Valorisation of zinc containing residues

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H2 FOR GREEN STEEL 3rd INTERNATIONAL CONFERENCE meets A CIRCULAR ECONOMY DRIVEN BY THE EUROPEAN STEEL

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PRIMETALS TECHNOLOGIES

Project key facts

Consortium – 7 partners from 4 EU countries

- Acciaierie d'Italia, Italy
- Centre de Recherches Métallurgiques, Belgium
- Linde, Sweden
- ORI Martin, Italy
- RINA Consulting Centro Sviluppo Materiali, Italy
- Swerim (coordinator), Sweden
- Tata Steel Nederland Technology, Netherlands

Duration: 42 months | Budget: 3.0 MEuro | Call topic: RFCS-02-2022-RPJ

Oct. 2023 → 2024 → 2025 → 2026 → Mars 2027

Sensitivity: general

This project has received funding from the Research Fund for Coal and steel (RFCS) under project No. 101112631

Background

The steel industry contributes greatly to the global economy, but at the same time generates significant amounts of emissions and residues.

Most residues are valorised by internal recycling or external use. Still significant values in terms of carbon and iron units can't be recycled – the zinc content in the dust and sludge is too high, but too low to be sent to zinc producers.

Zinc content of EAF dust will be lower in the future as DRI/HBI partly or fully will replace steel scrap.

Dust and sludge that is not recycled, causes both raw materials losses and additional costs for preparing safe deposits and conducting landfilling.

Objectives

Project objectives: to develop technologies securing high raw material efficiency by extracting more from existing raw material streams, enabling the reuse of low-zinc residues produced in the current and future steelmaking routes.

- Improved material efficiency
- Less need for landfill
- Improved feed material flexibility

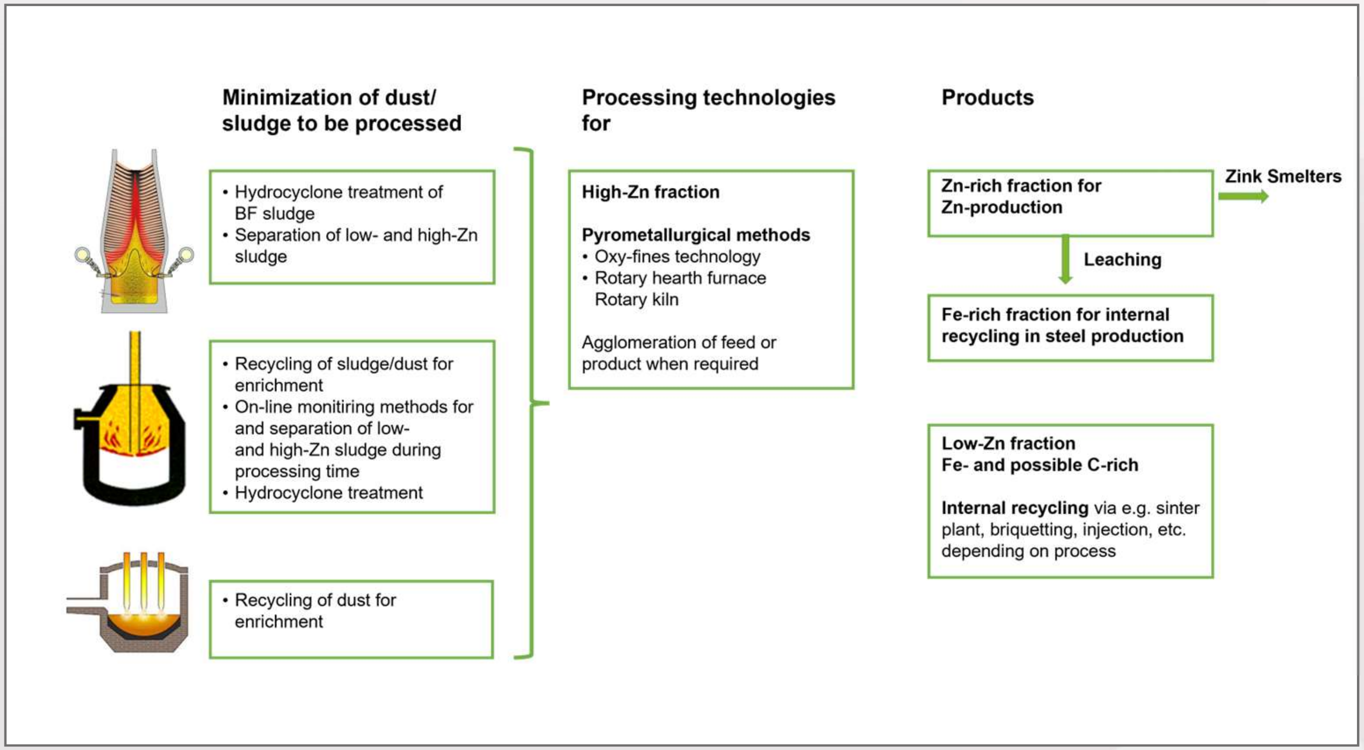
Development of technology for separation and treatment of low-zinc iron and steelmaking residues.

Improved knowledge regarding zinc containing residues and upgraded secondary materials from the iron- and steelmaking industry to realize valorisation of valuable contents in steelmaking or externally.

Evaluation of concepts for increased material efficiency/ reduced landfill by utilization of developed technologies.

Overall project concept

- Physical, chemical and mineralogical characterization of residues samples from steel production for selection of treatment method
- Development of technologies, with relatively low starting TRL, for separation and treatment of low-zinc residues from steel plants
- Evaluate Zn-rich and Fe-rich fractions for industrial use
- Design the most sustainable recycling routes for different residues regarding environmental impact, energy consumption and CO_2 emissions, as well as cost-effectiveness.



Characterisation of residues for hydrocyclone treatment

First part of the project is focused on the collection and characterisation of BF, EAF dust and BF, BOF sludge:

This initial part of the project is useful to describe; **Amounts, characteristics, and the variation of dust and sludges generated in BF, BOF and EAF**, but also useful as input for the sizing of all treatment processes considered for the recovery of Zinc

