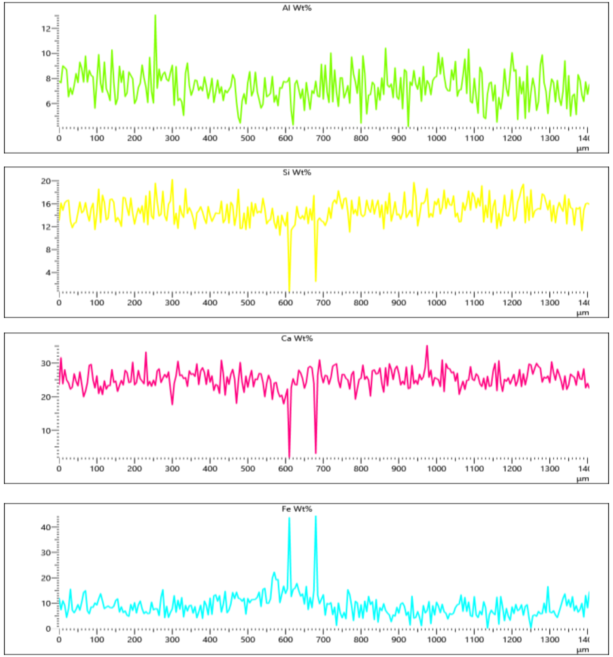


- Accretion disintegrated into fragments and decomposed i.e. onset of dissolution.
- Tiny fragments of accretion is visible under the microscope.
- Increase in slag FeO% across the crucible.

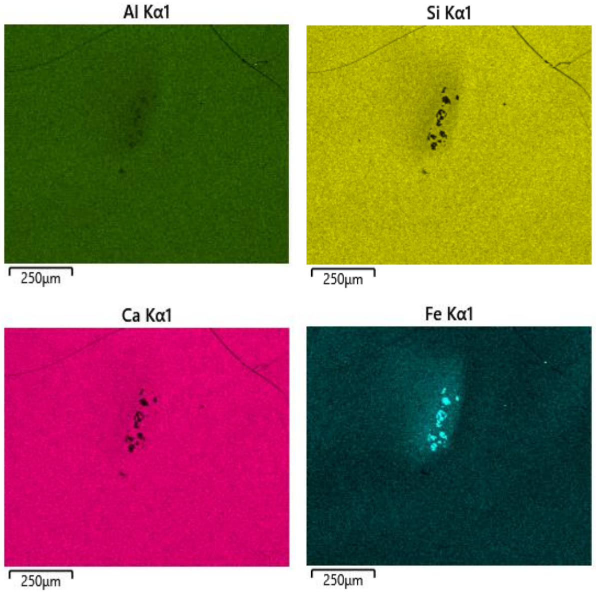
20g Slag – 2.5g Accretion – 3 minutes dissolution



