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## Sulfide precipitation kinetics and particle size distribution in Zn-Ni-Co system

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VTT

<https://h2020-nemo.eu/>

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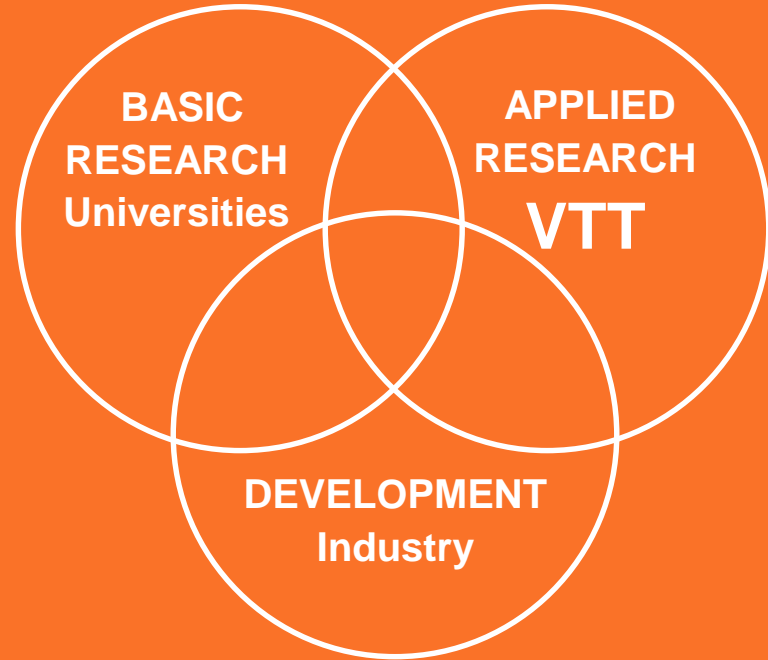


# Content

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- Introduction
- Materials and methods
- Results and discussion
- Acknowledgement

## VTT's status as performer of R&D work



# Zero-Waste mining concept

(Main current jointly funded R&D portfolio)

Academy of Finland EcoTail 300 k€

EU SCREEN 190 k€

EU MSP-REFRAM 65 k€

EIT SOLVOFLEX 180 k€

EIT BIOFLEX 4 k€

Challenge Finland  
SECO-MIM 700k€

Academy of Finland  
CERATAIL 370k€



EU METGROW+ 1.25 M€

EU BioMOre 290 k€

EIT RIGat 190 k€

Academy of Finland  
REE-PG 80 k€

**EU NEMO 1.5 M€**

EU ITERAMS 1.1 M€

TEKES MIWARE 450 k€



# NEMO – Why?

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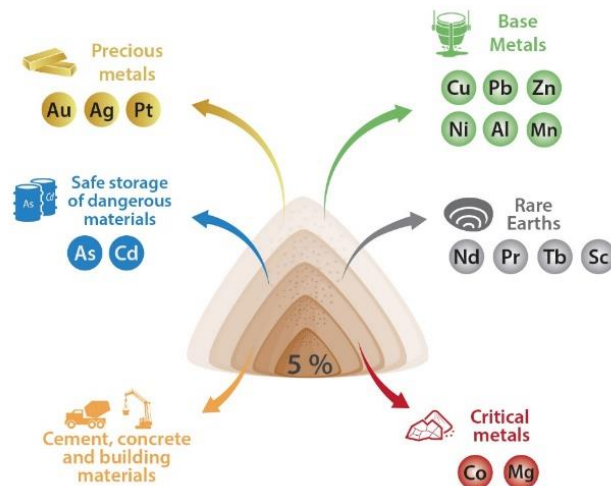
## Near-zero-waste recycling of low-grade sulphidic mining waste for critical-metal, mineral and construction raw-material production in a circular economy

The mining of non-ferrous metals and precious metals produce the largest volume of metal-containing, extractive waste in Europe.

**TAILINGS = potentially valuable material of enormous volumes.**



>28,000 Mt stock in EU!



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# NEMO – Why?

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EUROPEAN INNOVATION PARTNERSHIP ON RAW MATERIALS

Raw Materials Scoreboard, DG GROW, 2016

In the EIP's 2016 Raw Materials Scoreboard report, mining residues are earmarked as one of the key waste streams in Europe for future valorization:

- ❑ Extractive waste involves one of the largest waste streams in Europe.
- ❑ Unmanaged tailings may represent an environmental hazard and may jeopardise the Social License to Operate for mining and metallurgical companies.
- ❑ These residues contain materials that are considered critical for the EU economy.



# Sulfide precipitation

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- Selective, good settling properties and the tolerance to the metallic impurities (Mg, Ca, Al)
- Both high and low pressure/temperature process considerations can be utilized in sulphide precipitation.
- The first plant to utilize sulphide precipitation was commissioned in 1954 using high temperature and pressure.<sup>3</sup>
- The hydrogen sulphide gas is most commonly used in industrial scale
- Stoichiometry of the precipitation of a metal ion  $M^{2+}$  from solution
  - $M^{2+}(aq) + H_2S(g) = MS(s) + 2H^+$

