Electrolytic treatment of highly contaminated effluents from copper smelters

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RWTH Aachen
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Highly contaminated effluents from RTB Bor, Serbia

Wastewater from Electrolyte-, precious metals and electrolyte regeneration plant

Flow rate:
45 m^3 /day
(50.000 t Cu/a)
Cu:approx. 8 g/l
pH: 0 - 0.27

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Highly contaminated effluents from RTB Bor, Serbia

	Concentration, g/dm^3	Analytical method
Cu	8.33	AAS
Ni	0.66	AAS
As	0.63	AAS
Se	0.26	ICP-AES
Fe	0.086	AAS
Sb	0.075	ICP-AES
Te	0.068	ICP-AES
Al	0.04	ICP-AES
Zn	0.034	AAS
Bi	0.028	ICP-AES
Si	0.022	ICP-AES
Pb	0.0034	AAS
Mn	0.0011	AAS
Cd	0.0001	AAS
H_2SO_4	120.79	T/V
Cl-	0.07	TU

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Main aims

- electrochemical pre-treatment of highly contaminated and strong acidic industrial wastewaters
- applying a continuous technology with high specific surface area - using of rotating disc cathodes
- metallic recovery of copper as powder product
- determination of best process operation conditions regarding metal deposition rate as well as solution and metal purity
- optimized current density to avoid the formation of arsine – safety issue

