

Hephaestus: Zn recovery from electric furnace dust (EAFD)

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Prometia, 12th Scientific Seminar, Naples, 26/11/2025



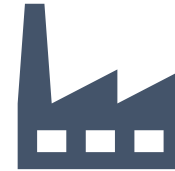
HEPHAESTUS

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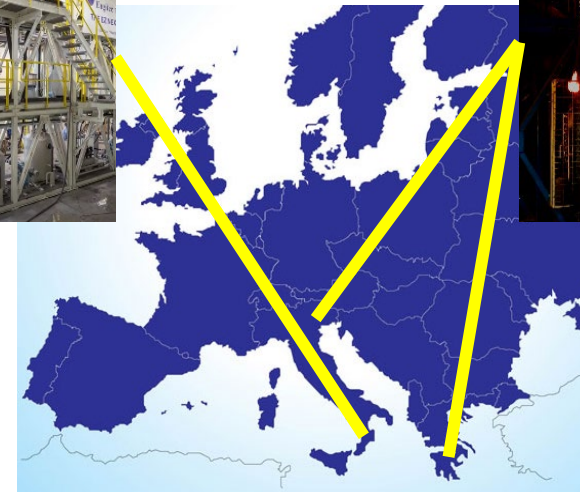


Electric Arc Furnace Dust (EAFD)

- Steel and stainless-steel production generates EAFDs
- Hazardous waste => landfilled or treated by Waelz process (70%)
- Hephaestus 2 demo site



0.5 - 1.5 M tons in EU



HEPHAESTUS project concept



EAFD (AST acciai speciali Terni)
Fe-Ni dusts (LARCO)

Arvedi AST



KU LEUVEN

Solvomet
AAC route



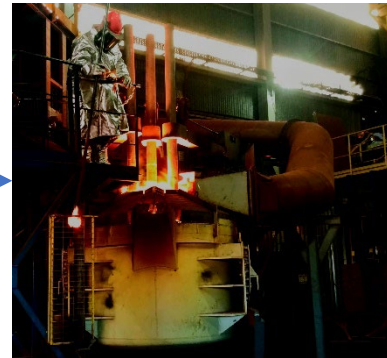
AdMiRIS

- Zn and Pb vaporise
- Zn is degrading and polluting the lining of the furnaces
- ZnO needs energy to be reduced
- Cl, K, Na unwanted



Metlen
Energy & Metals

1MVA Cleantech® => Greece (Metlen)
5MVA Cleantech® => Italy (AIT)



CO₂ to methanol (CC)
Greece NTUA



Engitec Technologies

EZINEX® => Italy (Engitec)