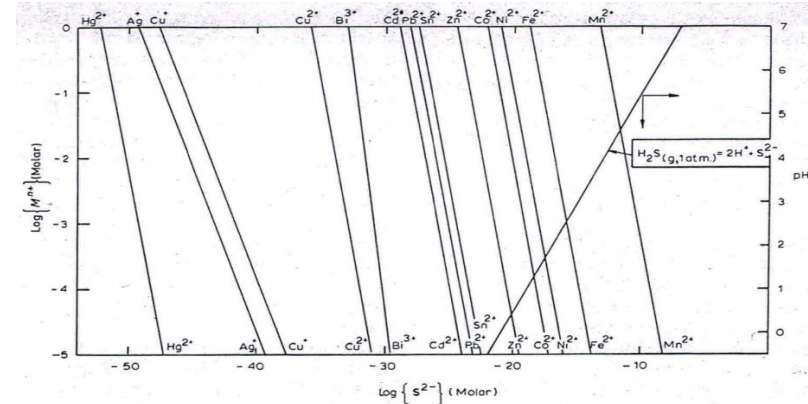


Fig. 2 Sulphide precipitation diagram, 25°C

Source: Monhemius, A. J. (1977) 'Precipitation diagrams for metal hydroxides, sulfides, arsenates and phosphates', *Transactions Institution of Mining & Metallurgy*, 86(Section C), pp. C202–C206.

#### Sources:

- Molina, N. (2009) 'Nickel and cobalt sulphide precipitation, a proven method of selective metal precipitation in laterite process flowsheets', in *Hydrometallurgy of Nickel and Cobalt 2009*.
- Lewis, A. E. (2010) 'Review of metal sulphide precipitation', *Hydrometallurgy*. Elsevier, 104(2), pp. 222–234. doi: 10.1016/j.hydromet.2010.06.010.
- Sandström, J. and Hämäläinen, M. (1972) 'Sulphide Precipitation as a Hydrometallurgical Separation Method', *Kemian Teollisuus*, 10, pp. 697–709.
- Simons, C. S. (1964) 'Hydrogen Sulfide as a Hydrometallurgical Reagent', *Unit Processes in Hydrometallurgy*, pp. 592–616.



# Materials and methods

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- Batch scale experiments conducted with artificially prepared solution and commercially available ZnS product as a precipitation seed
- Pre-adjusted pH value using H<sub>2</sub>SO<sub>4</sub> and experiments conducted with continuous base (15 m-% NaOH) feed to meet the target pH value

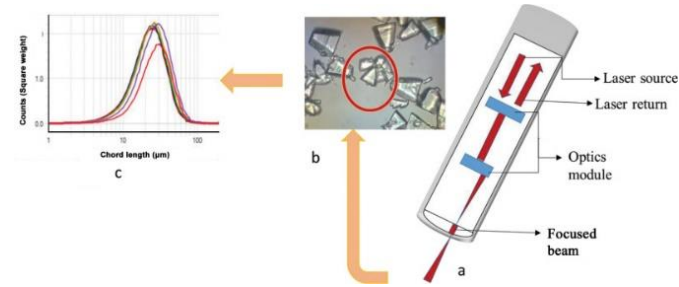




# Materials and methods

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- Particle size
  - ▣ Focused Beam Reflectance Measurement (FBRM)
  - ▣ Mettler Toledo G600
  - ▣ 0.5 to 2000  $\mu\text{m}$
- Particle shape and size
  - ▣ Particle Vision Measurement (PVM) V19
  - ▣ Optical resolution  $> 2\mu\text{m}$  with 1300 x 890  $\mu\text{m}$  view area
- FBRM is a versatile technique for in situ monitoring of chord length distribution and rate of change in crystal size.

