

Recovery of metals contained in residues of metallurgical plants, and the synthesis of nanoparticles

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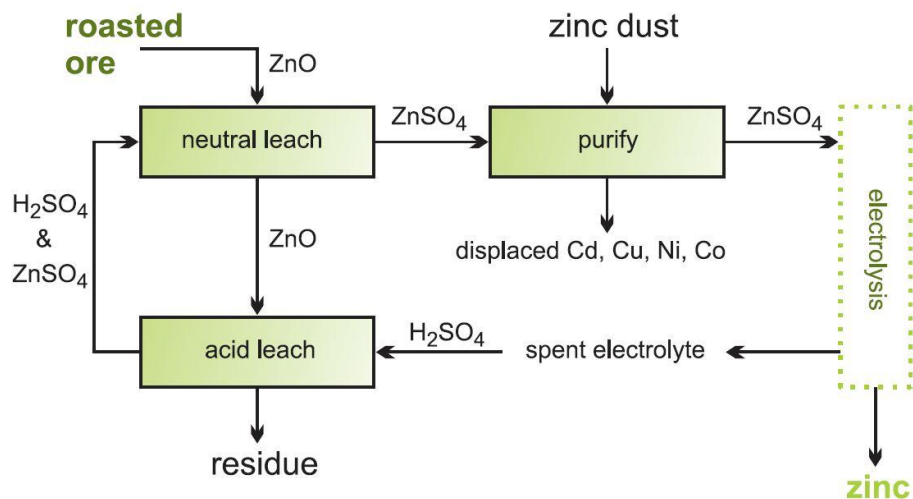
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Zinc refining and residues

More than 80% of the world's zinc production is obtained from zinc sulfide concentrates by the Roasting-Leaching-Purification-Electrolysis process

In the Zinc Electrolytic Plant in San Luis Potosí, in the various purification stages, secondary products rich in copper, cobalt and zinc are generated

The copper cement, sold to a copper refining plant, contains mainly copper, but also cobalt in small quantity





Crystallization stripping

Steps in a conventional solvent extraction: extraction, scrubbing and stripping. In the last step, the solute is returned from the organic to an aqueous phase for recovery

An interesting modification of this hydrometallurgical process is the addition of a crystallization operation, where any kind of low-solubility metal salts, such as oxalates, oxides, sulfides, or even vanadates, can be precipitated (precipitation stripping)