Concept of Metal Removal

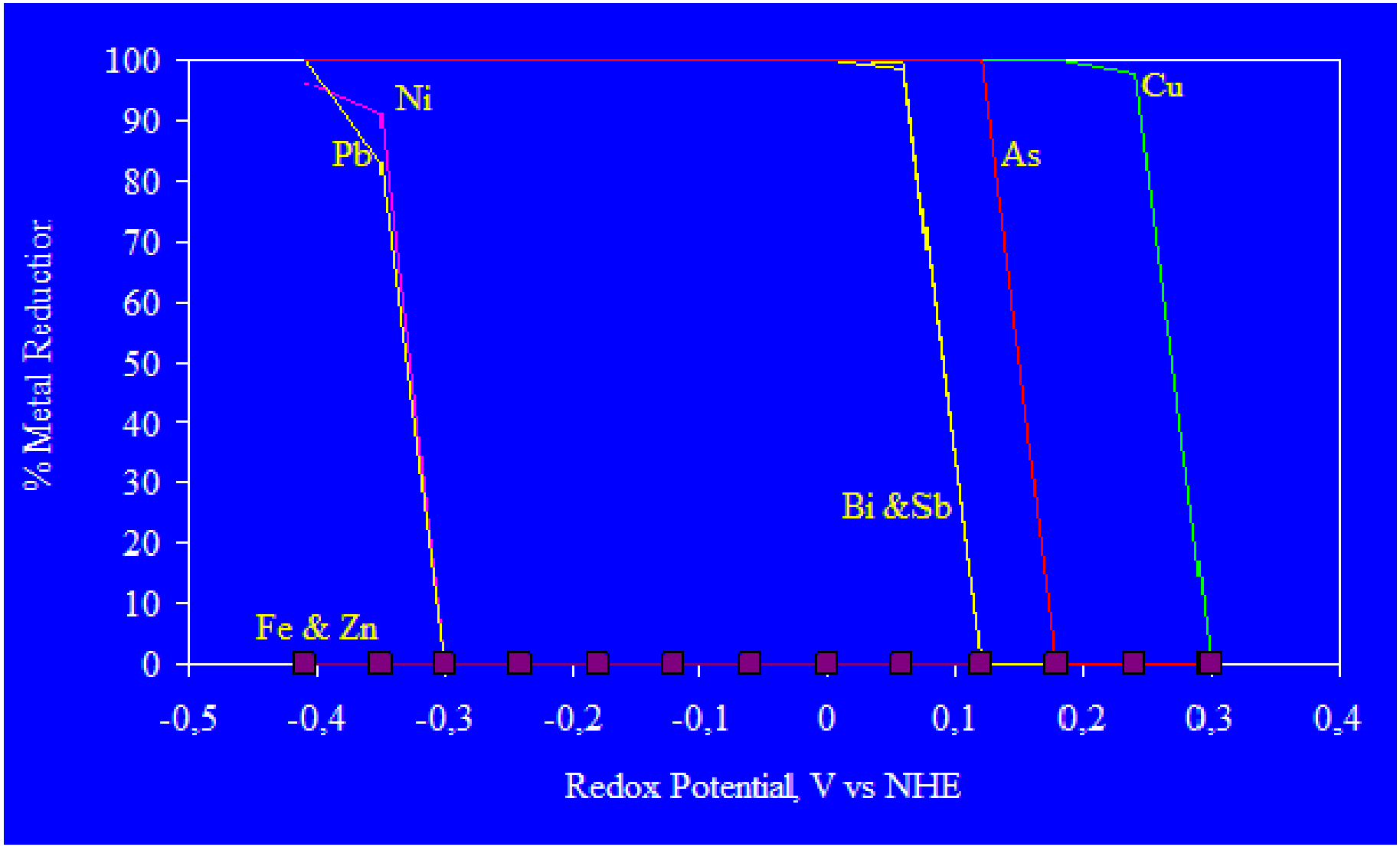
wastewater

electrolytic treatment with rotating discs

continuous precipitation

purified wastewater

Theoretical Background of Electrolytical Treatment



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Challenges of electrolytic treatment of As-solutions

Joint deposition of other metals (Se, As, Sb,..) with Cu:

Cathode: $Cu^{2+} + 2e^- = Cu$

Competing cathode reaction: $2\ H^+ + 2e^- = H_2$

Anode: $H_2O = 2\ H^+ + ½\ O_2 + 2e^-$

Formation of highly toxic AsH_3 (ARSINE) and SbH_3 (STIBINE)

$2\ As^{3+} + 3H_2 = 2\ AsH_3 + 6\ e^-$

$2\ Sb^{3+} + 3H_2 = 2\ SbH_3 + 6\ e^-$

Prevention of AsH_3-formation by $FeAsO_4$-deposition or by avoiding hydrogen formation (optimized current density)

