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Hydrometallurgical recovery of tin and copper from mobile phone printed circuit boards.

GDR Prométhée Scientific Days

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INSTITUT CARNOT Icéel

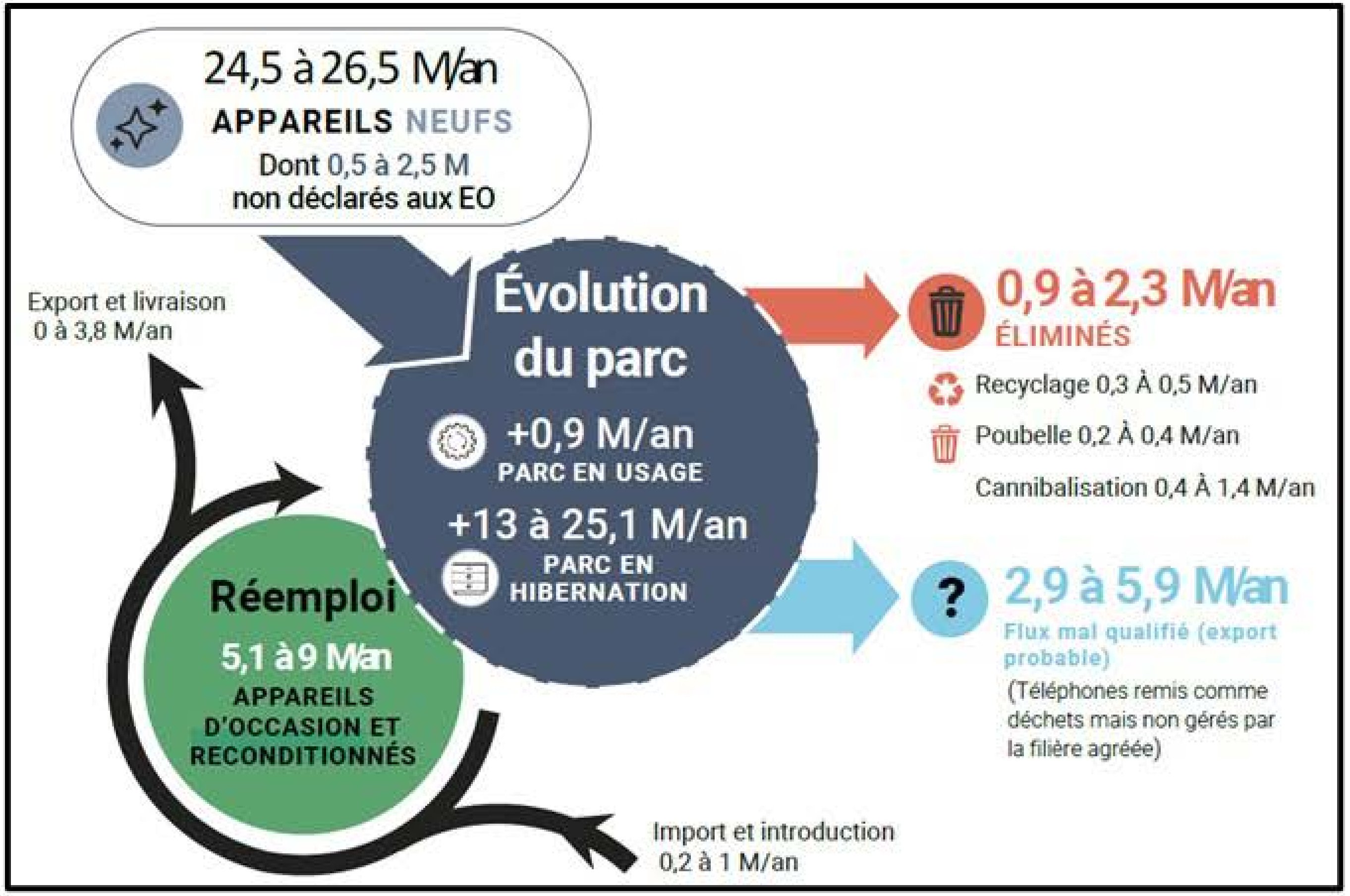
geo Ressources

TJFU

LRGP LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

THYMO Project (HYdrometallurgical Treatment of MObile phones)

Over 120 millions mobile phone remain in French drawers !



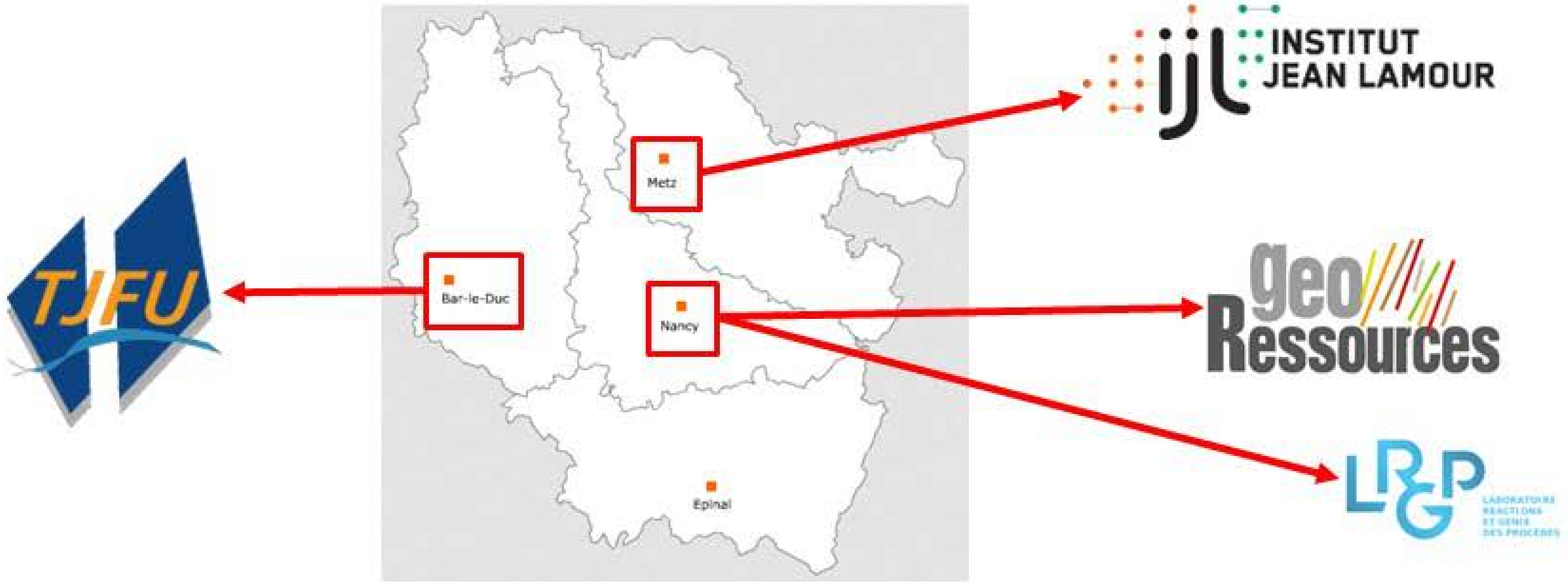
Flows and fleets of mobile phones in France in 2018. [1]

