NORSEP

"Fra avfall til råvare" Extraction of metal products from MSWI fly ash

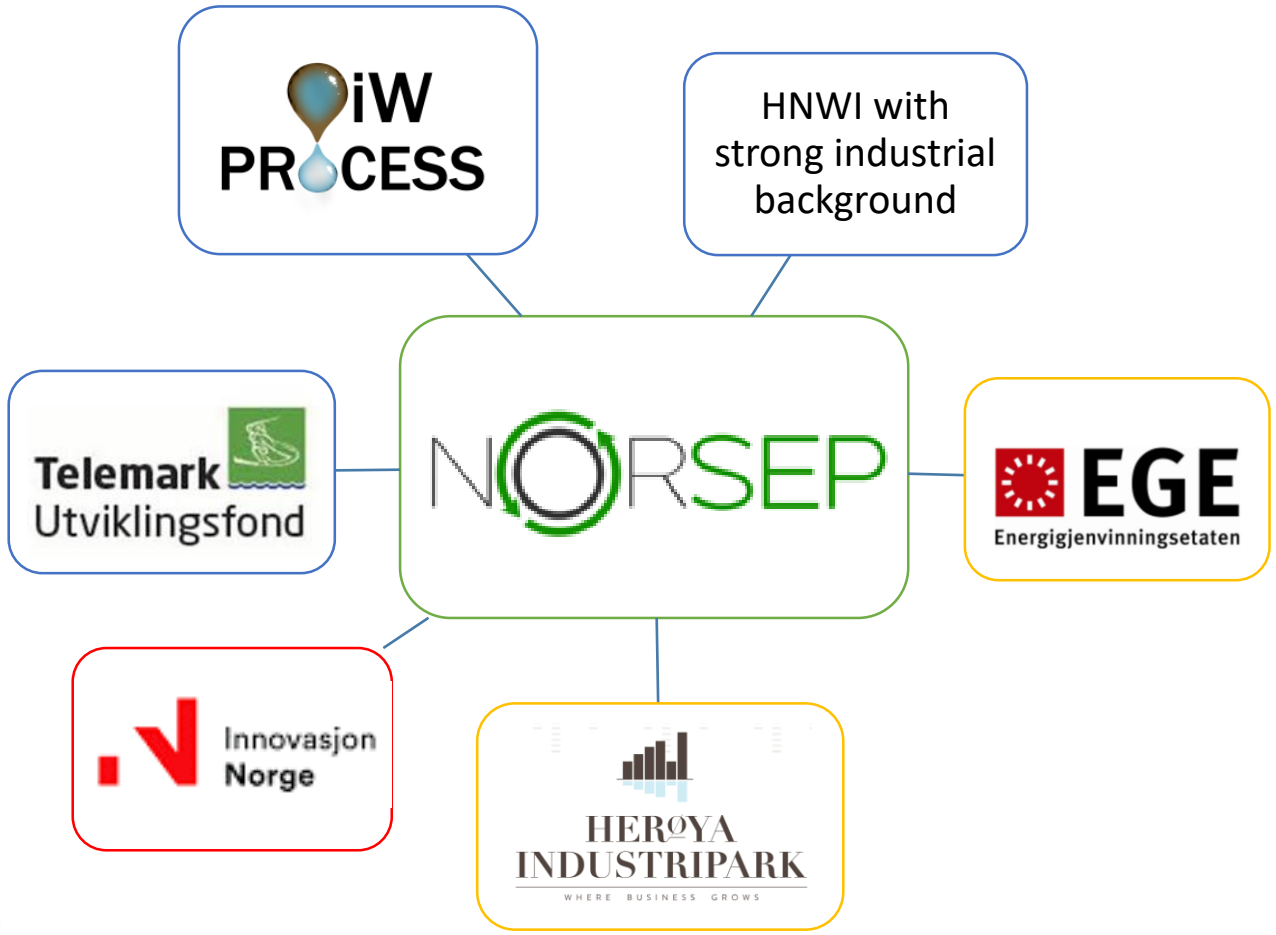
Per Bakke, OiW Process AS

4th Hydrometallurgy Seminar in Oslo

OiW PROCESS

Norsep AS – owners and partners

- R&D and consultancy in process technology
- Developing world leading technology for water purification
- 9 employees (PhD, MSc, BSc) with diversified background in Porsgrunn and Molde, Norway
- Owners:
  - The founders 80%
  - AF Gruppen 20%



The Research Council of Norway

REGIONALE FORSKNINGSFOND OSLOFJORDFONDET

Waste treatment in Norway – opportunity for moving the boundaries for Circular economy?

Langøya 2013

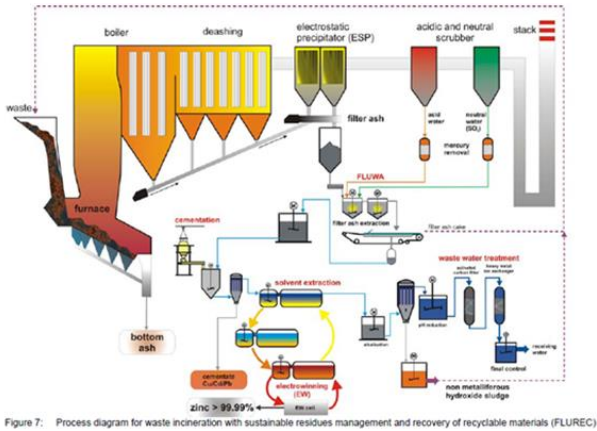
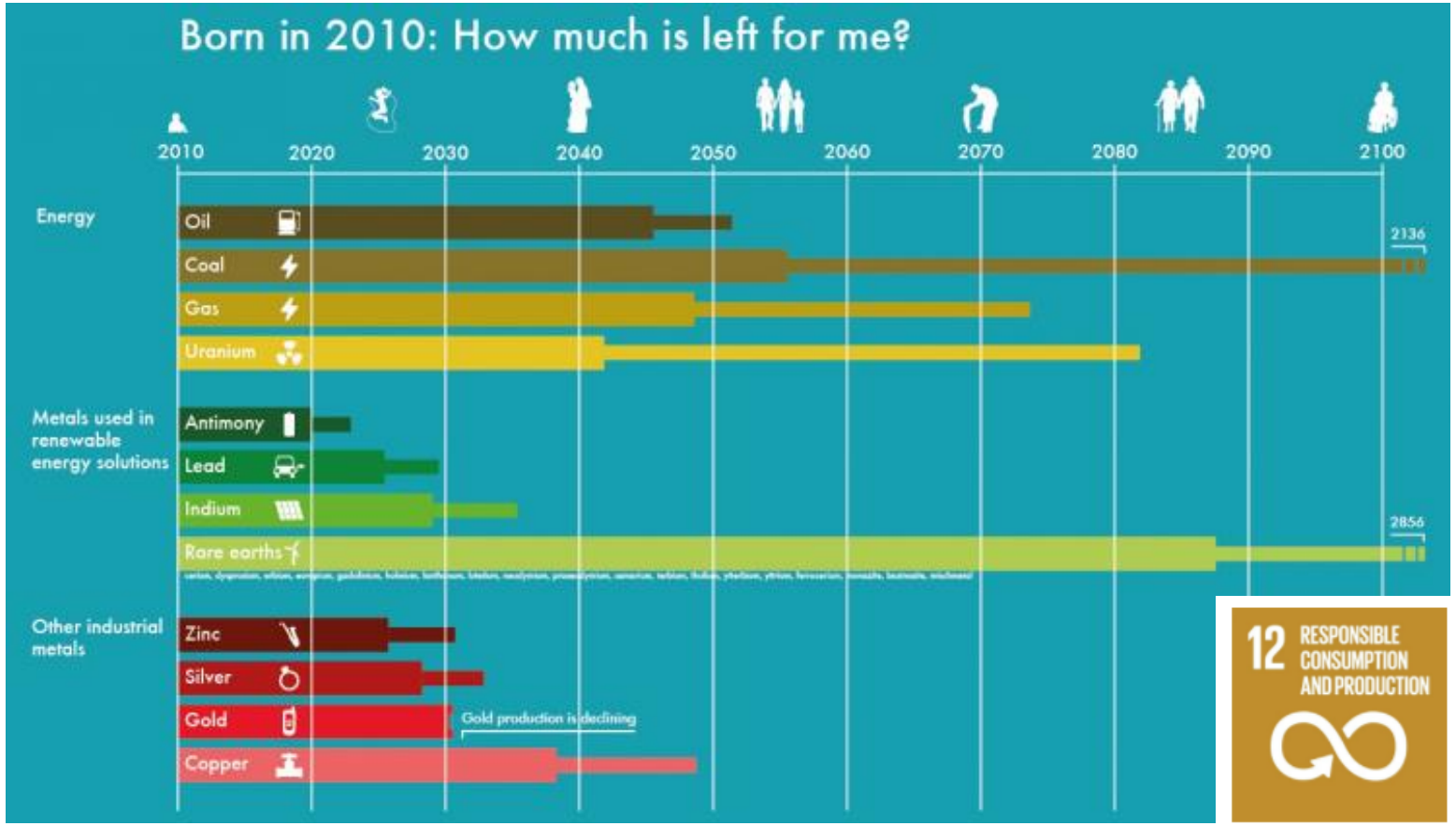


