SECOND INTERNATIONAL
SLAG VALORISATION SYMPOSIUM
THE TRANSITION TO SUSTAINABLE MATERIALS MANAGEMENT

TU Delft
Delft University of Technology

High Temperature Processing of Secondary Metallurgical Resources

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centre

SMART-PRO²

Overview

- **Introduction**
- **Research overview (TU Delft)**
  - Municipal solid waste incineration (MSWI) bottom ash
  - Zinc bearing residues
  - Vanadium containing fly ashes
- **Resource recovery from MSWI bottom ash**
- **Conclusions**

Secondary metallurgical resources

- **Scrap (metallic)**
  - New (prompt) scrap; old scrap
- **Metal bearing waste (non-metallic)**
  - Solid waste generated during (metallurgical) processing
    - Slags
    - Flue dust
    - Solid residues and ashes
  - Concentration tailings
  - Urban mines/landfill mines

Processing waste

Mining waste

EOL waste

Mine tailings

Metallurgical slags, residues

Urban mines: EOL products

Global flow of metals

- **Where the metals go?**
  - **Production of 1 ton of refined zinc: 420 kg of zinc loss**
  - **Where are the loses?**
    - **Tailings 34%; slags/solid residues 11%; landfill 55%**

Prompt scrap is recycled back to refined metal!

Metal	Zn (1994)	Cu (1994)	Ag (1997)	Ni (2000)	Cr (2000)
Mine metal (ore, kt)	7.800	9.490	20.200t	1.338	5.140
Refined metal (kt)	7.210	11.800	24.600t	1.120	3.900
Total metal loss (kt)	3.033	3.350	9.400t	509	1.910
Metal loss/Refined metal	0,42	0,28	0,38	0,45	0,49
Tailings (kt)	1.030 (34%)	1.400 (42%)	4.000t (42.5%)	167 (32.8)	740 (39%)
Slag (kt)	330 (11%)	150 (4%)	1.400t (15%)	74 (14.5%)	590 (31%)
Metal to landfill (kt)	1.673 (55%)	1.800 (54%)	4.000t (42.5%)	268 (52.7%)*	580 (30%)
Reference	Gordon et al.,2004	Lifset et al., 2002	Johnson et al., 2006	Reck & Gordon, 2008	Reck & Gordon, 2008

Metal loss during Concentration-smelting	~17%	~16%	~27%	~18%	~26%

Other potential sources of metals

- Residues from non-metallurgical industry
  - Power generation industry
    - Fly ashes
  - Thermal waste processing industry
    - Fly ashes
    - Bottom ashes
  - Petrochemical/chemical industry
    - Spent catalysts
- Not all metals are feasible for recovery.
  - Reactive and light metals such as Al, Mg, Si, Ca etc. in the slags or ashes

Am I forgetting any other sources of metals?

Research overview (TU Delft)

- **Metal recovery from secondary resources**
  - **Ash utilisation:** metal recovery, vitrification
    - MSWI bottom ash: vitrification
      - Metal recovery and refining
      - Slag formation and slag chemistry
  - **Residue treatment:** metal recovery
    - **Zinc recovery:** from various solid residues
      - Galvanising (HDG) bottom dross
      - Brass recycling flue dust
      - Industrial Zn-bearing residues (similar to EAF dust)
    - **Smart processing:** waste + waste = product
      - Fe-V production (using BOF dust + power plant fly ash)

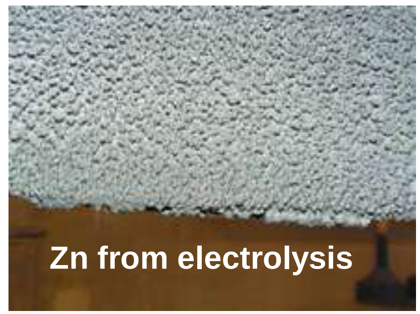
From solid residues to zinc metal

- Rotterdam Harbour: 5000 tons Zn residues stored for 17+ years without solutions.
- Dutch brass recycling industry generates a few thousands tons of filter dust and slag rich in zinc.
- Dutch steel industry: over 5000 tons of Zn metal lost as flue dust (EAF, BOF, BF)
  - 30 mt/year flue dust (worldwide)
- Galvanising industry: 500 tons almost pure zinc lost as dross
- Zinc ferrites and Gahnite spinels in flue dust: difficult to recover!

From solid residues to zinc metal

- TU Delft: Pyro- and Hydrometallurgical processes

Product: Zinc metal



Na_2CO_3 Roasting

NaOH leaching

Electrowining

Brass recycling flue dust

Carbothermic reduction

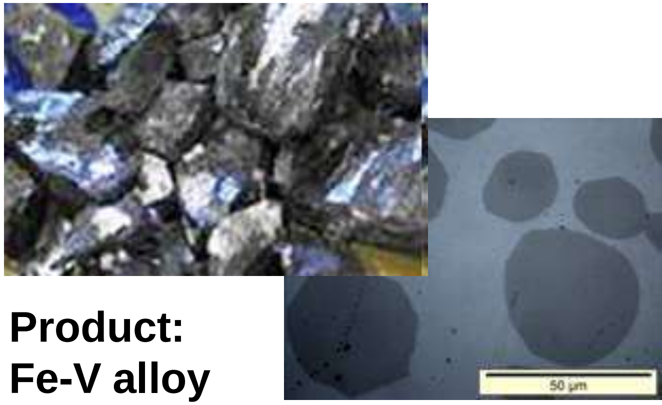
ZnO or Zn metal

Smart processing of multi-wastes

- **Waste + Waste = Products!**
- Example: FeV alloy production
  - Fly ash from oil-fired power plant: source of V and C
  - Flue dust from BOS steelmaking: source of Fe