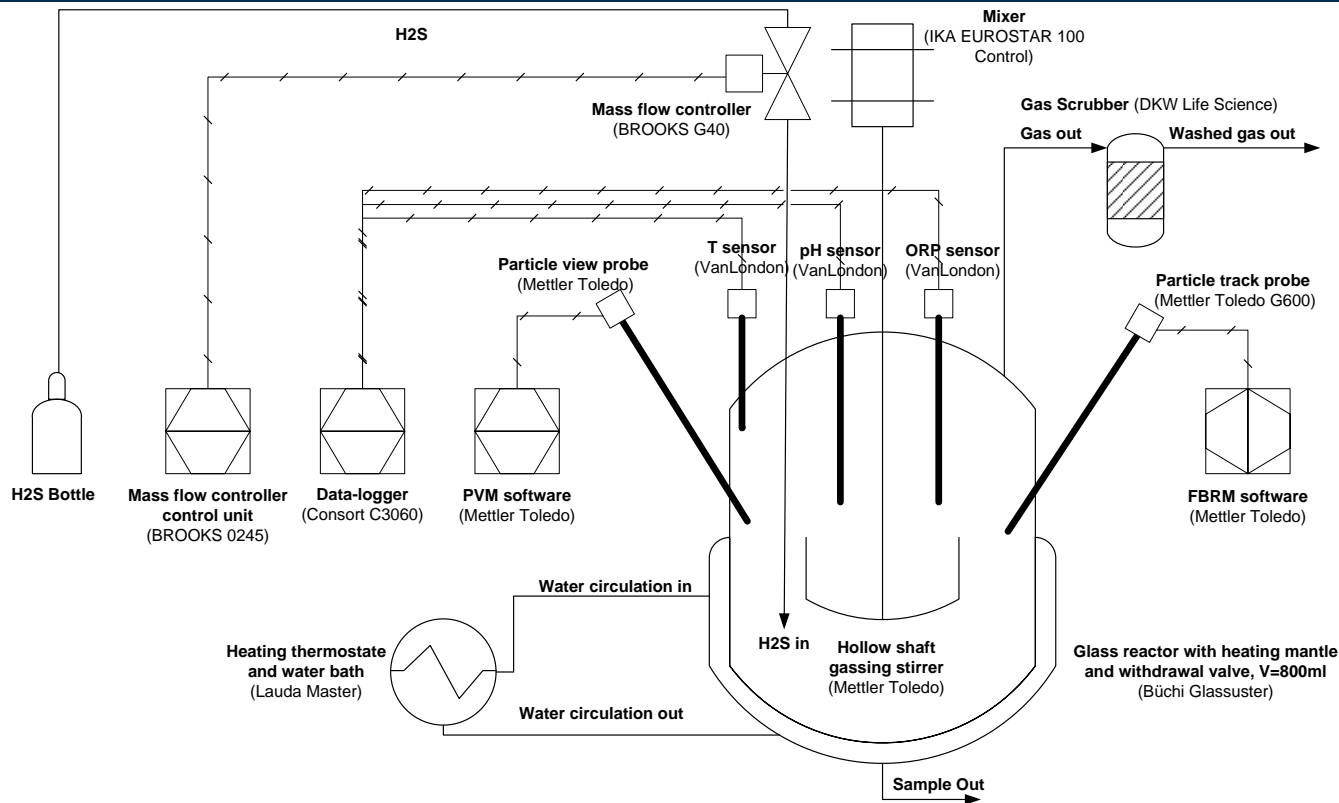


Source: Pandalaneni, K & Amamcharla, J (2016) Focused beam reflectance measurement as a tool for in situ monitoring of the lactose crystallization process, *Journal of Dairy Science* vol: 99 (7) pp: 5244-5253



# Experimental setup

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# Results and discussion

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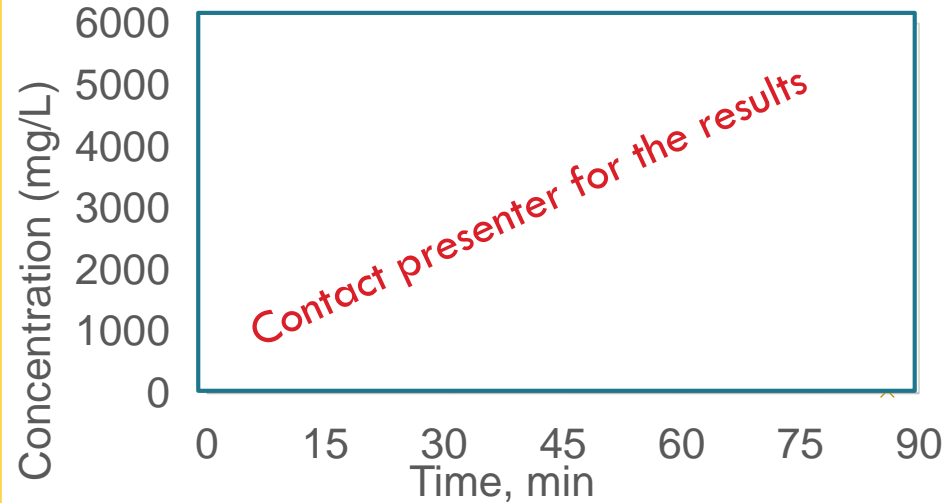
Experiment	T (°C)	pH	Gas feed (sccm)	Seed conc. (g/l)	Zn (mg/L)	Ni (mg/L)	Co (g/L)
E1	25	1,5	21,13	0	5000	2500	40
E2	75	1,5	21,13	0	5000	2500	40
E3	25	1,5	21,13	100	5000	2500	40
E4	75	1,5	21,13	100	5000	2500	40
E5	25	4,5	21,13	0	5000	2500	40
E6	75	4,5	21,13	0	5000	2500	40
E7	25	4,5	21,13	100	5000	2500	40
E8	75	4,5	21,13	100	5000	2500	40

# No Seed – Room temperature



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## Continuous pH control at 1.5