Figure 7: Process diagram for waste incineration with sustainable residues management and recovery of recyclable materials (FLUREC)

- In Norway large amounts of hazardous waste has been safely landfilled at Langøya since the early 1990's
  - >300 000 tons of flyash (FA) from Scandinavia is annually neutralised with contaminated H_2SO_4 from industry to form gypsum
  - Heavy metals in FA and acid are stabilised and the risk for future leakage and contamination of the surroundings is minimised
  - The Langøya site is filled up by 2023
  - State-of-the-art solutions for waste treatment as of the 1990's may be challenged
- Potential for new technology to move the boundaries for circular economy, significantly reducing the volumes for landfill
  - Valuable materials in the waste streams are lost
  - Metal recovery from fly ash implemented in Switzerland
  - Development projects in Sweden/Denmark
  - Activities also in Japan.

Sources: Vurdering av deponeringskapasitet for farlig avfall, Miljødirektoratet 2015; http://www.noah.no/samfunnsansvar/deponiovervaking-langoya/ ;
Avfall Norge, *Potensialet for økt materialgjenvinning av farlig avfall i Norge*, Rapport nr.: 02/2017, 13.01.2017; http://www.recydepotech.at/media/2.3_Weibel_1.pdf ;
http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=search.dspPage&n_proj_id=5787; JP2005272955(A), 2005 (Dowa Mining); JP2007186761(A), 2007; Mitsui Mining;

Fly ash contains non-renewable resources the world can run out of within the next generation

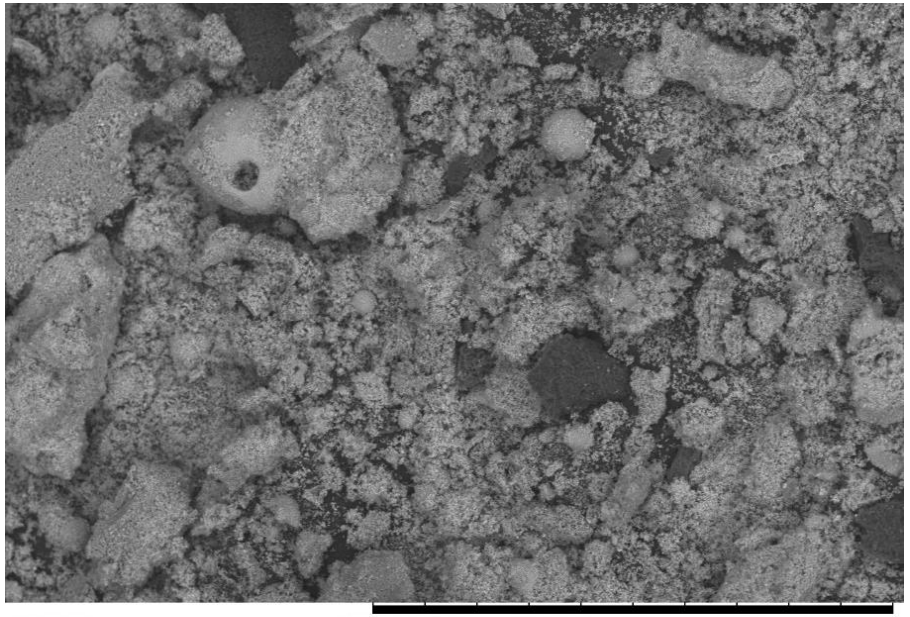


Zinc

- Estimated *reserves* in traditional ores ~220 mill tons
- Annual consumption 13.1 mill tons (2010-2014 average)
- Current recycling rate 31%
- ~25 years until depletion of natural Zn reserves
- Despite this, Zn is *not* on EU's Critical Raw Materials list.

Sources: https://visual.ly/community/infographic/environment/born-2010-how-much-left-me;
https://publications.europa.eu/en/publication-detail/-/publication/6f1e28a7-98fb-11e7-b92d-01aa75ed71a1/language-en

Analyses av fly ash – Sample from EGE Haraldrud, Oslo



Prøve merket: **Flyveaske**		*Semikvantitativ XRF-analyse*
Parameter	**Enhet**	
Ca, Kalsium	%	23
Cl, Klor	%	18
Na, Natrium	%	10
K, Kalium	%	7
S, Svovel	%	4
Si, Silisium	%	2,6
Al, Aluminium	%	1,9
Ti, Titan	%	1,5
P, Fosfor	%	1,0
Br, Brom	%	0,2

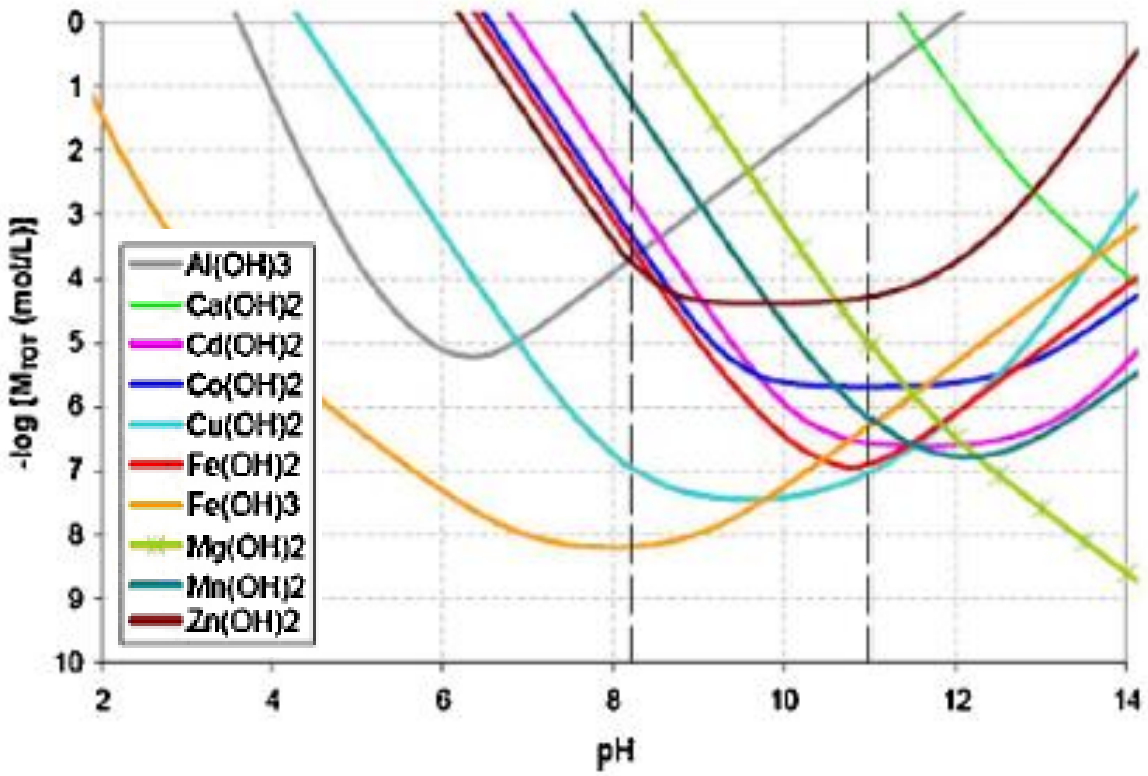
Prøve merket: **Flyveaske**		**Oppslutting i mikrobølgeovn*	*Grenseverdi farlig avfall*
Parameter	**Enhet**		
As, Arsen	mg/kg	35	1 000**
Cd, Kadmium	mg/kg	79	1 000**
Cr, Krom	mg/kg	300	1 000****
Cu, Kobber	mg/kg	640	2 500**
Hg, Kvikksølv	mg/kg	19	1 000***
Ni, Nikkel	mg/kg	53	1 000**
Pb, Bly	mg/kg	1000	2 500***
Zn, Sink	mg/kg	**11000**	2 500**

**Etter oppslutting og analyse med ICP-AES. Bestemmelse av Hg bestemt ved CV-AAS*
***Grenseverdier for oksider av parameter i den europeiske stofflisten.*
****Grenseverdier for kvikksølvforbindelser og blyforbindelser i den europeiske stoffli.*
*****Grenseverdi for kromat i den europeiske stofflisten.*