SEM Image – 1 – Bottom Top

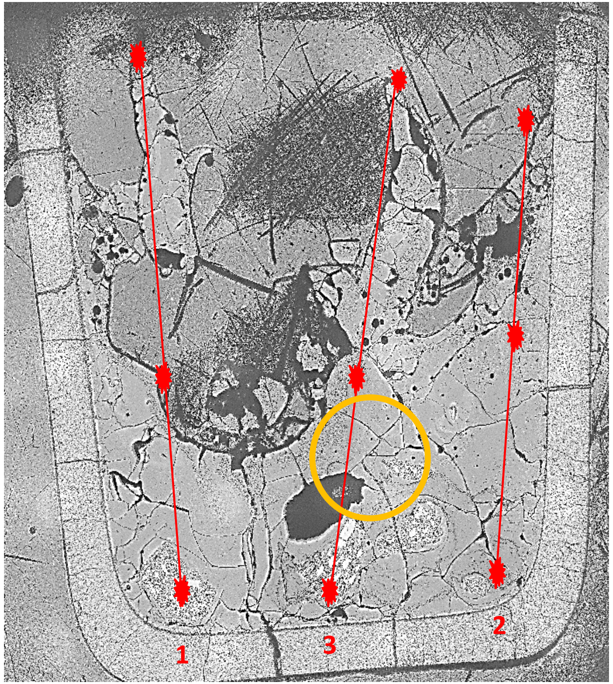


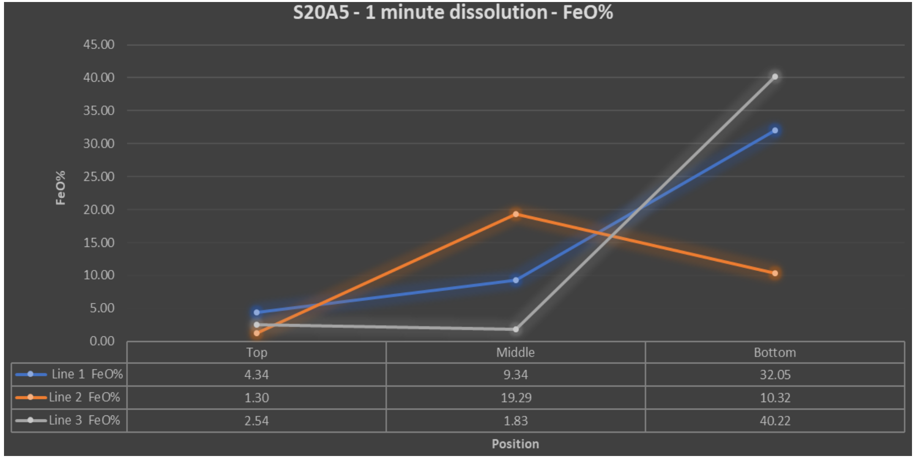
Line scan



EDS Map scan

20g Slag – 5g Accretion – 1 minute dissolution

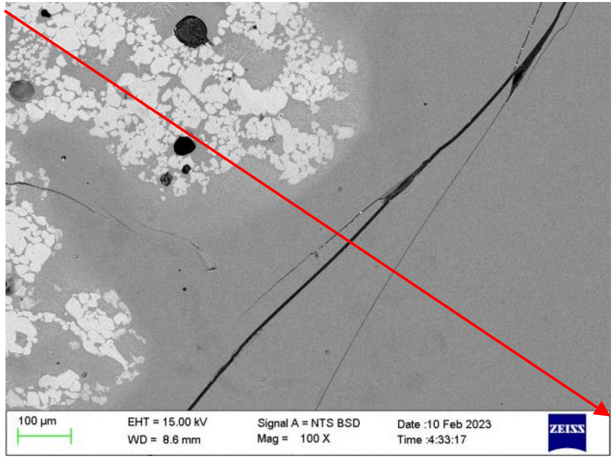




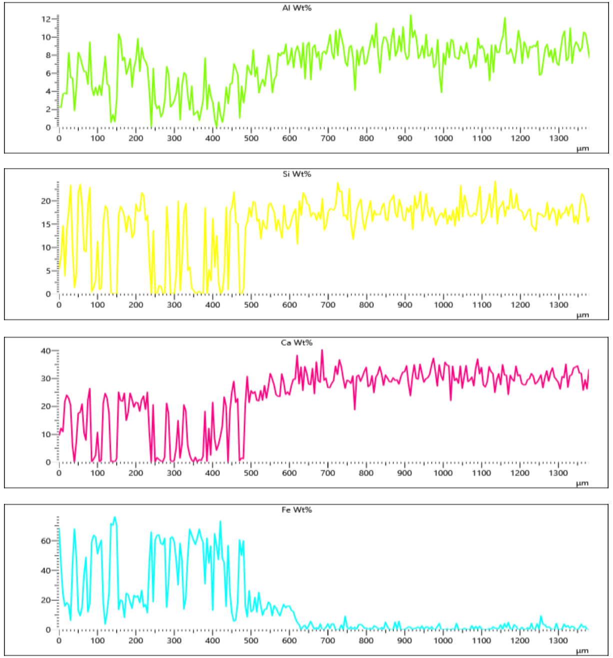
	Top	Middle	Bottom
Line 1 FeO%	4.34	9.34	32.05
Line 2 FeO%	1.30	19.29	10.32
Line 3 FeO%	2.54	1.83	40.22

- Accretion disintegrated into fragments and settled at the bottom of crucible.
- Tiny fragments of accretion is visible under the microscope in top and middle part of the crucible.
- Increase in slag FeO% around the accretion in the slag but low FeO% away from the accretion.