$Fe^{2+} - e^- = Fe^{3+}$ and $As^{3+} - 2e^- = As^{5+}$

$Fe^{3+} + 2\ O_2 + As^{5+} = FeAsO_4 + 8\ e^-$

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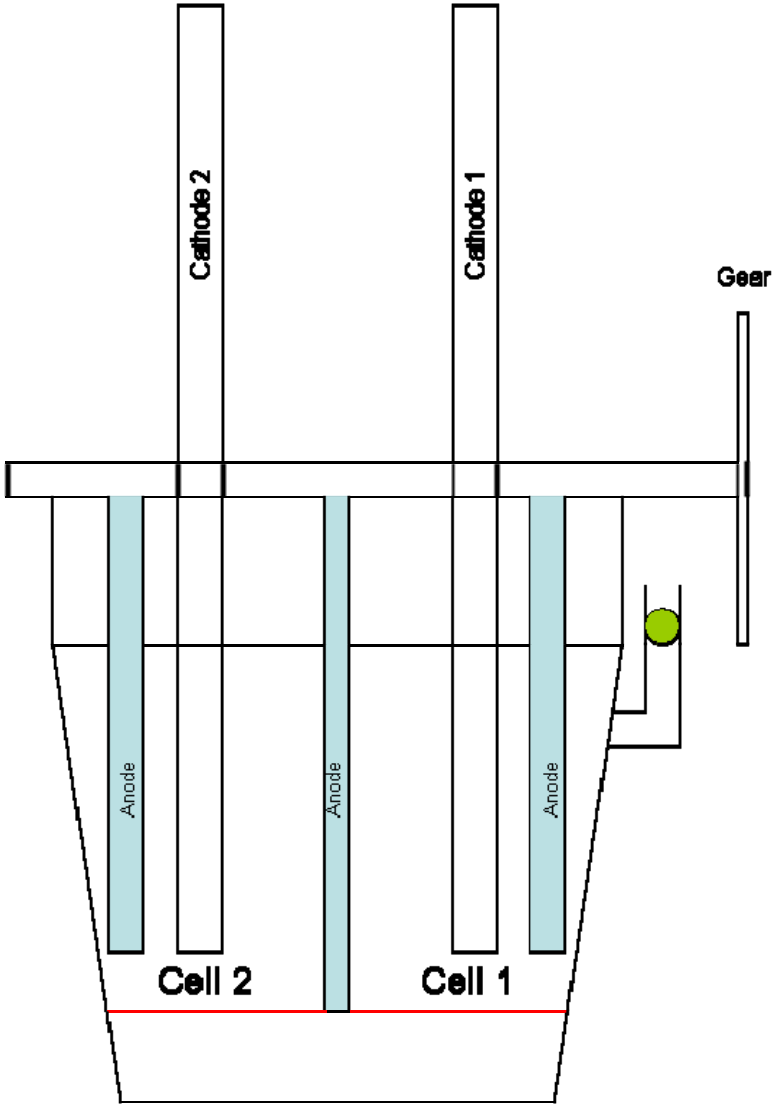
Electrolytic Treatment – Experimental Setup



Technical data of the electrolytic cell:

cell length/width/height: 34/13/20 cm
working cell volume: 3l (both cells)

cathode type: stainless steel discs
cathode diameter: 30 cm
total immersed cathode area: 940 cm^2
two cathode discs parallel

anode type: basket with titanium grid
basket length/width/height: 30/2,5/15 cm

electrolyte flow:

a) from cell to cell
b) through basket to cathode

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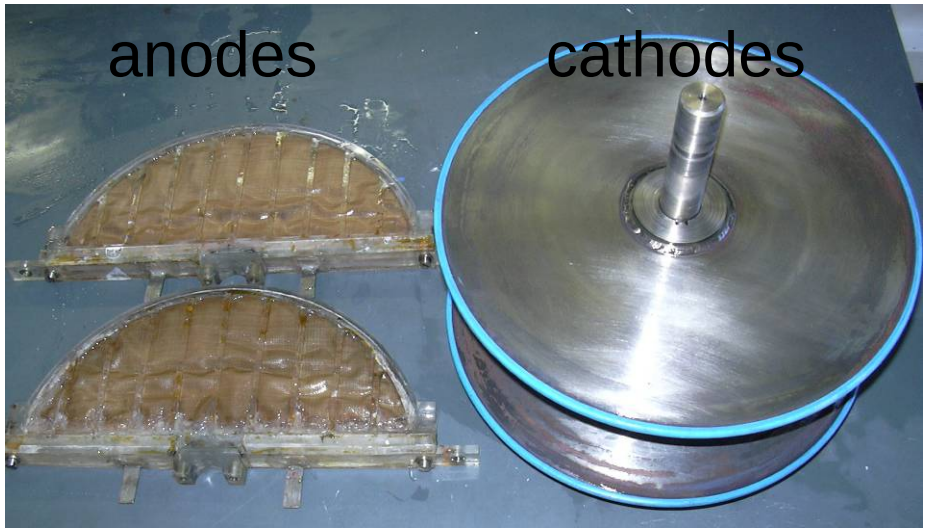
Electrolytic treatment – Experimental Parameters

Parameters:

temperature:	20-22°C (!)
deposition time:	5, 10 and 20 h
average cell voltage:	2.3 V
current density:	50 – 80 - 100 A/m^2
current:	4.7 - 7.5 – 9.9 A
cathode revolutions:	2 rpm (!)
flow rate:	0.5 - 1.0 - 2.0 l/h
active surface:	0,094 m^2
c-c distance:	30 mm
c-a distance:	15 mm