(V+C)-bearing power plant fly ash

BOF steelmaking Flue dust



Product: Fe-V alloy

MSW Incineration bottom ash

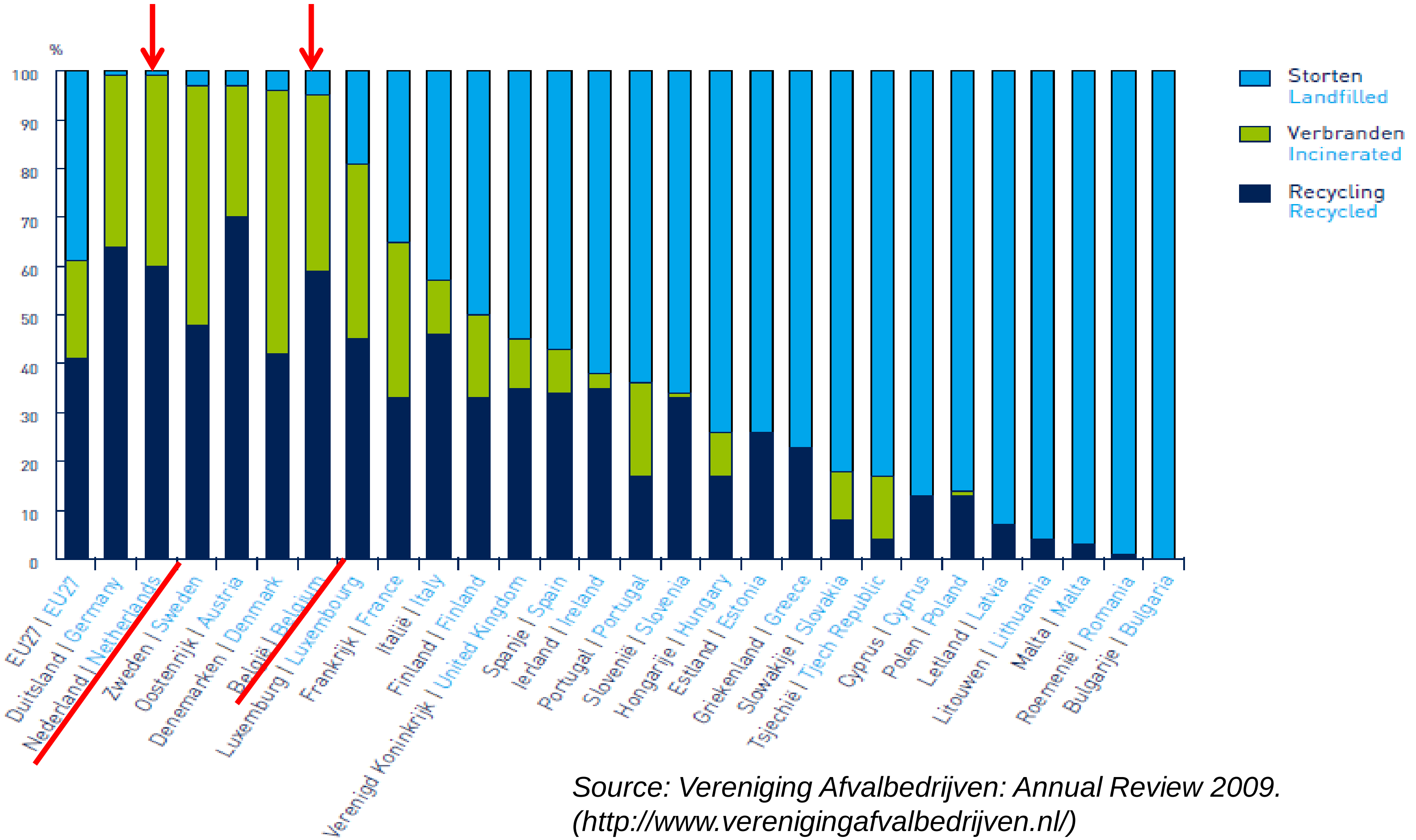
- **Metal recovery and slag utilisation**
  - MSW incineration (Waste-to-Energy)
  - European Union
    - 60 million tons annual processing
    - Generation of more than 10-20 million tons of bottom ash
  - Netherlands (2008)
    - Processing over 6 million tons of MSW in 11 MSWI
    - 3000 GWh electricity, 3000 TH thermal energy
    - 11% sustainable energy
    - **1,321 kt bottom ash, 85 kt fly ash**
    - **115 kt ferrous scrap, 21,5 kt non-ferrous scrap (from bottom ash)**

European policy "Stimulating recycling & energy recovery"!

Dutch national policy "Stimulating materials recycling"!

MSW Incineration bottom ash

- EU MSW processing: recycling, combustion, landfill (2008)



Source: Vereniging Afvalbedrijven: Annual Review 2009. (http://www.verenigingafvalbedrijven.nl/)

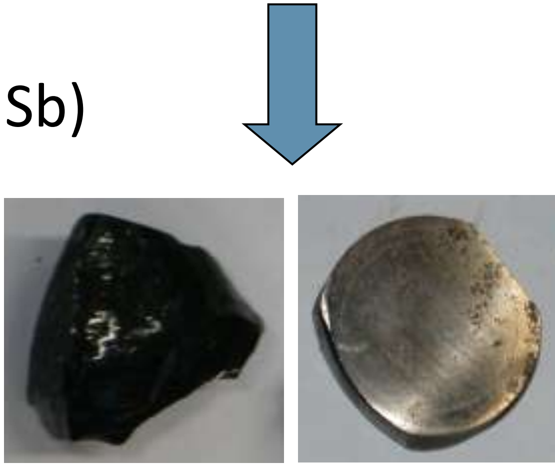
MSWI and the bottom ash

- MSW Incineration

- Bottom ash (BA)
  - 20-25% of the MSW
  - Valuable resource of metal
  - 15 -20% metal in the BA
  - Only 60% metal recovered

Bottom ash treatment

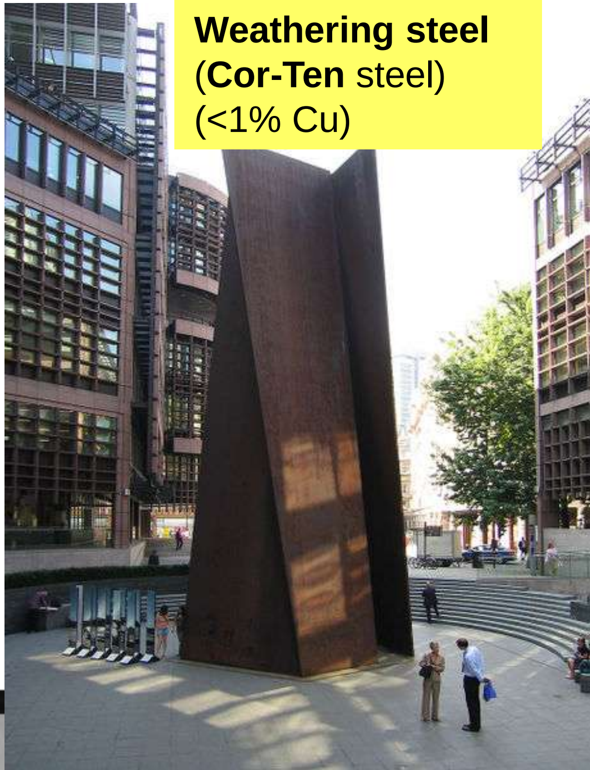
- **Current practice**
  - Physical separation of metal (partial)
    - Magnetic separation
    - Dry or wet eddy current separation
  - Construction material (low grade)
  - Unstable and leaching problems(Cu, Mo, Sb)
- **Vitrification: safer option**
  - Melting the ash at above 1400^{o}C
  - 2 useful products: **metal + slag**
  - Option for safe ash disposal/utilisation
  - Conversion of ash to stable glassy slag
  - Metals recovered as an alloy