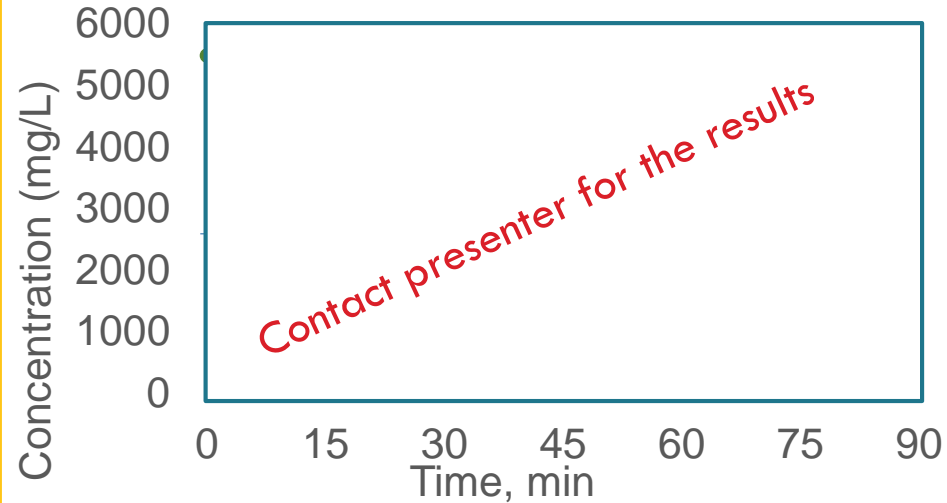


✕ Zn E1 - T=25C, pH=1.5, SC=0 g/L

\* Ni E1 - T=25C, pH=1.5, SC=0 g/L

— Co E1 - T=25C, pH=1.5, SC=0 g/L

## Continuous pH control at 4.5



● Zn E5 - T=25C, pH=4.5, SC=0 g/L

+ Ni E5 - T=25C, pH=4.5, SC=0 g/L

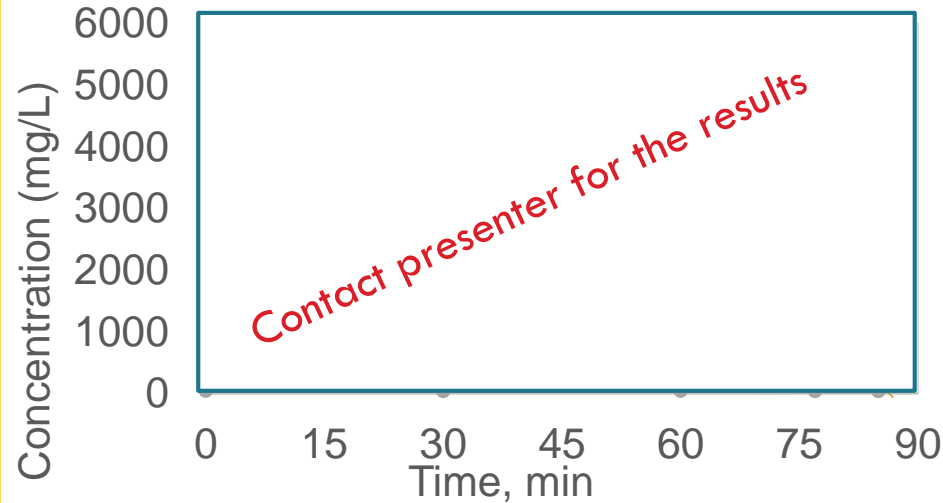
— Co E5 - T=25C, pH=4.5, SC=0 g/L

# No Seed – Increased temperature



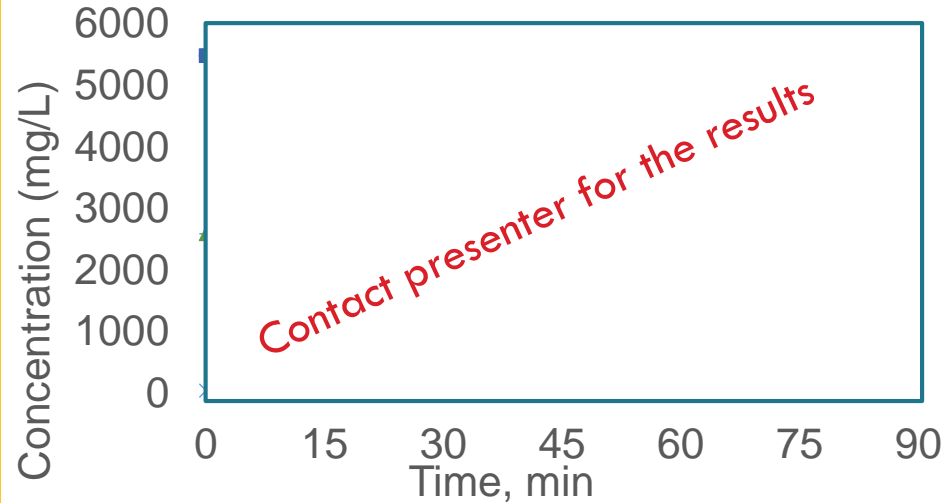
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## Continuous pH control at 1.5



- ✖ Zn E1 - T=25C, pH=1.5, SC=0 g/L
- ✖ Ni E1 - T=25C, pH=1.5, SC=0 g/L
- Co E1 - T=25C, pH=1.5, SC=0 g/L
- ✖ Zn E2 - T=75C, pH=1.5, SC=0 g/L
- ✖ Ni E2 - T=75C, pH=1.5, SC=0 g/L
- Co E2 - T=75C, pH=1.5, SC=0 g/L

## Continuous pH control at 4.5



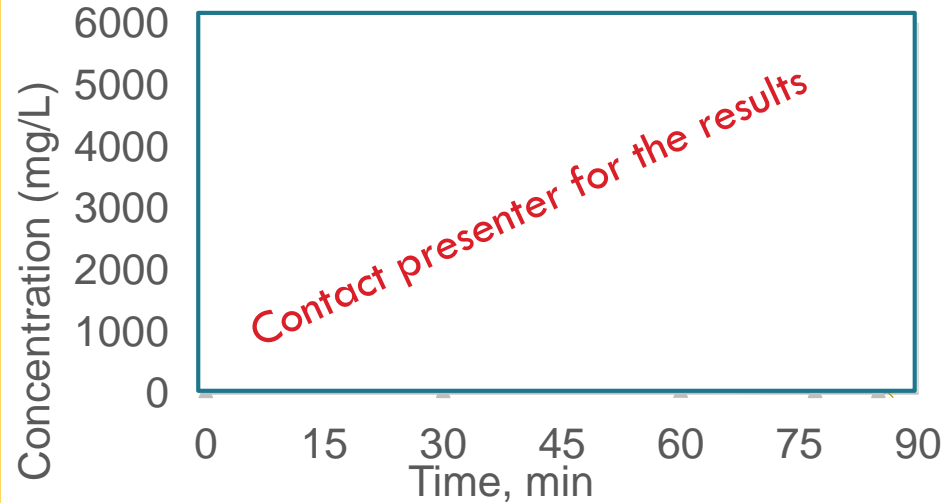
- Zn E5 - T=25C, pH=4.5, SC=0 g/L
- + Ni E5 - T=25C, pH=4.5, SC=0 g/L
- Co E5 - T=25C, pH=4.5, SC=0 g/L
- Zn E6 - T=75C, pH=4.5, SC=0 g/L
- ▲ Ni E6 - T=75C, pH=4.5, SC=0 g/L
- ✖ Co E6 - T=75C, pH=4.5, SC=0 g/L