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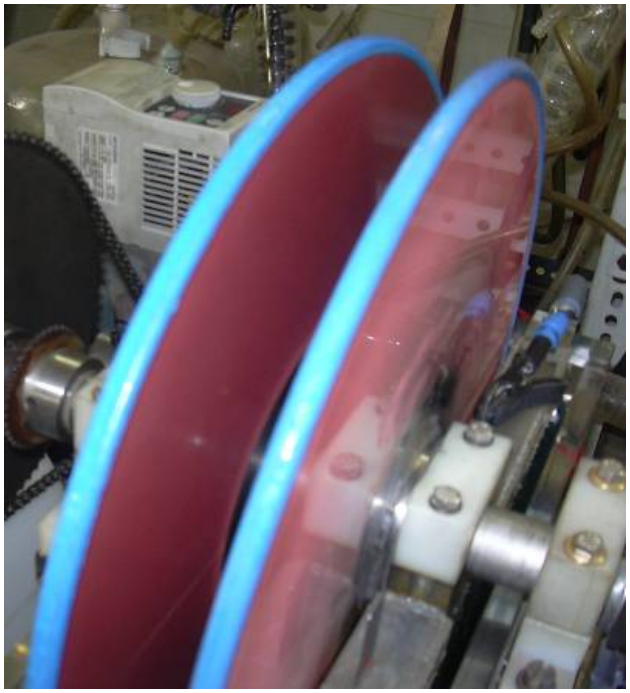
Electrolytic treatment - Experimental part

Experiment No.	current density (A/m^2)	Volume flow (l/h)	solution type
1	240	0.5	Synthetic
2	80	0.5	Synthetic
3	50	0.5	Synthetic
4	80	1.0	Synthetic
5	80	2.0	Synthetic
6	50	0.5	Real
7	80	0.5	Real
8	100	0.5	Real
9	80	1.0	Real
10	80	2.0	Real

Electrolytic treatment - Results (deposition)