Bottom ash treatment

- **Vitrification product – recovered alloy** (AVR case)
  - ~ 8% of total bottom ash
  - Chemical composition:
    - **Fe-Cu** based
    - 82% **Fe** – 12% **Cu** – 2% **P** – 1.5% **S** – 1.5% **C** + 1% other impurities
  - Market for the alloy?
    - Direct applications?
    - Steel scrap?
    - Copper scrap?
  - **Purification necessary!**

Star-40 crucible steel
(1%Cu, 3% Ni, 1.5%Mn…)



Weathering steel
(**Cor-Ten** steel)
(<1% Cu)

Bottom ash treatment: Fe-Cu separation

- **Copper removal** from steel and Fe-based alloys
  - Cu as a harmful impurity in steelmaking
    - Steel scrap tolerance: 0.5-1.0% Cu
  - Fe-Cu alloy from MSWI ash vitrification: high in Cu
    - Over 10% Cu, no commercial or any research results available
- **Possibilities**
  - Vacuum refining, chlorination, filtration
  - Sulfide treatment: FeS-based sulphide mixture
- **Current research Objective:** sulphide treatment
  - Cu recovered as a matte: Cu_2S-FeS --> copper smelter
  - Steel scrap: low in Cu (market in steelmaking industry)

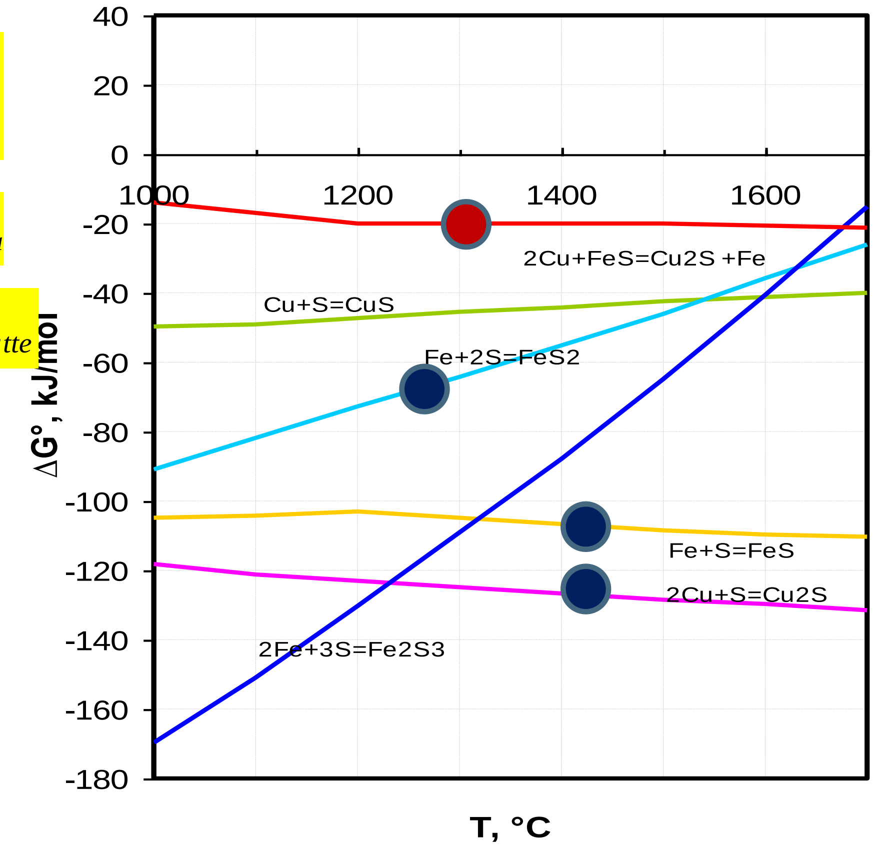
Fe-Cu separation: sulphide treatment

- **Principles**

$$2[Cu]_{alloy} + MeS = [Me]_{alloy} + (Cu_2S)_{matte}$$
$$(Fe, Zn, Al, Na, Ni, etc.)$$

$$2[Cu]_{alloy} + FeS = [Fe]_{alloy} + (Cu_2S)_{ma}$$

$$2[Cu]_{alloy} + ZnS = Zn_{gas} \uparrow + (Cu_2S)_{matte}$$



- **Challenges**
  - New impurities?
    - FeS best option
  - Phase separation
    - Fluxing agent needed
    - Carbon saturation: critical

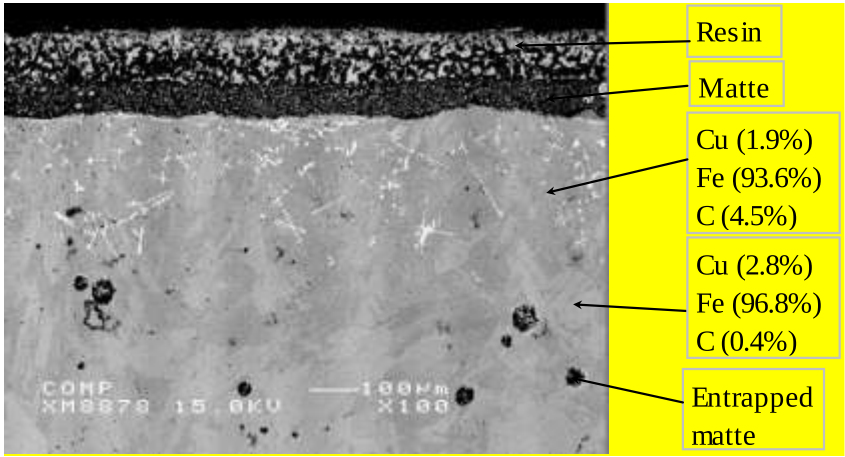
Experiments

- **Furnace:** vertical tube furnace
- **Synthetic Fe-Cu alloy**
  - 87.2% Fe + 12.8% Cu
- **Temperature:** 1500°C
- **Atmosphere:** N_2 flow (100 l/h)
  Reaction time: 2-4 hours
- **Reaction system:**
  - Graphite crucible; C-saturation
- **S/Cu ratio:** 2-8 stoichiometric
- **Analysis:** XRF, SEM, EMPA