# Seed 100 g/L – Room temperature



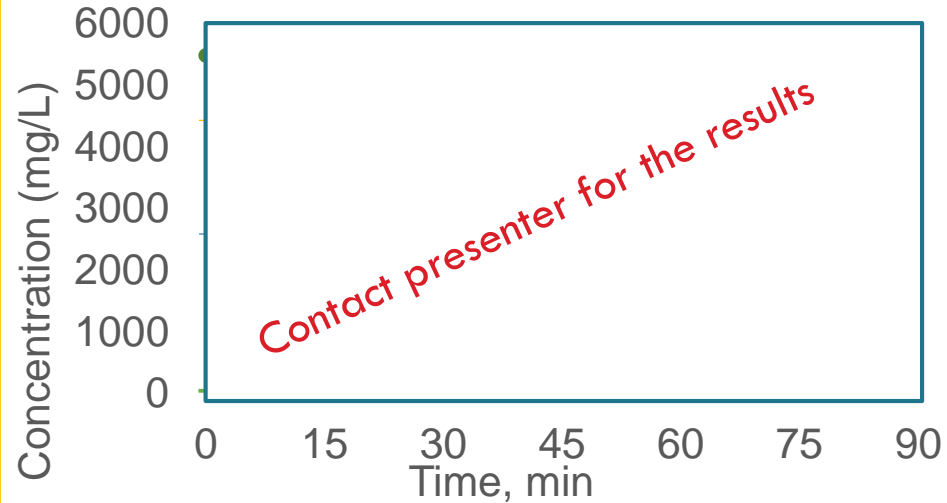
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## Continuous pH control at 1.5



- ✕ Zn E1 - T=25C, pH=1.5, SC=0 g/L
- \* Ni E1 - T=25C, pH=1.5, SC=0 g/L
- Co E1 - T=25C, pH=1.5, SC=0 g/L
- ◆ Zn E3 - T=25C, pH=1.5, SC=100 g/L
- Ni E3 - T=25C, pH=1.5, SC=100 g/L
- ▲ Co E3 - T=25C, pH=1.5, SC=100 g/L

## Continuous pH control at 4.5



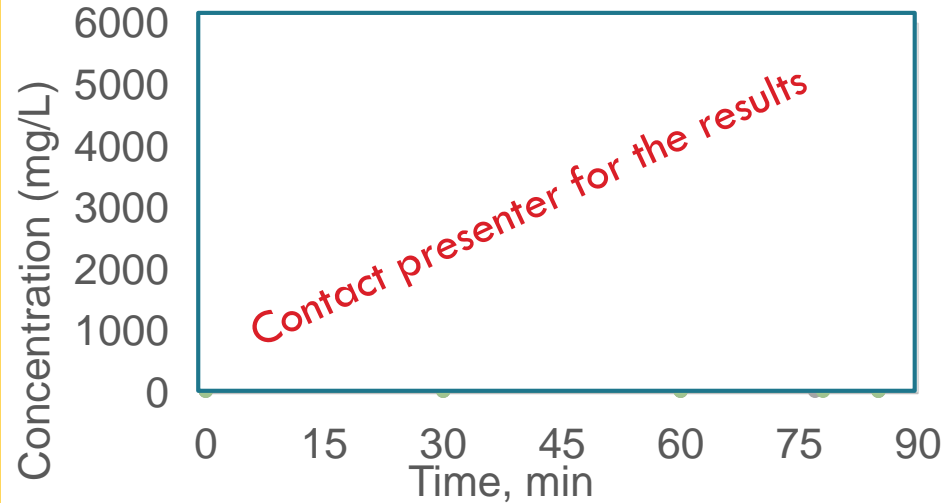
- Zn E5 - T=25C, pH=4.5, SC=0 g/L
- + Ni E5 - T=25C, pH=4.5, SC=0 g/L
- Co E5 - T=25C, pH=4.5, SC=0 g/L
- ✕ Zn E7 - T=25C, pH=4.5, SC=100 g/L
- Ni E7 - T=25C, pH=4.5, SC=100 g/L
- Co E7 - T=25C, pH=4.5, SC=100 g/L