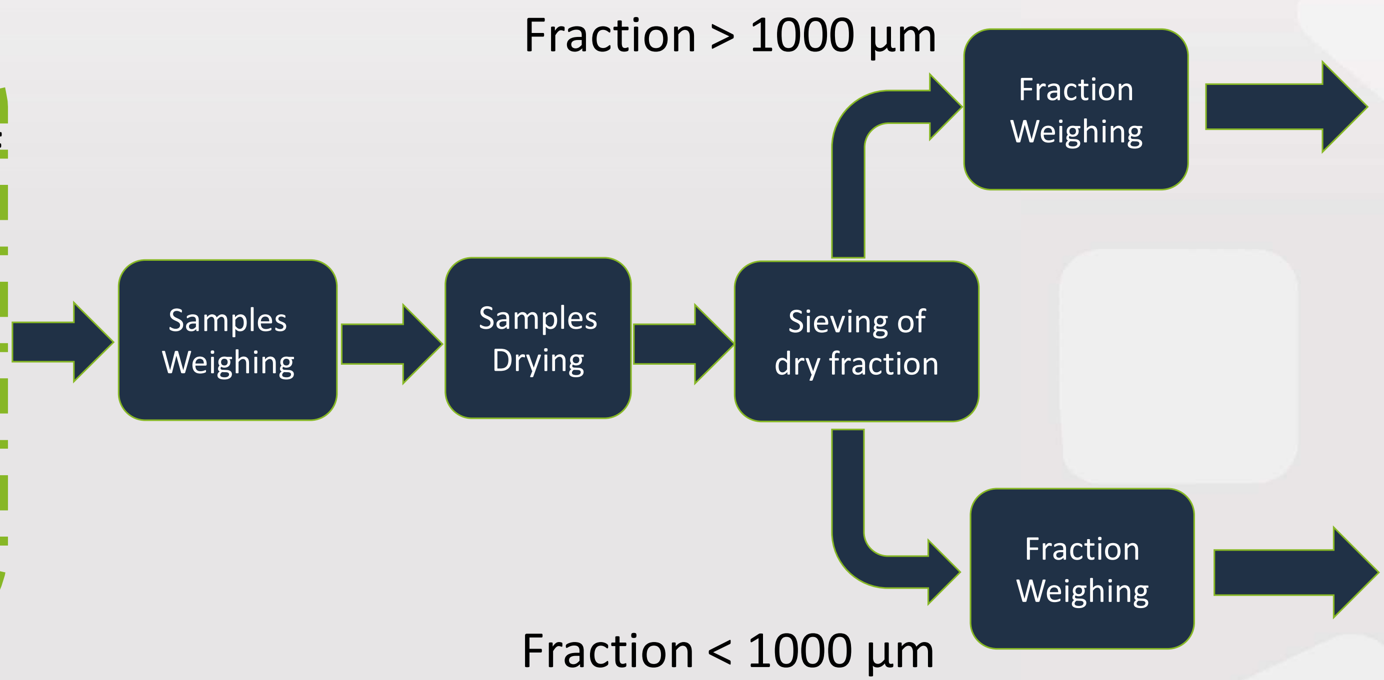
Physical and chemical characterization will be based on the determination of:

1. Grain size curve of BF, BOF Sludge and BF, EAF Dust ,
2. Particles distribution
3. Moisture content
4. Zinc content correlated as a function of the grain size,
5. Chemical composition of each fraction,
6. Check if zinc is found in the form of oxide or ferrite

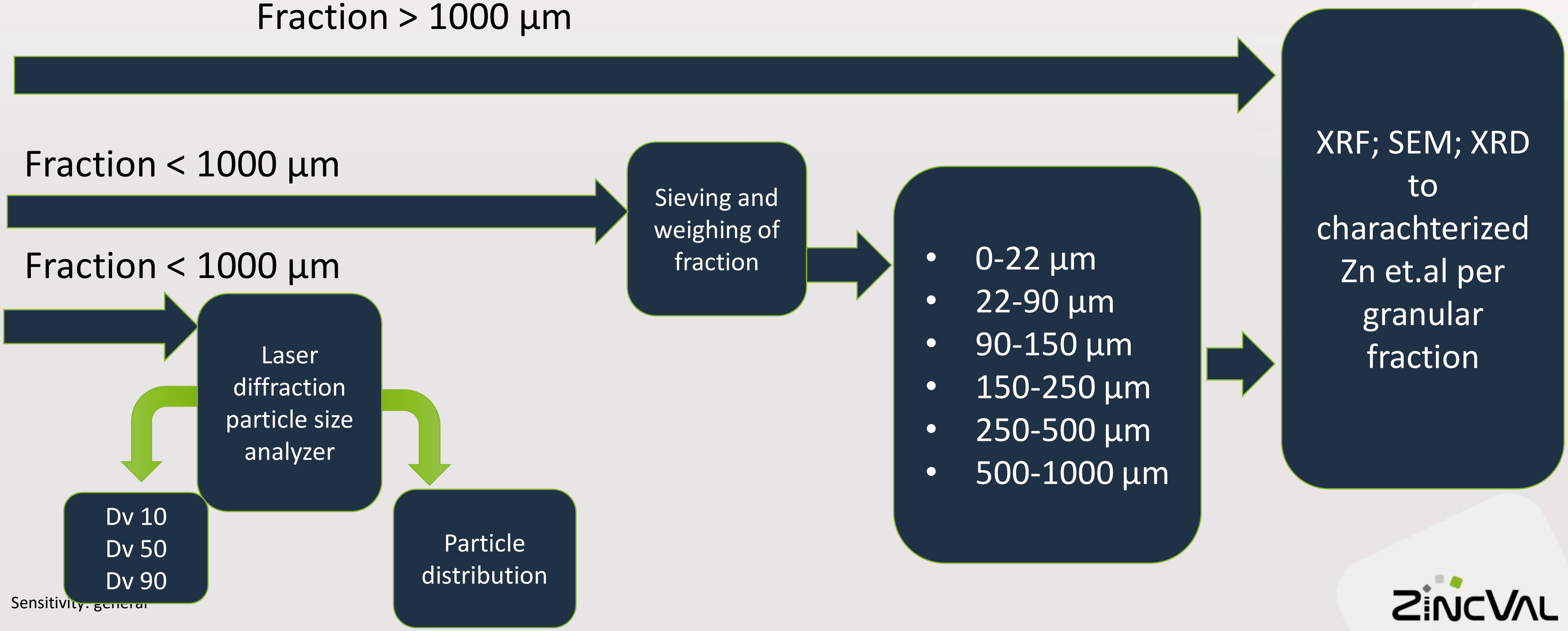
Characterisation of residues for hydrocyclone treatment

Collection and labbeling of samples of BF and BOF Sludge and BF end EAF dust

Sample	Type	Label
BF1	*SLU*	F
BF2	*SUL*	E
BF3	*SLU*	A
BF4	*SLU*	D
BOF	*SLU*	B
BF Dust	*DUS*	C
EAF	*DUS*	G



Characterisation of residues for hydrocyclone treatment



Characterisation of residues for hydrocyclone treatment

Sample Description	Acronym	type	Zn content (% m/m)
Blast Furnace sludge (0 – 22 µm)	BFS	SOLID	2.90
Blast Furnace sludge (22 – 90 µm)	BFS	SOLID	1.75
Blast Furnace sludge (90 – 150 µm)	BFS	SOLID	1.67
Blast Furnace sludge (> 150µm)	BFS	SOLID	2.21
Blast Furnace Dust	BFD	SOLID	0.15
Basic Oxygen Furnace Sludge	BOFS	SOLID	0.25
Pre-separated Steelmaking Sludge - Grit	GRIT	SOLID	0.04
Steelmaking Sludge dehydrated	BOFD	SOLID	0.36

The table lists the materials identified and characterized because they are considered potentially interesting for the project. The fundamental criterion for selection is their zinc content. In fact, for the scope of the project, BFS were taken into consideration because their high zinc content compromises their recycling possibilities, so it makes sense to experiment with systems to remove it. On the other hand, the other materials analyzed have a zinc content too low to justify a removal treatment and can already be reused in the steel industry.
The chemical compositions were obtained with the XRF and LECO methodologies, while the grain size separation and distribution were obtained using sieves and balances.