Lab-scale furnace

Fe-Cu separation: sulphide treatment

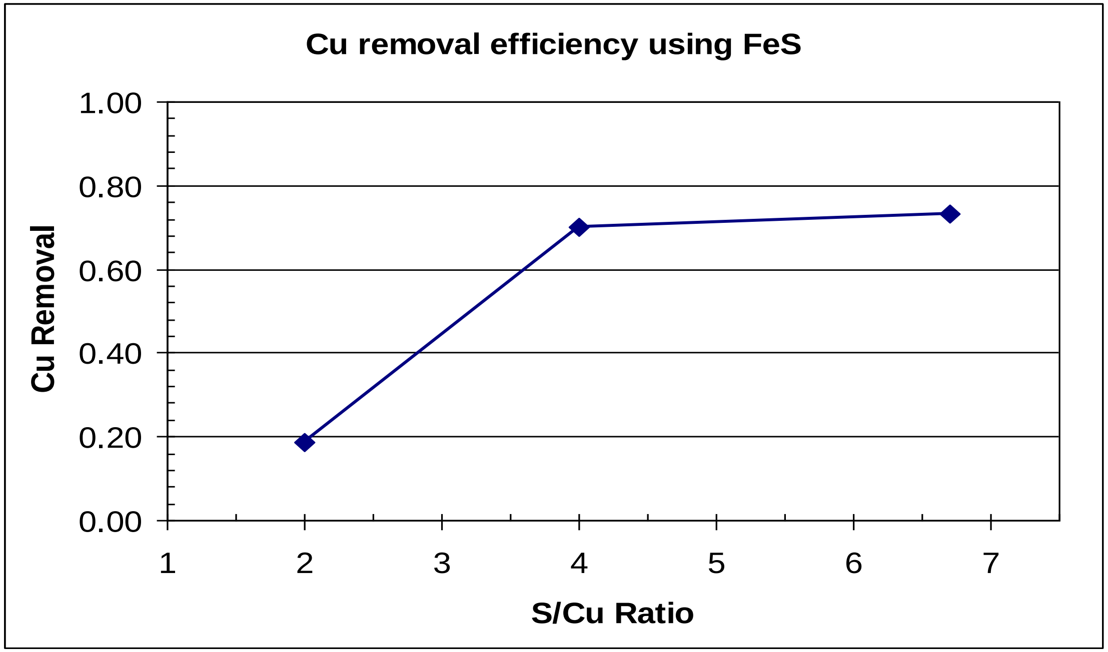
- If no C-saturation, no phase separation
  - Matte ($FeS-Cu_2S$) – alloy (Fe-Cu) fully mixed
- Under C-saturation, separate matte layer
- Cu in the alloy: reduced (pushing out by carbon)



S/Cu=4.0 at 1500°C

Fe-Cu separation: sulphide treatment

- FeS alone is ineffective
  - Effect of S/Cu ratio



Fe-Cu separation: sulphide treatment

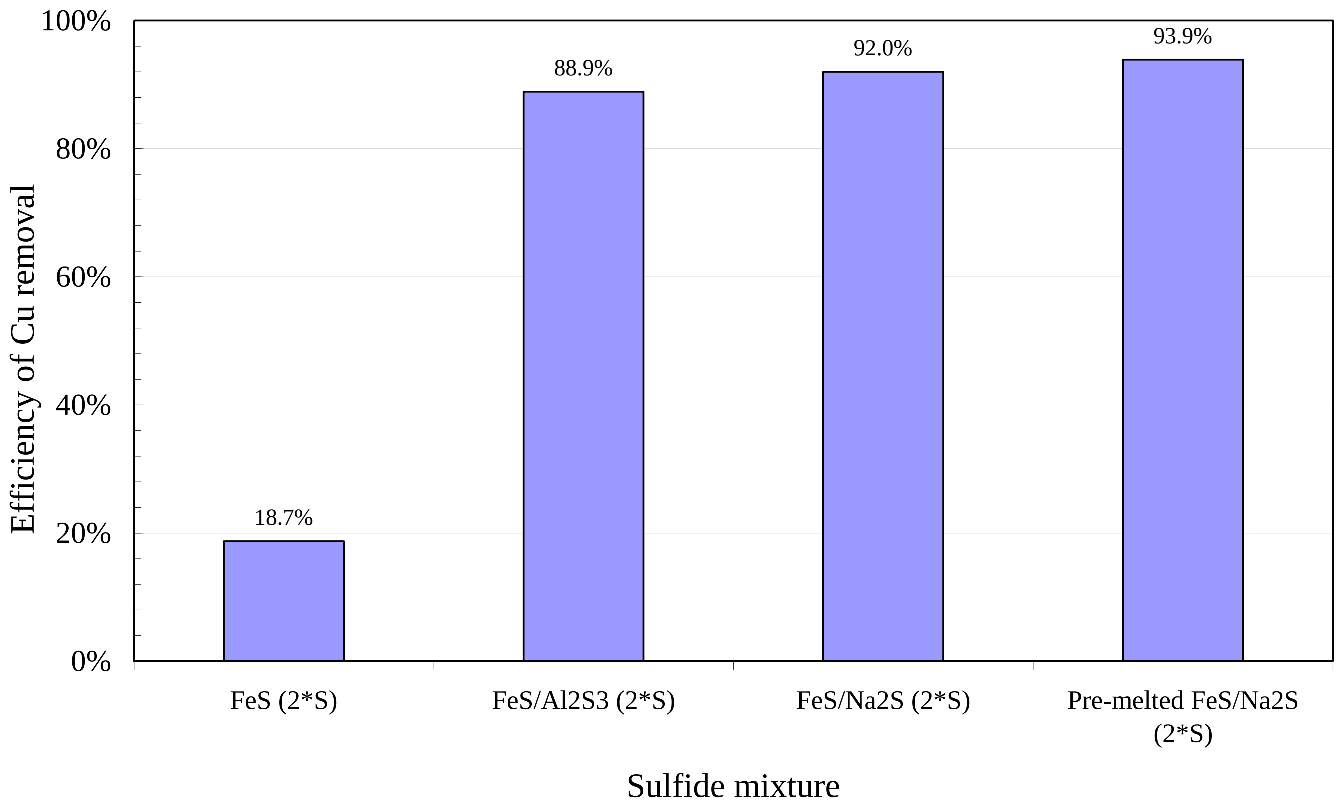
- **Effect of sulphide additives**
  - Lowering the melting point of sulphides
  - Decreasing the activities of Cu_2S
  - Possibly participating the reaction.