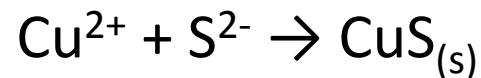
Extraction



Stripping

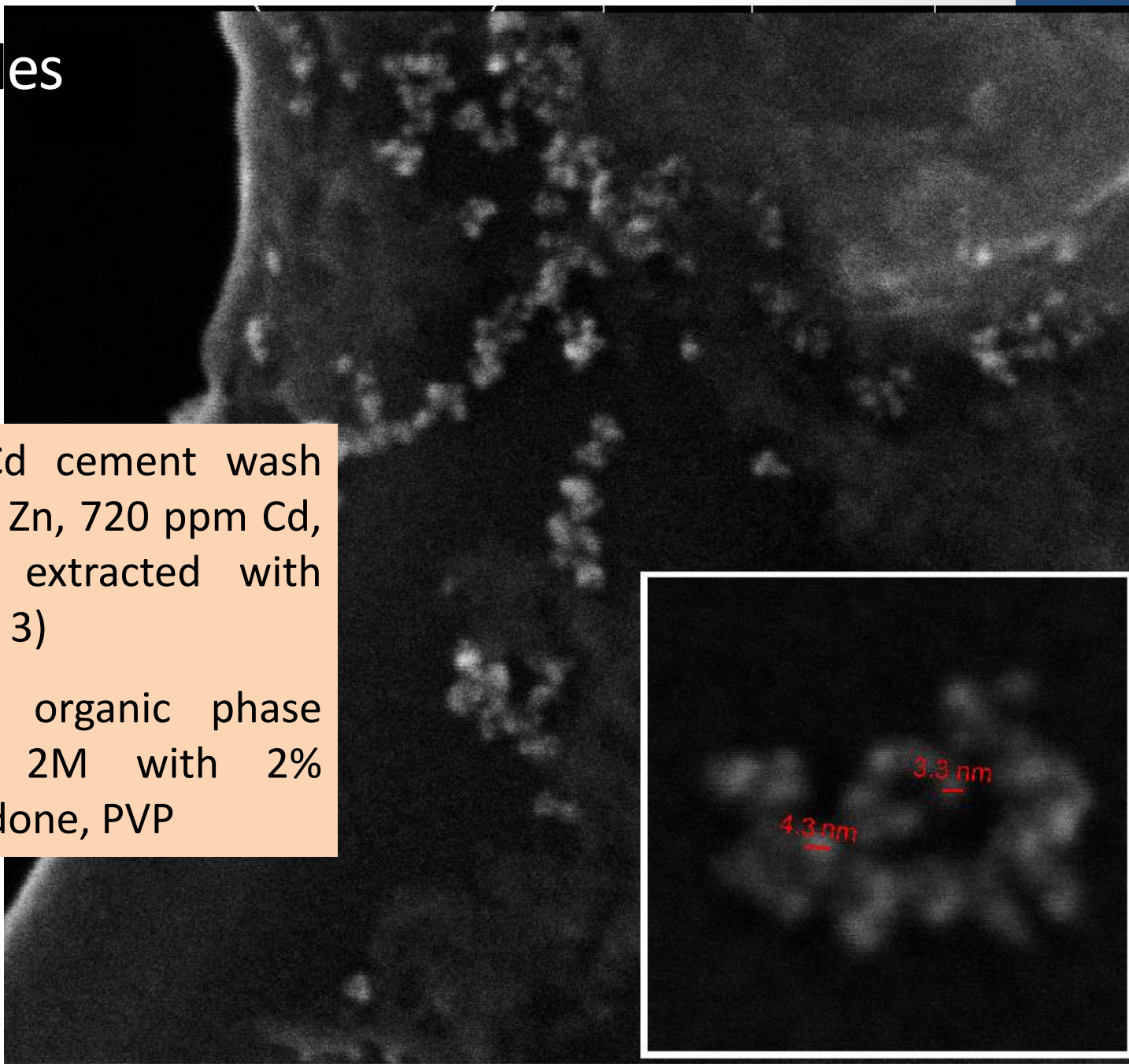


Crystallization





Nanoparticles



Zn from the Cd cement wash solution (74 g/L Zn, 720 ppm Cd, 244 ppm Co) extracted with Cyanex[®]923 (pH 3)

Stripping from organic phase using (NH₄)₂S 2M with 2% polyvinylpyrrolidone, PVP

HV 5.00 kV mag 250 000 x

200 nm X8 (IPICYT-LINAN)