NORSEP

Sources: SINTEF Molab, *Basiskarakterisering av flyveaske*. Rapport 64910, 09.12.2016

Fly ash partly dissolves in strong acids - metals in solution precipitate as hydroxides with increasing pH



Solubility of metal hydroxides increases with decreasing pH. Most metal hydroxides have minimum solubility in the pH range 6-11

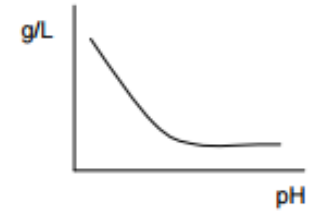
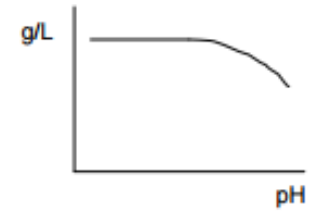
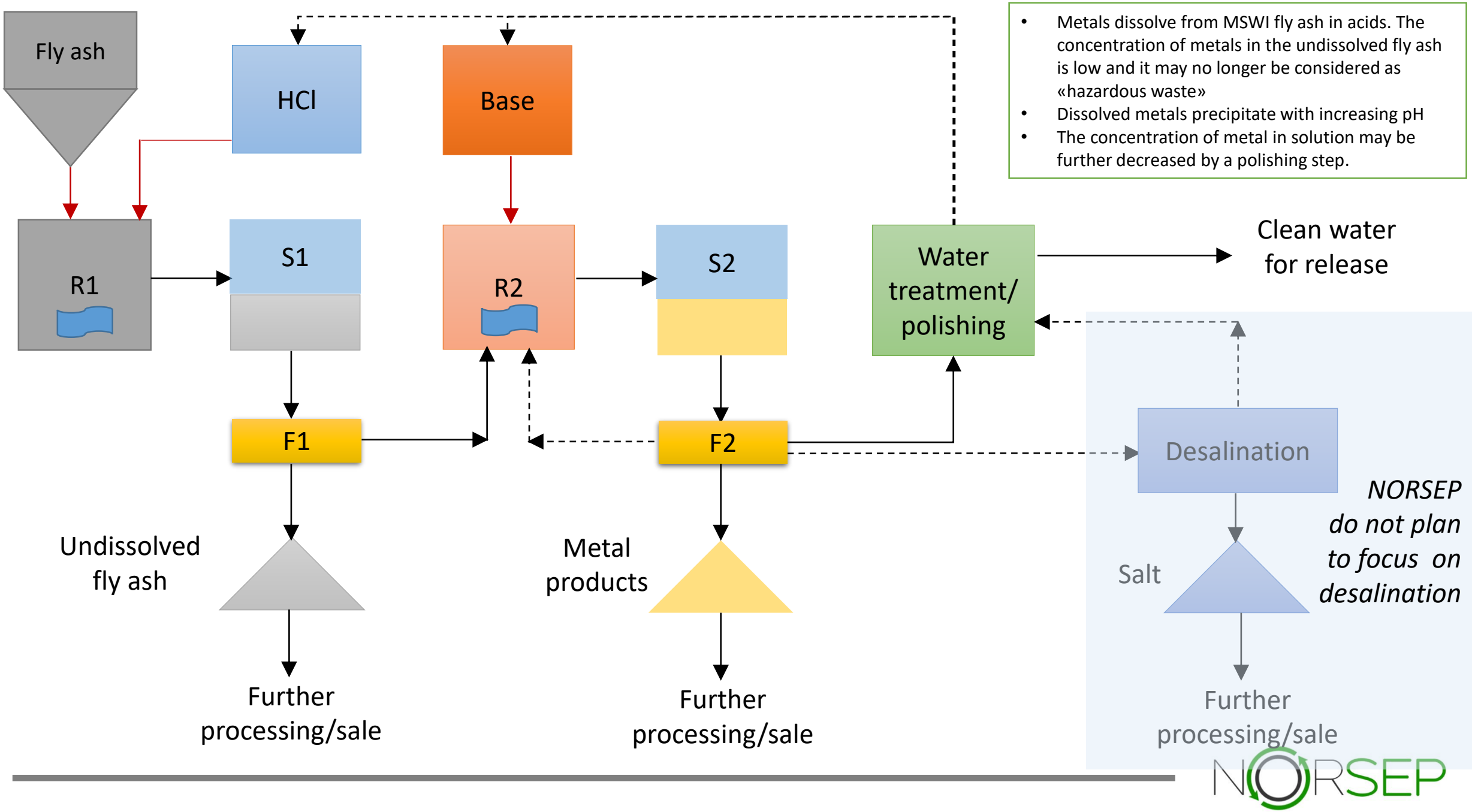
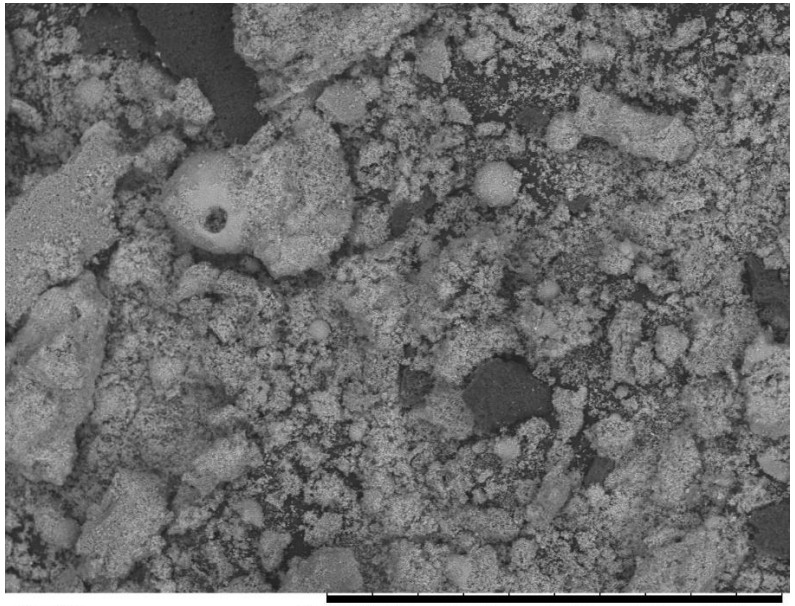
Species	Metals	Leachability vs. pH
Cation-forming and non-amphoteric elements Leaching is approximately constant at pH > 8	Ca	
Amphoteric elements Minimum leaching around pH 7	Al, Cd, Co, Cu, Ni, Pb, Zn	
Oxyanion-forming elements Leaching decreses at pH > 10	As, B, Cr, Mn, Mo, Sb, V	

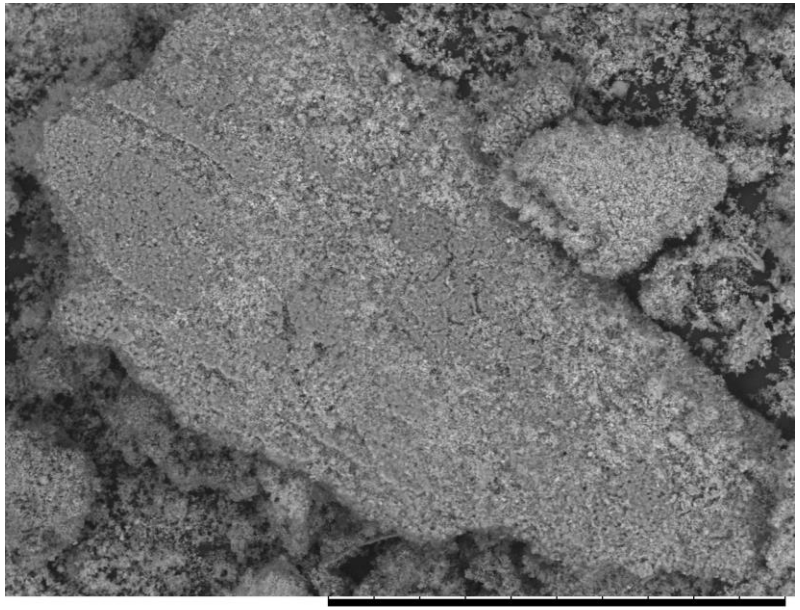
Figure 3.3. The influence of pH on the leaching of certain metals from MSWI ashes.