- **Use of Na_2S and Al_2S_3 additives**
  - Na_2S (72.5 mol%) – FeS (27.5 mol%) system
    - Pre-melting (1200^oC) or non pre-melting
  - Al_2S_3 (70 mol%) – FeS (30 mol%) system
  - S/Cu= 2.0 Stoichiometric ratio (based on FeS only)

- **Problem:** impurity pick-up in the alloy
  - Al: 2.8% (wt)
  - Na: 10 – 15%

Effect of additives on Cu removal

- Increased Cu-removal efficiency



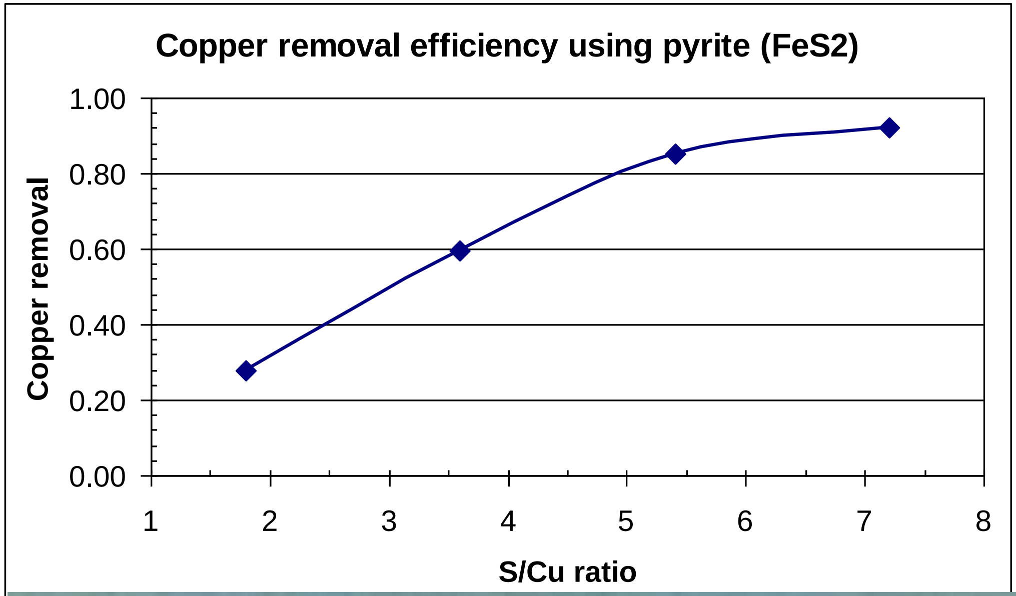
Pyrite treatment: Fe-Cu separation

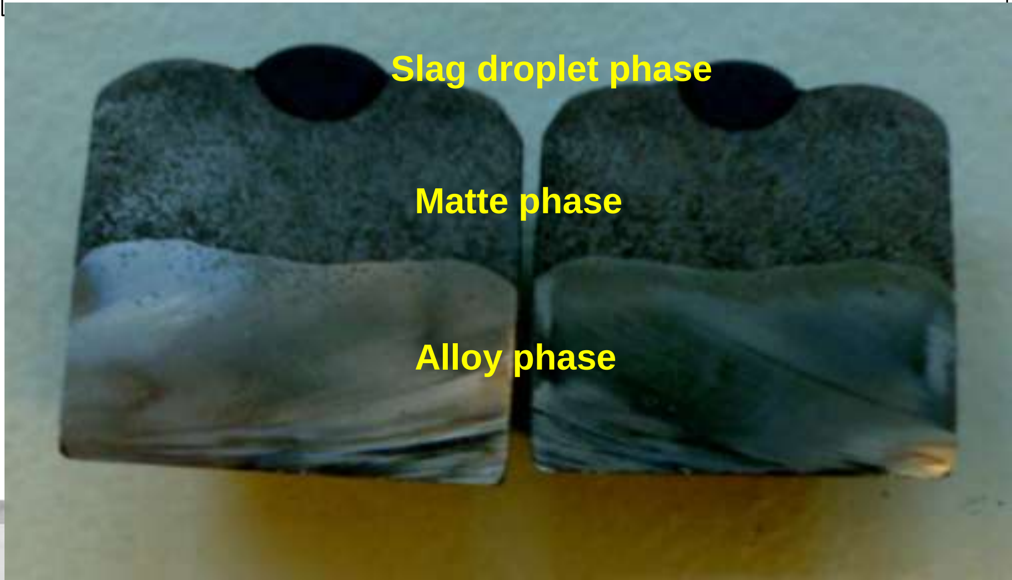
- **Pyrite concentrate**
  - 89.3% Fe_2S
- **Reactions**

$$FeS_2 + 4[Cu] = [Fe] + 2(Cu_2S)$$

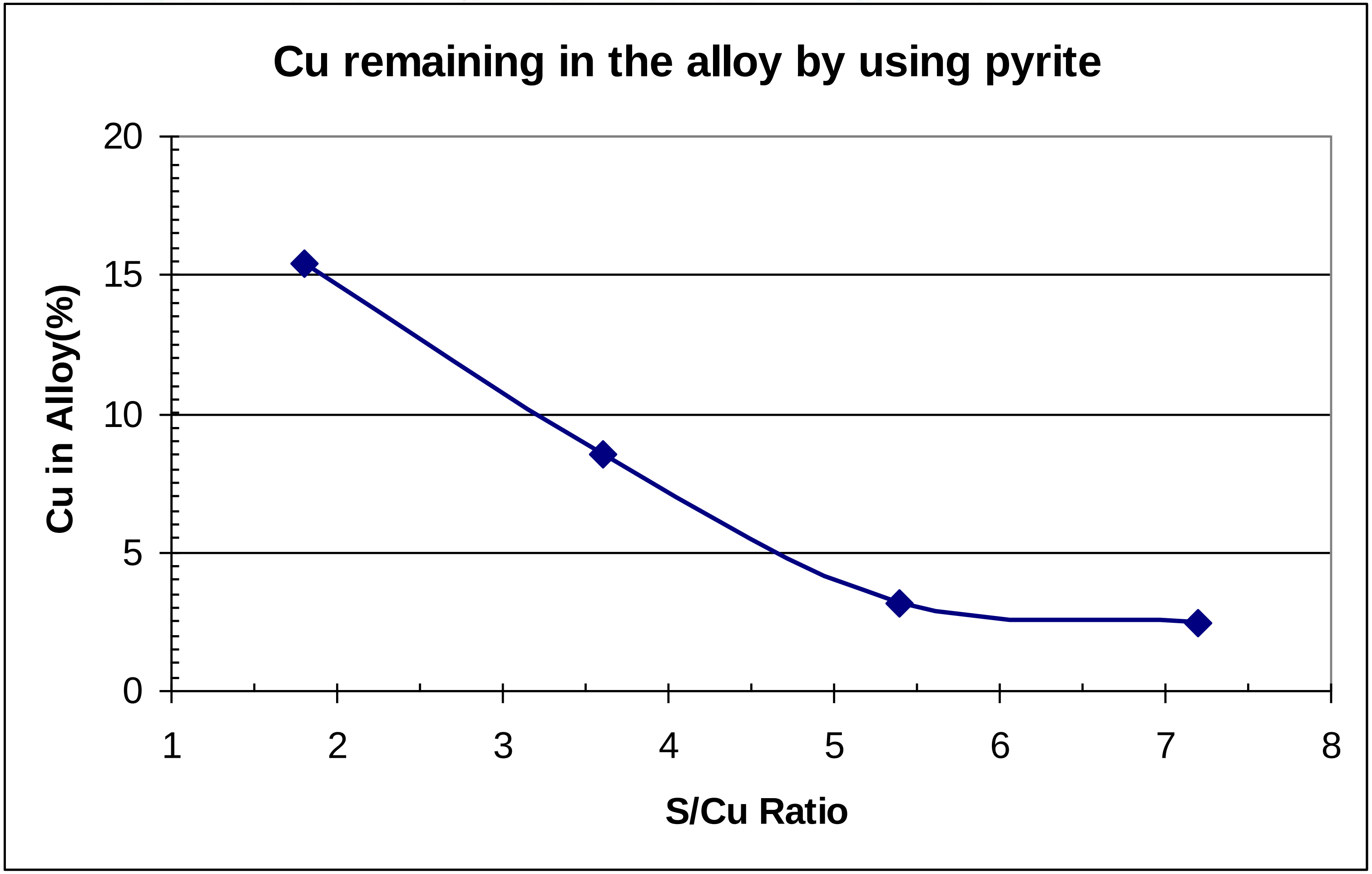
$$K = \frac{a_{[Fe]} \cdot a^2_{(Cu_2S)}}{a_{(FeS_2)} \cdot a^4_{[Cu]}} = 1.60 \cdot 10^6$$