synthetic wastewater



fine layer of powder

real wastewater

black powder directly after test start

a dark reddish gray deposition after 60 min

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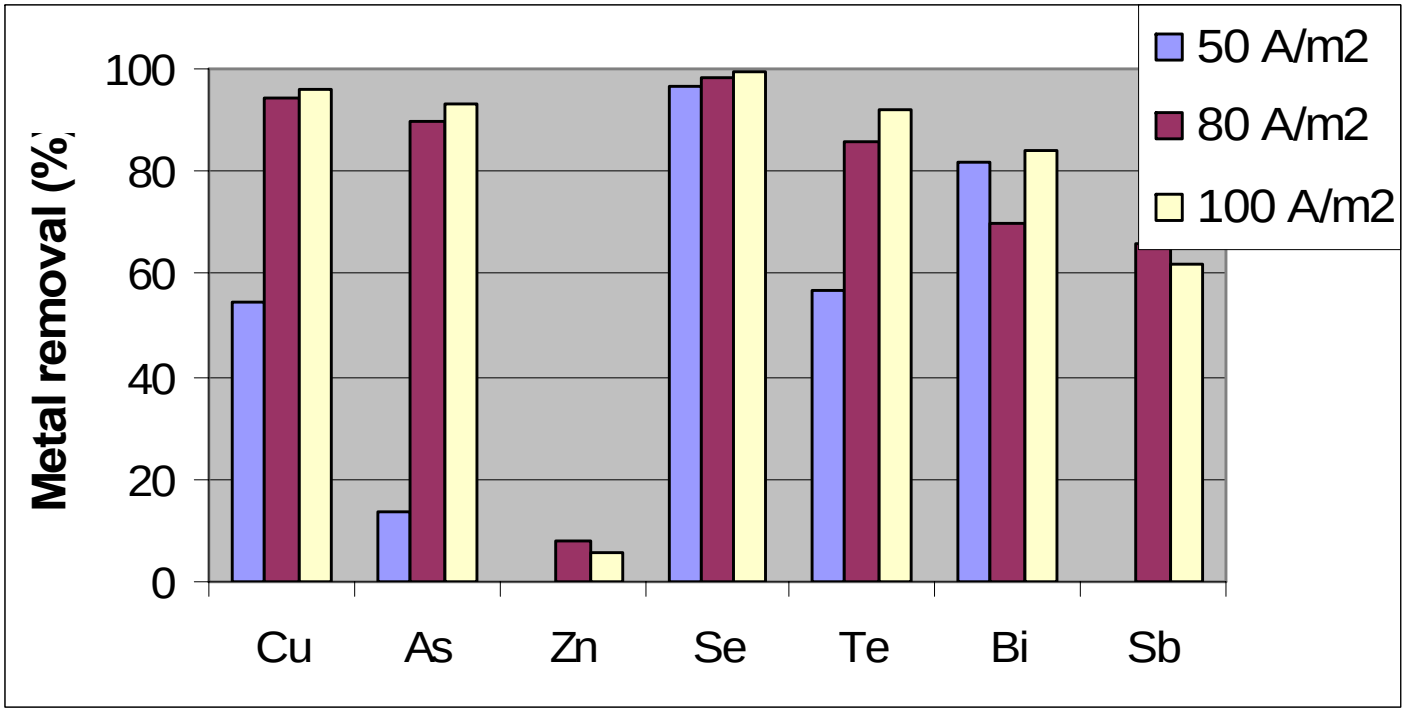
Electrolytic treatment- Results (current density)



- change of current density from 50 A/m^2 to 100 A/m^2 increases the metal removal for Cu, As, Te
- metal removal of Se is always high
- in case of Zn the current density has no influence

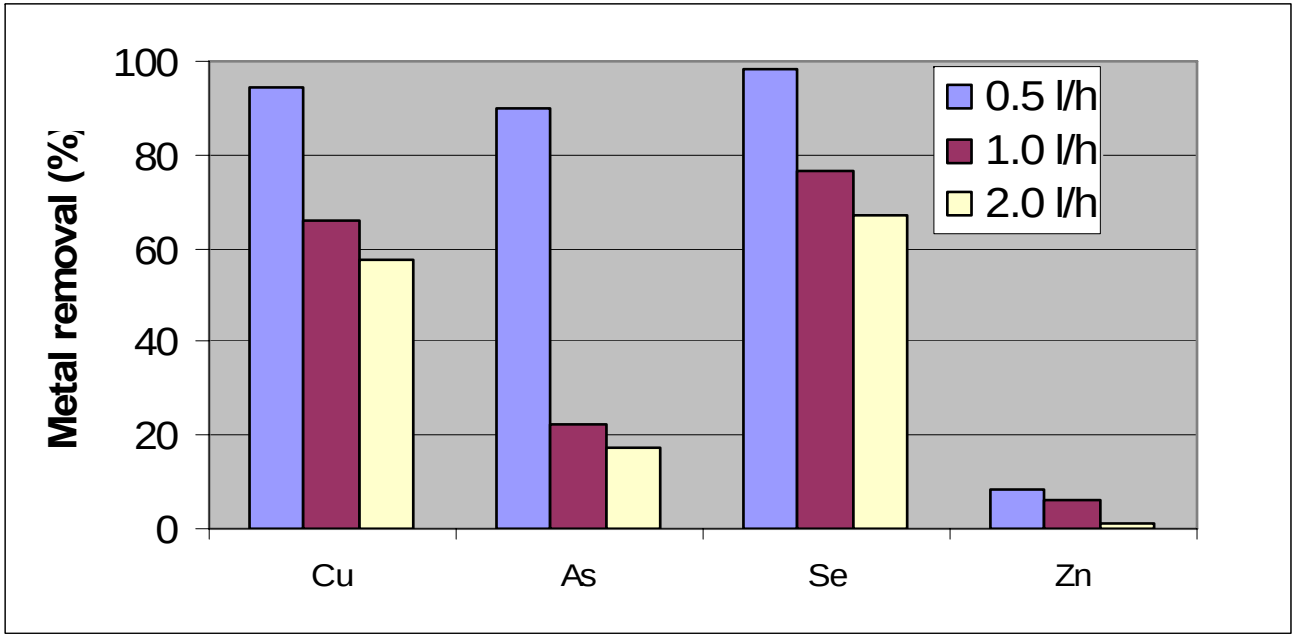
Electrolytic treatment - Results (current density)