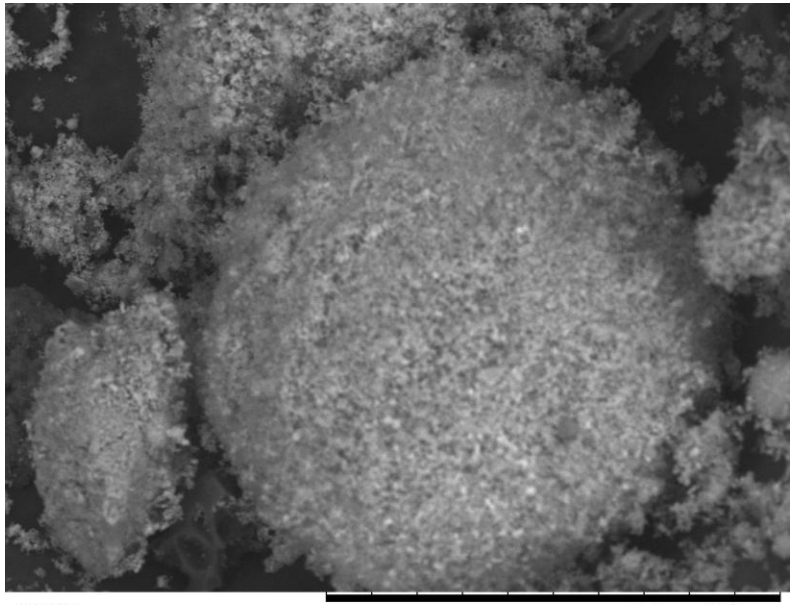
Sources: M.S. Oncel, *J. Env. Chem. Eng., 2013,* pp.989-995;
K.Karlfeldt Fedje, *Metals in MSWI fly ash – problems or opportunities?,* PhD thesis, Chalmers University of Technology, Gothenburg, Sweden, 2010

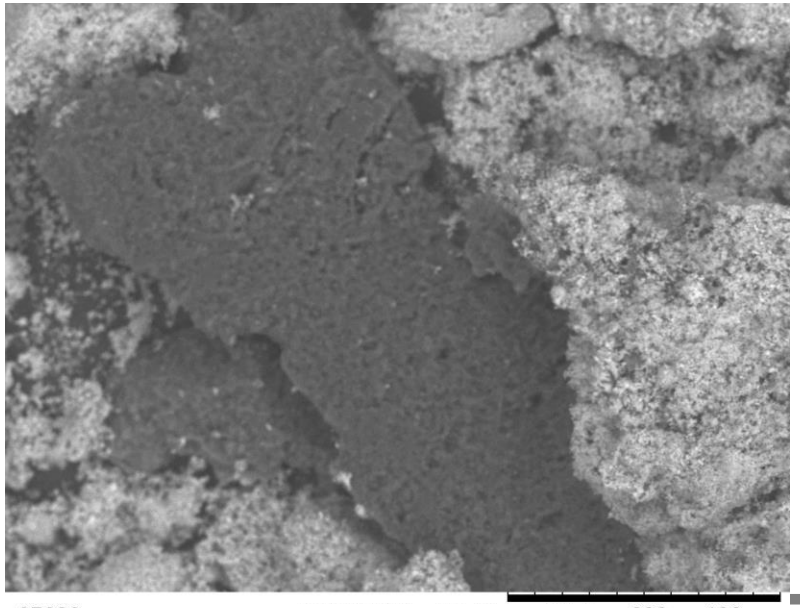


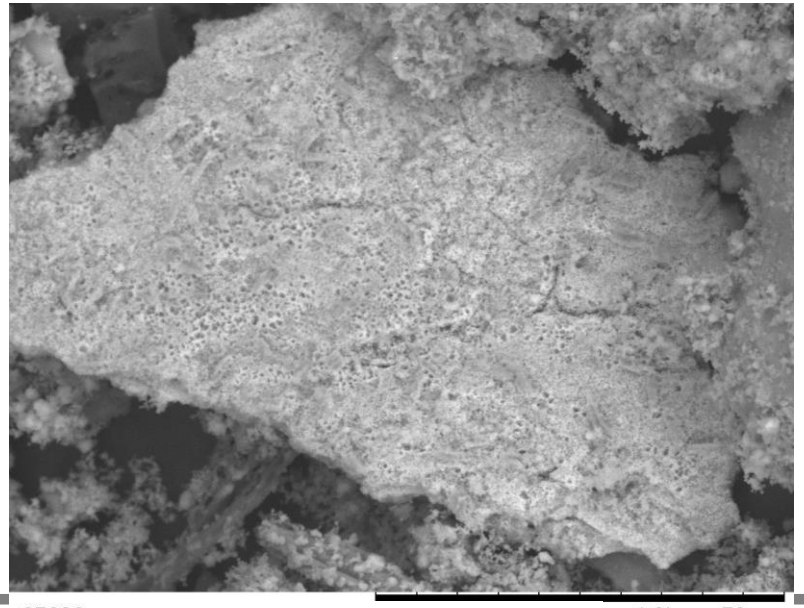
- Metals dissolve from MSWI fly ash in acids. The concentration of metals in the undissolved fly ash is low and it may no longer be considered as «hazardous waste»
- Dissolved metals precipitate with increasing pH
- The concentration of metal in solution may be further decreased by a polishing step.