[1] Sofies and Bio Innovation Service (2019). Étude du marché et parc de téléphones portables français en vue d'augmenter durablement leur taux de collecte.

THYMO Goals

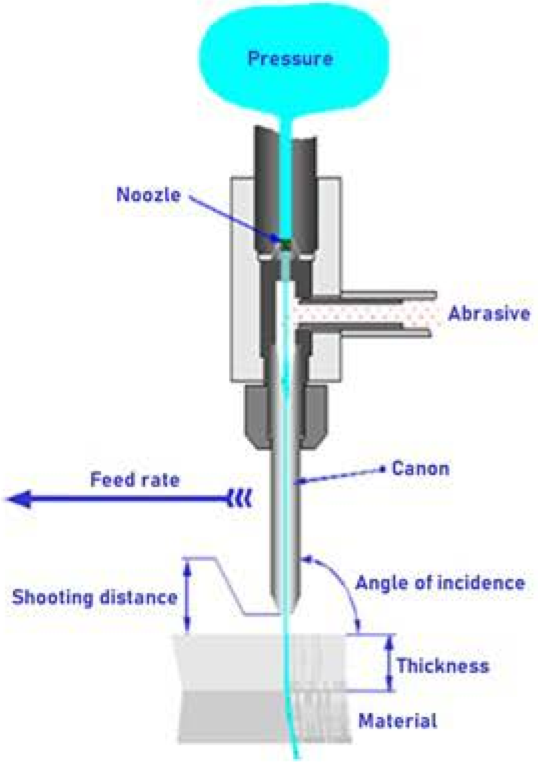
- Develop an innovative process for recycling cell phone circuit boards:
  - low environmental impact
  - energy-efficient
  - enables maximum recovery of metals
  - enables the “polymer” part of the board to be recovered

- Use a significant quantity of circuit boards to obtain realistic raw material



Collection of over 19000 mobiles phones

Automated process by CRITT-TJFU



Printed circuit boards or PCBs
Theoretical industrial rate : up to 400 phones per minute

Pre-treatment

PCBs from CRITT TJFU

Shredding to 8 mm

Magnetic sorting
Eddy Current

Shredding (hammer mill)

Sizing < 500 µm

Shaking table

- **Light fraction :** epoxy resin, glass fibers, aluminum
- **Heavy fraction :** metals, ceramics ($BaSO_4$, Al_2O_3)