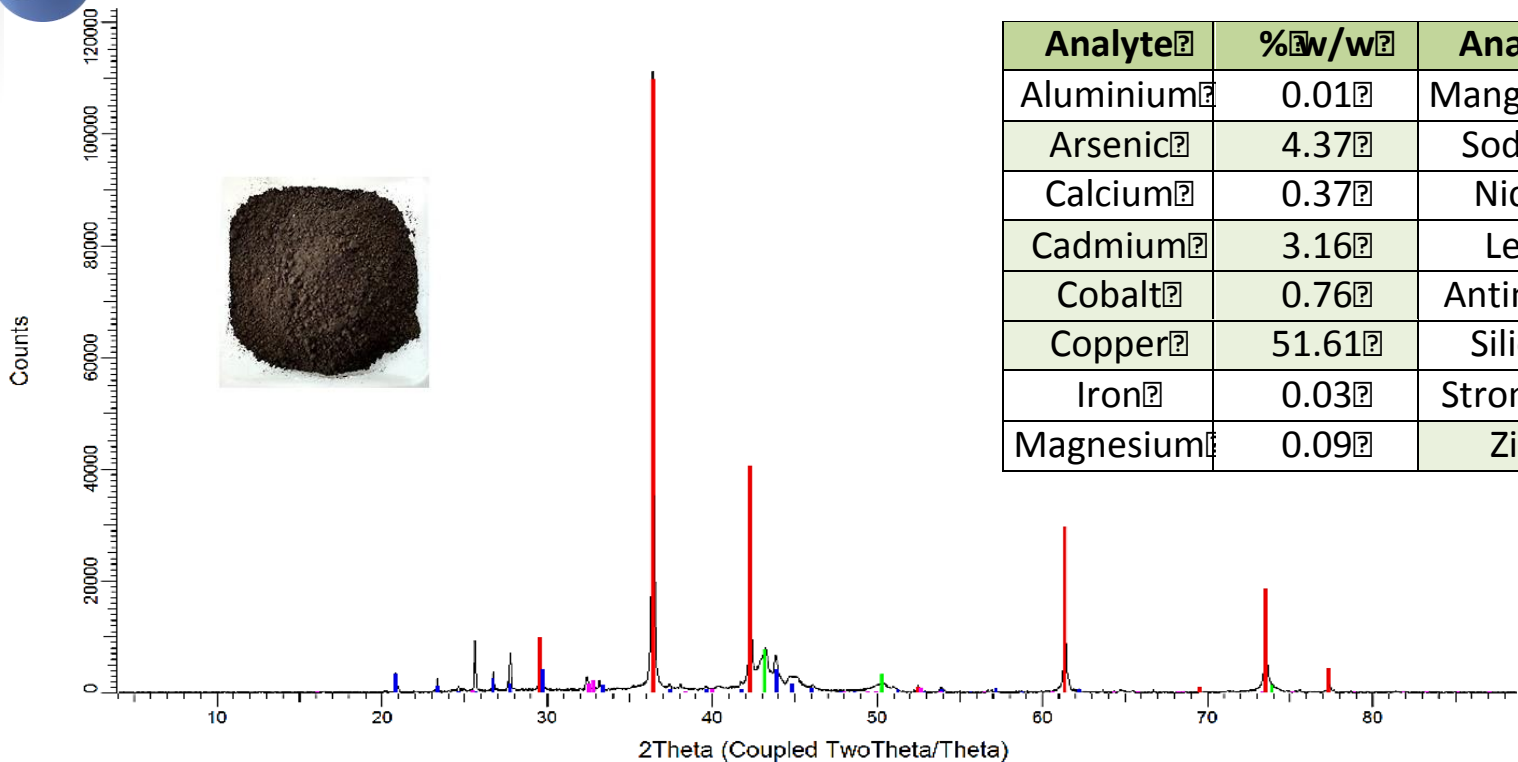
Objective

The recovery of cobalt from a copper cement by solubilizing the metal in a washing step, and the separation of copper by acid leaching

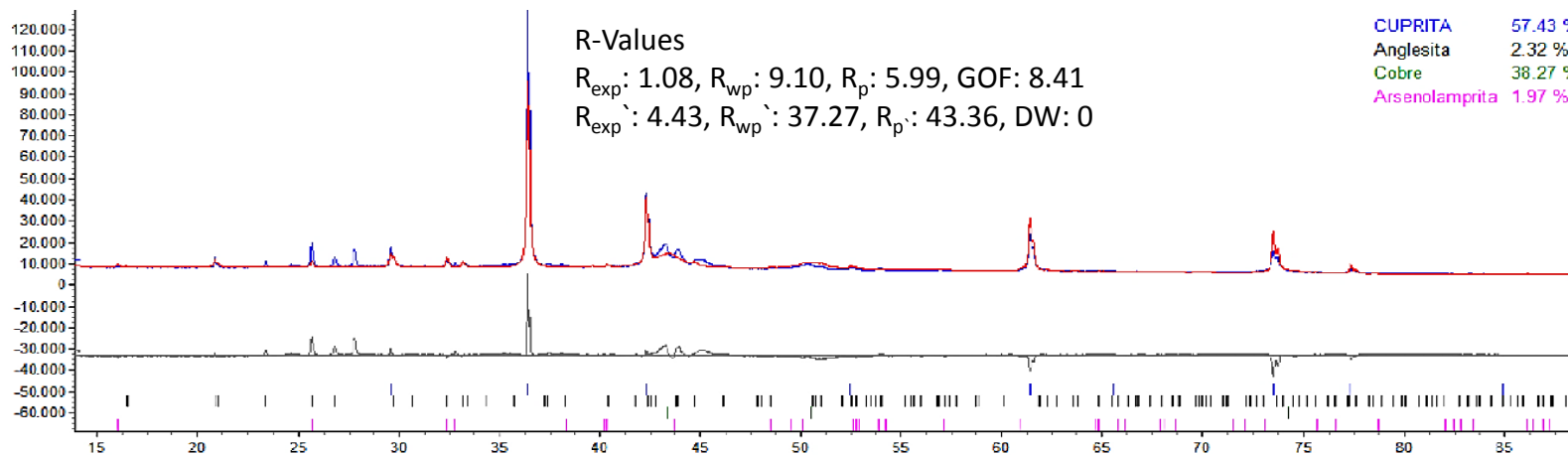
Both metals recovered from the aqueous solution using solvent extraction and acid stripping, and the strip solutions used to synthesize metal sulphide nanoparticles

Results: Solid characterization

X-Ray Diffraction, Rietveld refinement, ICP-OES analysis



Analyte	%w/w	Analyte	%w/w
Aluminium	0.01	Manganese	0.11
Arsenic	4.37	Sodium	0.1
Calcium	0.37	Nickel	0.06
Cadmium	3.16	Lead	2.21
Cobalt	0.76	Antimony	0.08
Copper	51.61	Silicon	0.07
Iron	0.03	Strontium	0.55
Magnesium	0.09	Zinc	3.02



$$\chi^2 = R_{wp}/R_{exp}$$



Leaching of the cement

Wash step **Solution S1**, metal dissolved, ppm

Solid (30 g) + water (100 mL),
50 °C, 10 min

Element?	40° C?	50° C?	60° C?
Arsenic??	3.6?	5.3?	7.4?
Cadmium?	289.6?	329.3?	345.8?
Cobalt?	2184.6?	3448.0?	3501.56?
Copper?	182.3?	281.3?	297.6?
Zinc?	103.5?	119.3?	124.7?