- **Efficiency:** 92%
- Phase separation
  - Good!





Pyrite treatment: Fe-Cu separation



1500°C for 4.0 hours

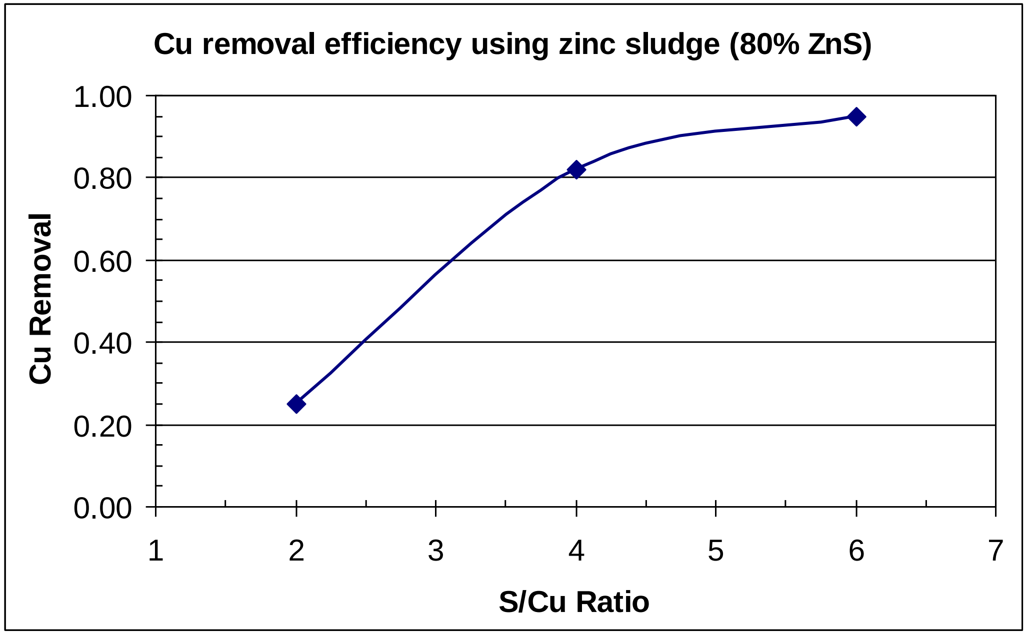
Cu removal with zinc sludge (ZnS)

- **Zinc sludge**
  - Waste from zinc smelter
  - 80% ZnS
- **Reactions**

$$(ZnS) + 2[Cu] = Zn_{(g)} + (Cu_2S)$$

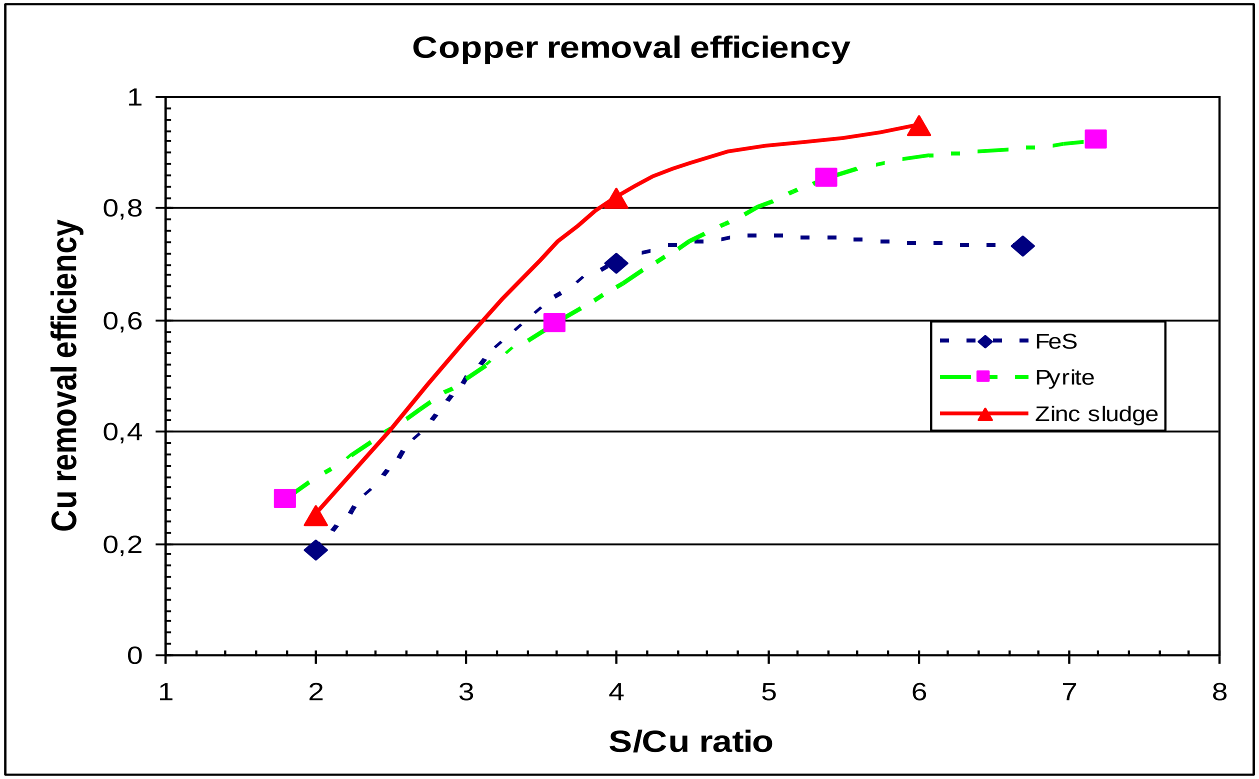
$$K = \frac{p_{Zn} \cdot a_{[Cu_2S]}}{a_{(ZnS)} \cdot a_{[Cu]}^2} = 20.46$$