Characterization protocol

Shredded PCBs → Homogenization

200 g

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3 replicates
500 mg

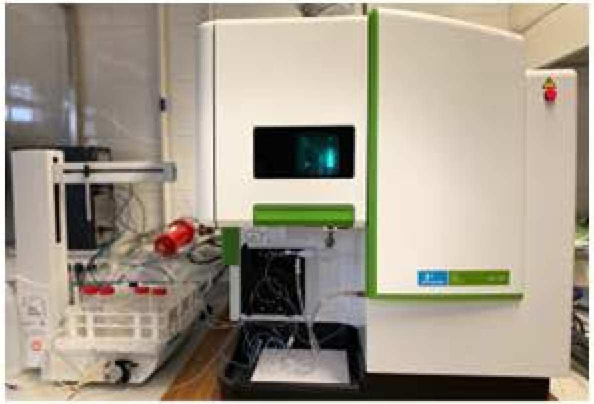
Aqua regia leaching
20 mL HNO_3/HCl

P_{max} = 1,8 kW T° = 220 °C t = 20 mn

Filtering 0,45 µm

Solid residues
XRD, CHNS

Leachate
ICP-AES
Elementary analysis



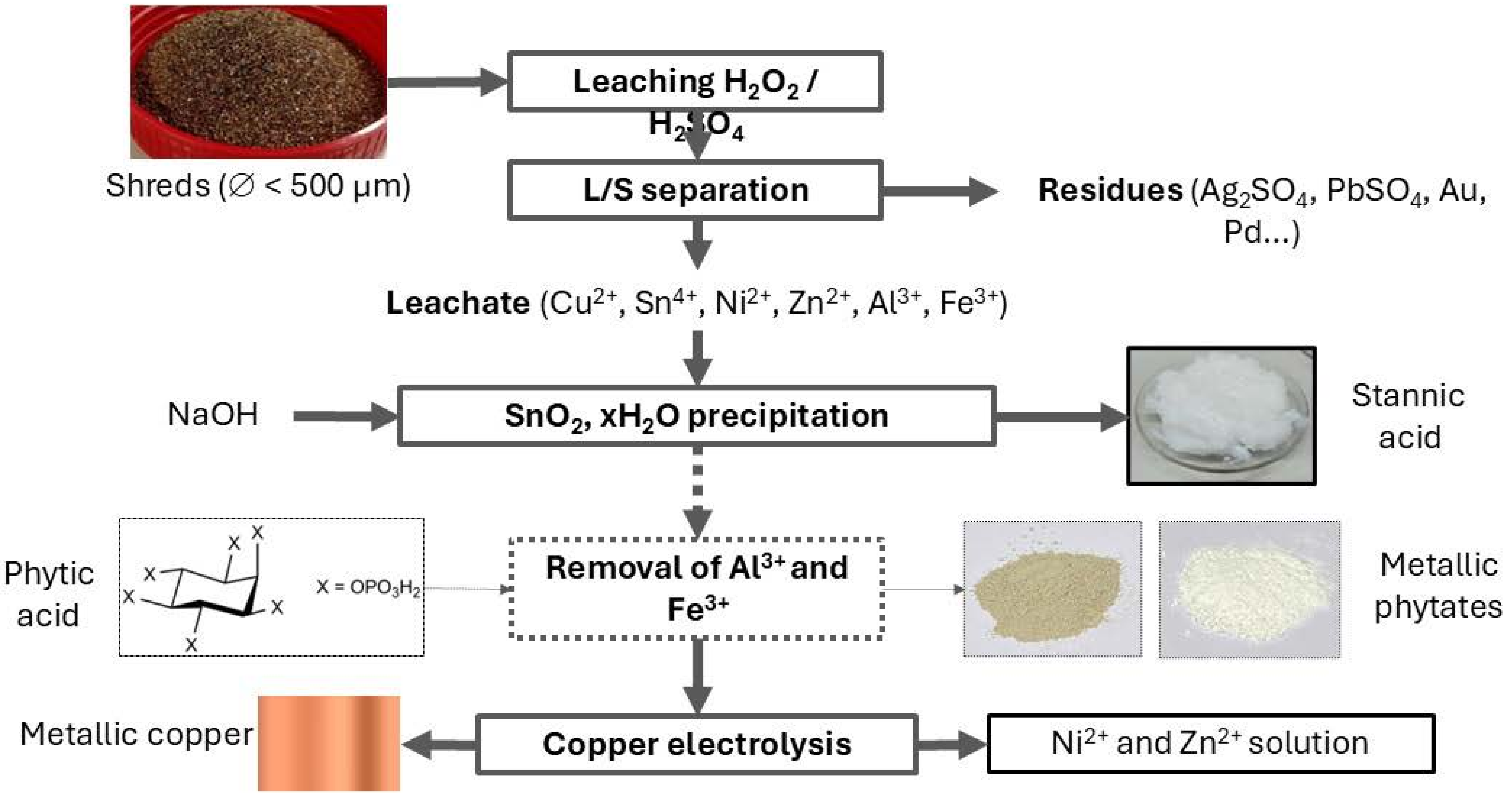
ICP-AES
Avio200 DV PERKIN-ELMER

PCB shred composition

Metals	Weight fraction (%)
Cu	52-70
Sn	7-15
Ni	2-4
Al	0.2-1.2
Fe	0.9-1.8
Zn	0.2-1.6
Pb	0.1-1
Ag	0.03-0.2
Au	0.1-0.15
Pd	< 0.05

90 % of market value

Process overview



Leaching step

Leaching step (1/3)

Reagents

H_2O_2-H_2SO_4 (H_2O_2 considered as a green oxidant)

$$Cu_{(s)} + H_2O_{2\,(aq)} + 2\,H^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + 2\,H_2O_{(l)}$$