Cobalt 45.1%
Copper 0.05%
Cadmium 1.04%
Arsenic 0.01%
Zinc 0.40%

Acid leaching **Solution S2**, metal dissolved, ppm

Solid (30 g) + 1 M H₂SO₄
(100 mL), 65 °C, 10 min

Element?	50° C?	65° C?	80° C?
Arsenic?	215.6?	291.3?	311.7?
Cadmium?	267.9?	362?	387.3?
Cobalt?	4504.6?	6087.3?	6513.4?
Copper??	78.1g/L?	105.6g/L?	112.9g/L?
Zinc?	335.9?	454?	485.8?

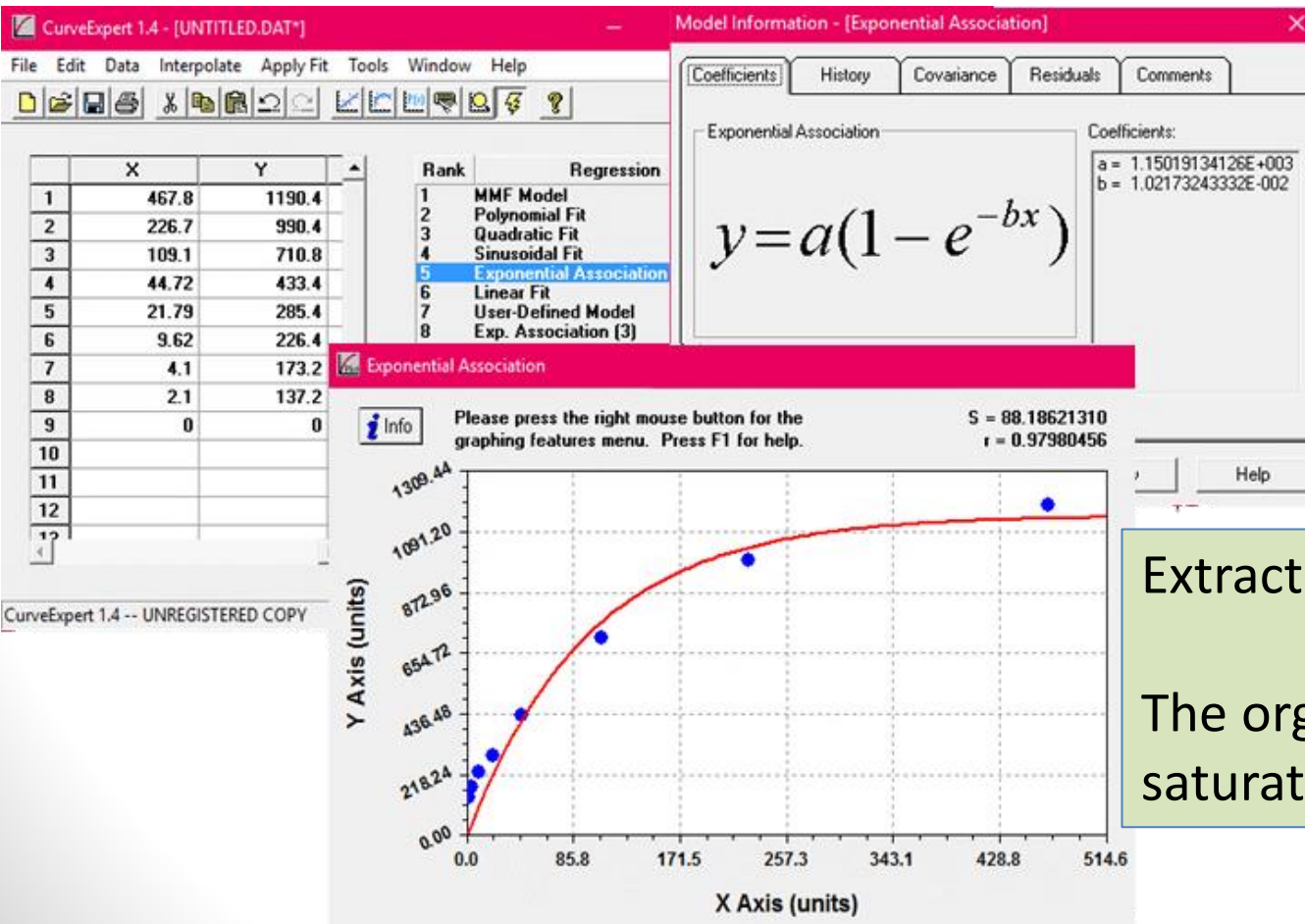
Cobalt 79.7%
Copper 20.4%
Cadmium 1.15%
Arsenic 0.67%
Zinc 1.51%