Characterisation of residues for hydrocyclone treatment

	particle size range	Elements	C	S	Ca	Fe	Zn	Fraction $\%_{m/m}$
BFS	0 - 22 µm	$\%_{m/m}$	28.78	1.18	6.04	45.93	2.90	4.2
	22 - 90 µm	$\%_{m/m}$	37.19	0.94	3.85	45.46	1.75	36.0
	90 - 150 µm	$\%_{m/m}$	51.62	1.26	3.62	32.02	1.67	21.5
	>150 µm	$\%_{m/m}$	42.95	2.53	5.15	35.73	2.21	38.3

The highest zinc content was found in BFS fractions of 0-22 microns and >150 microns, so the experimental treatment will be focused on the industrial separation of these fractions from the rest of the sludge.

BFS samples	DRY density (g/cm^3)	WET density (g/cm^3)
BFS1	1.04	0.98
BF2	0.81	0.85
BF3	0.87	0.83
BF4	0.79	0.88

The sampling of BFS was done in four different points and the values were obtained from the averages of these samples. Furthermore, the difference between the chemical composition of the various grain size ranges was investigated to explore the hydrocyclonic separation as a method of zinc removal. The hydrocyclone in fact separates the particles based on their size and density.

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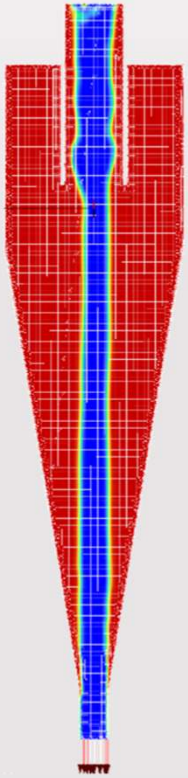
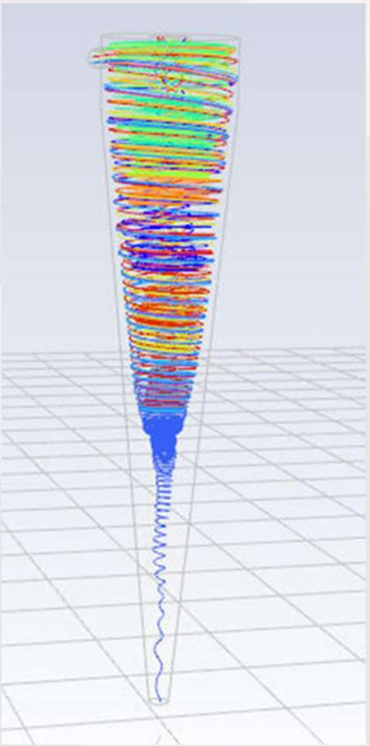
Hydrocyclone - introduction

Design a Hydro-cyclone pilot prototype, using CFD simulation

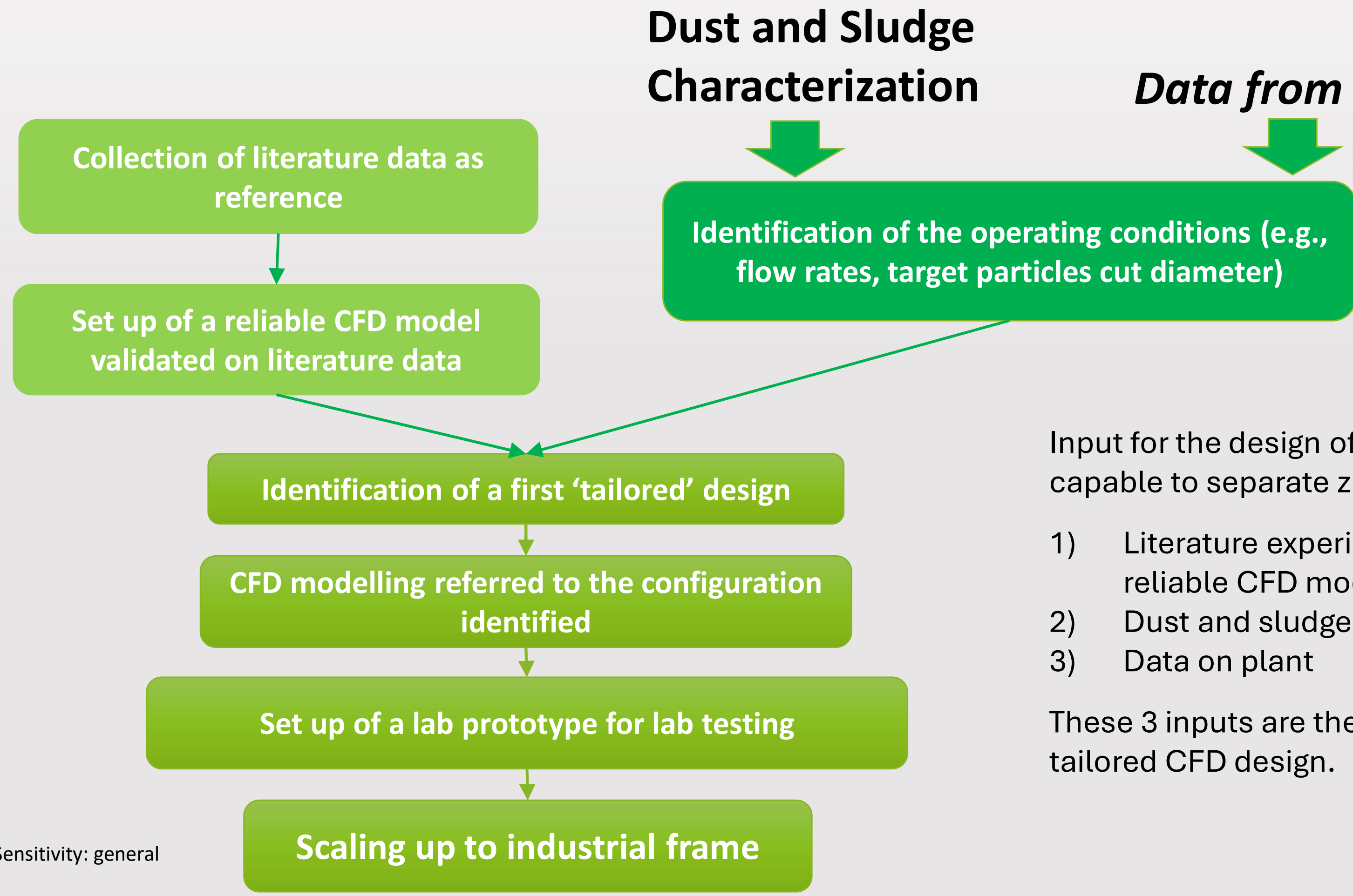
- Hydrocyclone units are used to separate particles dispersed in a fluid via physical phenomena
- ***Efficiency depends on layout and operating conditions, to be identified based on the expected performance***

Efficiency is defined as 'the separation of fraction of particles of a given size due to the force caused by the spinning gas stream in a cyclone.'