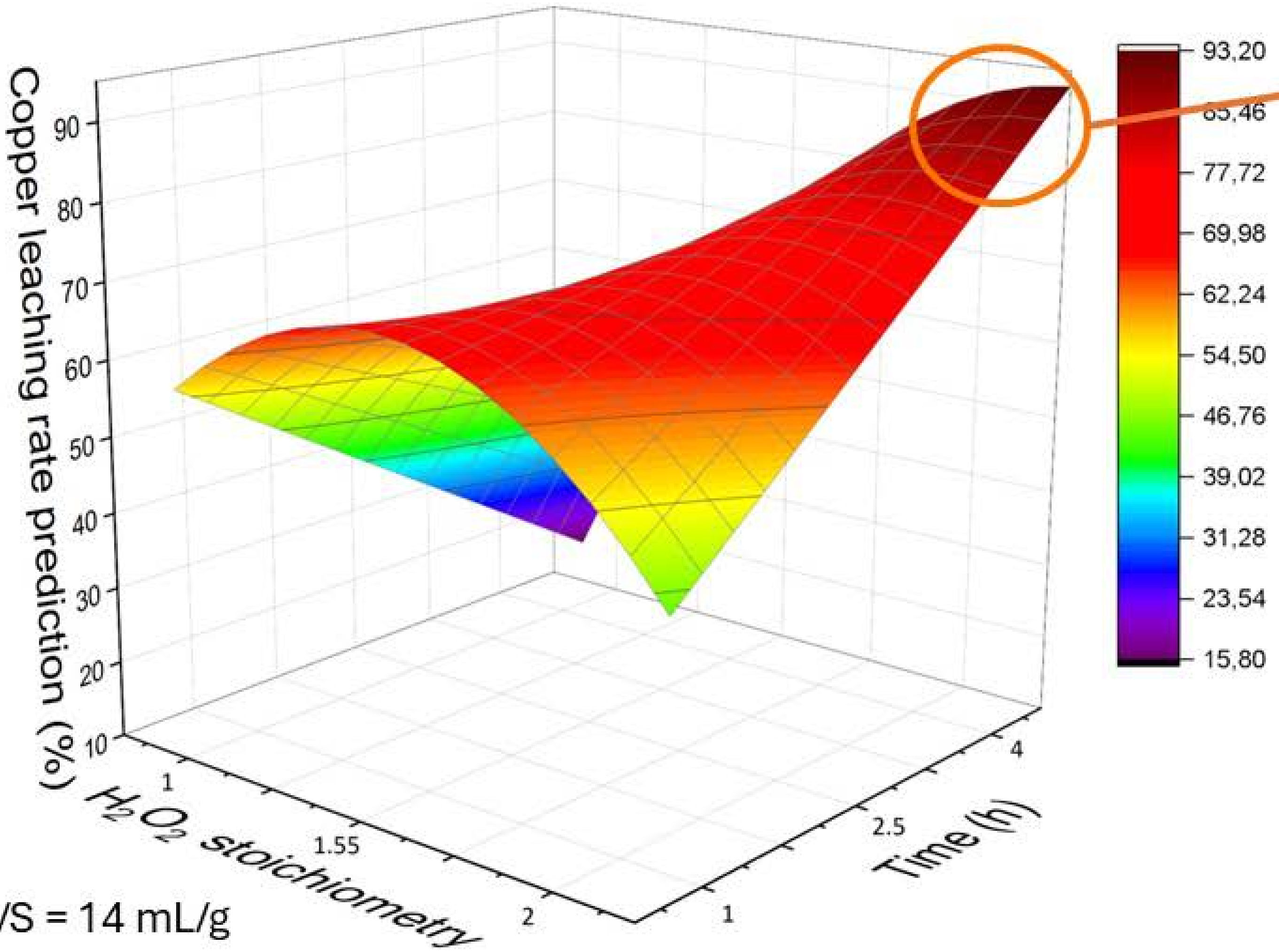
$$Sn_{(s)} + 2\,H_2O_{2\,(aq)} + 4\,H^+_{(aq)} \rightarrow Sn^{4+}_{(aq)} + 4\,H_2O_{(l)}$$

Constraints

- Limit H_2O_2 dismutation (temperature, catalysis by Cu^{2+}, Fe^{2+}, Fe^{3+})
- Avoid $CuSO_4$, $5H_2O$ precipitation (solubility of 207 g/L in water at 20°C)
- Avoid prematured precipitation of SnO_2, x H_2O

Optimization – Design of Experiments

Fractional factorial design 2^{4-1} then central composite design



L/S = 14 mL/g

Optimal conditions

n H_2O_2 / Σ n métaux = 2

n H^+ / Σ n métaux = 6

Leaching time = 4h

Liquid/Solid ratio = 14 mL/g

Cryostat set at 20°C

Stirring rate = 300 rpm

Tested on 3 leachings

Copper leaching rate : 82.8 ± 4.4 %

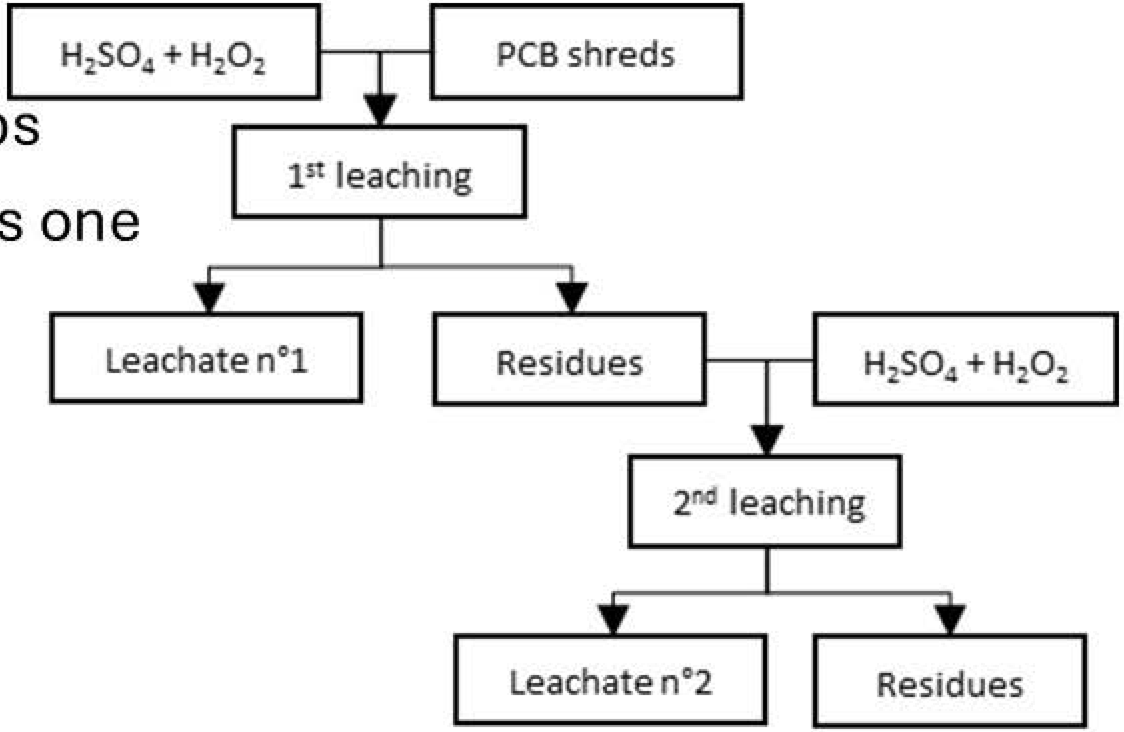
Tin leaching rate: 96.1 ± 0.5 %

Leaching step (3/3)