# Seed 100 g/L – Increased temperature



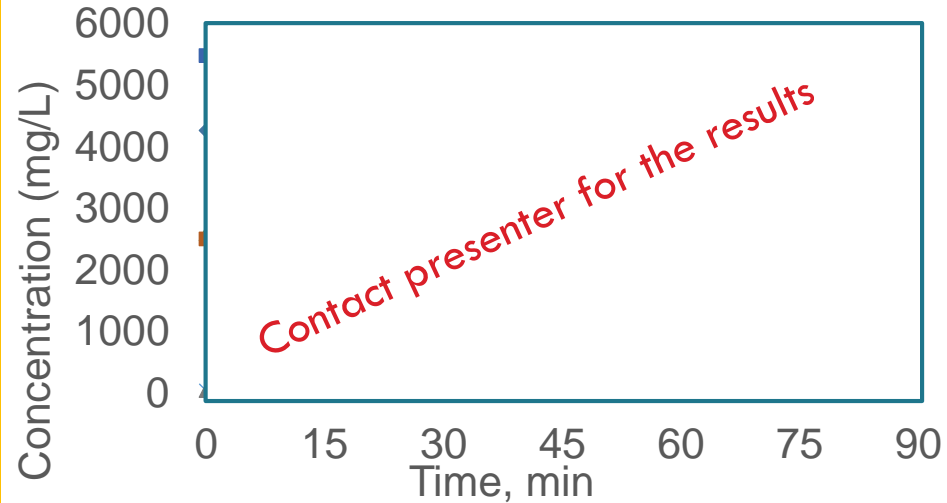
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## Continuous pH control at 1.5



- ◆ Zn E2 - T=75C, pH=1.5, SC=0 g/L
- ✱ Ni E2 - T=75C, pH=1.5, SC=0 g/L
- Co E2 - T=75C, pH=1.5, SC=0 g/L
- ✱ Zn E4 - T=75C, pH=1.5, SC=100 g/L
- ✱ Ni E4 - T=75C, pH=1.5, SC=100 g/L
- Co E4 - T=75C, pH=1.5, SC=100 g/L

## Continuous pH control at 4.5



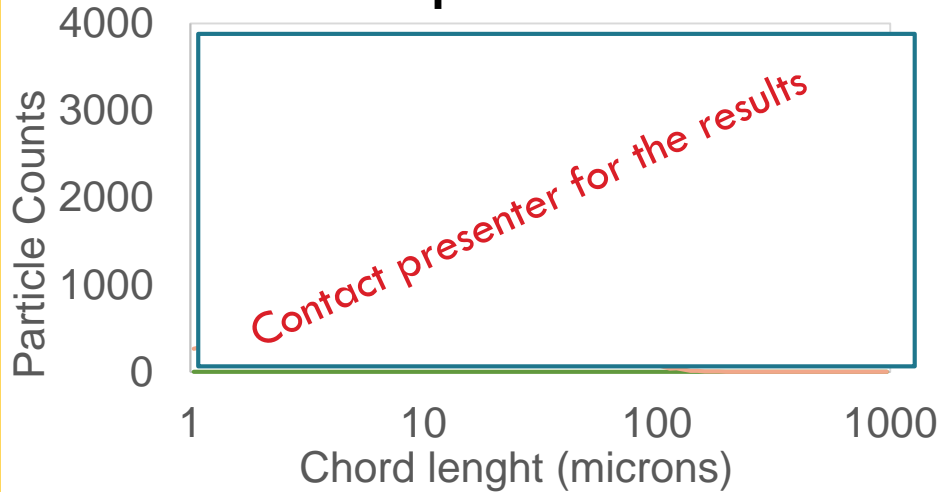
- ◆ Zn E6 - T=75C, pH=4.5, SC=0 g/L
- ▲ Ni E6 - T=75C, pH=4.5, SC=0 g/L
- ✱ Co E6 - T=75C, pH=4.5, SC=0 g/L
- ◆ Zn E8 - T=75C, pH=4.5, SC=100 g/L
- Ni E8 - T=75C, pH=4.5, SC=100 g/L
- ▲ Co E8 - T=75C, pH=4.5, SC=100 g/L

# Particle size distribution – No seed – Room temperature



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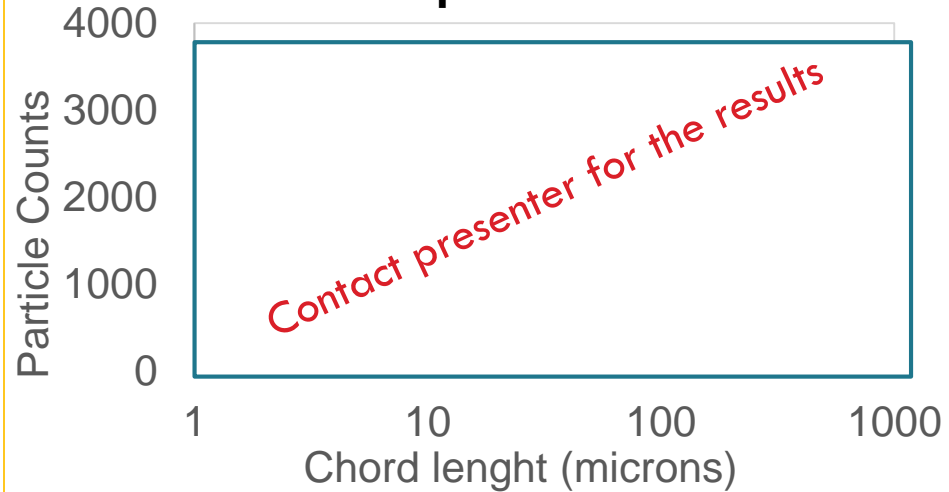
## Continuous pH control at 1.5



— START (E1 - T=25C, pH=1.5, SC=0 g/L)

— STOP (E1 - T=25C, pH=1.5, SC=0 g/L)

## Continuous pH control at 4.5



— START (E5 - T=25C, pH=4.5, SC=0 g/L)

— STOP (E5 - T=25C, pH=4.5, SC=0 g/L)