Hydrocyclone - Technical Roadmap



Input for the design of CFD model of a hydro-cyclone capable to separate zinc fraction are:

1) Literature experimental data useful to validate a reliable CFD model.
2) Dust and sludge charactherization
3) Data on plant

These 3 inputs are the input for the design of the first tailored CFD design.

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Hydrocyclone - model set – check on turbulence approach/options reliability

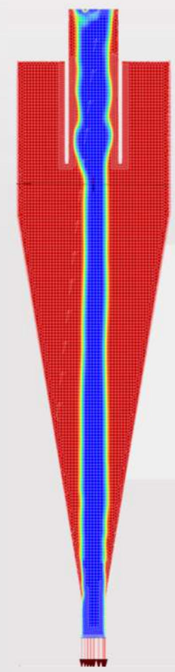
The inputs to build the model are:

1) Mesh
2) Turbulence
3) Particles and how they are present in the fluid (dispersed)

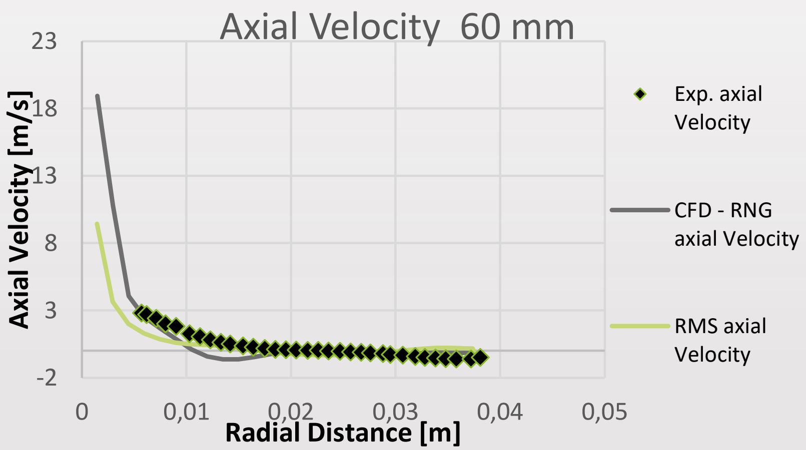
Different kinds of models presented in literature were tested in Ansys-Fluent code to identify the best and reliable design.

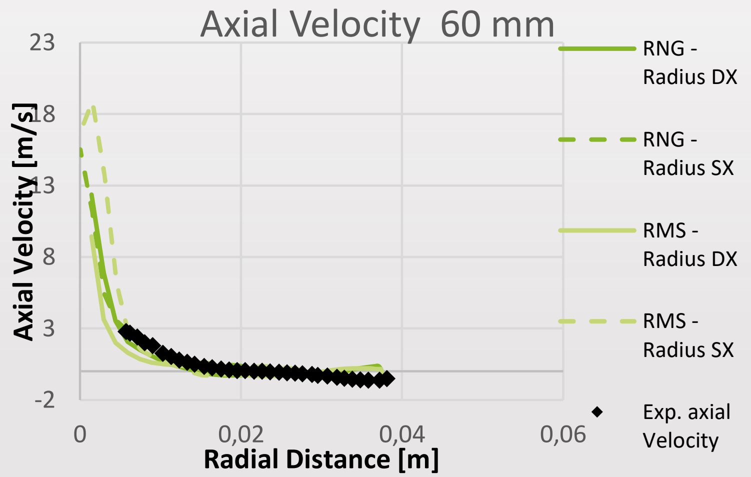
<u>Turbulence Models tested to identify the most reliable in validation</u>:

- K-eps: RNG & wall Functions (2 eq.)
- Reynolds Stress Model (7 eq.)



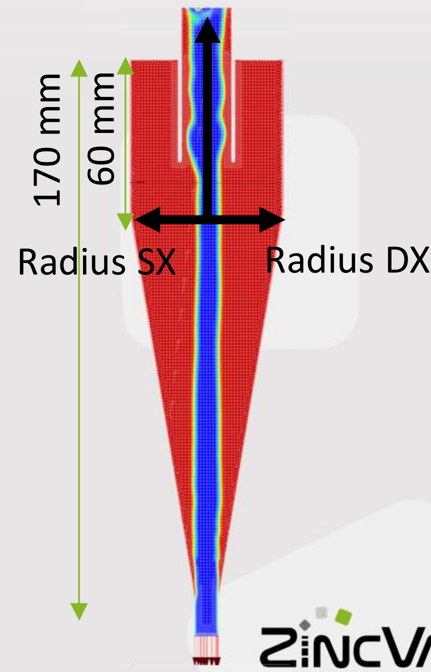
Hydrocyclone - model set – check on turbulence approach/options reliability