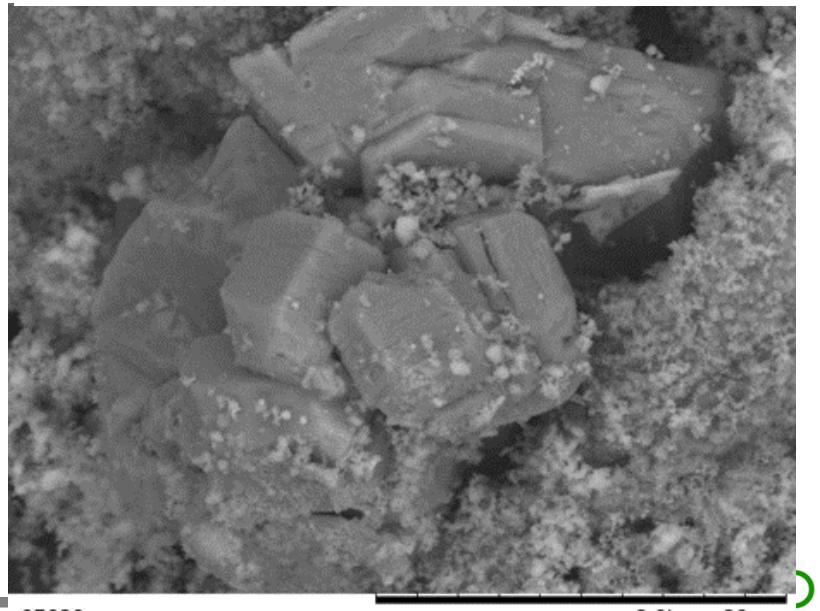

65630
x200 500 um
Flyveaske


65630
x500 200 um
Flyveaske

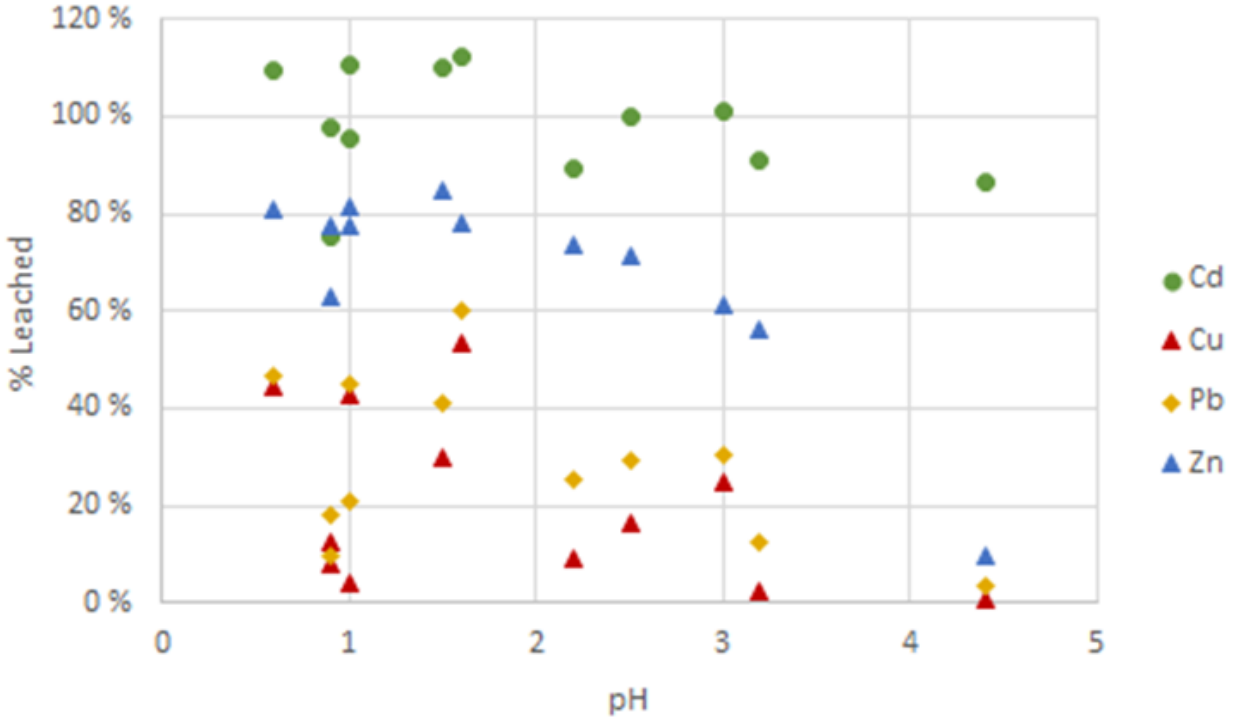

65630
x1.0k 100 um
Flyveaske


65630
x600 100 um
Flyveaske


65630
x1.8k 50 um
Flyveaske


65630
x3.0k 30 um
Flyveaske

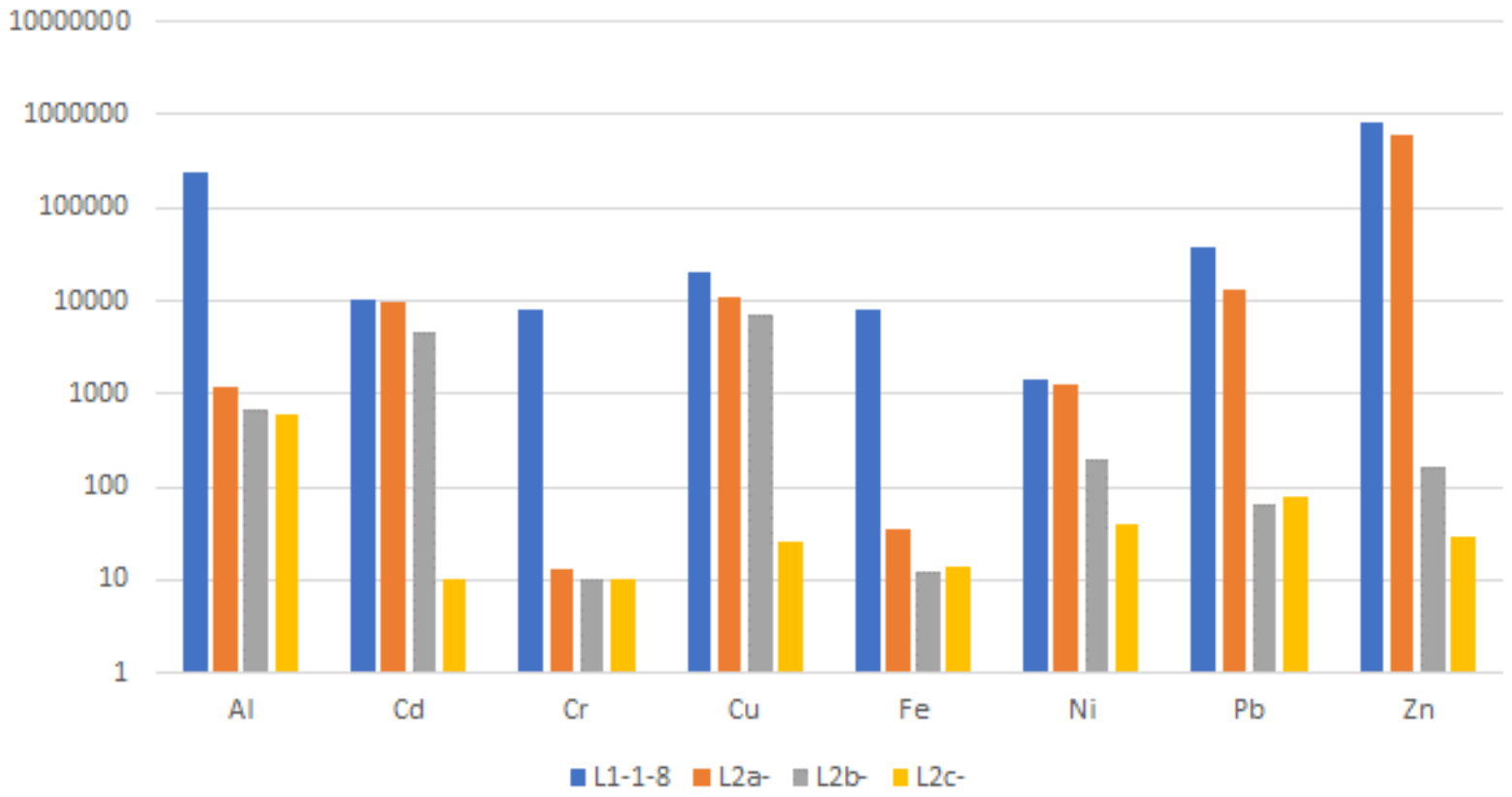
Leaching, C_0=1M



- % leached decerases with increasing pH
- 75% Zn dissolves even at pH = 2.5
- Cd dissolves 100% also at relatively high pH
- Pb and Cu dissolves <50%, inconsistent results.

- At low pH several of the compounds in the fly ash dissolve, causing pH to increase
  - The stronger the acid is initially, the more compounds dissolve
- When more fly ash is added, some compounds still dissolve, while other compounds that dissolved at the lower pH no longer dissolve
- At the same time some phases (hydroxides), may start to precipitate
  - At a certain pH range dissolution of some compounds and precipitation of others may occur simultaneously
- At higher pH dissolution ceases and precipitation dominates.

Precipitation – dissolved elements can partly be separered in different fractions

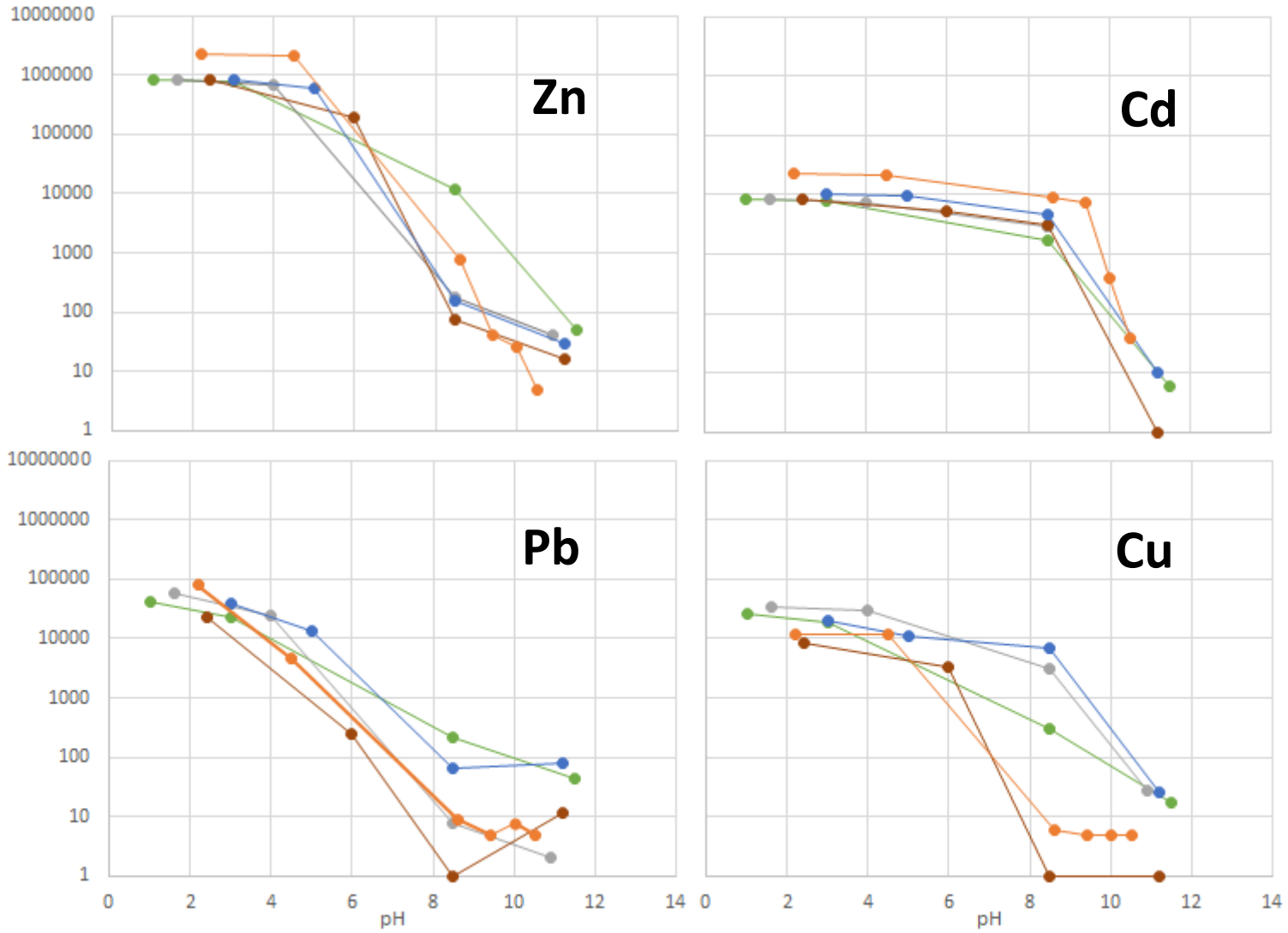


- pH(L1) < pH(a) < pH(b) < pH(c)