Optimization – Multi-step leaching

H_2O_2 quantity divided between 2 leaching steps

Second leaching on residues from the previous one



<u>3 protocols were studied</u>

- 1-step leaching with 100 % H_2O_2
- 2-steps leaching 50-50 % H_2O_2
- 2-steps leaching 75-25 % H_2O_2

Leaching protocol	One step: 100% H_2O_2	1st step: 50% H_2O_2 2nd step: 50% H_2O_2	1st step: 75% H_2O_2 2nd step: 25% H_2O_2
Final copper leaching rate (%)	82.8 ± 4.4	97.3 ± 1.1	95.9 ± 2.2
Final tin leaching rate (%)	96.2 ± 0.5	97.8 ± 0.2	97.6 ± 0.3

Recovery of tin

Recovery of tin (1/2)

Leaching H_2O_2 / H_2SO_4

↓

S/L separation

↓

Leachate (Cu^{2+}, Sn^{4+}, Ni^{2+}, Al^{3+}, Fe^{3+}, Zn^{2+})

↓

NaOH → **SnO_2, x H_2O precipitation** →

Stannic acid

Goal : Precipitate stannic acid selectively and quantitatively

Problems :

- Spontaneous precipitation of stannic acid at pH $\simeq 0.3 - 0.5$

- Precipitation delay
  - Important increase of pH → may decrease purity (goethite precipitation, Cu^{2+} adsorption)
  - Crystal seeding at lower pH → requires pre-made stannic acid

Recovery of tin (2/2)

Crystal seeding

Initial leachate $[H^+] > 1$ mol/L

↓ NaOH 5-6 mol/L

Leachate pH = 0

↓ Pur germs (50 g/L solution)
NaOH 5-6 mol/L

Leachate pH = 1

↓

Centrifugation + filtering →

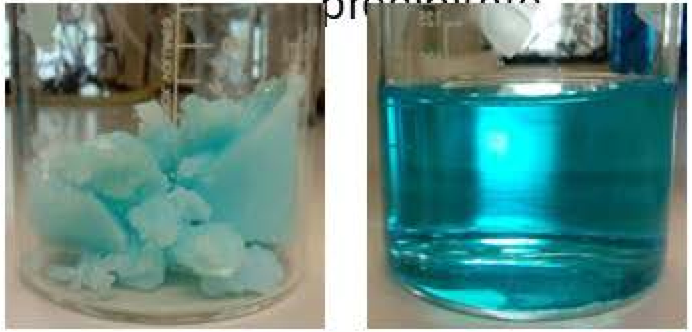
%Cu trapped = 2.4%

↓

Leachate
$[Cu^{2+}] = 3.76.10^{-1}$ mol/L or 24 g/L
$[Sn^{4+}] =$ $6.57.10^{-5}$ mol/L or 8 mg/L

<u>Washing by repulping:</u> 1 mL H_2SO_4 0,1 M per gram of precipitate

Washing 1



$[Cu^{2+}] = 1.72.10^{-1}$ mol/L
%Cu trapped = 1,8 %

Washing 2

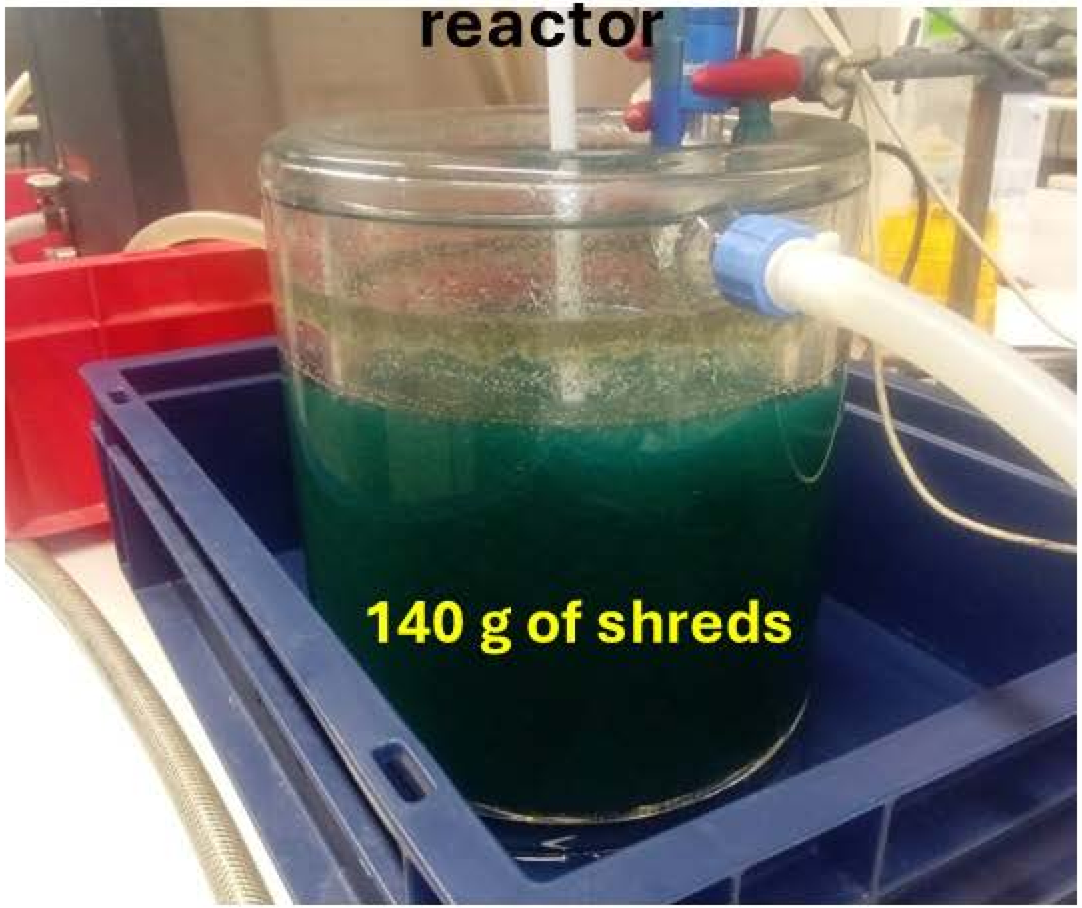
$[Cu^{2+}] = 7.96.10^{-2}$ mol/L
%Cu trapped = 1.4 %