CZO

zinc

ferroalloy
ingots

Fiberization unit



Slag

Mineral wool

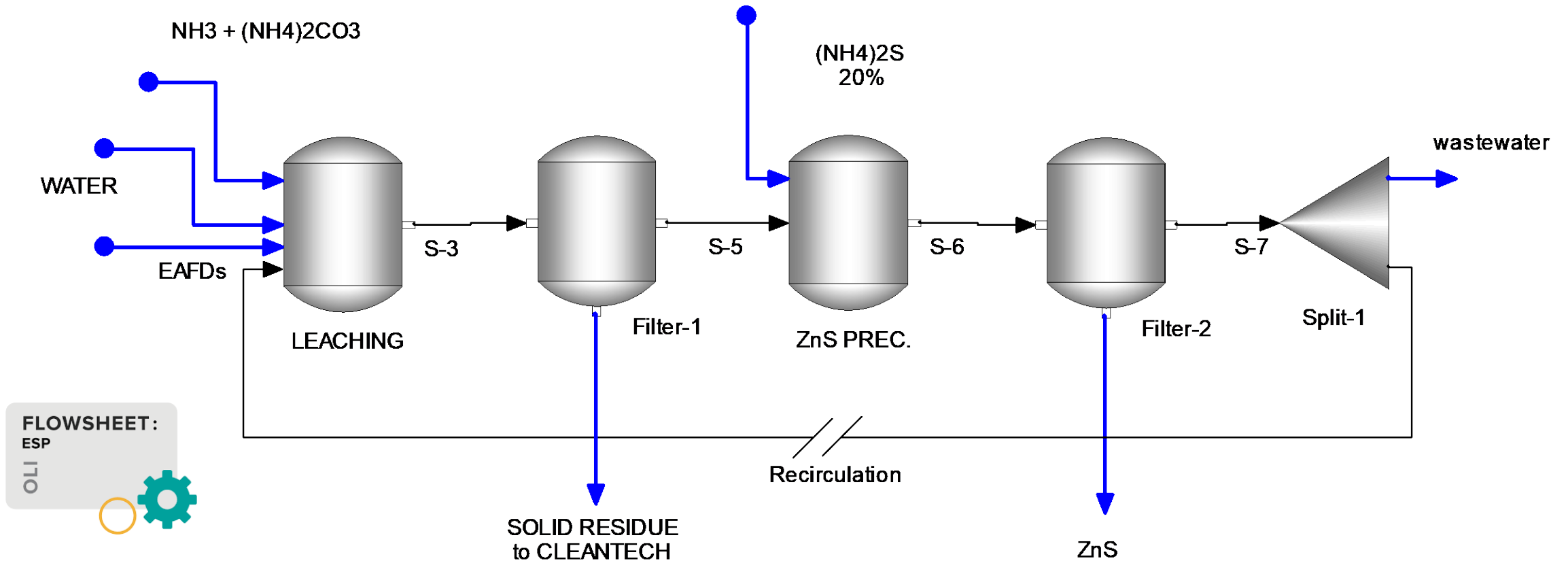


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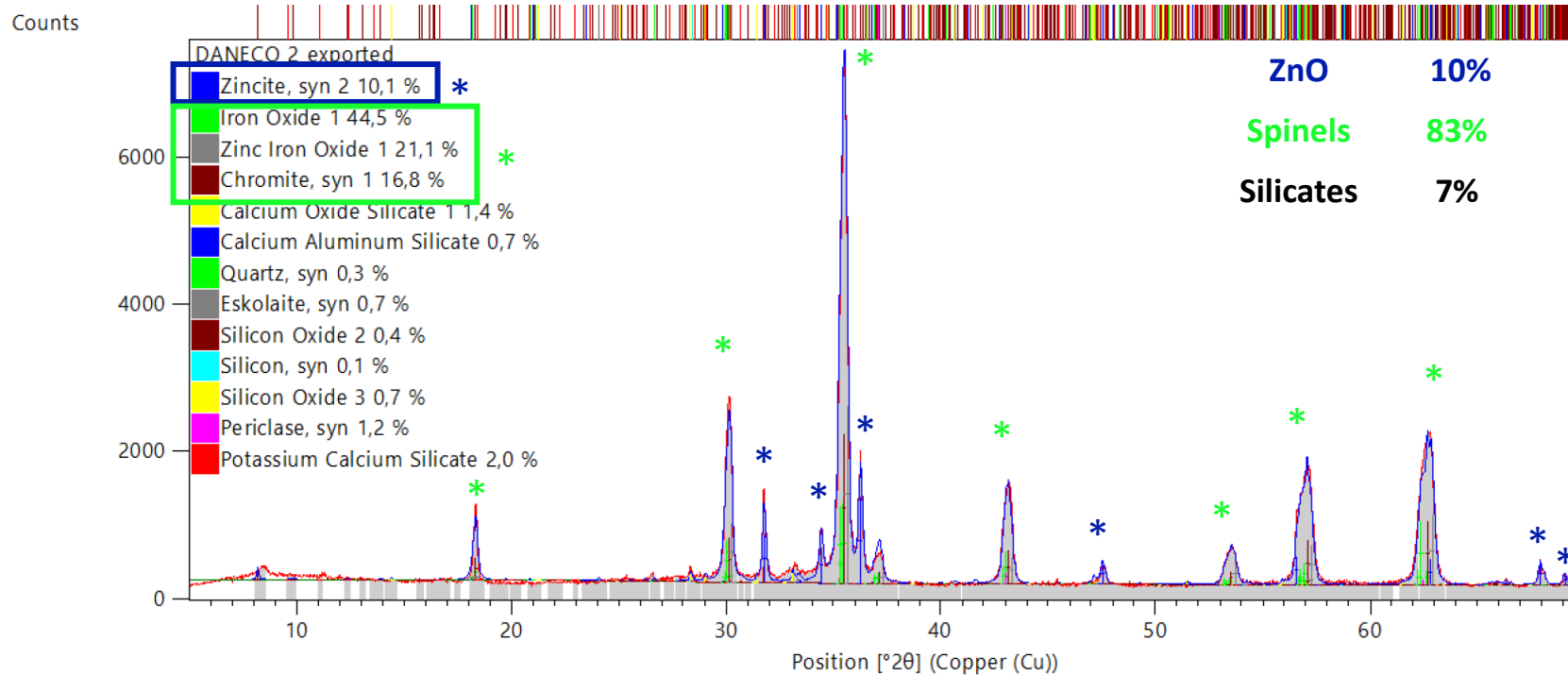
AAC (ammonia/ammonium carbonate) route



1) **Leaching:** $\text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+} + 2\text{OH}^-$

2) **Precipitation:** $\text{Zn}(\text{NH}_3)_4^{+2} + (\text{NH}_4)_2\text{S}_{(\text{aq})} \rightleftharpoons \text{ZnS}_{(\text{s})} + 2\text{NH}_4^+ + 4\text{NH}_3$

EAFD composition



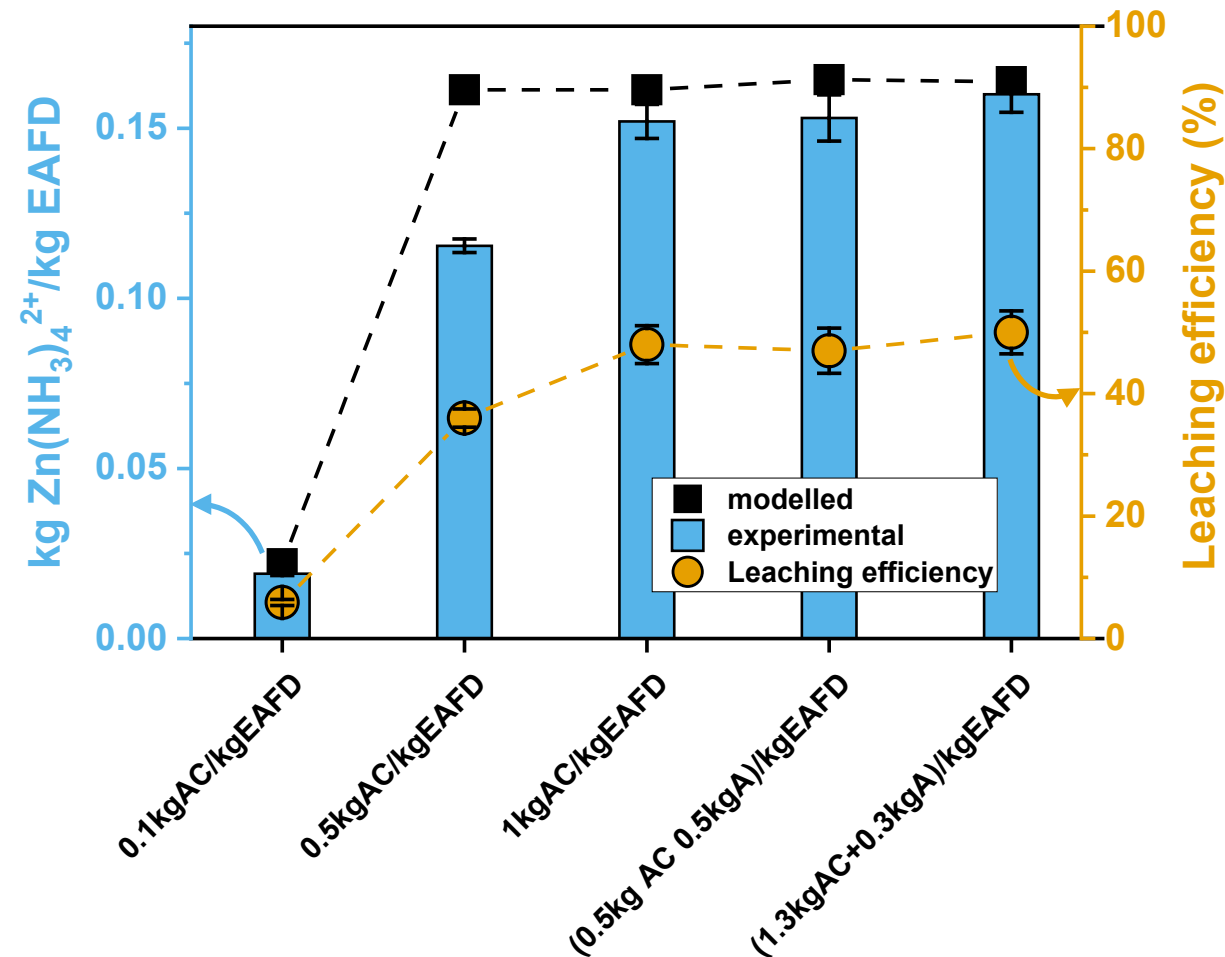
1) **Leaching:** $\text{ZnO} + 4\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Zn}(\text{NH}_3)_4^{2+} + 2\text{OH}^-$

Elem. %	Average	Std. Dev.
Fe	23.8	0.5
Zn	15	1
Cr	9.5	0.4
Ca	3.55	0.05
Mg	3.61	0.06
Si	3.4	0.1
Mn	2.16	0.03
C*	2.2	0.1
Ni	0.98	0.06
K	1.7	0.1
Pb	0.6	0.1
Cu	0.35	0.03
S	0.56	0.02
Al	0.6	0.1
Mo	0.23	0.03
Ti	0.12	0.02



AAC (ammonia/ammonium carbonate) leaching

- **OLI Studio** calculations on single elements, to progressively more complex representative sample (iterative comparison with leaching experiments)
- L/S 5, RT, (3h, 500 rpm) at various AAC compositions
- Consistently, **(1.3kgAC + 0.3kgA)/kg EAFD** gave higher Zn conc. (**15.3 ± 0.5** vs **14.2 ± 0.5 g·L⁻¹**) and lower Zn in the residue (**7.7** vs **8.8%**)