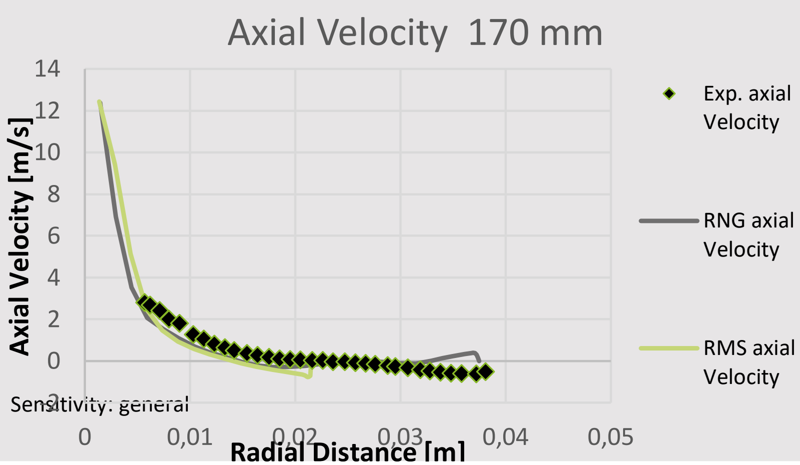


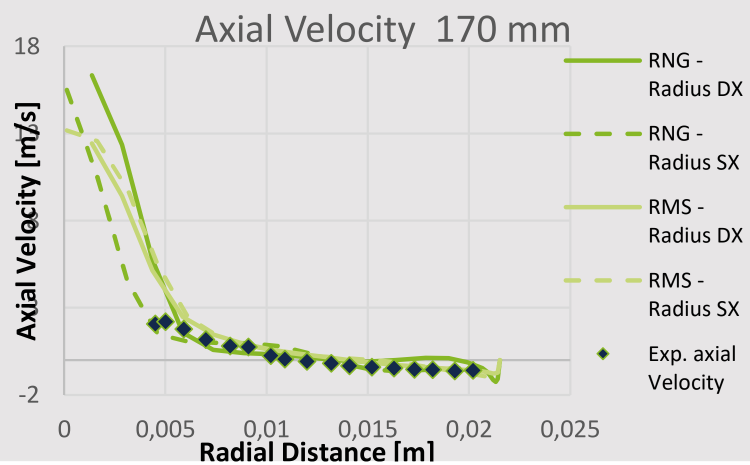


Dots = experimental literature points for validation

RMS preferred also for time calculations issues







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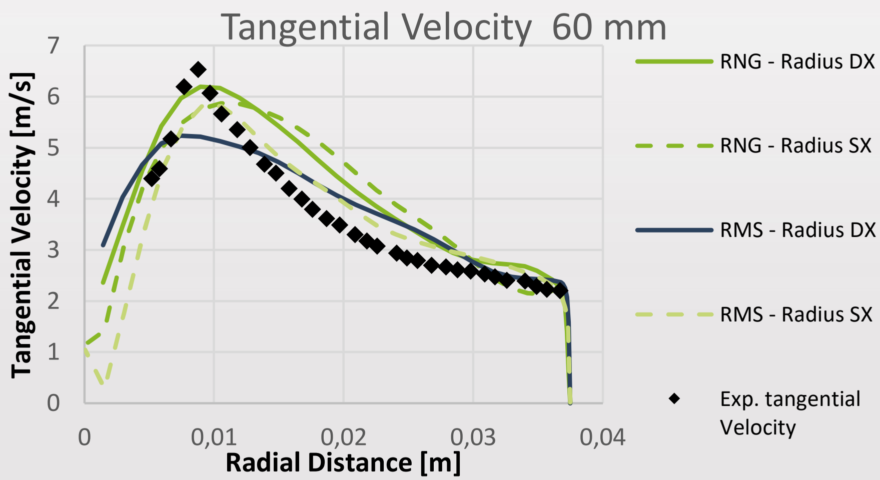
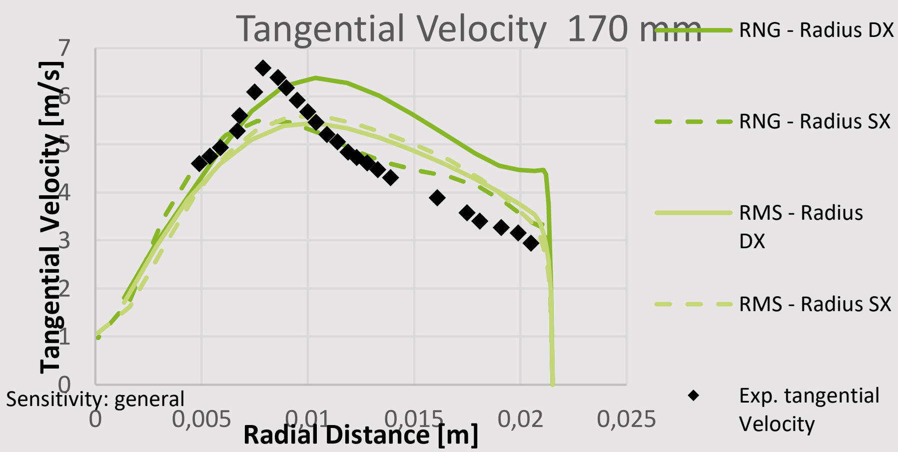
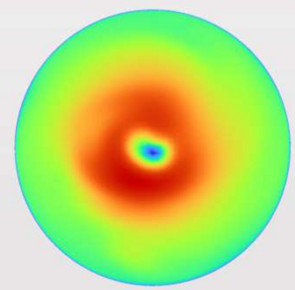
Hydrocyclone - model set – check on turbulence approach/options reliability

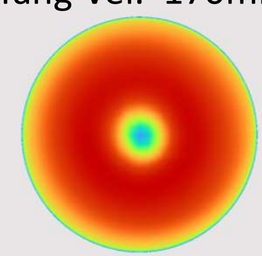




Tang Vel. 60 mm

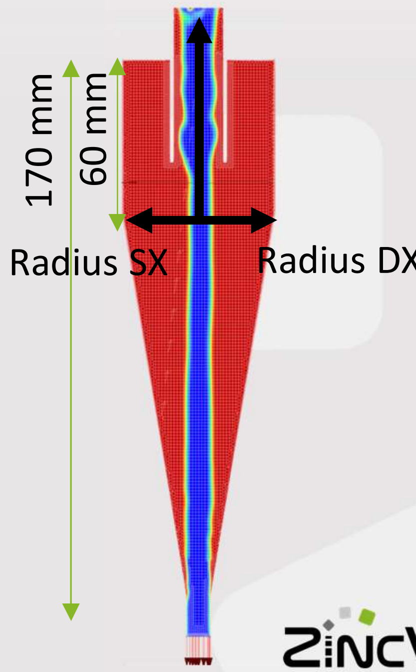


Tang Vel. 170mm



Dots = experimental literature points for validation

RMS preferred also for time calculations issues



Sensitivity: general

Hydrocyclone - Technical Roadmap

Dust and Sludge Characterization

Data from Plant

Collection of literature data as reference

Set up of a reliable CFD model validated on literature data

Identification of the operating conditions (e.g., flow rates, target particles cut diameter)

We are Here !!!

Identification of a first 'tailored' design

CFD modelling referred to the configuration identified

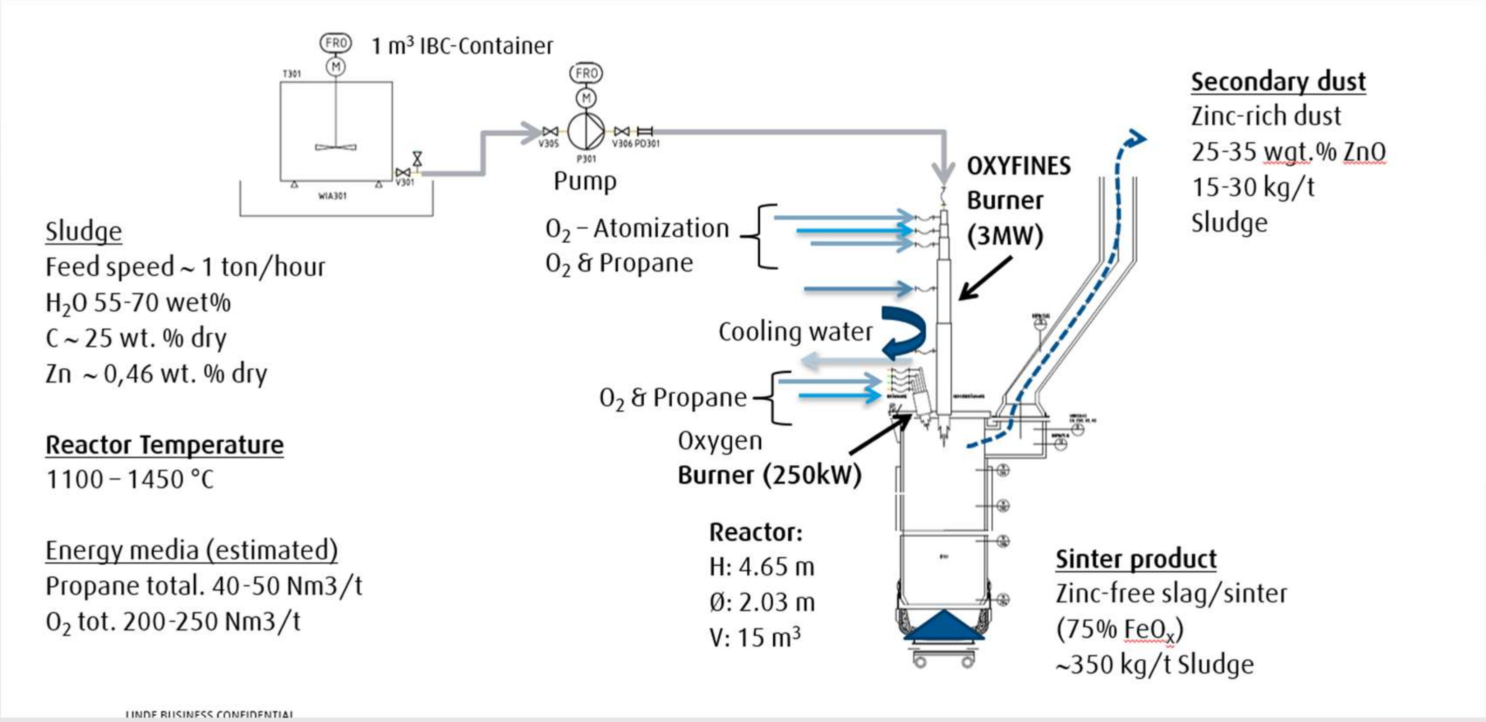
Set up of a lab prototype for lab testing