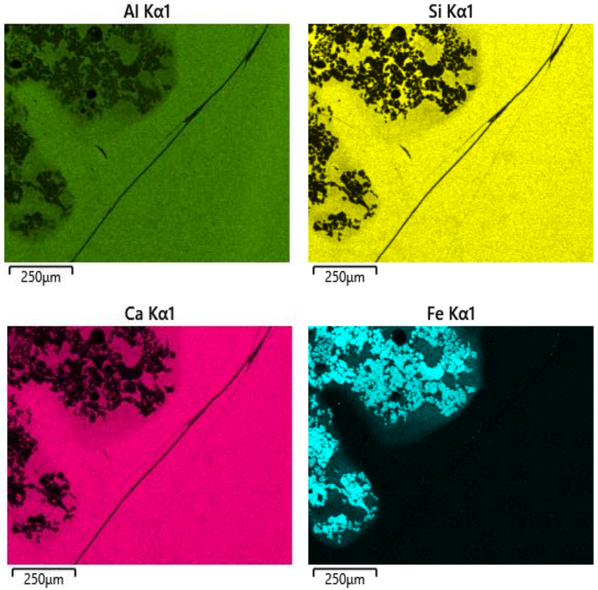
20g Slag – 5g Accretion – 1 minute dissolution



SEM Image – 3 – Middle Bottom

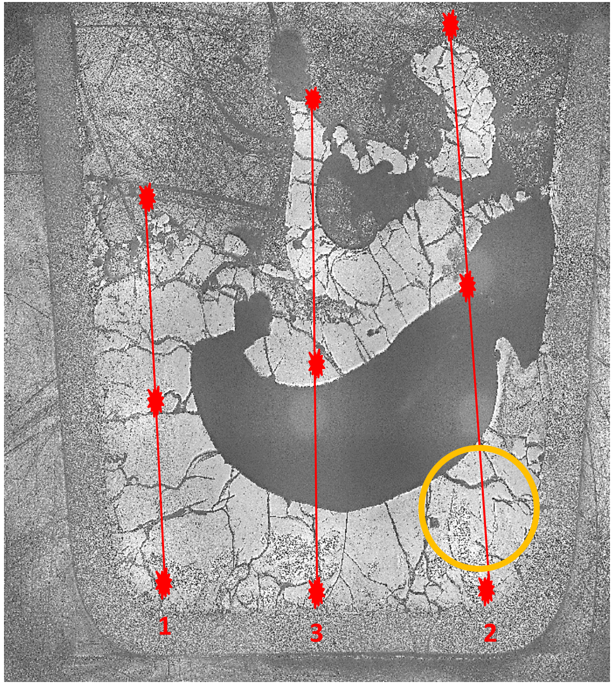


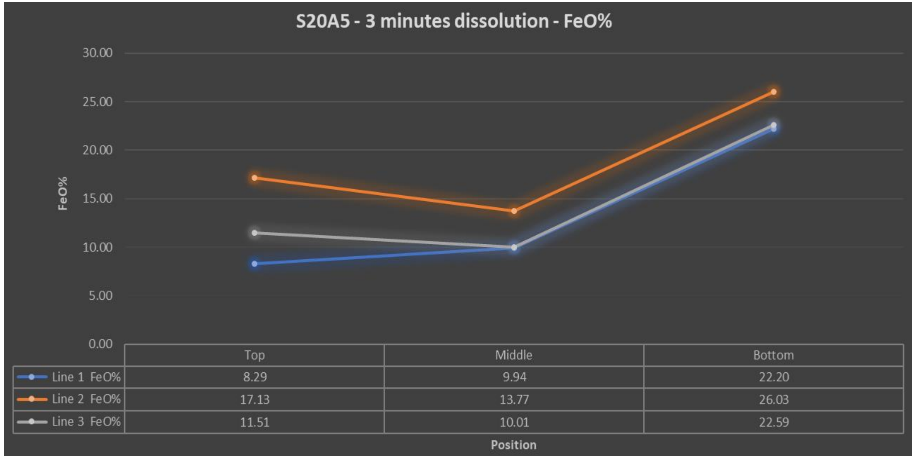
Line scan



EDS Map scan

20g Slag – 5g Accretion – 3 minute dissolution

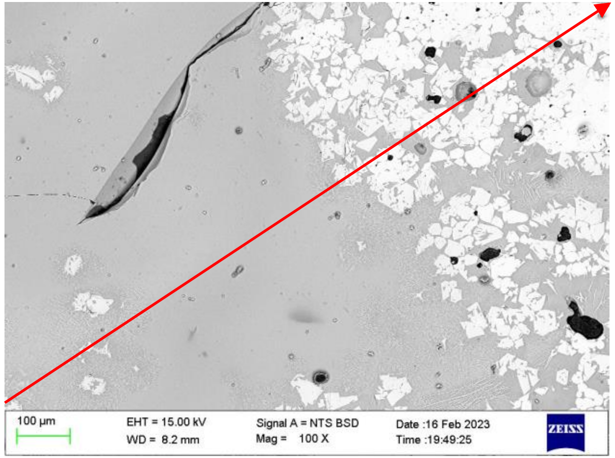




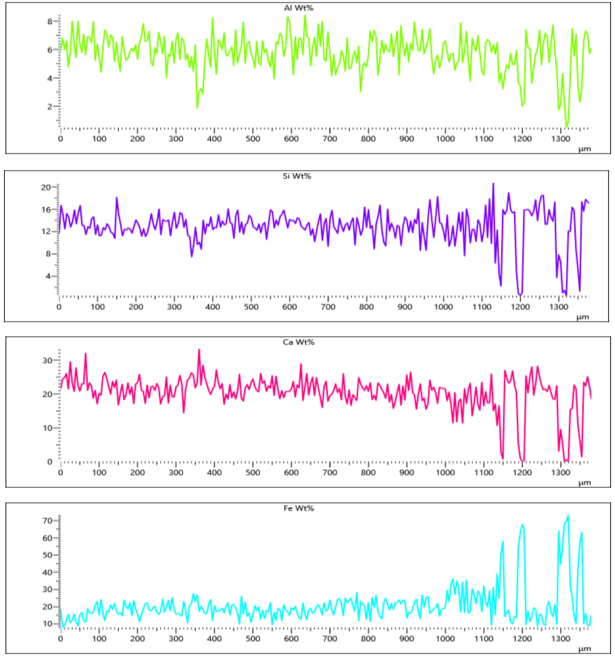
	Top	Middle	Bottom
Line 1 FeO%	8.29	9.94	22.20
Line 2 FeO%	17.13	13.77	26.03