current density (A/m^2)	Concentration (mg/l)						
	Cu	As	Zn	Se	Te	Bi	Sb
Start	**8330**	**630**	34	**260**	68	28	75
50	**3790**	**544**	35.8	**8.93**	29.4	5.1	80.3
80	**478**	**62.7**	31.2	**5.0**	9.6	8.4	25.7
100	**308**	**42.2**	32.1	**1.4**	5.5	4.5	29.4

Electrolytic treatment alone can not ensure metal concentration in the allowed values

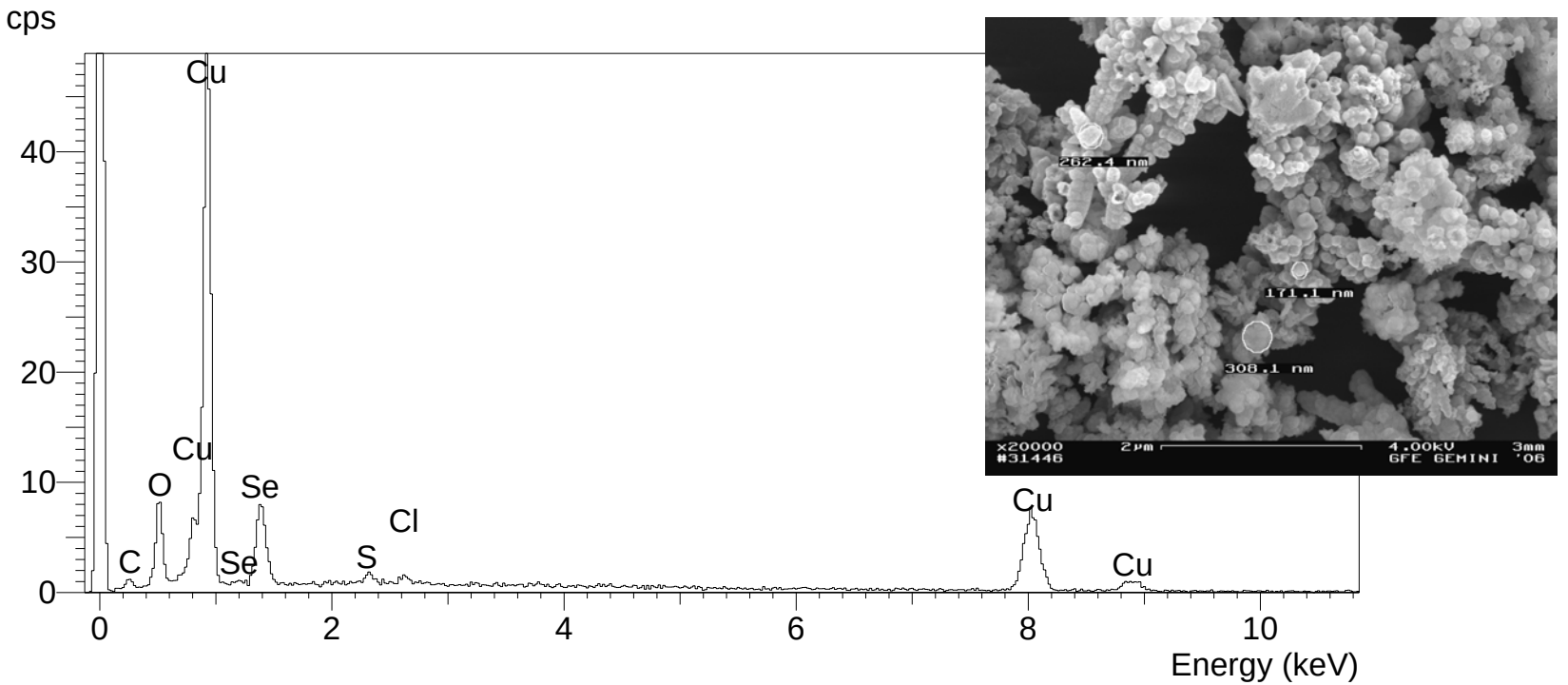
Electrolytic treatment - Results (flow rate)