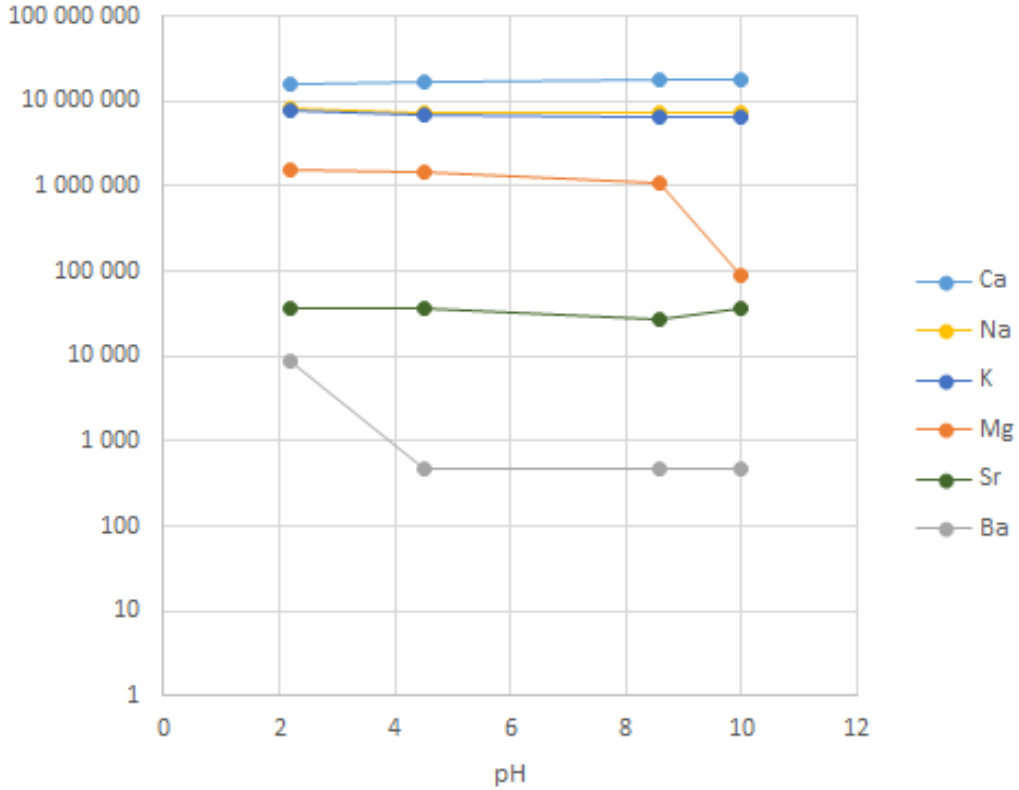
- Al, Fe og Cr precipitate mainly before pH level a
- Zn (and Pb) precipitates between pH levels a and b
- Cd (and Cu) mainly precipitates between pH levels b and c

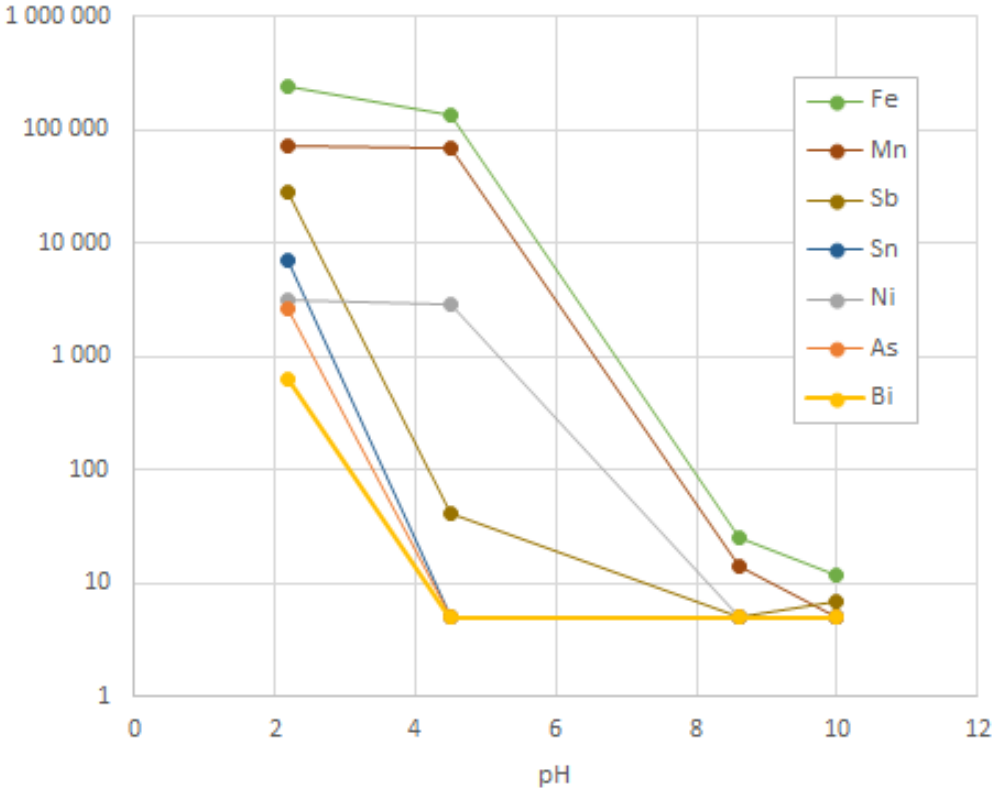
A Zn enriched metal product can be prepared by extracting precipitates at appropriate pH levels.