Scaling up to industrial frame

- Identification of the operating conditions (target particles cut diameter derived from the characterization)
- CFD modelling referred to the configuration identified;

Pyrometallurgical aspect

Oxyfines



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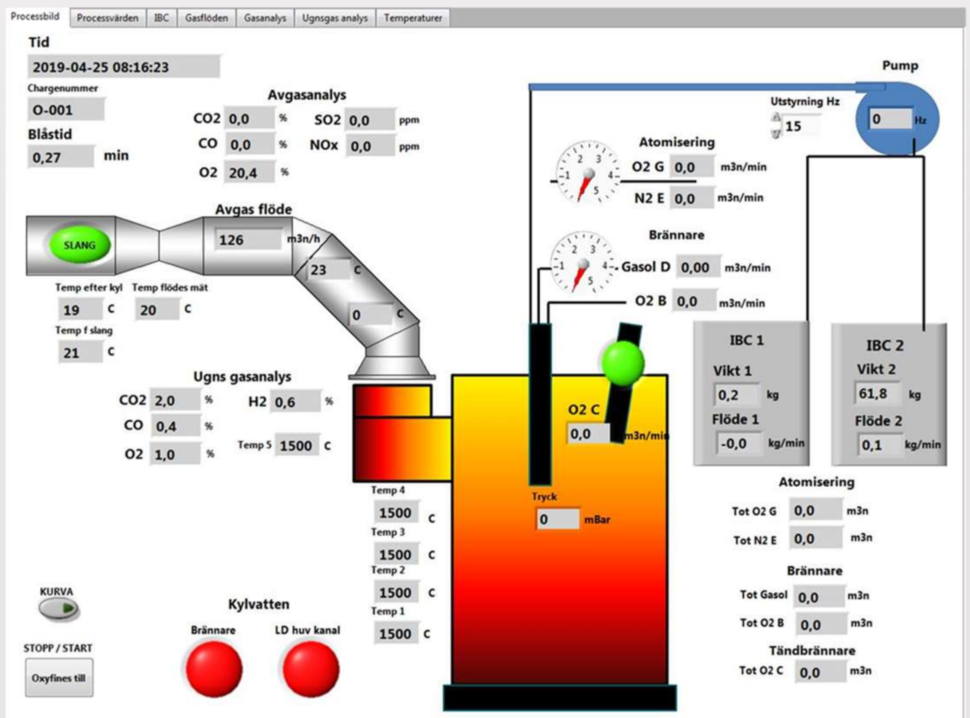
Pyrometallurgical aspect

Oxyfines

- Burner developed for recycling and processing waste materials
- Offers efficient combustion thanks to oxyfuel
- Reaches high temperatures
- Initiates carbon reactions
- Utilizes the energy in the mix

Pyrometallurgical aspect

Oxyfines



Pyrometallurgical aspect

Oxyfines - Results

- Processed app. 30 t BF sludge (50 – 65 wt% water)
- Formed 5 t iron-rich sinter later charged in BOF as cooling scrap
- 97% Zn removal from the sinter
- Secondary dust 45 kg/t BF sludge
- Developed for batch operation with very little refractory wear

Pyrometallurgical aspect

BF sludge deposits

ZincVal

Pyrometallurgical aspect

Best results

Process temperature1250C
Feeding rate 15 kg/min
CO in off gas 10 Vol%
60 Vol% H20

Removal
Zn 97%
Alkali 77%
(Na20 85% K20 68%)

Consumptions
Propane 76 Nm3/ton
Oxygen 264 Nm3/ton

Sinter product 420 kg/ton dry sludge (55 wt% Fe, 0,1 wt% C, 0,05 wt%) Zn

Secondary dust 95 kg/ton dry sludge (Reached 45 kg/ton)

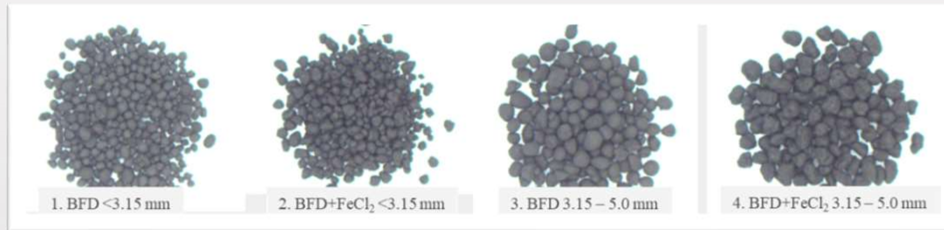
Pyrometallurgical aspect

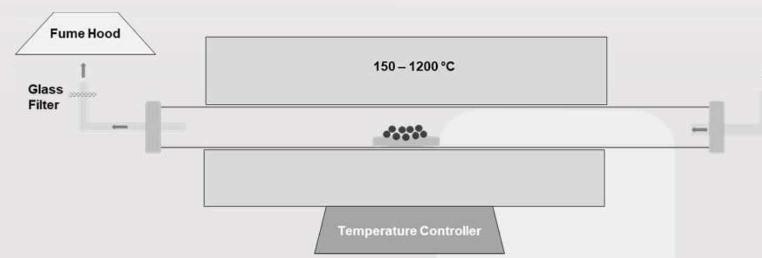
- Zinc removal and valorisation

- RHF, Waelz Kiln, DK Recycling ...
- R&D efforts
  - Oxidative pressure leaching
  - Alkaline selective leaching
  - Zinc fuming via EAF and plasma smelting
  - Selective harmful elements removal via carbochlorination
    - *initial motivation of waste co-processing: Zn-rich BF filter cake + Pickle liquor*

Carbochlorination *- lab scale experimental*

- Zn-rich BF dust as filter cake
  - Conditioning & characterization
  - Moisture, PSD, total chemistry & mineralogy
  - Zn (~2.8 wt%) is mainly present in ZnO, ZnS
- Agglomeration with bentonite binder
  - Mini-pellets – 2 sizes
  - Reference – without chloride addition
  - With stoichiometric $FeCl_2$ addition
- Carbochlorination experiments
  - Selective stage-wise heavy metal removal in horizontal tube furnace (50 grams)
  - Temperature 150 – 1100 °C;
  - Inert gas N_2 & Self-reducing nature
- Results evaluation
  - Residues
  - Flue dust captured