- **Results**
  - High efficiency
  - Zn to vapour phase
  - No contamination to alloy



From waste to metals

- Comparison of different sulphide treatment



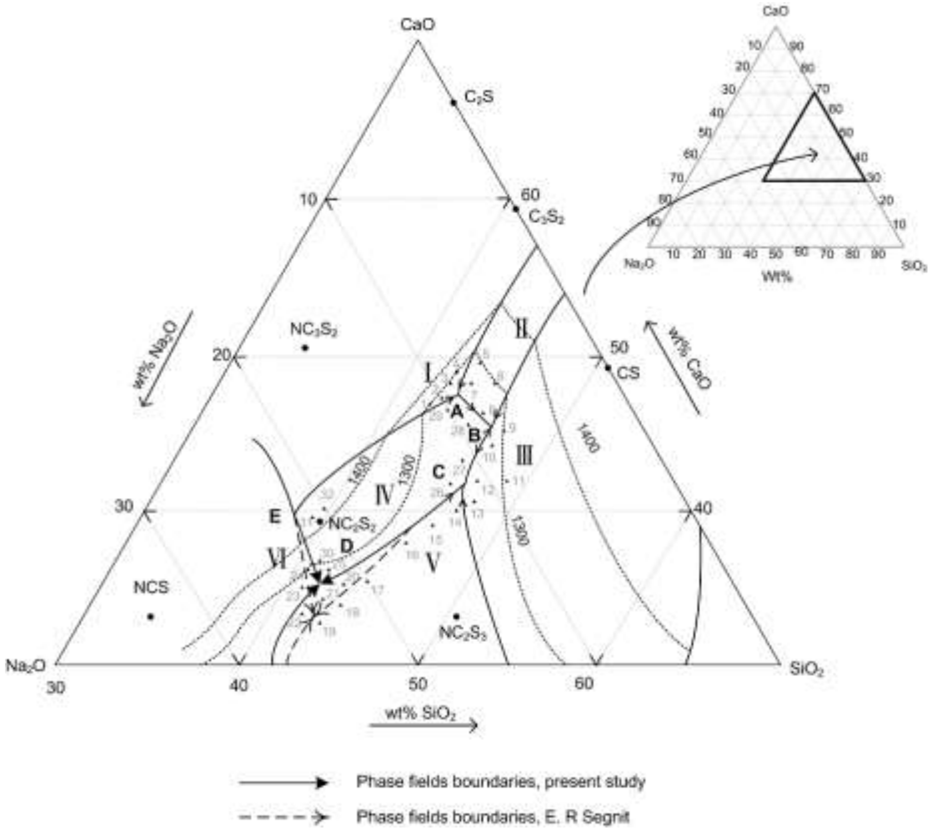
Thermodynamic study of MSWI slag

- MSWI bottom ash: vitrified slag (~1500°C)
  - *SiO_2 (52.1 %), CaO (16.2 %), Al_2O_3 (12.2 %), Fe_2O_3 (7.7 %), Na_2O (4.2 %) and MgO (2.3 %)*
- High in alkali: *Na_2O + K_2O*
  - Lack of information on thermodynamic data and phase relations
- Phase relations in SiO_2-CaO-N_2O slag system
  - Phase diagram: Liquidus temperatures
  - Experimental: thermal analysis (DSC) + phase equilibrium
  - Modelling: FactSage
  - A PhD project

Thermodynamic study of MSWI slag

Primary phase fields and liquidus surface projection: Na_2O-CaO-SiO_2 containing (0 - 40 wt%Na_2O and 30 - 70 wt%SiO_2).

The primary phase fields: Ca_2SiO_4, $Ca_3Si_2O_7$, $CaSiO_3$, $Na_2Ca_2Si_2O_7$, $Na_2Ca_2Si_3O_9$, and Na_2CaSiO_4 I, II, III, IV, V and VI).
(C=CaO; N=Na_2O; S=SiO_2).