content (g/l)	Initial	0.5 l/h	1.0 l/h	2.0 l/h
Cu	8.33	0.478	2.86	3.54
As	0.63	0.063	0.49	0.52
Se	0.26	0.005	0.0613	0.0862
Zn	0.034	0.0312	0.032	0.0337



Best results of metal removal obtained for 0.5 l/h

Electrolytic treatment- ICP, SEM and EDX Analysis



Typical EDX Analysis from the powder deposit

ICP analysis of powder composite in %:

80 Cu, 4 As, 3 Se, 0.6 Te, 0.4 Sb, 0.2 Bi,

0.2 Si, 0.1 Zn, 0.02 Pb, <0.01 Al, Ni, Mn, Cd

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Conclusions

- Copper was deposited with removal efficiencies of >95% from wastewater with 8.3 g/l Cu and 120.8 g/l H_2SO_4 in a continuous electrolytic cell with rotating discs at room temperature
- suitable operation parameters are 0.5 l/hour (flow rate) and 100 A/m^2 (current density) due to safety reasons
- current efficiency for 100 A/m^2 is 58 %
- electrolytic treatment alone can not ensure the legally prescribed metal concentration requirements

Next steps:

- used of platined titanium instead of stainless steel
- improving of the collection method

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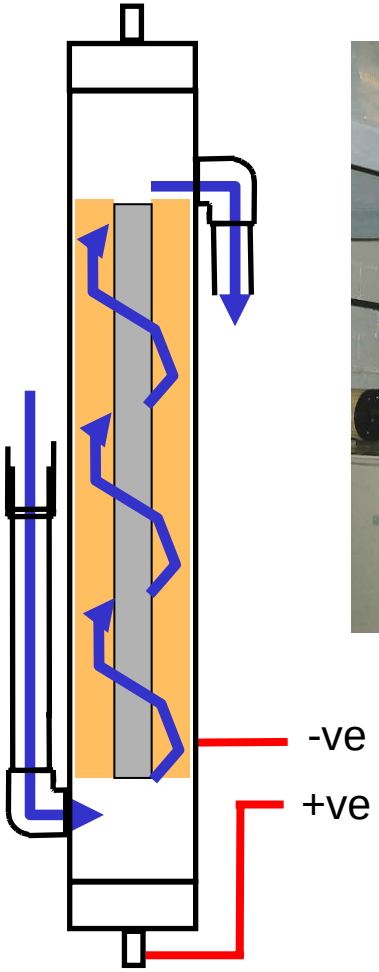
Existing Technologies for electrolytic WW-treatment

Two companies offer rotating cylinder electrode technology:

1. Electrometals Electrowinning EMEW® Cell- Australia
2. “Elektrolyse und Umweltschutz” Eilenburg

The electrolyte is circulated rapidly past the anode and cathode at a higher flow rate, allowing for improvements in efficiency and recovery. The electrolyte is pumped through the cell from the bottom.



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