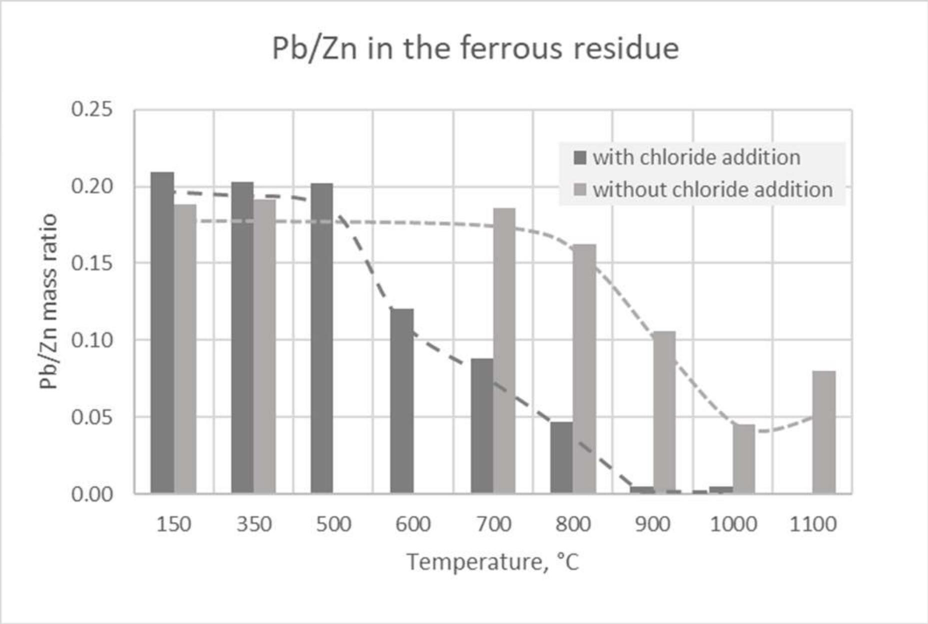




Schematic diagram of horizontal tube furnace for carbochlorination tests

Sample	Size, mm	Cl, wt%	C, wt%	Ca, wt%	Cd, wt%	Fe, wt%	Mg, wt%	Mn, wt%	Pb, wt%	S, wt%	Ti, wt%	V, wt%	Zn, wt%	Si, wt%
1	<3.15	0.14	40.80	1.63	0.01	24.45	0.62	0.10	0.51	1.10	0.09	0.02	2.77	2.70
2	<3.15 (with $FeCl_2$)	2.22	38.00	1.63	0.01	25.15	0.58	0.09	0.49	1.04	0.08	0.02	2.48	2.60
3	3.15 - 5	0.13	40.65	1.65	0.01	24.65	0.63	0.10	0.56	1.11	0.09	0.02	2.83	2.70
4	3.15 - 5 (with $FeCl_2$)	2.10	38.95	1.59	0.01	24.75	0.57	0.10	0.51	1.06	0.08	0.02	2.60	2.50

The mass ratio of Pb to Zn in the residues and accumulated filter dust

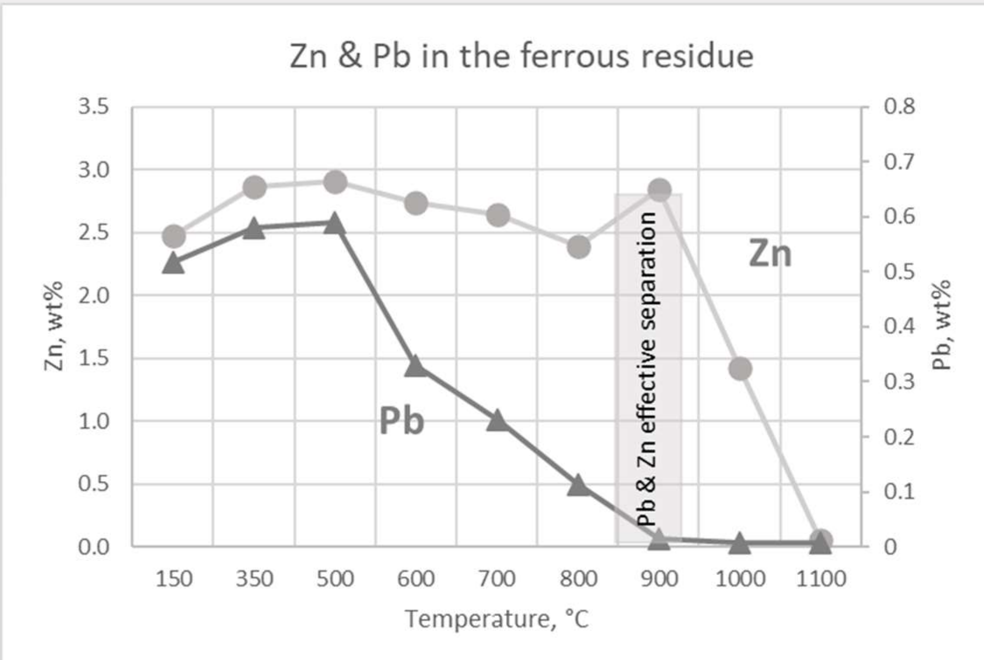


Observations

- Earlier removal of Pb starting from 600 °C.
- >97% of Pb removed at 900 °C with $FeCl_2$ addition, where the majority of zinc still remains in the solid residues
- Limited amount of secondary flue dust captured on the glass filters.
- Pb/Zn ratio determined with ICP-OES analyses following certified procedures