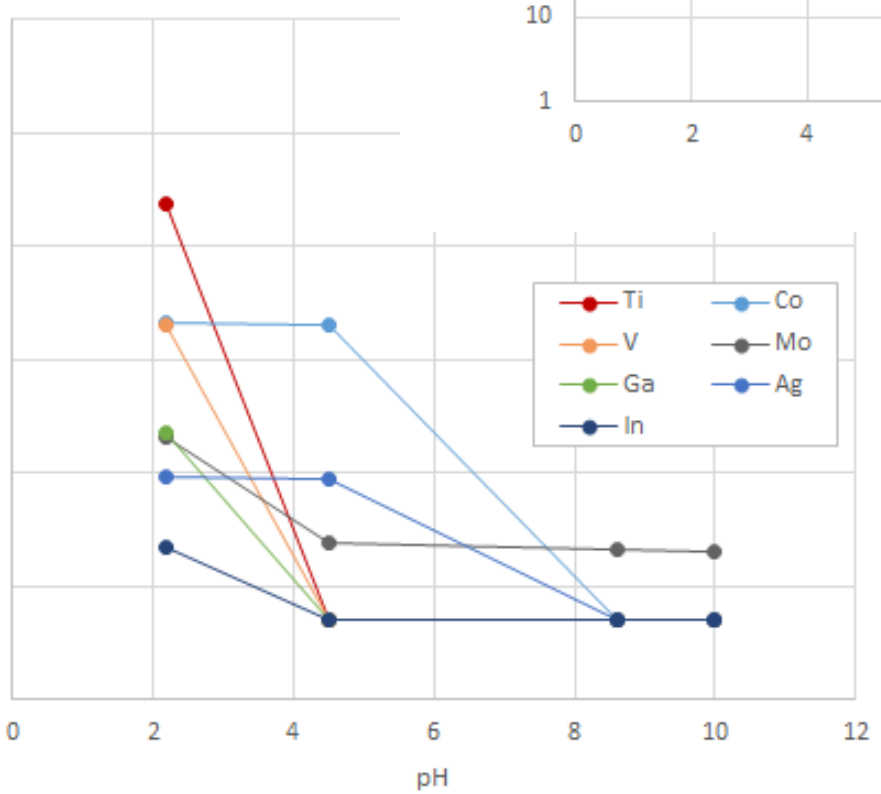
Precipitation vs. pH: Zn, Pb – Cd, Cu



Precipitation vs. pH – other elements

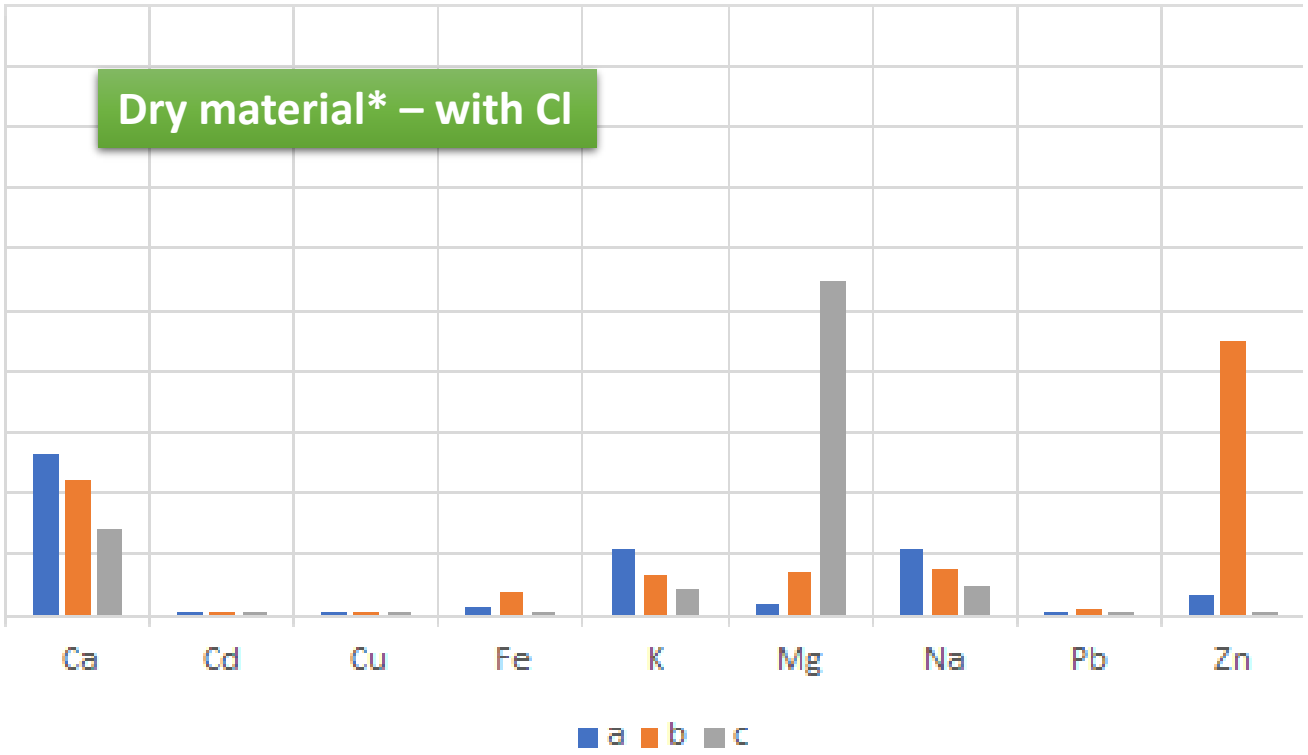


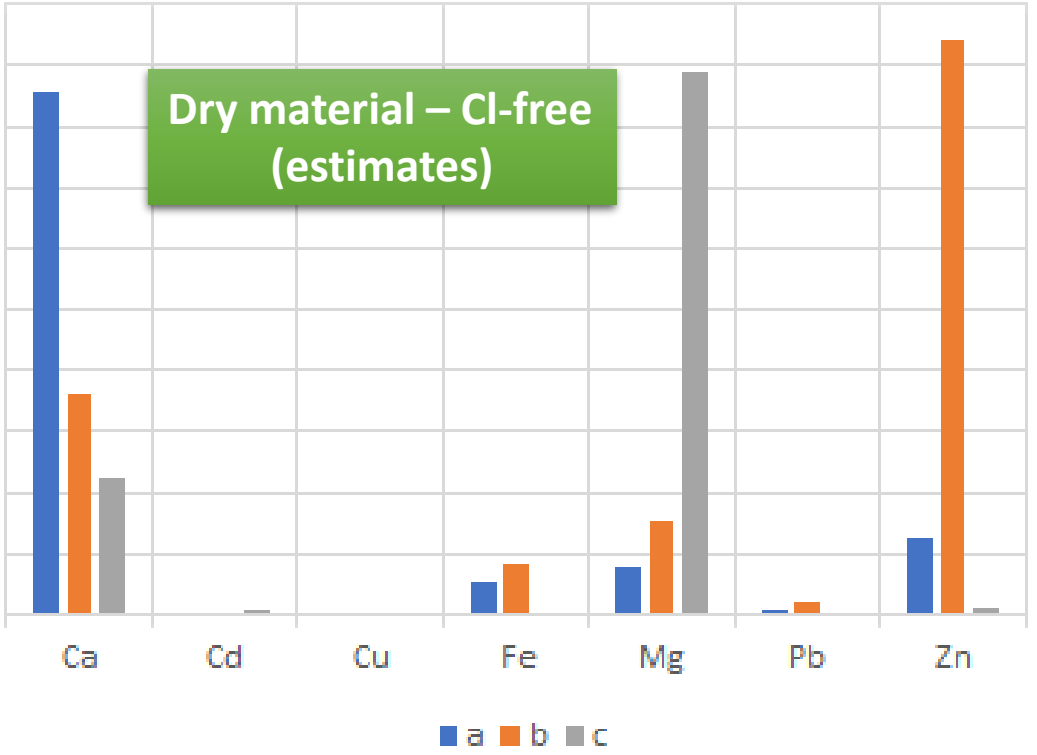




NORSEP

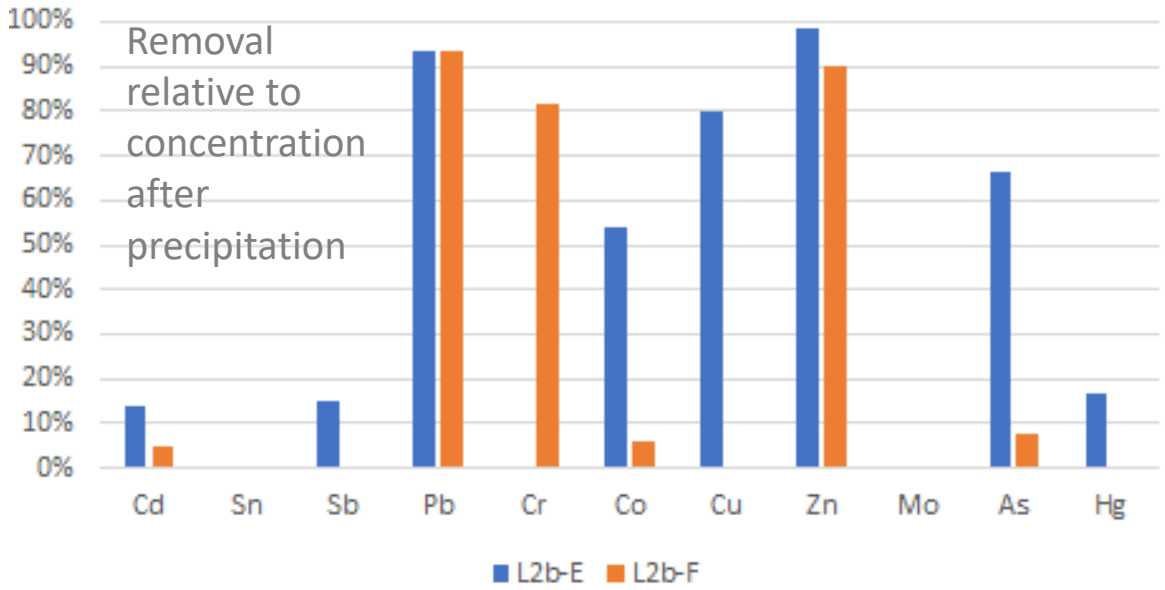
Precipitated matierials



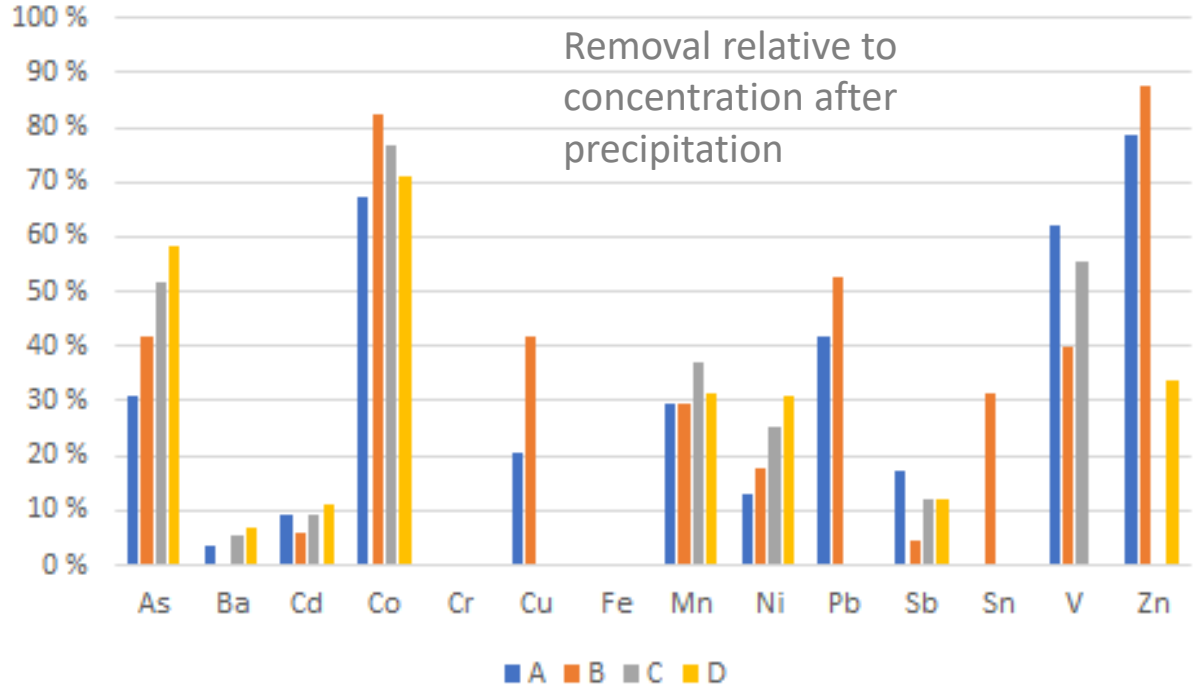


* Drying at 105°C. Chlorides in moisture precipitates during evaporation and contaminate the surfaces.

Polishing of NORSEP wastewater using different adsorbents (A-F)



- Different adsorbents (E and F) can selectively decrease the metal contents significantly
- Additional removal of >90% have been demonstrated for Pb and Zn, approx. 80% for Cr and Cu, and 50-70% for Co and As
- Adsorption of Co, Sb and Mo is limited for the adsorbents tested.



- Different adsorbents (A, B, C and D) can selectively decrease the metal contents significantly
- From the solution with pH adjusted to level b, additional removal of 70-90% have been demonstrated for Co and Zn, and above 50% for As, Pb and V
- Ba, Cd, Mn, Ni and Sb exhibit limited response to adsorption, at least for the adsorbents A-D tested.

Phase 2 of NORSEP project - ongoing

- Lab-activities
  - Verify process – create interest
  - Input for design of pilot
  - Prepare test material for evaluation of process equipment
- Pilot - preparations
  - F-park Herøya – June 2018
  - Equipment
- Application for EU-funding phase 3 for building of a demonstration facility at a WtE -plant
  - Prepare and submit application – deadline May 2018