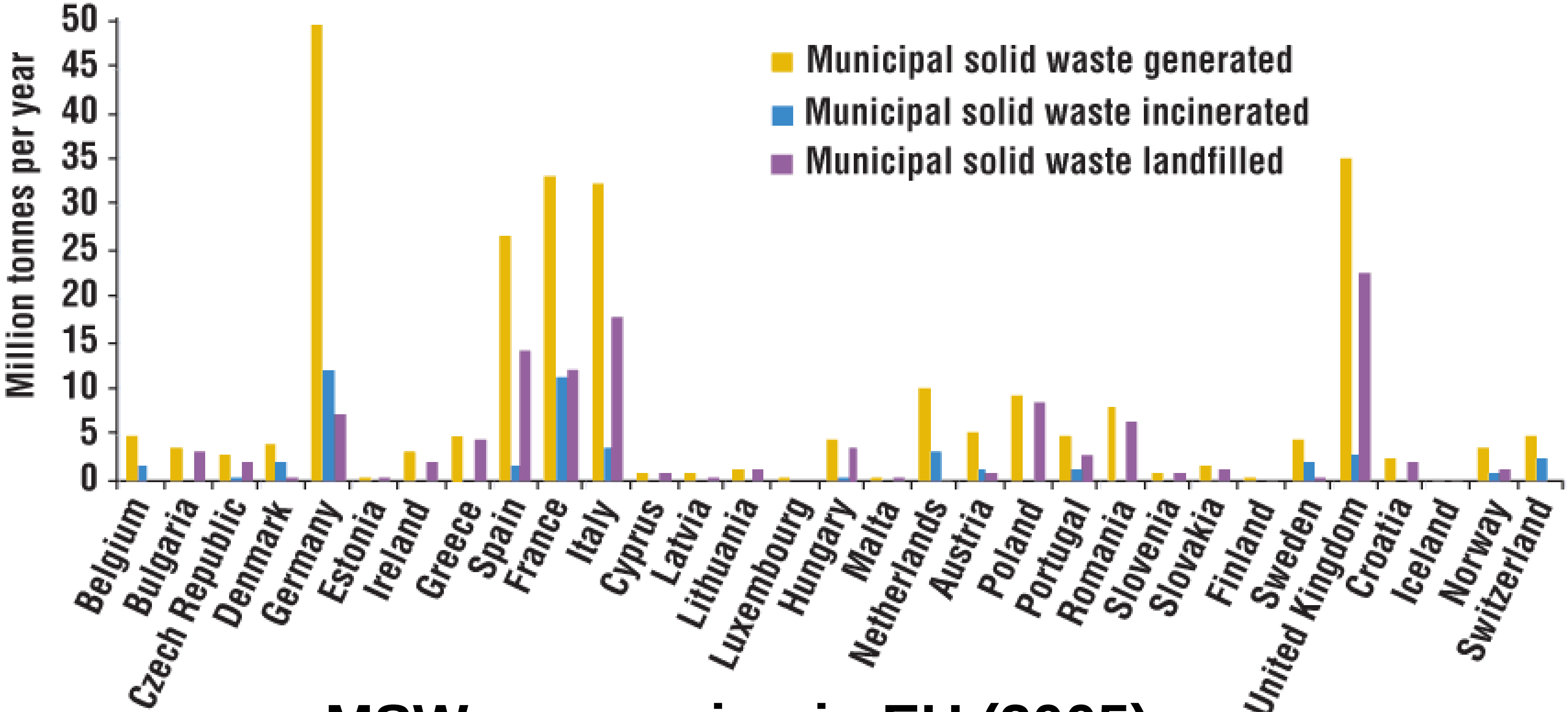


Conclusions

- Carbon is essential in sulfide treatment
- High S/Cu ratio is beneficial for Cu removal
- Reaction rate: fast (first 10 min. completed)
- Sulphide additives (Na_2S and Al_2S_3) improve Cu-removal but bring new impurities (Na, Al).
- Pyrite and zinc sludge are good alternatives with high Cu removal efficiency & no pollution to the alloy
- Cu removal below 1-2% in the alloy is more difficult and multi-step treatment is an option.

Thank you!

MSW Incineration bottom ash



MSW processing in EU (2005)

Source: Waste Management World: ***Management of bottom ash in Europe***
(Lenka Muchovà and Peter Rem; http://www.waste-management-world.com/

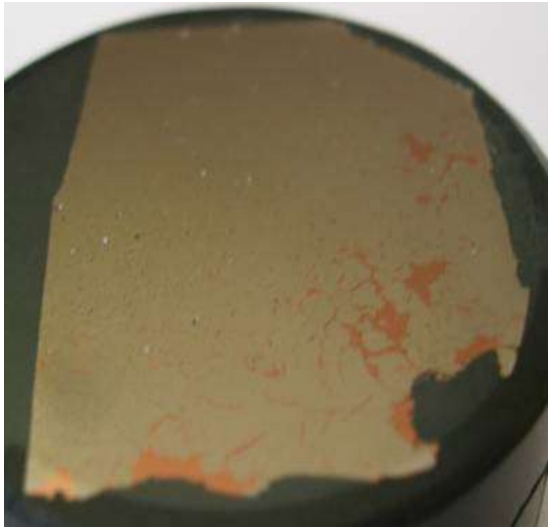
MSWI bottom ash

- **Current disposal/utilisation alternatives**
  - Landfill (after possible partial metal recovery (>10 mm))
  - Construction materials
    - Partial recovery of metals (>10 mm))
    - Deep dry metal recovery (>4 mm)
    - Wet separation metal recovery (0.1 mm)
  - Metal recovery
    - Magnetic and eddy current separation
    - Ferrous and non-ferrous scrap

The role of carbon saturation

Carbon promote Cu – Fe separation

- In the absence of sulphide
  - C-saturation forming Fe-Cu-C ternary alloy
  - Solubility of copper in iron: decreased
  - Copper was precipitated to certain extent
  - Phase separation: still difficult!



Raw materials

- Petroleum fly ash (PFA)
  - Main constituents (%): V (27.56), C (36.5), S (12.3), Ni (5.9)
  - Main phase: $VOSO_4 \cdot 3H_2O$, $NiS_2O_6 \cdot 6H2O$ (XRD)
- BOF steelmaking flue dust
  - Coarse fraction and fine fraction (BOF-CF; BOF-FF)
  - Fe/FeOx, CaO, MgO
- Chemical analysis

Element, wt%	Fe	V	Ni	Si	Ca	Al	Mg	S	P	Na	K
PFA	0.767	27.56	5.925	0.269	0.788	0.058	2.645	12.75	0.023	1.386	0.080
BOF-CF	36.03	0.033	0.008	0.705	42.55	0.222	7.400	0.049	0.008	0.053	0.045
BOF-FF	82.95	0.026	0.000	0.740	8.535	0.043	1.247	0.053	0.050	0.203	0.033

Element, wt%	Ti	Cr	Mn	Zn	Pb	Cu	Cd	Cl	C (LECO)	SUM	S (LECO)
PFA	0.133	0.000	0.022	0.052	0.059	0.049	0.000	0.000	36.5	89.1	12.3
BOF-CF	0.070	0.015	0.625	0.193	0.011	0.010	0.000	0.027	0.570	88.6	0.002
BOF-FF	0.024	0.028	1.429	0.370	0.065	0.000	0.012	0.012	1.650	97.5	0.039

Results of smelting tests

- Conditions: 1550°C for 2 hours in Ar
- Metal yield: 27-32%
- Weight loss (off-gas + dust): 32-42%
- Slag yield (balance): 29-37%

Test	Charge, g				BOO FA to BOF-CF ratio	Total weight, g	Weight loss, %	Metal yield, %	Remarks
	BOO FA	BOF-CF	SiO_2	C					
B-1	1.28	1.59	0.96	---	0.8	3.83	38.4	32.6	Good metal/slag separation
B-2	1.07	1.33	0.81	0.07	0.8	3.28	42.4	---	No metal agglomeration
B-3	0.95	1.59	0.95	---	0.6	3.49	31.8	31.4	Metal yield in total ash mixture
B-4	16.0	20.0	12.0	---	0.8	48.0	36.4	27.3	

Results of smelting tests

- Major compositions of slag and metal
  - Metal: 62-63% Fe, 18-22% V, 1-2% Ni
  - Slag: $CaO-SiO_2-MgO-VO-NiO$

Test	Slag, wt%						Metal, wt%		
	CaO	SiO_2	MgO	FeO	VO	NiO	Fe	V	Ni
B-1	28.3	35.6	6.50	15.6	0.13	0.07	63.0	18.2	1.89
B-3	26.0	44.8	5.25	12.4	0.19	0.05	62.2	20.8	1.15
B-4	33.6	38.6	7.23	4.58	0.96	0.10	62.4	22.6	1.88

Experimental results

Element distribution (test B-4 during smelting)

Elemental distribution, %	Slag	Metal	Off-gas/flue dust
Fe	12.4	83.5	4.1
V	4.2	50.1	45.7
Ni	2.0	19.5	78.5
Si	79.8	14.2	6.0
Ca	71.1	0.4	28.5
S	77.3	3.1	19.6
Na	63.1	0.6	36.4
Zn	0.0	1.8	98.2
Pb	0.0	10.7	89.3
Cu	26.8	31.6	41.6