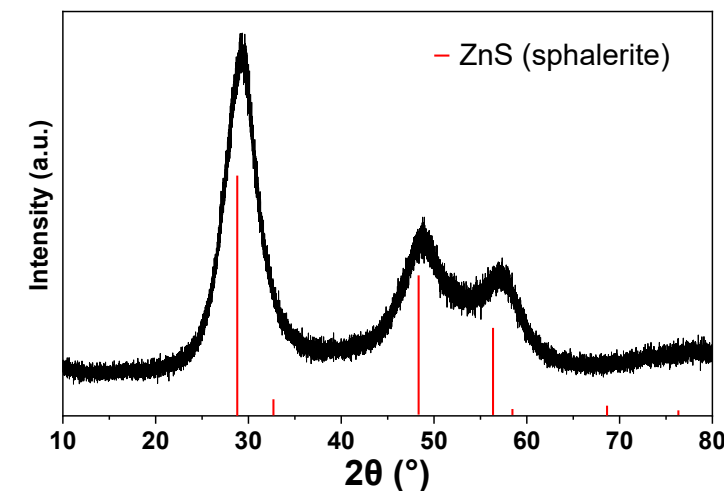
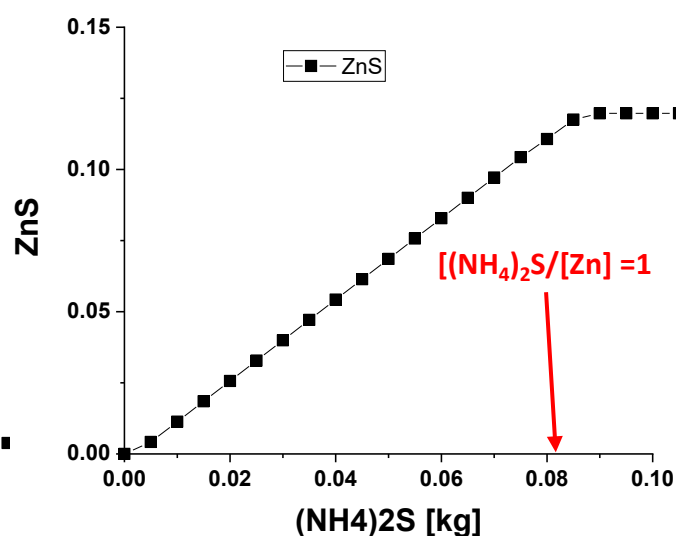
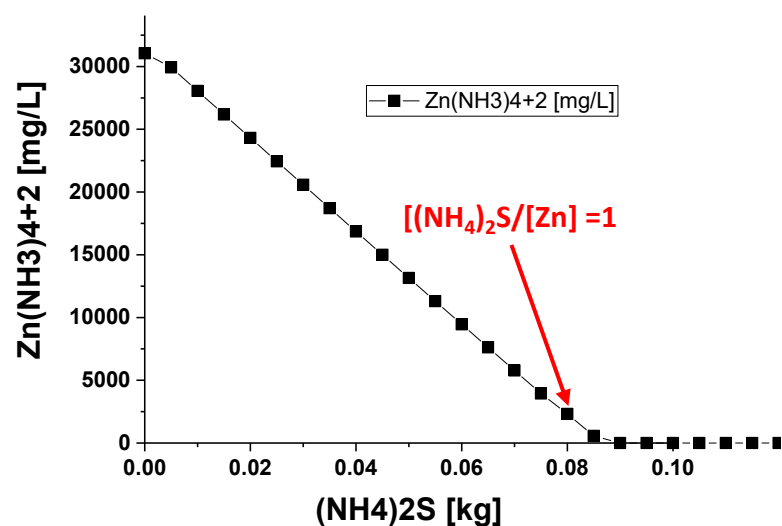


species	kg/kg EAFD
ZnO	0.1
Fe3O4	0.83
SiO2	0.07
CuO	5E-04
PbO	1E-03
FeO	1E-04
CrO3	1E-04
KCl	1E-03
NaCl	1E-03
MoO3	1E-03
Total	1.0037

ZnS precipitation



> 99.5% leached zinc precipitated

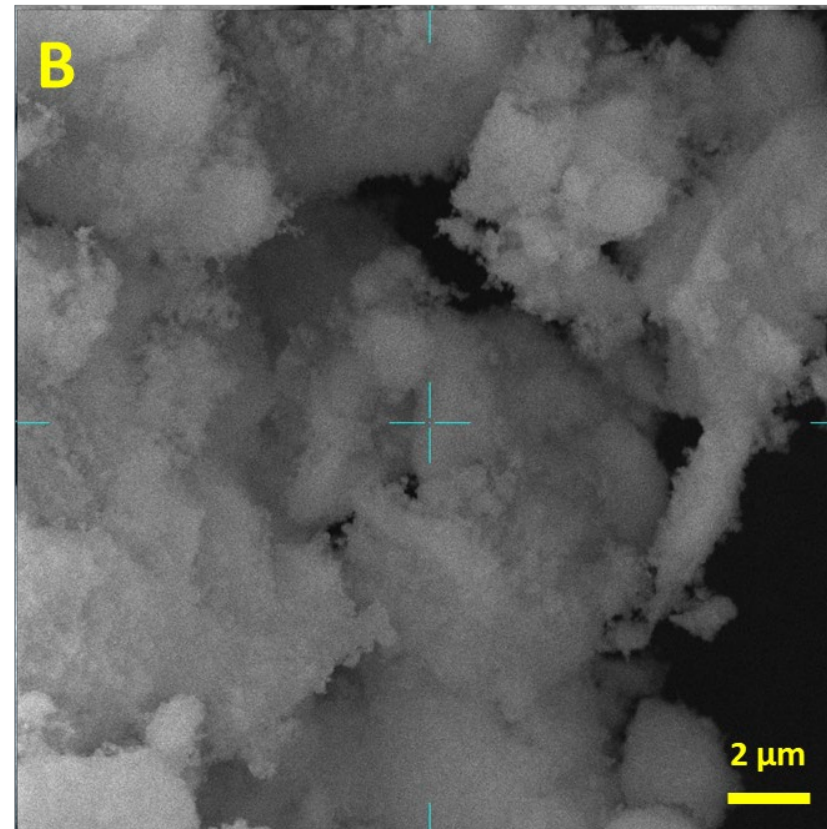
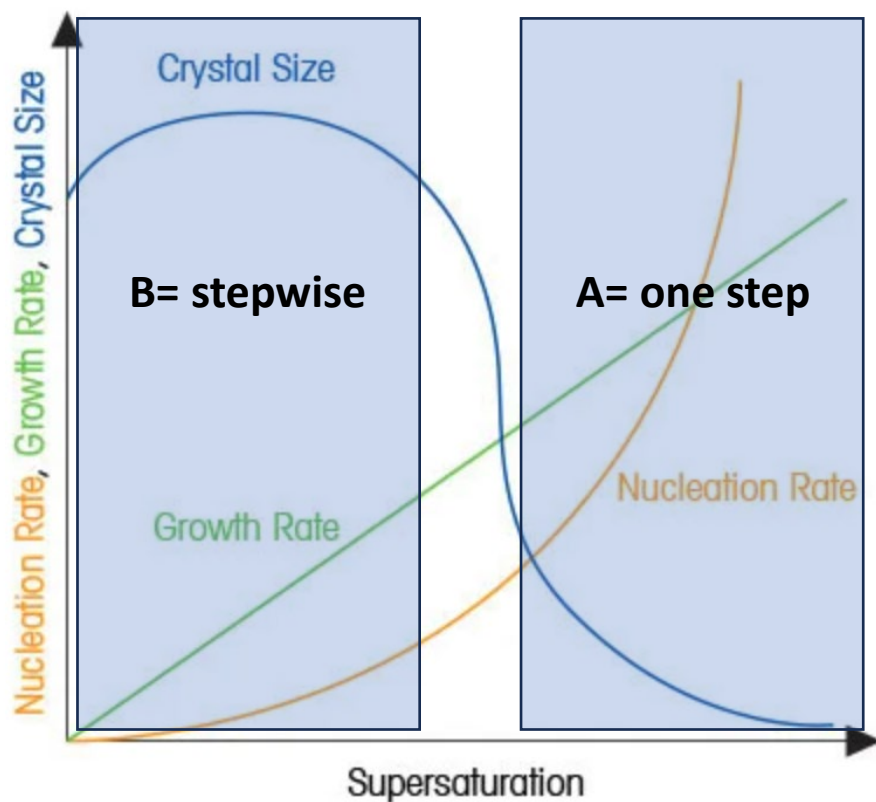