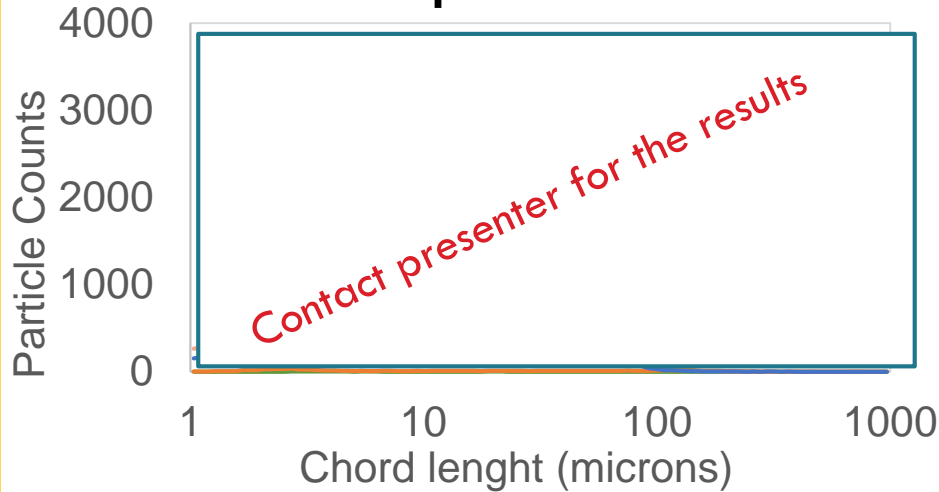


# Particle size distribution – No seed – Increased temperature



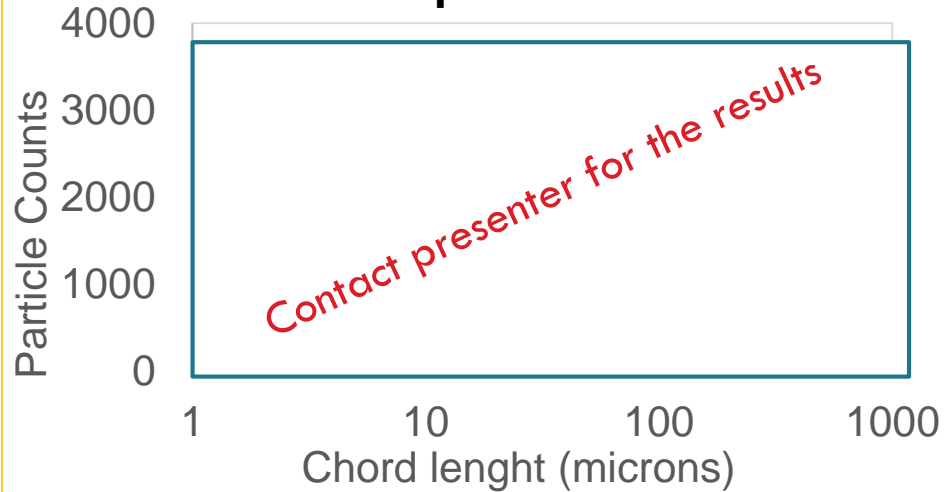
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## Continuous pH control at 1.5



- START (E1 - T=25C, pH=1.5, SC=0 g/L)
- STOP (E1 - T=25C, pH=1.5, SC=0 g/L)
- START (E2 - T=75C, pH=1.5, SC=0 g/L)
- STOP (E2 - T=75C, pH=1.5, SC=0 g/L)

## Continuous pH control at 4.5



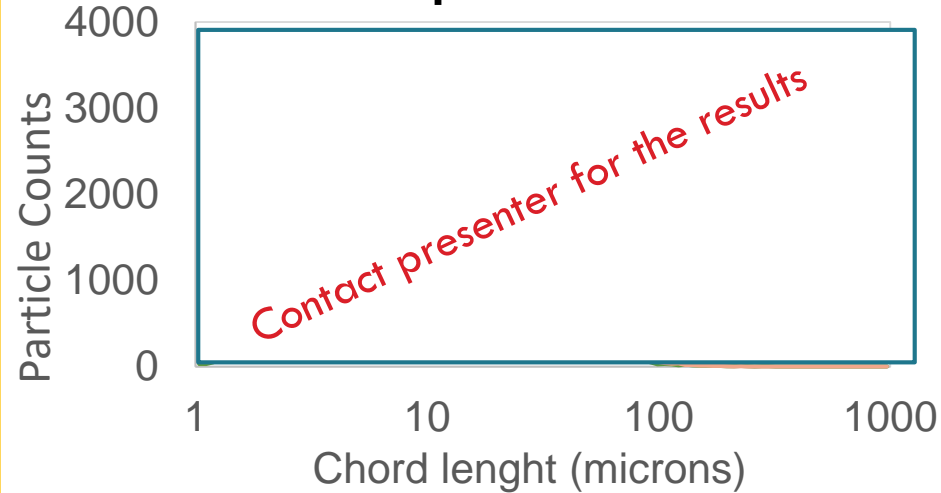
- START (E5 - T=25C, pH=4.5, SC=0 g/L)
- STOP (E5 - T=25C, pH=4.5, SC=0 g/L)
- START (E6 - T=75C, pH=4.5, SC=0 g/L)
- STOP (E6 - T=75C, pH=4.5, SC=0 g/L)