Washing 3

$[Cu^{2+}] = 4.94.10^{-2}$ mol/L
%Cu trapped = 1.1 %

Scale-up

Two-step leaching in optimal conditions in a 3 L reactor



Optimal conditions

$n\ H_2O_2\ /\ \Sigma\ n$ métaux = 2 (50-50)

$n\ H^+\ /\ \Sigma\ n$ métaux = 6

Leaching time = 4 h

Liquid/Solid ratio = 14 mL/g

Cryostat set at 20°C

Stirring rate = 300 rpm

Leachates gathered into

Metals	Concentration (g/L)	Concentration (mol/L)	Leaching rate (%)
Cu	**37.93**	$5.97*10^{-1}$	**> 95**
Sn	**5.63**	$4.8*10^{-2}$	**> 95**
Ni	0.83	$1.4*10^{-2}$	
Zn	0.49	$7.5*10^{-3}$	
Fe	0.17	$3.0*10^{-3}$	
Al	0.02	$7.4*10^{-4}$	

Scale-up (2/3)

Leaching step

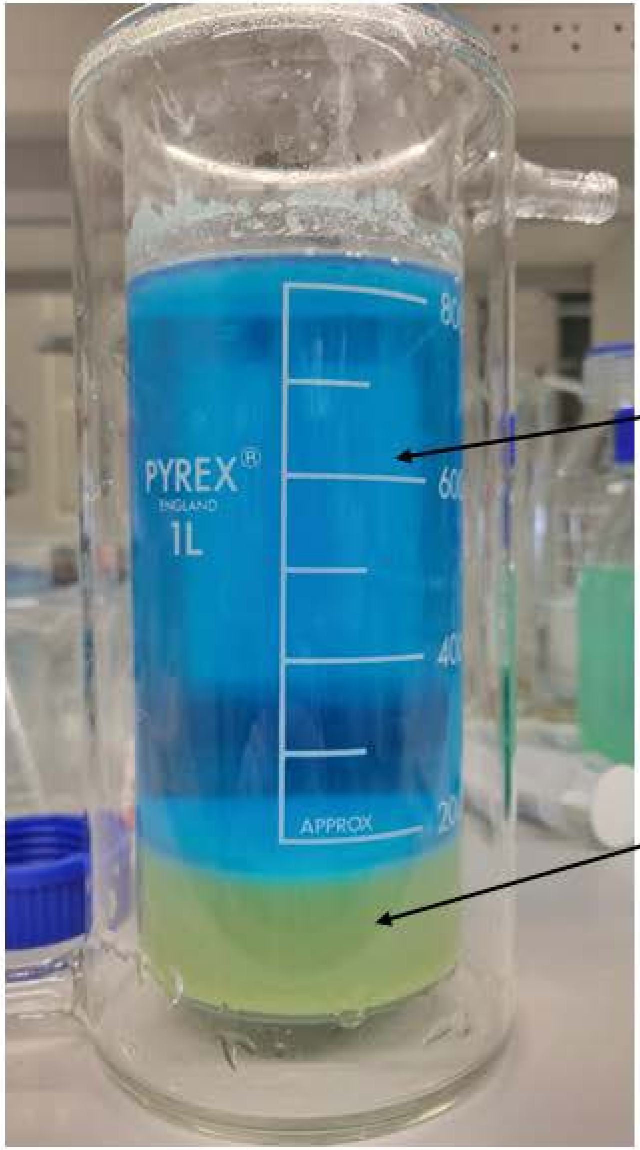
BEFORE

Mass loss ≃ 82%

AFTER

Metals	Cu	Sn	Ni	Zn	Fe
Mass content (%)	69.3	12.2	2.6	1.6	0.9
Metals	**Al**	**Pb**	**Ag**	**Au**	**Pd**
Mass content (%)	0.2	0.9	0.2	0.09	0.05

Metals	Cu	Sn	Ni	Zn	Fe
Mass content (%)	21.2	2.6	6.4	0.6	5.5
Metals	**Al**	**Pb**	**Ag**	**Au**	**Pd**
Mass content (%)	0.6	5.7	1.1	0.26	0.17



Best results at pH = 2.5

Metals	Concentration (g/L)	Concentration (mol/L)
Cu	23.21	$3.65*10^{-1}$
Sn	0.10	$8.4*10^{-4}$
Ni	0.46	$7.8*10^{-3}$
Zn	0.29	$4.4*10^{-3}$
Fe	0.10	$1.8*10^{-3}$
Al	< 0.01	$< 3.7*10^{-4}$

After 1 wash : 1% copper remaining in precipitate

Low amount of aluminum and iron
-> **phytates precipitation step is skipped**

Next steps :

- Copper electrolysis
- Recovery of nickel and zinc (chelating resin)

Conclusion

- Maximization of both copper and tin leaching from PCB shreds (< 500 µm) by Design of Experiments methodology

- Savings in H_2O_2 consumption with two-step leaching process

- Leaching rates of copper and tin > 97 %

- Production of a tin precipitate richer than cassiterite

  SnO_2, 2 H_2O (around 1% Cu trapped) represents around 70 % SnO_2
  $\Rightarrow$ production of tin via pyrometallurgy or electrolysis in alkaline medium

Prospects

- **Electrolysis of copper incoming**
  - Purity of at least 99,99 % required
  - Avoid co-deposition of nickel

- **Mineralurgical characterization of leaching residues** (at least 100 g required)

- **Development of precious metals enrichment process** according to density, electrical conductivity, magnetic susceptibility of different phases

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Questions?