Solvent extraction

Cobalt extraction

Extraction using **S1** (dilution 2/3) and Cyanex[®]272, bis(2,4,4-trimethylpentyl)phosphinic acid, 20% in Exxsol[™]D60

Highest extraction values for cobalt reached at pH>6 (98.6 %)



Extraction isotherm

The organic phase reach saturation at 1190.4 mg Co/L



Solvent extraction

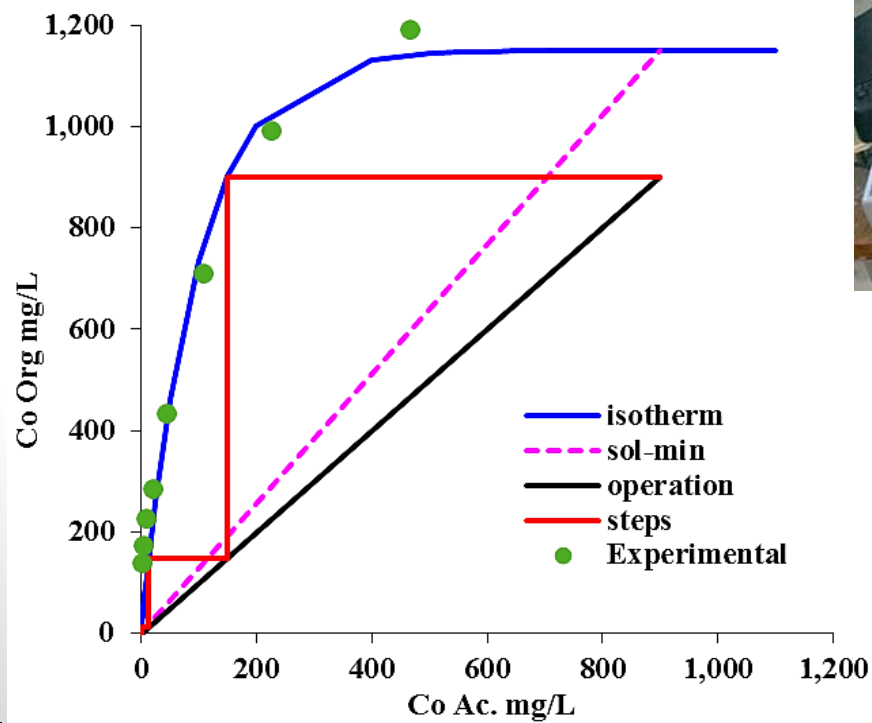
Cobalt extraction



McCabe-Thiele diagram for cobalt, equilibrium pH 5.5, O/A 1.3



Counter current experiments with four stages for cobalt in mixer-settlers



	$[M]_{\text{feed}}$, mg/L	$[M]_{\text{raffinate}}$, mg/L	Extraction, %
Cd	65.9	51.2	22.2
Co	760.5	38.5	94.9
Cu	56.2	55.8	0.85



Solvent extraction and synthesis

Copper extraction

- As copper concentration in liquor **S2** was high, extraction in a single step performed (2-hydroxy-5-nonyl-salicylaldoxime, Acorga®M5774, pH 2)
- 99% of the copper extracted

