UNIVERSITAT POLITÈCNICA DE CATALUNYA
BARCELONATECH
Escola d'Enginyeria de Barcelona Est

r2em
RESOURCE RECOVERY
& ENVIRONMENTAL
MANAGEMENT

Research at Barcelona Research Center
of Multiscale Science and Engineering

Recovery of antimony and bismuth from arsenic-containing waste streams from the copper electrorefining circuit: an example of promoting critical metals circularity from secondary resources

J.L. Cortina, Barcelona Tech-UPC (Spain)

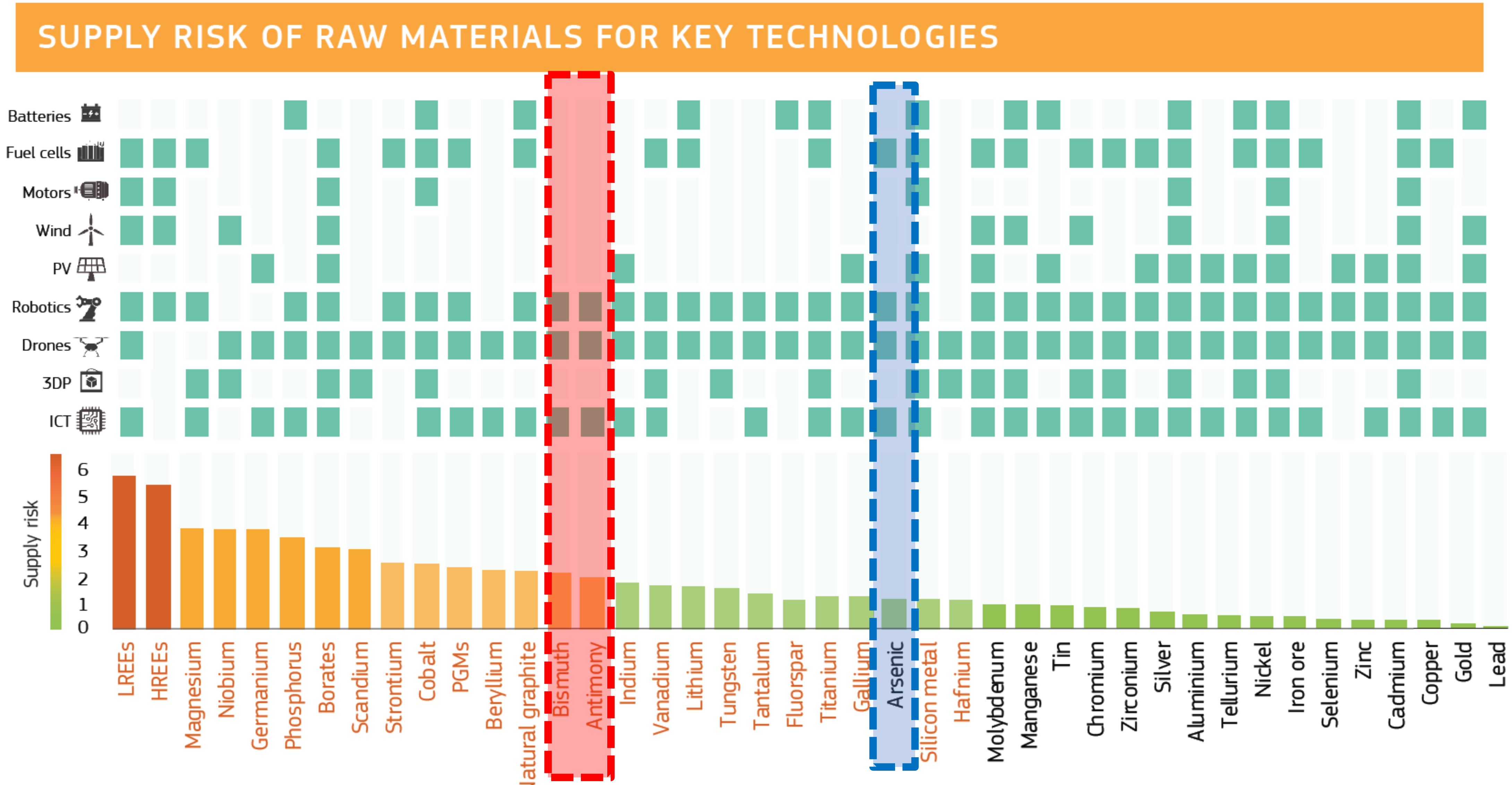
10th Scientific Seminar, November 28-30th, 2023, Lisbon (Portugal)

PROMETIA
Mineral Processing and Extractive Metallurgy
for Mining and Recycling Innovation Association

Index

- Introduction: why/where/how Sb and Bi could be recovered in Cu metallurgical circuits.
- Scientific and technology challenges and recovery principles.
- Back-flow to EITRM: efforts on commercialization routes of technologies/products.
- Out-look and next stages.