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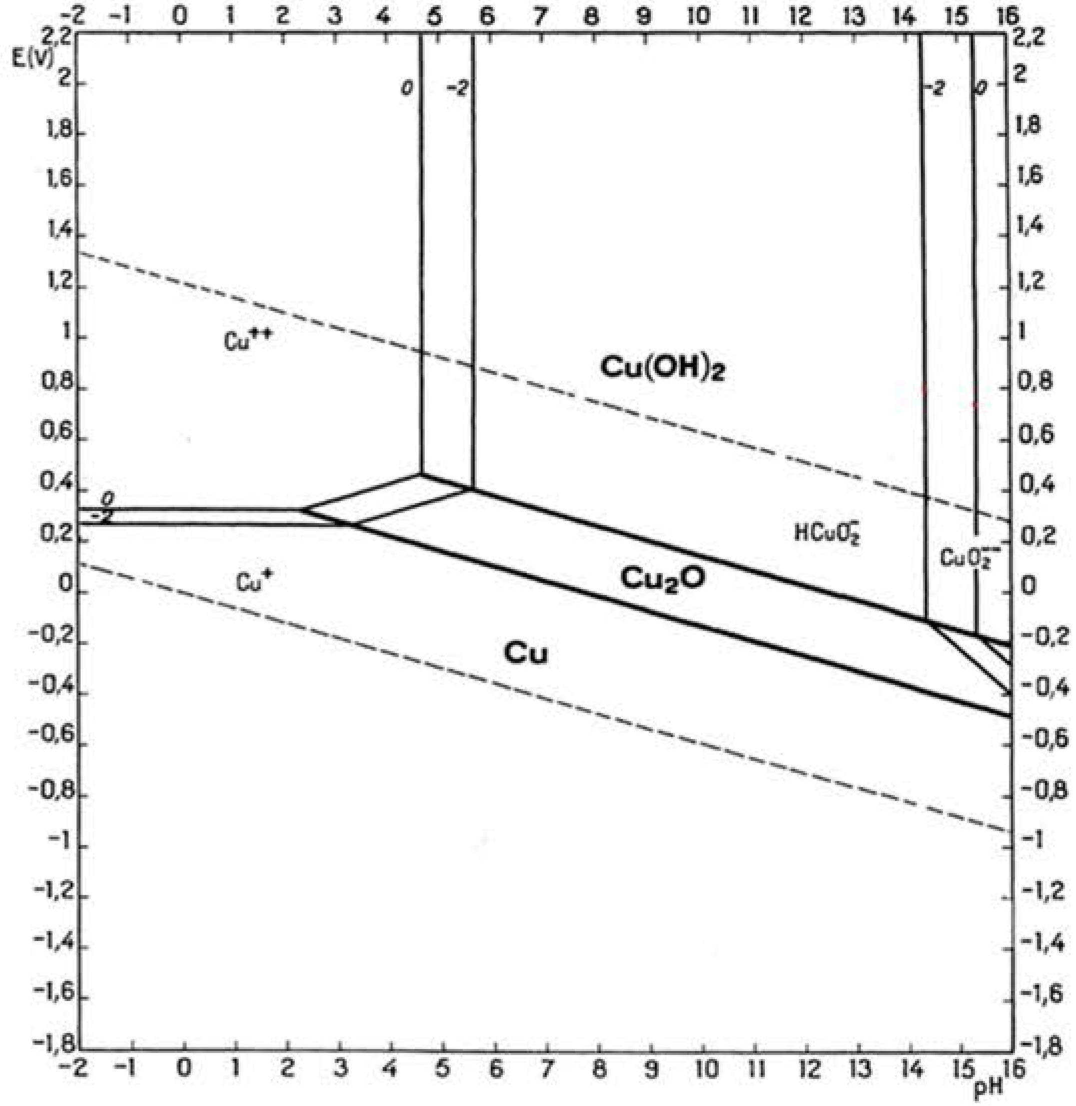
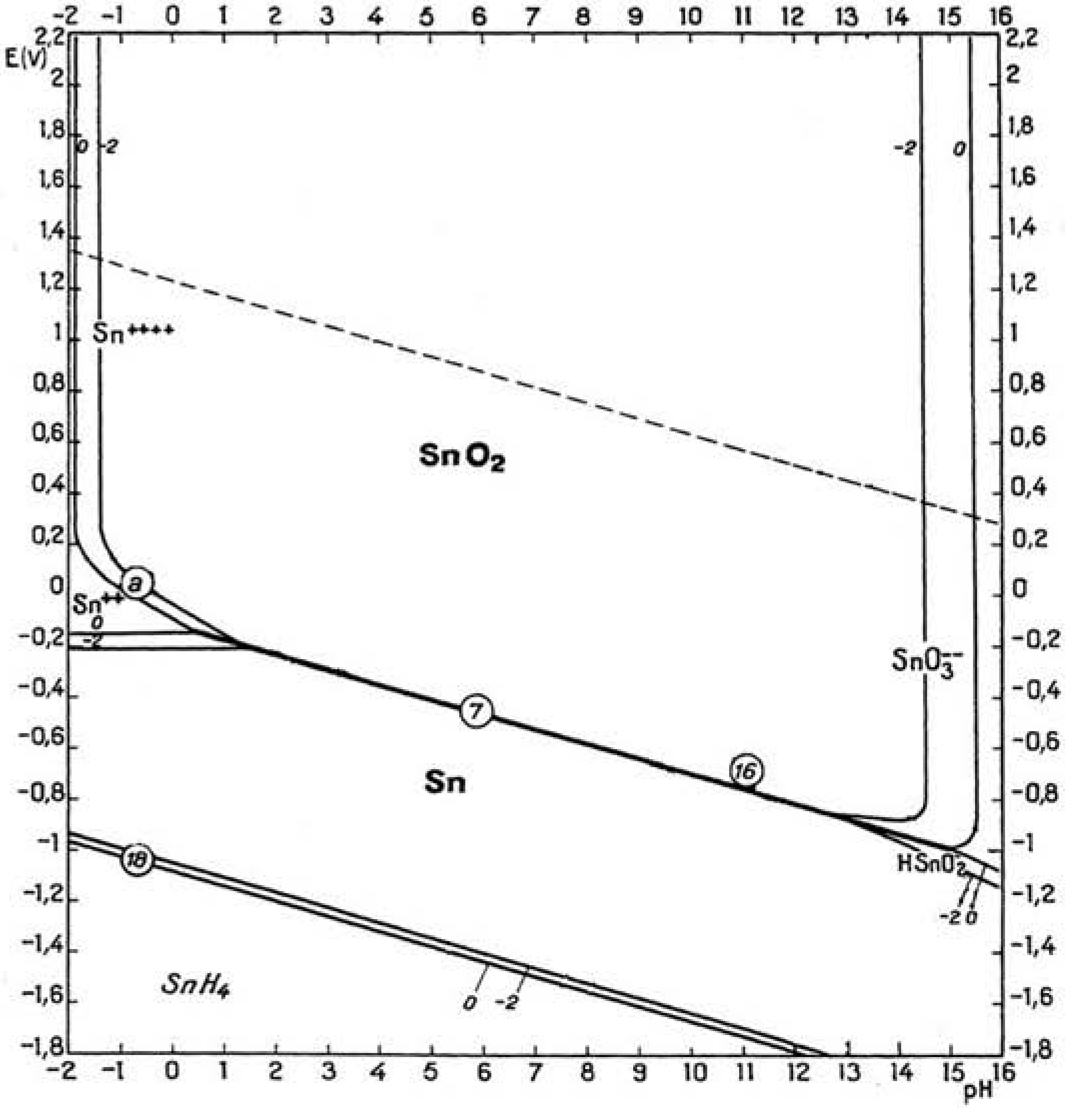
Thank you for your attention