Elem. (%)	Zn	Cr	Cu	Pb	Na	K	Fe	Si	Cl	Purity (%)
ZnS	55.6	0.3	0.6	0.6	0.4	0.5	0.3	0.5	0.3	82%



ZnS precipitation: enhance filtration

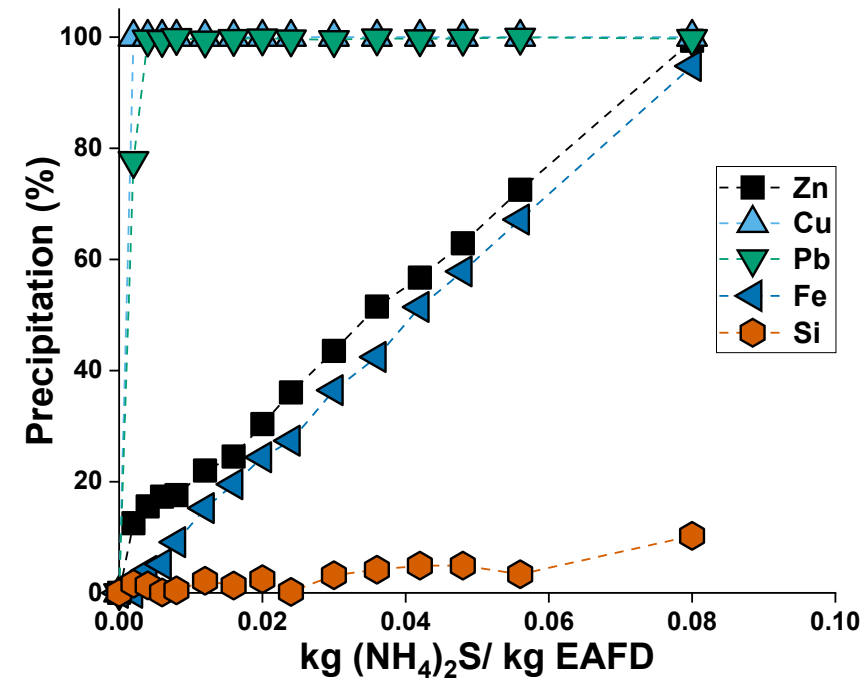
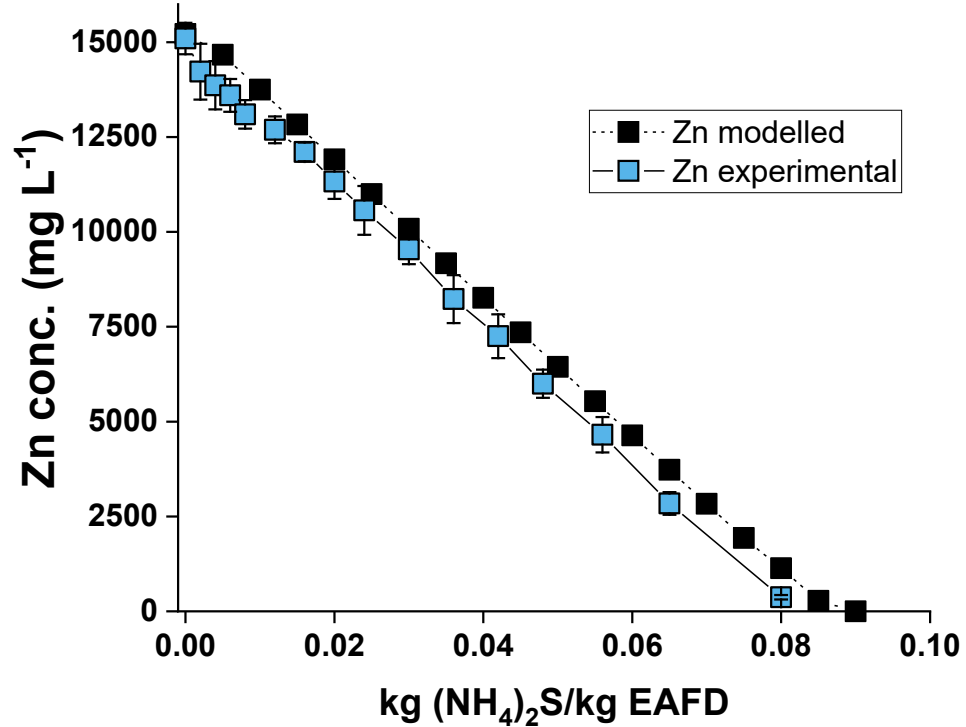
reduce the rate of nucleation by lowering the relative supersaturation: adding reagents slowly with good mixing