Line 3 FeO%	11.51	10.01	22.59

- Accretion disintegrated into fragments and settled in the middle and the bottom of the crucible.
- Tiny fragments of accretion is visible under the microscope across different locations in the crucible.
- Increase in slag FeO% around the accretion in the slag but low FeO% away from the accretion.

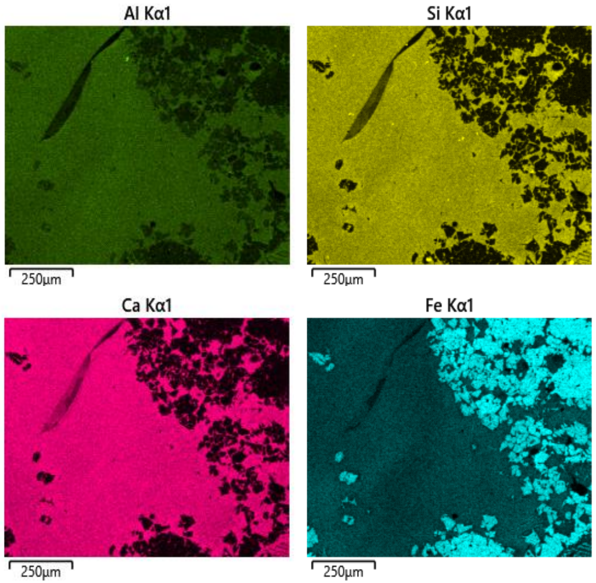
20g Slag – 5g Accretion – 3 minute dissolution