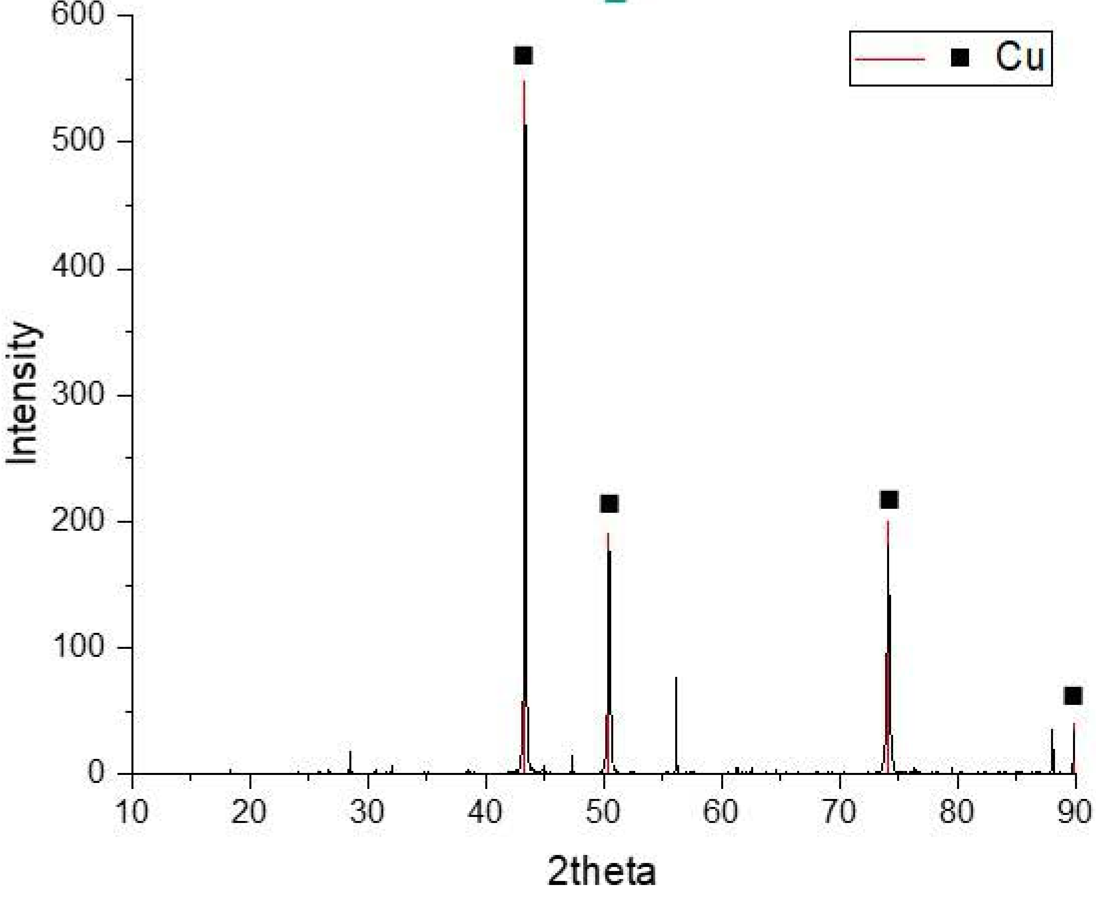
Pourbaix Diagramm





Residues XRD

BEFOR E



AFTER