Major results of experiments

- Zn & Pb in the solid residue for the samples with $FeCl_2$ addition

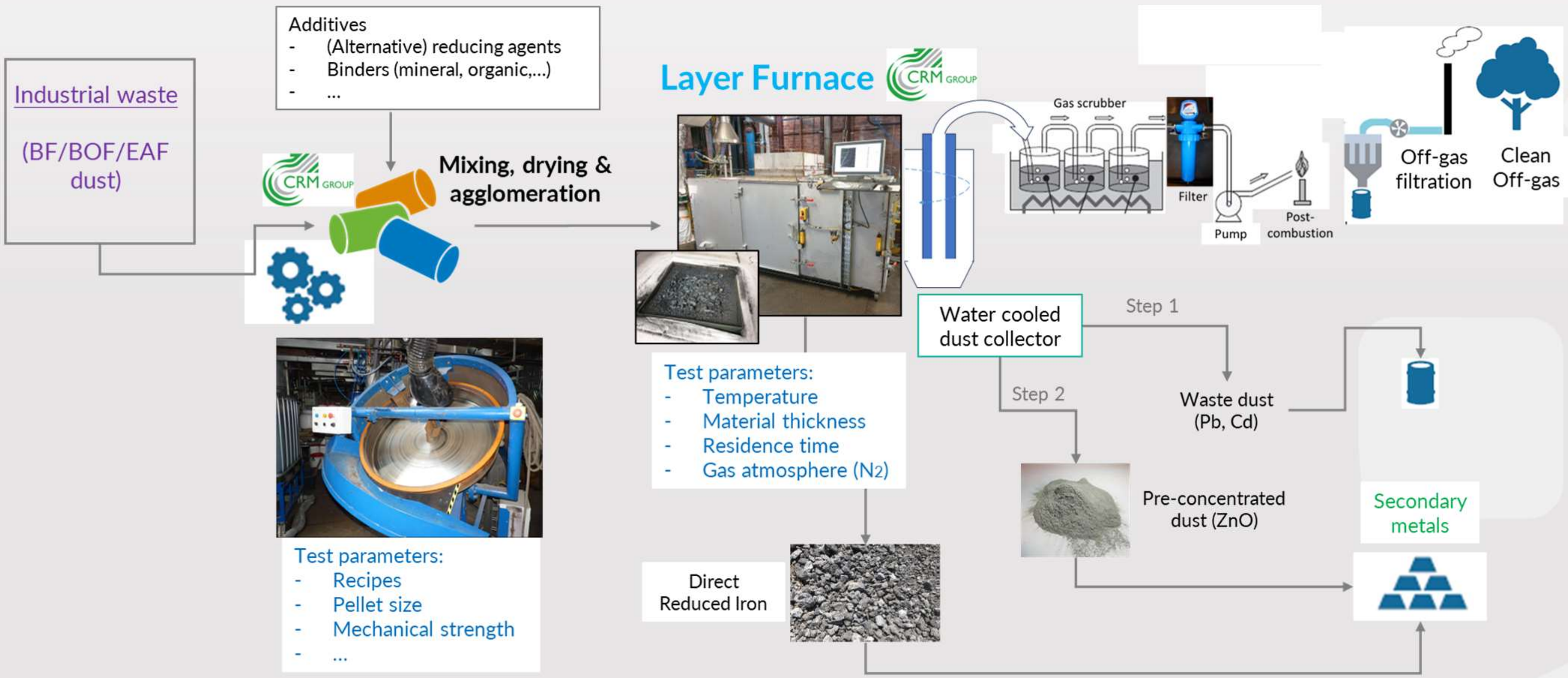


A NEW 2-steps processing route:

Reactor 01: 800- 900°C for Cd/Pb removal
Reactor 02: ≥ 1000°C for Zn enrichment/recovery

Upscaling tests by CRM in the EU RFCS ZincVal project

Scale-up testing for optimum conditions



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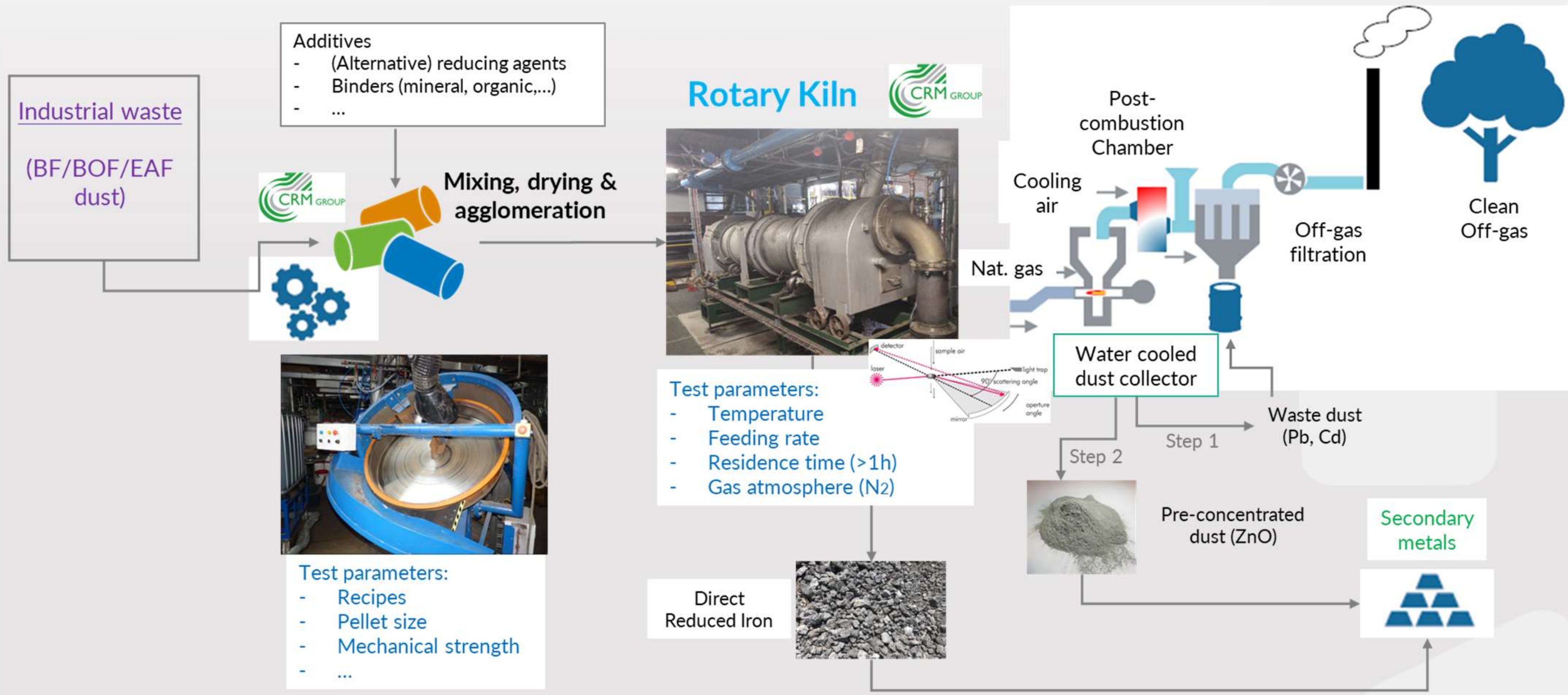
Rotary kiln simulation



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Hydrometallurgical processing of the secondary flue dust generated from RFCS-ZincVal pyro-processing

- **Direct leaching of BF/BOF/EAF dust – challenges due the presence of sulfides and ferrites**
- **Assessment of the secondary flue dust for zinc purification and recovery**
  - *Characterisation of collected flue dust from pyro-treatment processes*
  - *Leaching - acidic and/or alkaline solutions with varying pH;*
  - *Liquid-solid separation;*
  - *Solution purification;*
  - *Zinc precipitation for valorization.*
- **The behaviour of zinc, lead and other minor and trace elements in different processes will be monitored**
- **Application of the results in the follow-up flowsheet modelling for the technical, economic and environmental assessment**

Technology benchmarking

- Individual process models for each step will be developed and integrated into a flow sheet model that represents the entire steel production process.
- Reliable data from both new and existing technologies are necessary for an accurate evaluation.
  - *This data may include consumption rates per process step, efficiency of raw materials and reaction agents, energy usage, specific metal or element yields, landfill requirements etc.*
- The comparison results will be generated with outcomes presented relative to a BAT reference case (e.g. RHF, Waelz kiln).
- Results with recommendations will aid steelmakers in making informed decisions.

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the European Union

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