SEM Image – 2 – Bottom

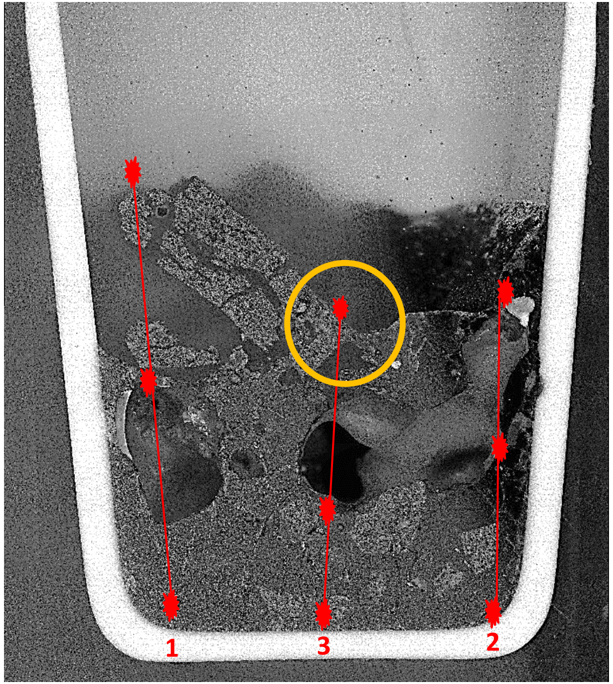


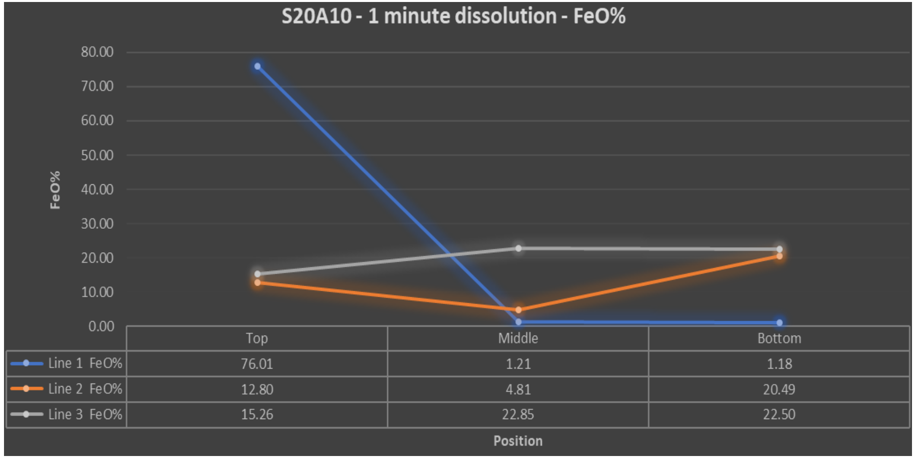
Line scan



EDS Map scan

20g Slag – 10g Accretion – 1 minute dissolution

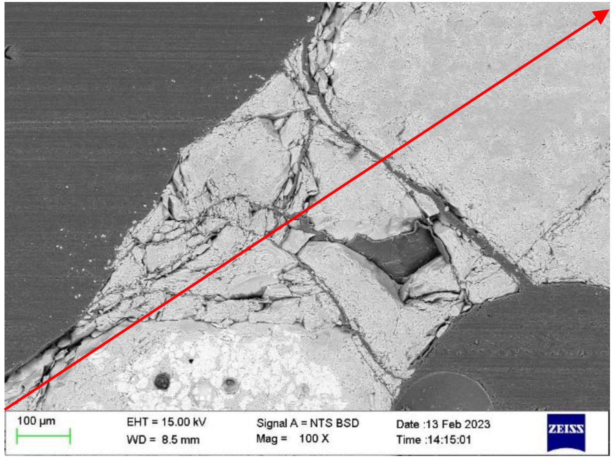




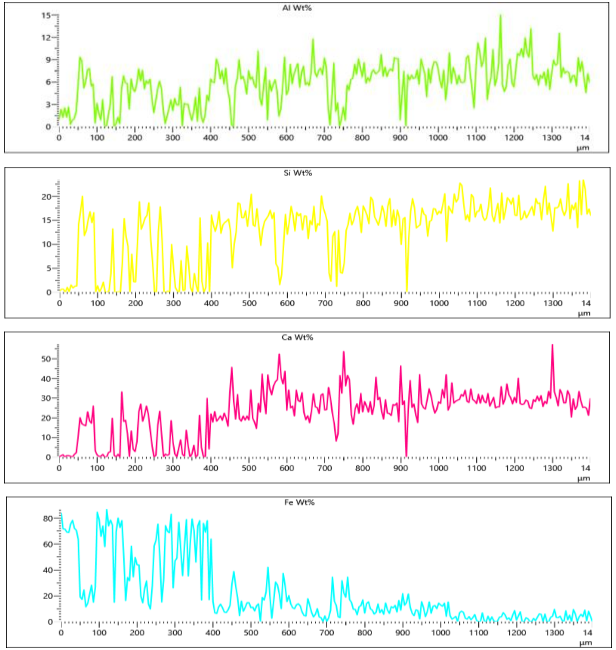
	Top	Middle	Bottom
Line 1 FeO%	76.01	1.21	1.18
Line 2 FeO%	12.80	4.81	20.49
Line 3 FeO%	15.26	22.85	22.50

- Big chunk of accretion deformed and slightly disintegrated into fragments which are settled at the bottom.
- Large area of accretion remains inert at the top.
- Increase in slag FeO% around the accretion in the slag but low FeO% away from the accretion.(Line 1)