Synthesis of metal sulfide nanoparticles

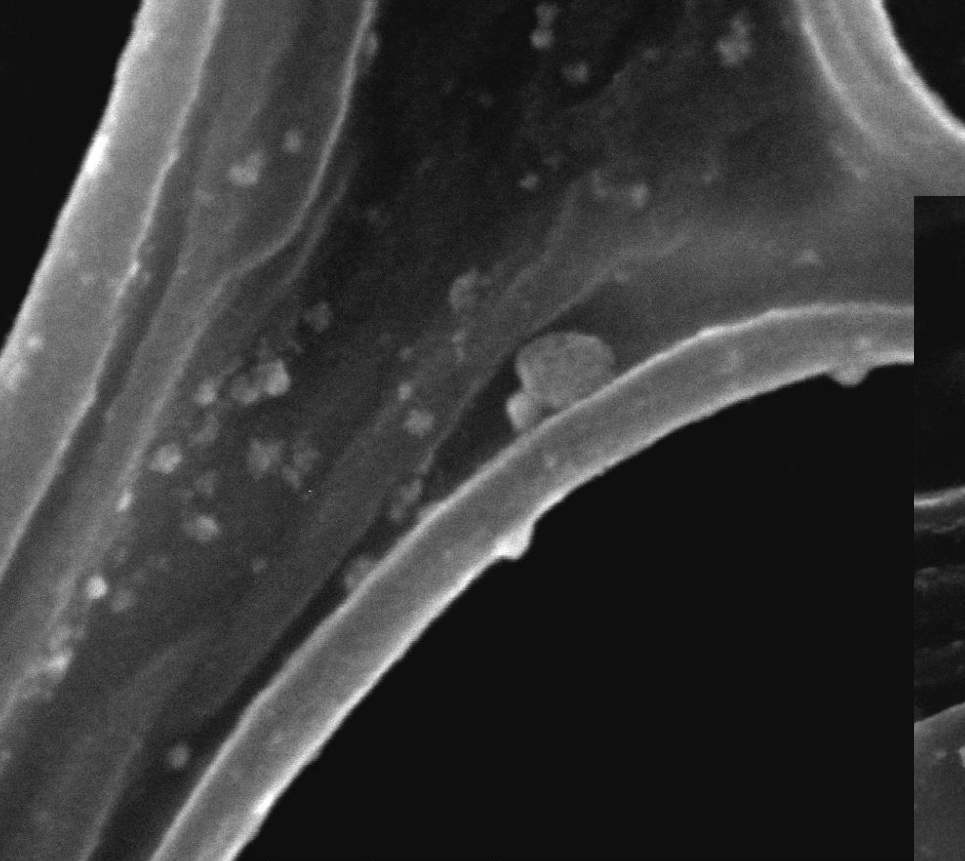
- Metal recovered from the organic phase using sulfuric acid solution, both strip solutions used for the preparation of nanoparticles
- Synthesis 1 of Co_xS and CuS : 3 mL strip solutions added dropwise to 2 M $(\text{NH}_4)_2\text{S}$, with 2% polyvinylpyrrolidone
- Synthesis 2: 3 mL organic solutions added dropwise to 2 M $(\text{NH}_4)_2\text{S}$, with 2% polyvinylpyrrolidone



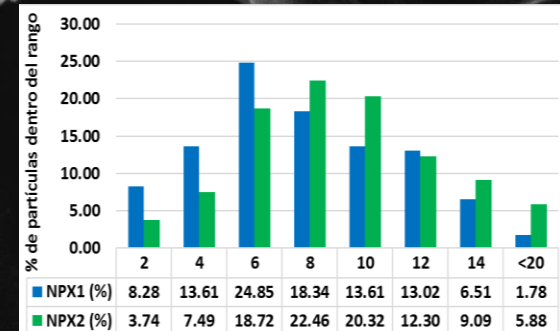
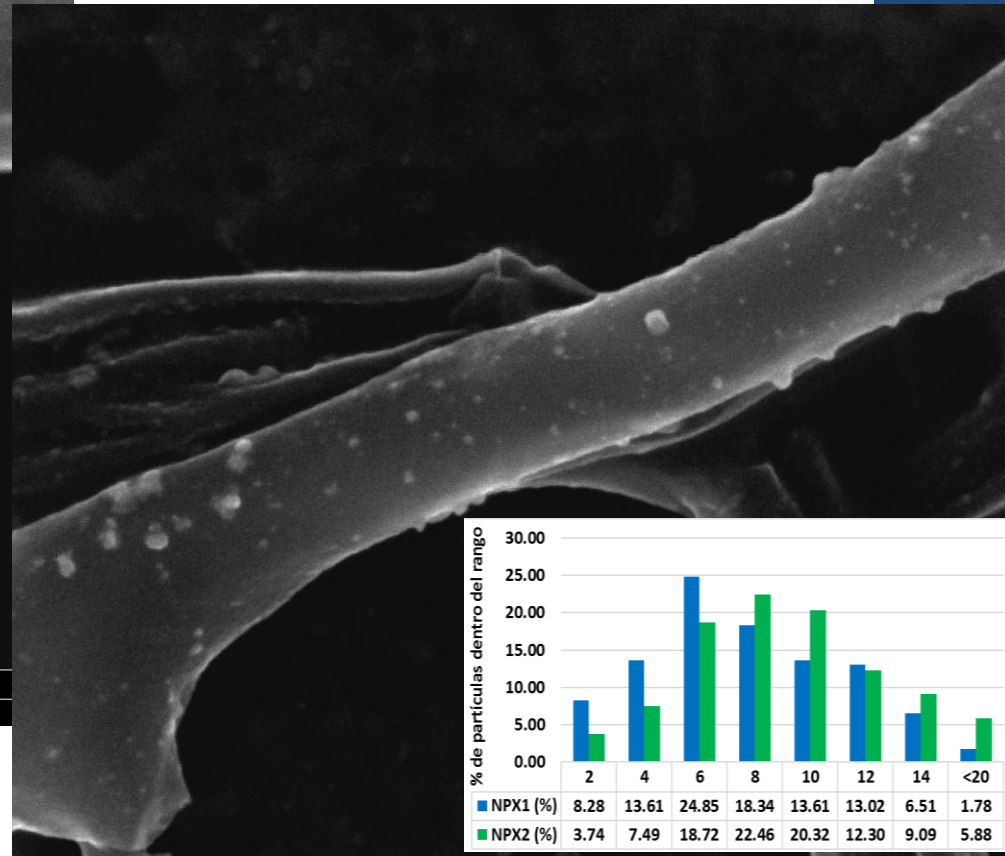
Synthesis of nanoparticles