  - Professional assistance in the application process

A compact NORSEP -facility

Compact fly ash treatment facilities at existing or new MSWI sites

- Utilise acid already available from wet scrubbers
- May utilise existing water treatment system
- Less variation in fly ash composition
- Infrastructure for energy recovery in place.

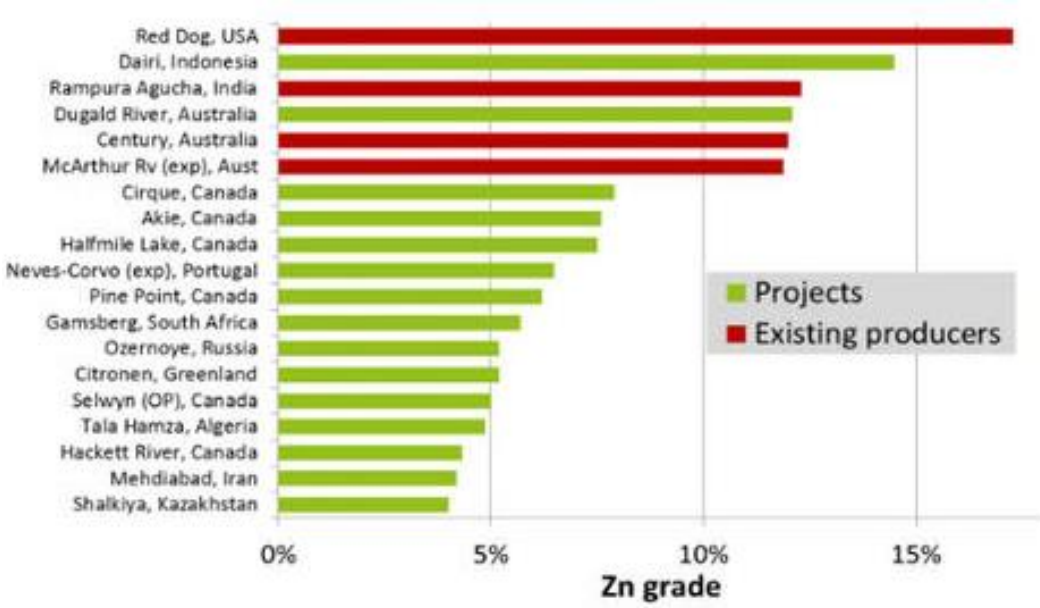
Centralised plants, e.g. at the sites of companies utilising main material streams.

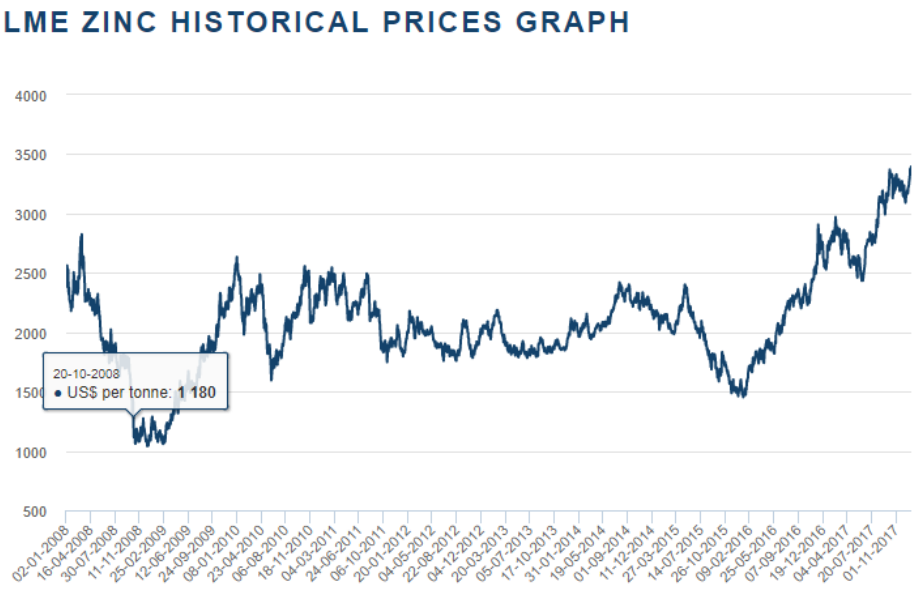
- CAPEX/ton

Urban Mining from fly ash becomes competitive ?

- One or more material streams from NORSEP-process will mainly consist of metal hydroxides
- With Zn content of 20-50% the metal hydroxide concentrate(s) could be tailored to become commercially attractive for subsequent production of oxides and/or extraction of metals
  - Mining projects with zinc grades of 4% are considered for realisation

Example: 300.000 tons of FA containing ~1.5% Zn may yield 4500 tons of Zn, representing ~10 mill €





Sources: http://www.mining.com/web/a-stealth-bull-market-coming-for-a-particular-metal-and-one-way-to-play-it/ ; http://www.lme.com/en-gb/metals/non-ferrous/zinc/#tab2

NORSEP – materials produced from waste streams

Haraldrud MSWI plant, Oslo, Norway. Capacity 100000 tons/yr.

- Raw materials
  - Flyash
  - Waste acid
  - Waste base
- Products
  - Undissolved flyash
  - Metal concentrates
  - (Salts)

Commercially attractive products may be prepared from a combination of waste streams, with minimum use of virgin raw materials