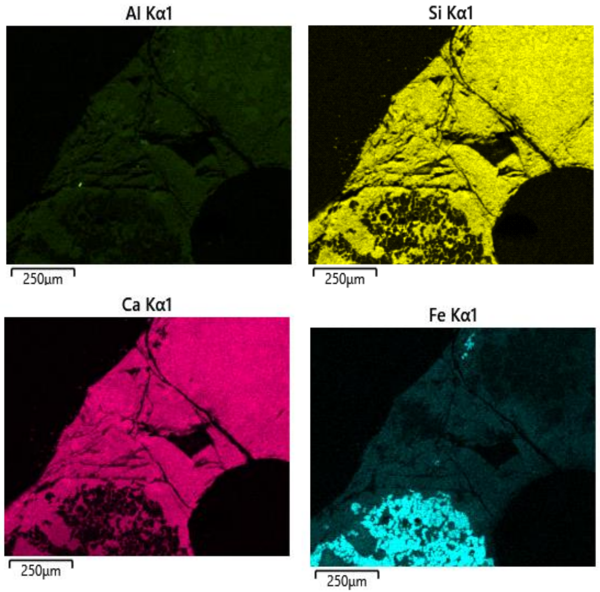
20g Slag – 10g Accretion – 1 minute dissolution



SEM Image – 3 – Top

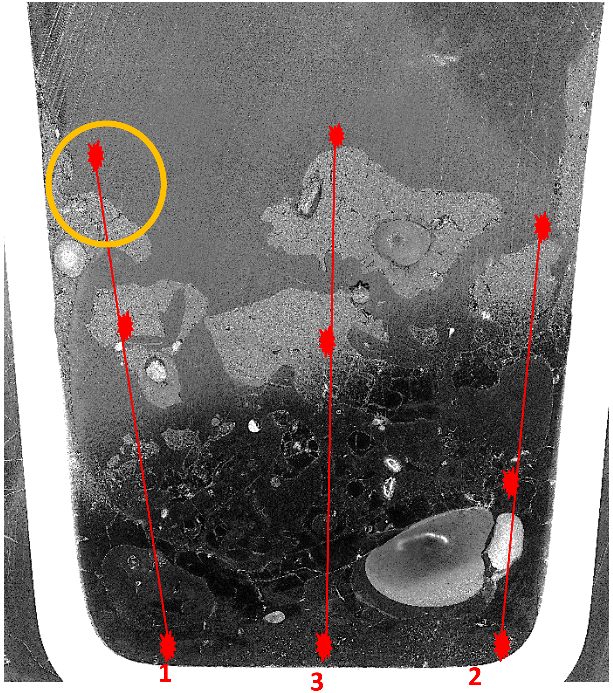


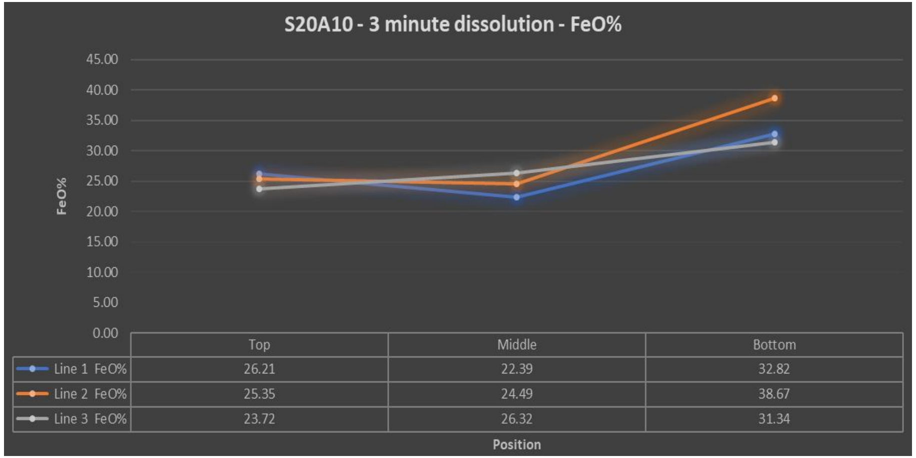
Line scan



EDS Map scan

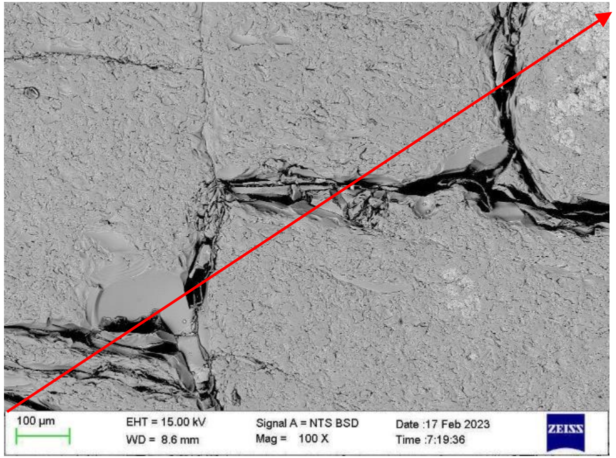
20g Slag – 10g Accretion – 3 minute dissolution