Very fast filtration and decantation



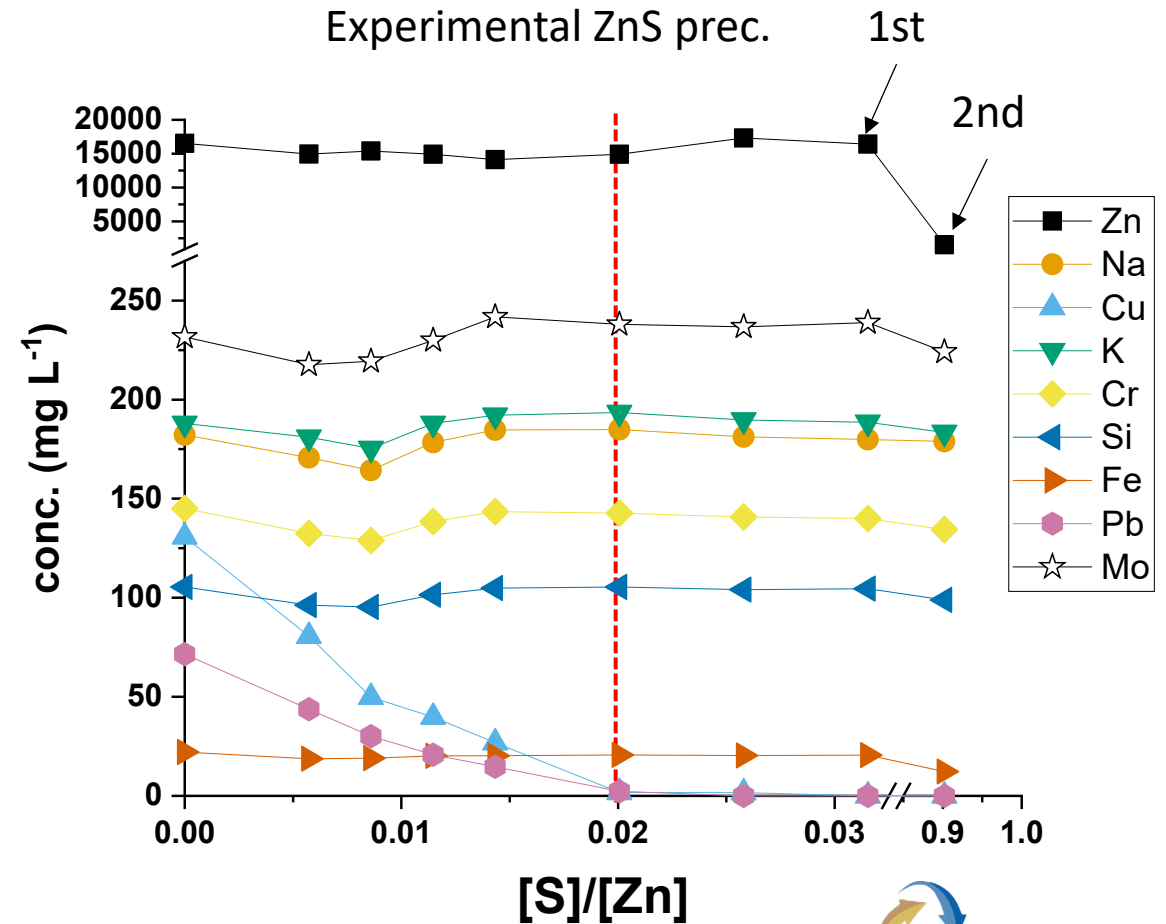
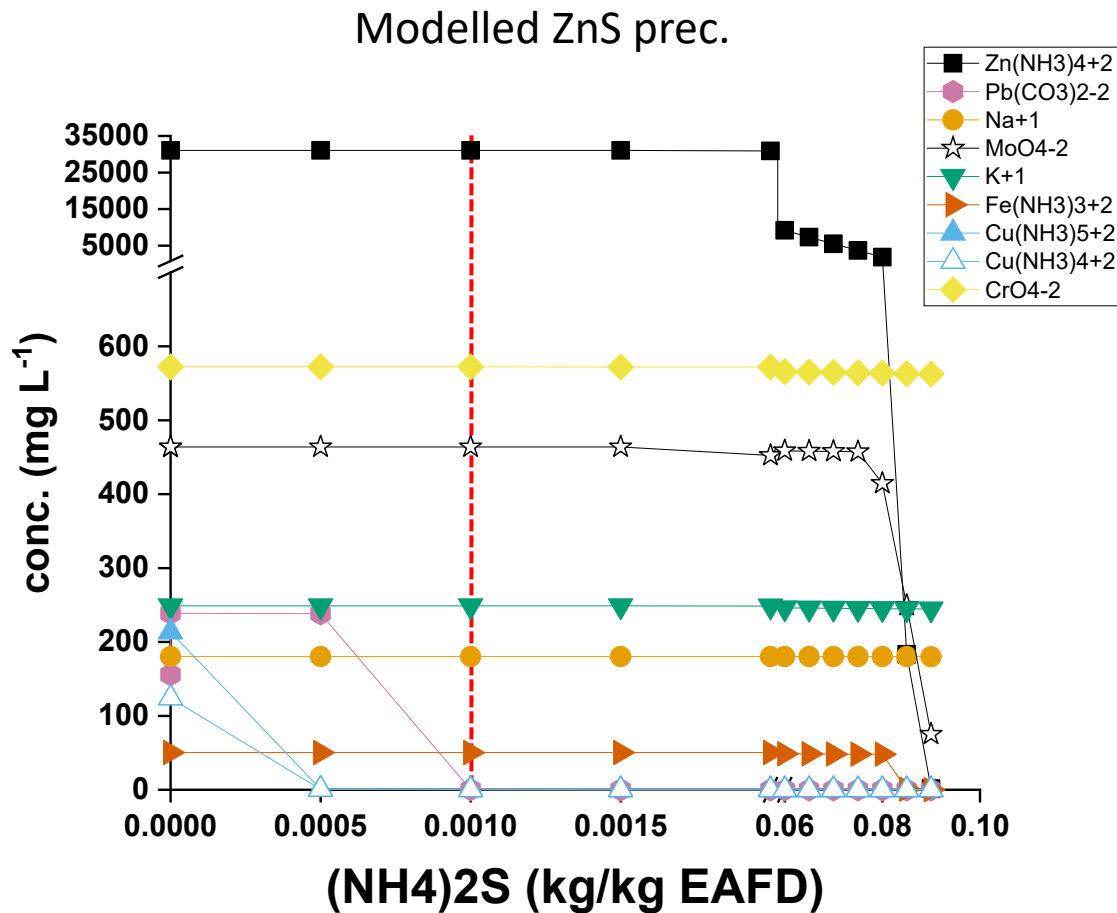
ZnS precipitation: enhance purity



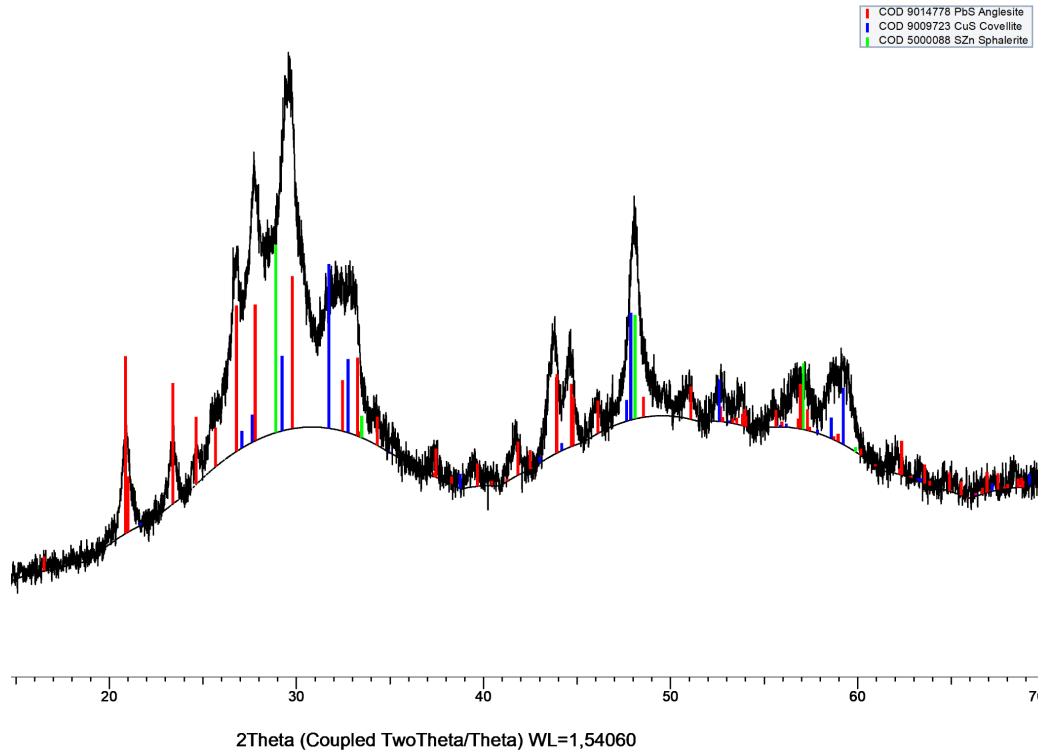
%	Zn	Na	K	Ca	Cu	Fe	Si	Cr	Pb	Cl	Mo	Purity (%)
ZnS	58-59	<LOD	<LOD	<LOD	0.52-0.56	0.15-0.20	0.1-0.16	<LOD	0.3-0.45	<LOD	<LOD	87-88