Cobalt sulfide nanoparticles

Particles well dispersed (size 2 to 20 nm)



det	WD	curr	HV	mag	田	100 nm	
TLD	4.1 mm	86 pA	5.00 kV	350 000 x		CoS17	(LINAN-IPICYT)



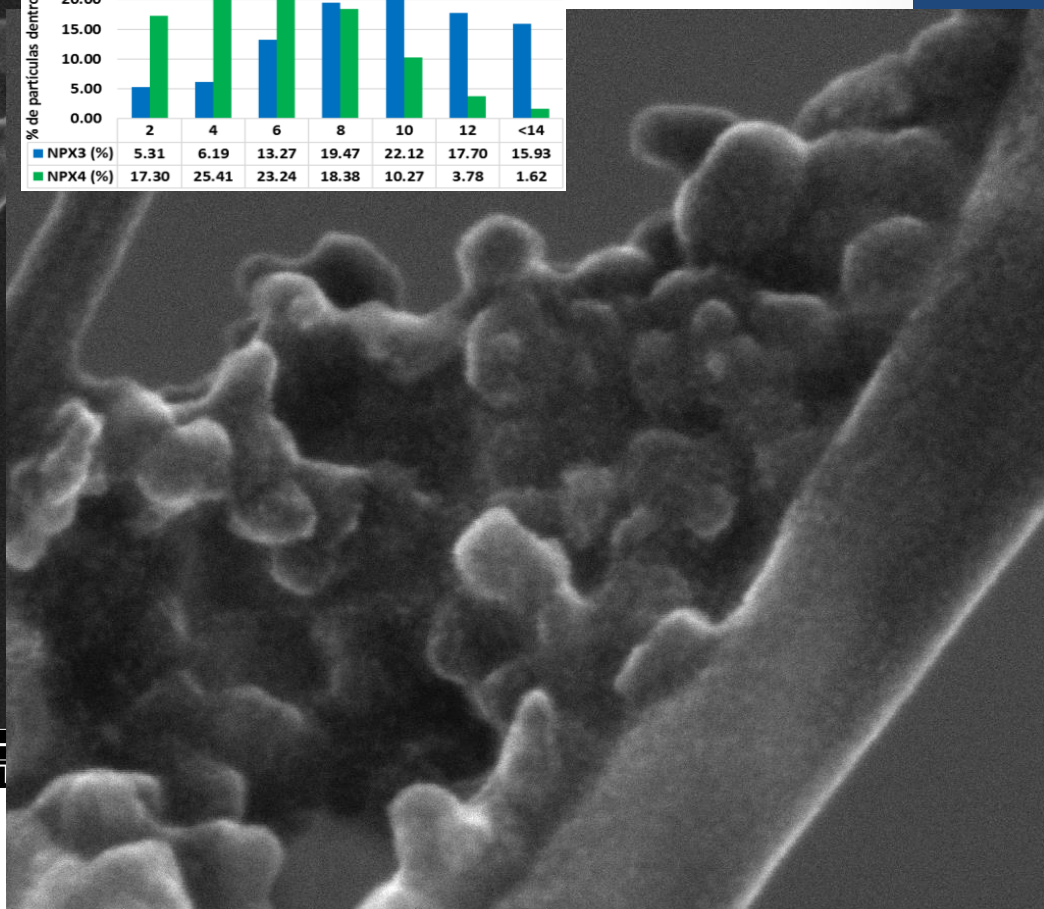
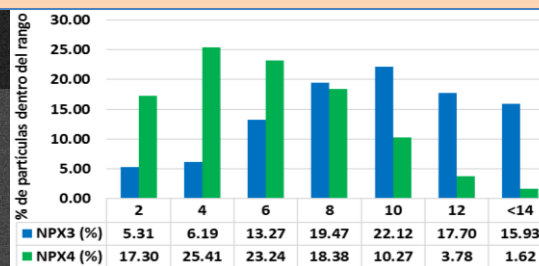
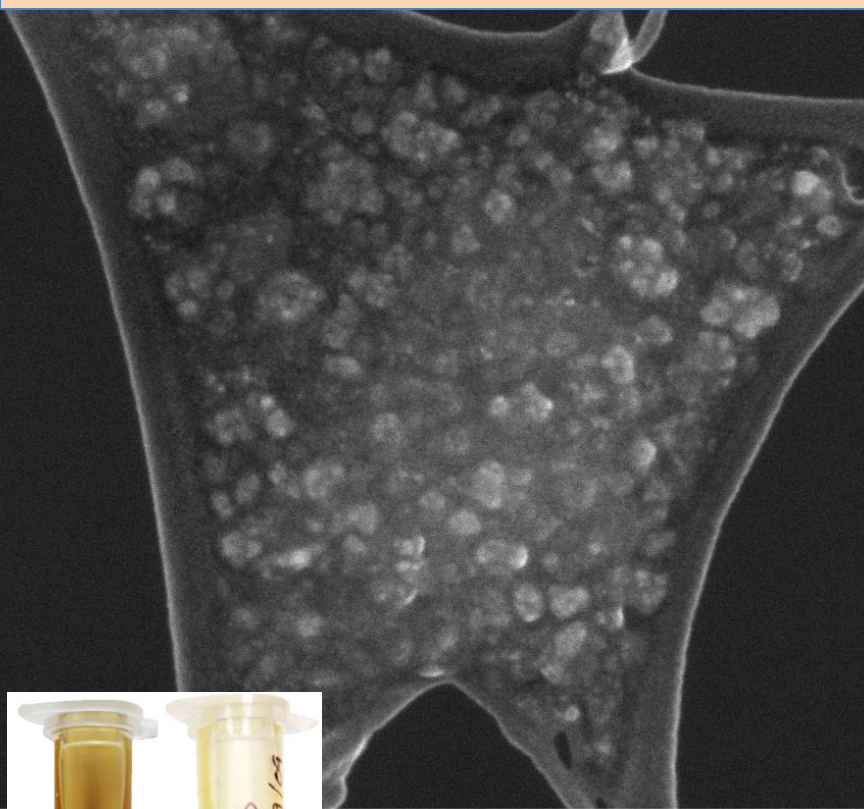
det	WD	curr	HV	mag	田	400 nm	
TLD	4.1 mm	86 pA	5.00 kV	150 000 x		CoS17	(LINAN-IPICYT)

Synthesis

Copper sulfide nanoparticles

Nanoparticles from 2 to 14 nm

$\text{Cu}_{1.8}\text{S}$, card 01-089-2073, and covellite (CuS , card 00-001-1281)



mag 150 000 x 400 nm CuS17 (LINAN-IPICYT)

det TI D 3.8 mm 86 pA 5.00 kV 350 000 x 100 nm CuS17 (LINAN-IPICYT)



Conclusions

Cobalt in the copper cement obtained by a wash step at 50°C, extraction performed at pH=5.5. Efficiency of counter current extraction 94.9%

Copper recovered by acid leaching and extracted in a single step, efficiency of 99%

Acidic and precipitation stripping allowed the preparation of dispersed nanoparticles of cobalt sulfide (2-20 nm), and copper sulfide (2-14 nm)

$\text{Cu}_{1.8}\text{S}$, card 01-089-2073, and covellite (CuS , card 00-001-1281)



Acknowledgements

Obrigado, Gracias, Thank you

Xóchitl Macías is grateful to CONACYT for the postgraduate grant

Project SER-CONACYT México-Argentina de Nanotecnología, 191145 “Recuperación de metales de efluentes metalúrgicos para preparar materiales nanométricos, y su uso en sensores ambientales”

We thank M. Rosa Lina Tovar for the XRD support and Dr. Daniel Bien (Exxon Mobil Co.) for the useful advice, and Cytec Co. and ExxonMobil for the diluent samples