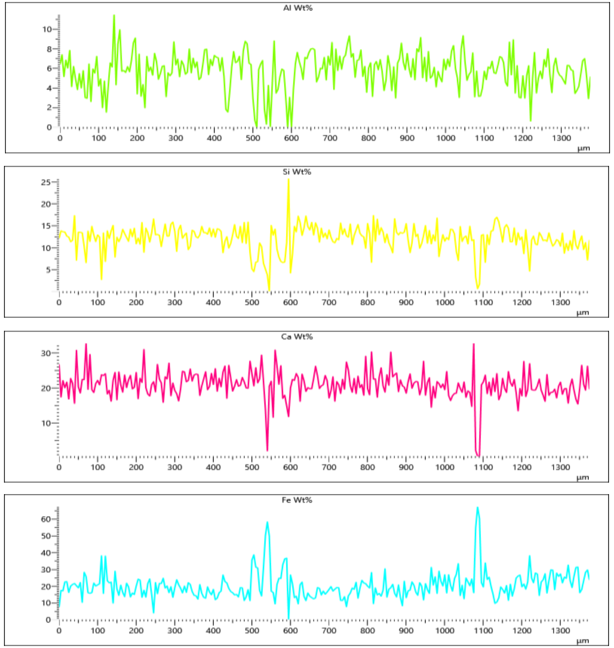


- Accretion disintegrated into fragments and scattered across the crucible and visible under the microscope.
- Increase in slag FeO% around the accretion in the slag and increasing FeO% away from the accretion.

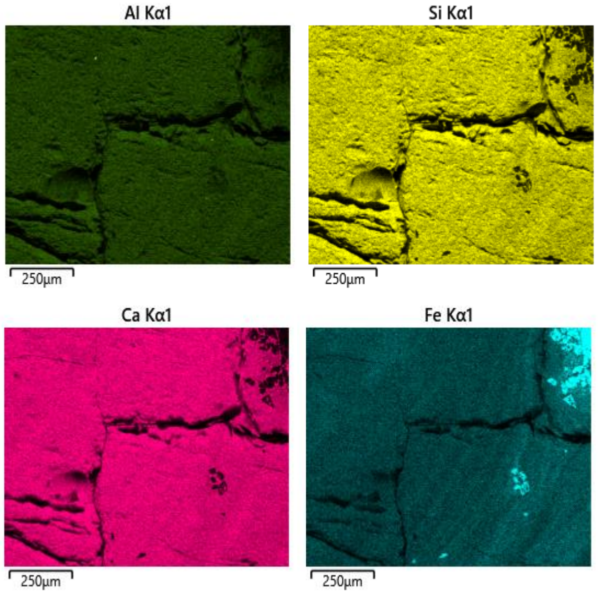
20g Slag – 10g Accretion – 3 minutes dissolution