ZnS precipitation: enhance purity



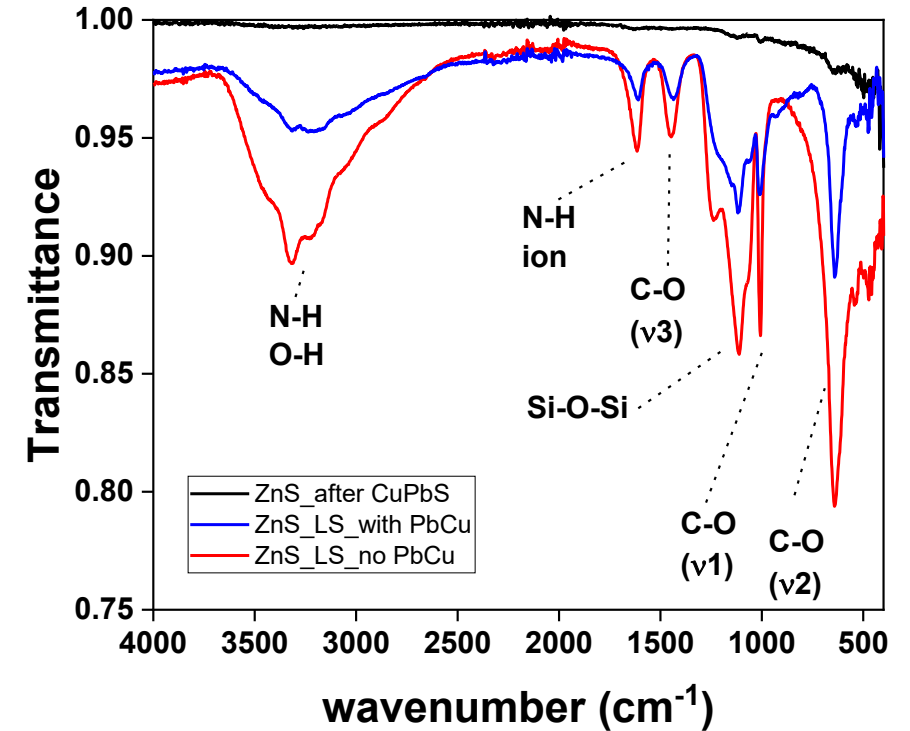
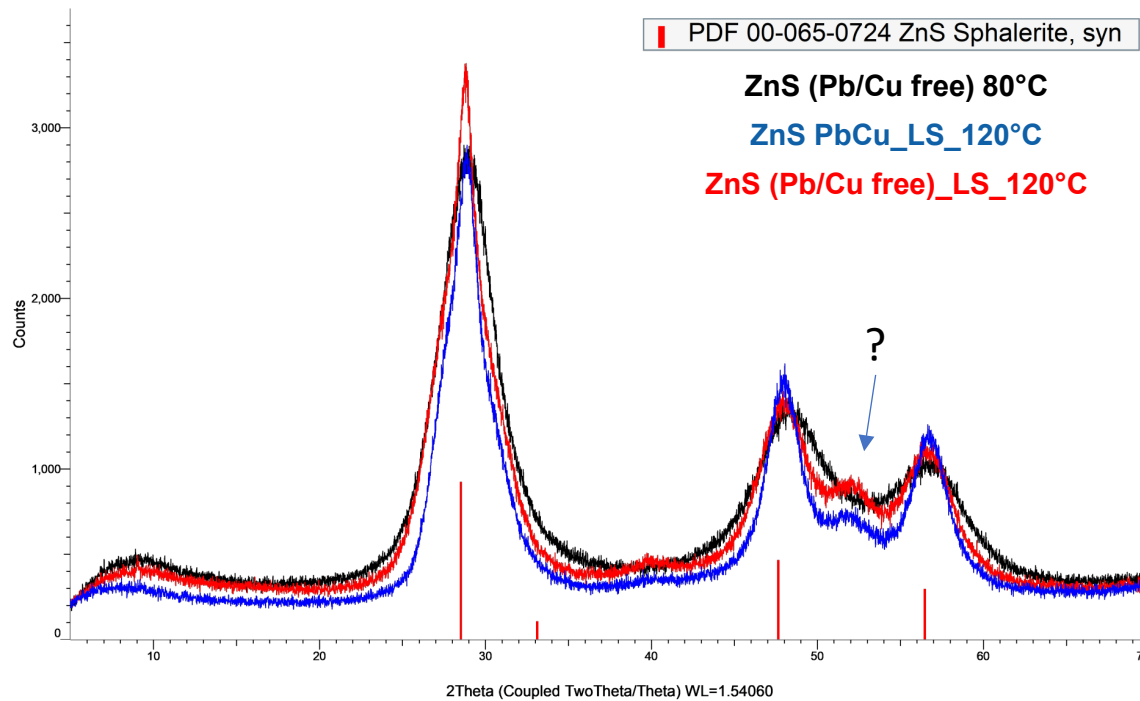
ZnS precipitation: removal of Pb and Cu



- Pb and Cu were removed 100%
- Zn losses < 0.1%

%	Zn	Na	K	Ca	Cu	Fe	Si	Cr	Pb	Cl	Mo
Pb Cu prec.	40.7	<LOD	<LOD	<LOD	8.9	<LOD	<LOD	<LOD	5.3	n.a.	<LOD

ZnS precipitation: enhance purity



%	Zn	Na	K	Ca	Cu	Fe	Si	Cr	Pb	Cl	Mo	Purity (%)
ZnS (Pb/Cu free) 80°C	62.2	/	/	/	/	/	0.01	/	/	/	/	92
ZnS PbCu_LS_120°C	53.1	/	/	/	0.49	0.01	0.12	/	0.43	/	0.01	80
ZnS (Pb/Cu free)_LS_120°C	55.5	/	/	/	/	/	0.05	/	/	/	0.03	83

AAC flowsheet modelling

FLWSHEET: ESP

ITO



EAFDs	
Mass (kg/hr)	1.0037
Volume (L/hr)	0.208969
ZnO (Zincite) (kg/hr)	0.1
Fe3O4 (Magnetite) (kg/hr)	0.83
SiO2 (Quartz) (kg/hr)	0.07
NaCl (Halite) (kg/hr)	1.0e-3
KCl (Sylvite) Solid (kg/hr)	1.0e-3
FeO (Wustite) (kg/hr)	1.0e-4
CuO (kg/hr)	5.0e-4
CrO3 (kg/hr)	1.0e-4
PbO (Massicot) Solid (kg/hr)	1.0e-3