# Particle size distribution – Seed 100 g/L – Room temperature

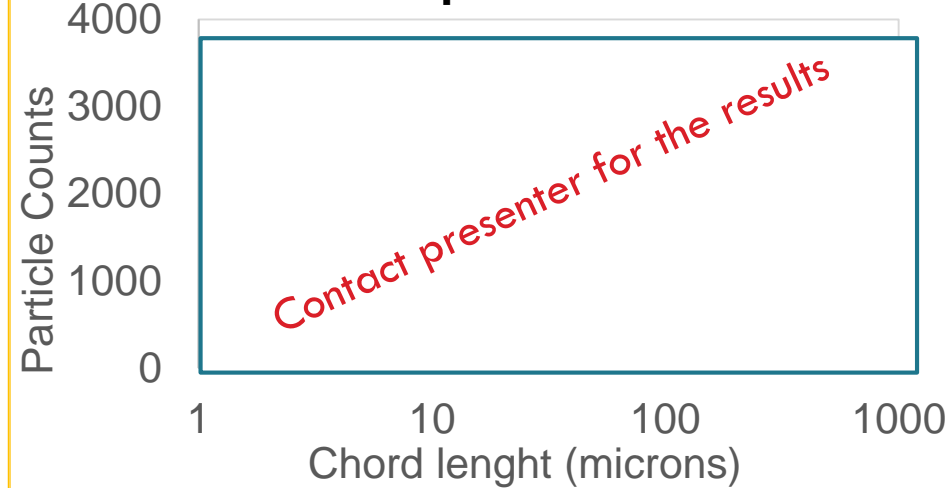


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## Continuous pH control at 1.5



## Continuous pH control at 4.5

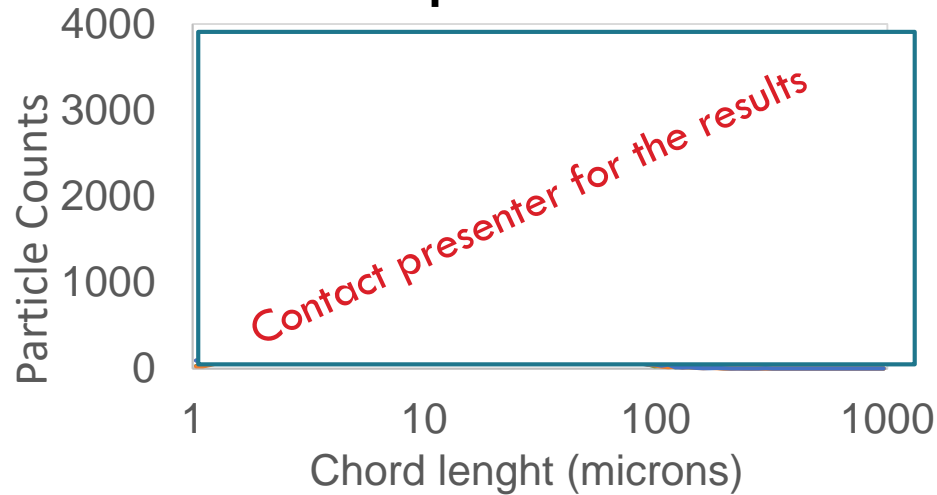


# Particle size distribution – Seed 100 g/L – Increased temperature



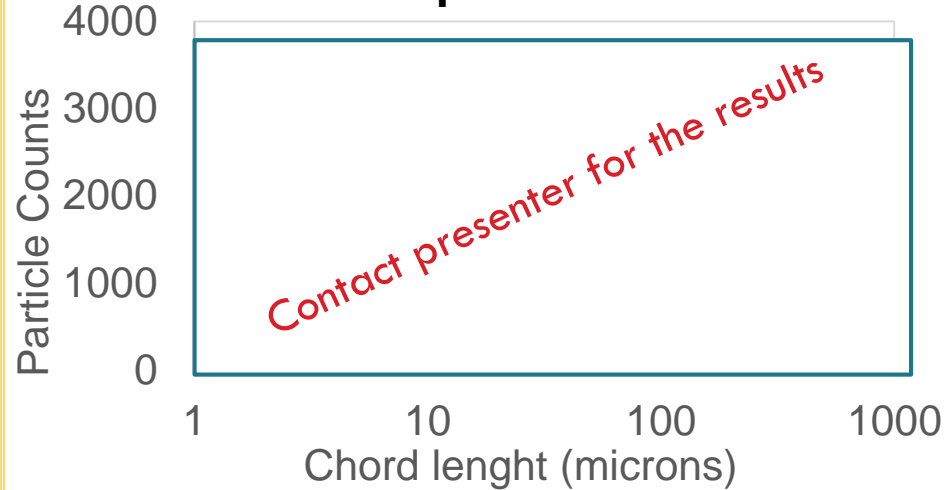
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## Continuous pH control at 1.5



- START (E3 - T=25C, pH=1.5, SC=100 g/L)
- STOP (E3 - T=25C, pH=1.5, SC=100 g/L)
- START (E4 - T=75C, pH=1.5, SC=100 g/L)
- STOP (E4 - T=75C, pH=1.5, SC=100 g/L)

## Continuous pH control at 4.5



- START (E7 - T=25C, pH=4.5, SC=100 g/L)
- STOP (E7 - T=25C, pH=4.5, SC=100 g/L)
- START (E8 - T=75C, pH=4.5, SC=100 g/L)
- STOP (E8 - T=75C, pH=4.5, SC=100 g/L)



# Acknowledgement

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# QUESTIONS?

<https://h2020-nemo.eu/>