SEM Image – 1 – Top

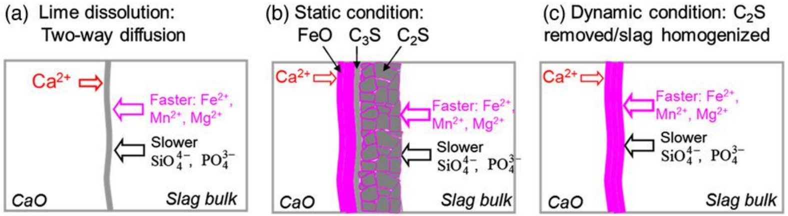


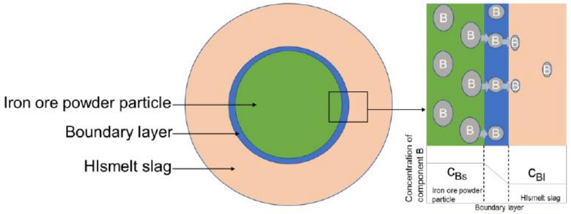
Line scan

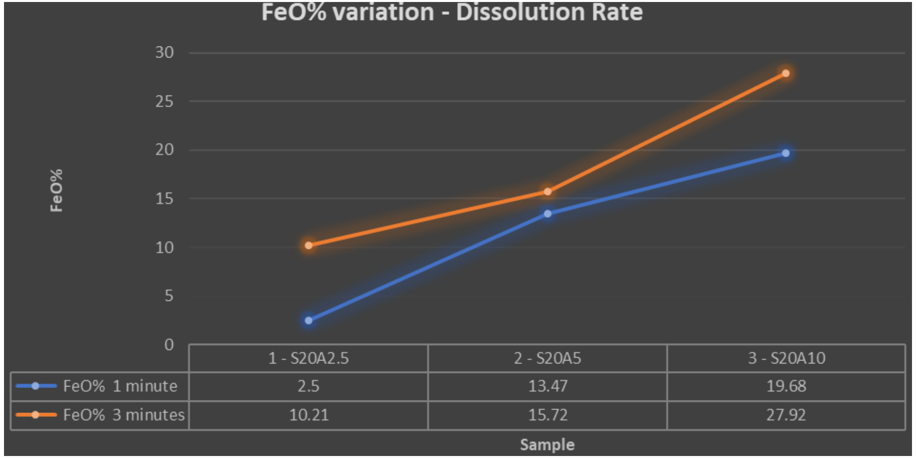


EDS Map scan

Analysis - Discussion







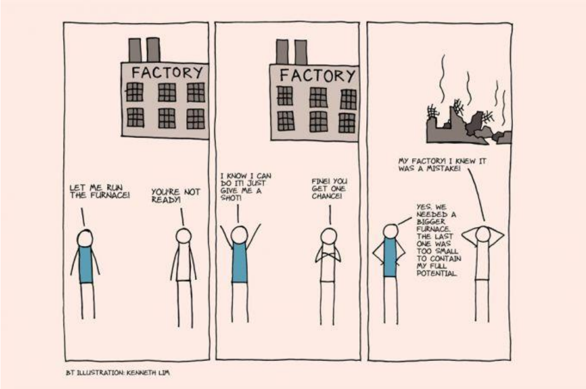
- ❖ FeO% in the slag increases as the dissolution time increases.
- ❖ FeO% in the slag increases rapidly as the weight of the accretion reduces and dissolution time increases.
- ❖ Dissolution rate is the controlling parameter for accretion-slag reaction.
- ❖ Decomposition of accretion is initial parameter before dissolution sets in.
- ❖ Spinel/slag dissolution is a 2 – way process, forming Di/tri – Calcium silicate along the boundary.

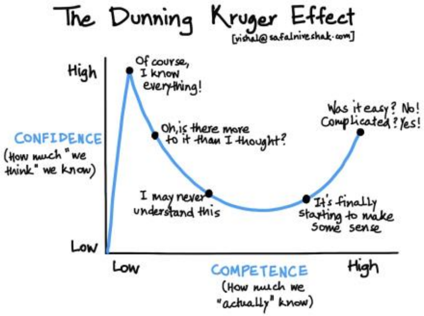
* J. Pang, Z. Wang, J. Zhang, S. Zhang, P. Hu and J. Rao: *ISIJ Int.*, (2022), https://doi.org/10.2355/isijinternational.ISIJINT-2022-261

Observation:

- The chemical composition of **accretion is similar to that of the iron ore** used in the Hisarna furnace.
- The absence of volatile elements like **gases, water, goethite and kaolinite**, skips the endothermic reactions of the accretions.
- Since the accretion has higher percentage of Hematite, curves are mainly exothermic in behaviour due to the reduction of hematite to magnetite to wüstite, releasing energy – transforming phases.
- The physical appearance of Tata steel's accretion was brittle, porous and hard. (difficult to break by hand)
- The 24 hours sintered accretion in Muffle furnace exhibits similar microstructure properties with more porosity with that of the industrial sample.
- 1 minute dissolution (drop method) throws light on penetration behaviour of the slag into the porous matrix of accretions.
- Fe% in the slag varied from ~1-28% within 3 minutes of the dissolution - EDS analysis.

Pun intended and who are we…..?





Thanks You
For Your Attention

Do u have

Any
QUESTION?