NH3 + (NH4)2CO3	
Mass (kg/hr)	0.0588312
pH	10.1396
Volume Aq (L/hr)	0.0362287

S-3	
T (°C)	25.0
P (atm)	1.0
pH	11.2389
Zn(NH3)4+2 Aq (mg/L)	33191.6

(NH4)2S 20% 2	
Mass (kg/hr)	0.356722
Volume (L/hr)	0.363169
H2O Aq, True (kg/hr)	0.285378

Recirculation 1	
Mass (kg/hr)	3.88758
Volume (L/hr)	3.9003
pH	10.2955
Zn(NH3)4+2 Aq (kg/hr)	3.9003e-4
S-2 Aq (kg/hr)	3.09899e-10

wastewater	
Mass (kg/hr)	0.20461
Volume (L/hr)	0.205279
pH	10.2955

washing water	
pH	9.8794
Mass (kg/hr)	4.47162
Volume (L/hr)	4.49297
K+1 Aq (kg/hr)	4.7185e-3
Na+1 Aq (kg/hr)	3.4986e-3
NaCO3-1 Aq (kg/hr)	0.0

Washing water 1	
Mass (kg/hr)	5.48402
Volume (L/hr)	5.39185
pH	11.0784
CO3-2 Aq (mg/L)	11786.8
CO2 Aq, True (mg/L)	2.81115e-3
NH2CO2-1 Aq (mg/L)	1066.3
NH4+1 Aq (mg/L)	542.535
NH3 Aq, True (mg/L)	18809.3
Zn(NH3)4+2 Aq (mg/L)	26111.0

Washing water 2	
Mass (kg/hr)	5.34338
Volume (L/hr)	5.36058
pH	10.2637
CO2 Aq, True (kg/hr)	4.19411e-7
CO3-2 Aq (kg/hr)	0.0221102
HS-1 Aq (kg/hr)	1.77479e-8
NH3 Aq, True (kg/hr)	0.151969
NH4+1 Aq (kg/hr)	0.0252021
S-2 Aq (kg/hr)	1.28176e-10
Zn(NH3)4+2 Aq (kg/hr)	4.11962e-4

Washed ZnS	
Mass (g/hr)	697.175
Volume (L/hr)	0.621186
ZnS (Sphalerite) (g/hr)	102.033
NH3 Aq, True (mg/L)	28349.4
NH4+1 Aq (mg/L)	4701.38
Zn(NH3)4+2 Aq (mg/L)	76.8502
CO3-2 Aq (mg/L)	4124.59
SiO2 (Quartz) (g/hr)	1.43013
CuS (Covellite) (g/hr)	2.24707e-5
PbS (Galena) Solid (g/hr)	3.07969e-3

S-22	
CuS (Covellite) (g/hr)	0.540764
PbS (Galena) Solid (g/hr)	0.397053
SiO2 (Quartz) (g/hr)	0.112041
ZnO (Zincite) (g/hr)	0.13795
Mass Solid (g/hr)	1.18781

washed PbCuS	
Mass Solid (g/hr)	1.18781
Volume (L/hr)	0.286294
Fe3O4 (Magnetite) (kg/hr)	0.830101
ZnO (Zincite) (kg/hr)	6.38083e-4
Zn(NH3)4+2 Aq (kg/hr)	0.015643
SiO2 (Quartz) (kg/hr)	0.0681908

Washed SOLID RESIDUE	
Mass (kg/hr)	1.50897
Volume (L/hr)	0.788317
Fe3O4 (Magnetite) (kg/hr)	0.830101
ZnO (Zincite) (kg/hr)	6.38083e-4
Zn(NH3)4+2 Aq (kg/hr)	0.015643
SiO2 (Quartz) (kg/hr)	0.0681908

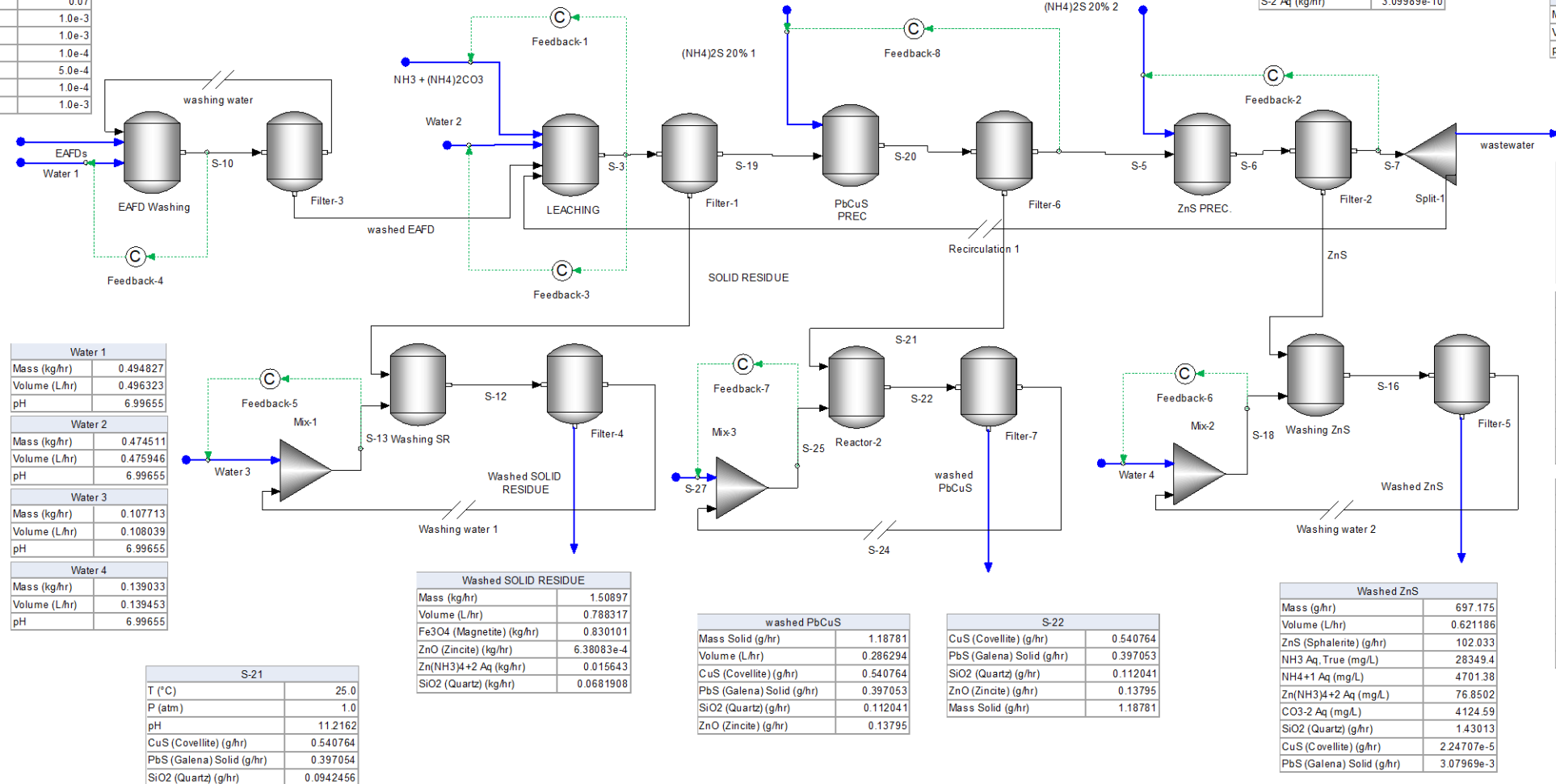
S-21	
T (°C)	25.0
P (atm)	1.0
pH	11.2162
CuS (Covellite) (g/hr)	0.540764
PbS (Galena) Solid (g/hr)	0.397054
SiO2 (Quartz) (g/hr)	0.0942456

Water 1	
Mass (kg/hr)	0.494827
Volume (L/hr)	0.496323
pH	6.99655

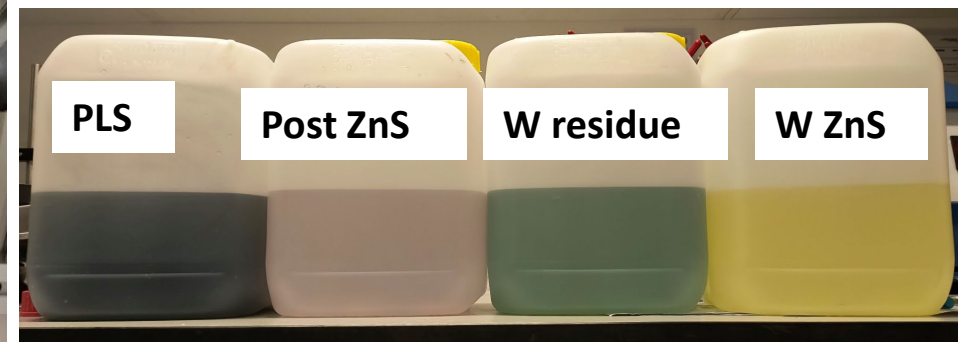
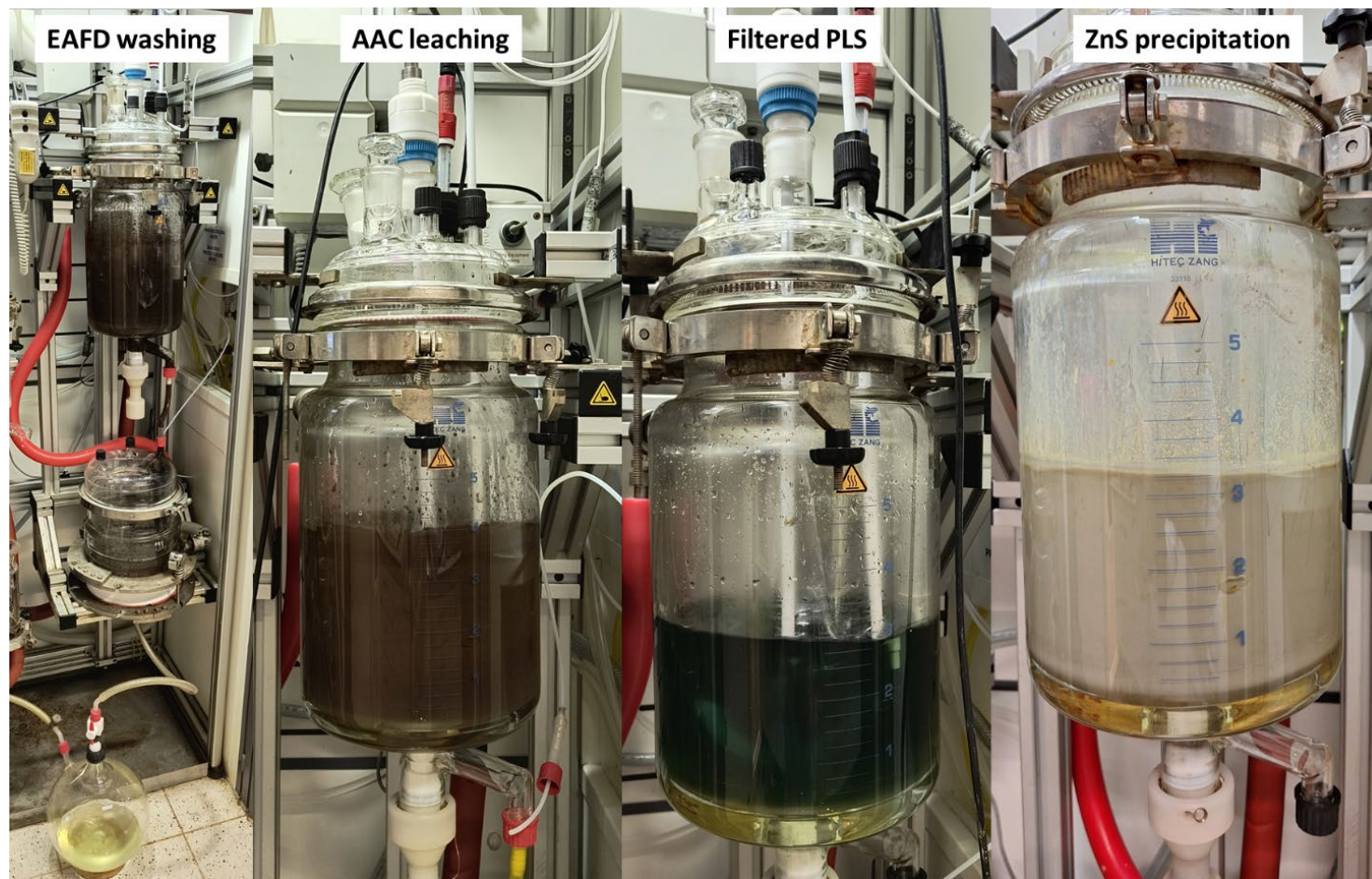
Water 2	
Mass (kg/hr)	0.474511
Volume (L/hr)	0.475946
pH	6.99655

Water 3	
Mass (kg/hr)	0.107713
Volume (L/hr)	0.108039
pH	6.99655

Water 4	
Mass (kg/hr)	0.139033
Volume (L/hr)	0.139453
pH	6.99655



Validate the AAC process



Conclusions



Funded by
the European Union

The process is almost circular

- 45-50% Zn leaching
- 10% in the washing of LR. LR to cleantech
- 90% ZnS
- ZnS purity 85-90% or > 90% with Pb/Cu removal
- 1 kg water/kg EAFD
- 0.08 kg (NH₄)₂S/kg EAFD = 0.38 kg (NH₄)₂S (20 wt. %) sol. /kg EAFD
- << 0.2 kg/kg EAFD

Is it economically viable?

- about 0.5 € per kg of EAFD (ammonium sulphide: 1.9-4.7 €/kg and zinc sulphide: 0.9-18 €/kg) => depends on ZnS purity

Outstanding points

- KCl recovery? Bleed of the closed-loop liquid streams after how many cycles?
- Recovery of Zn in washing of LR (+ 10%)?



Thank you for your attention!

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