What was the driving force of the recovery project ?

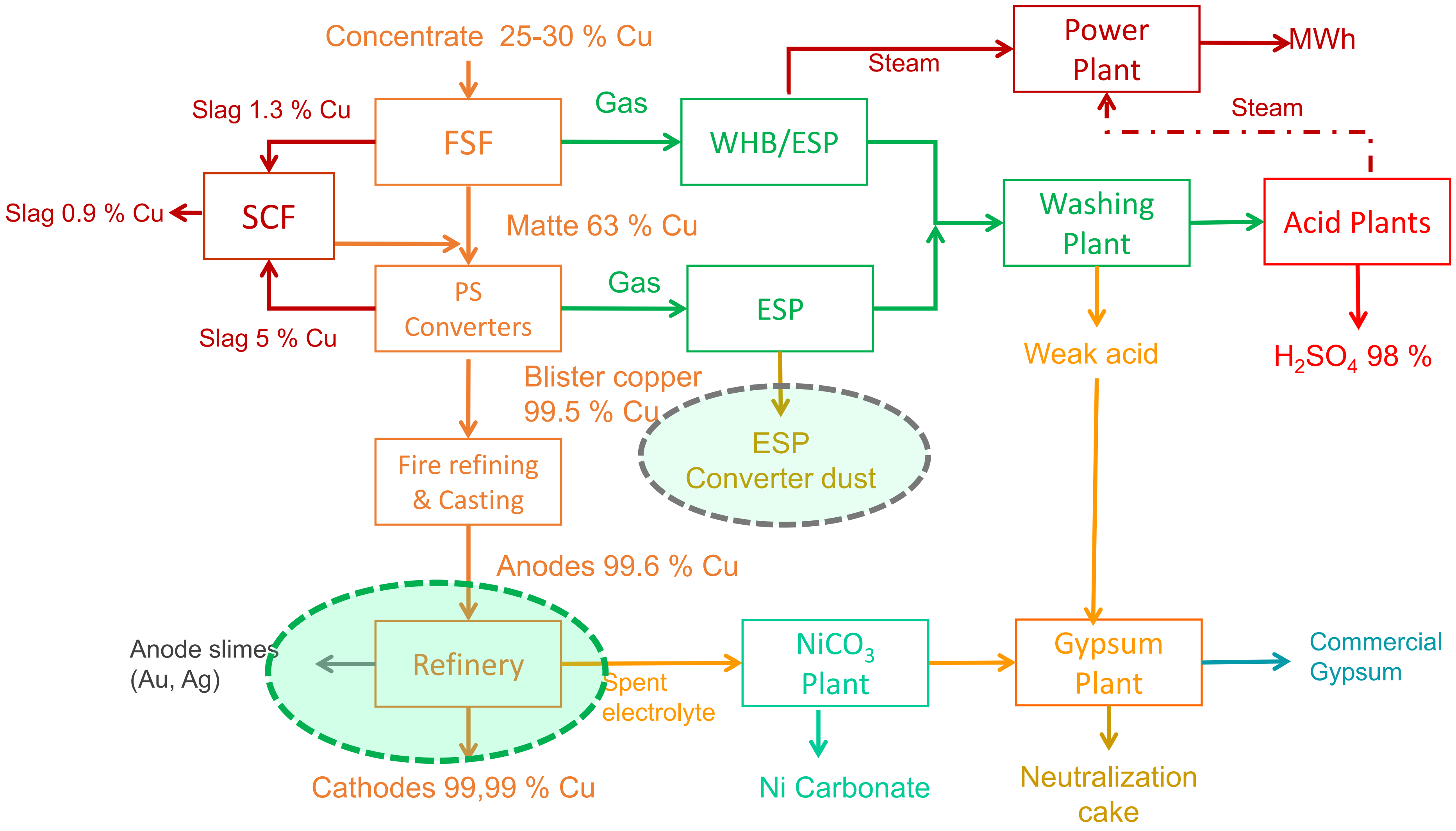


Both critics (2021, 2023) and Bi strategic (20203)

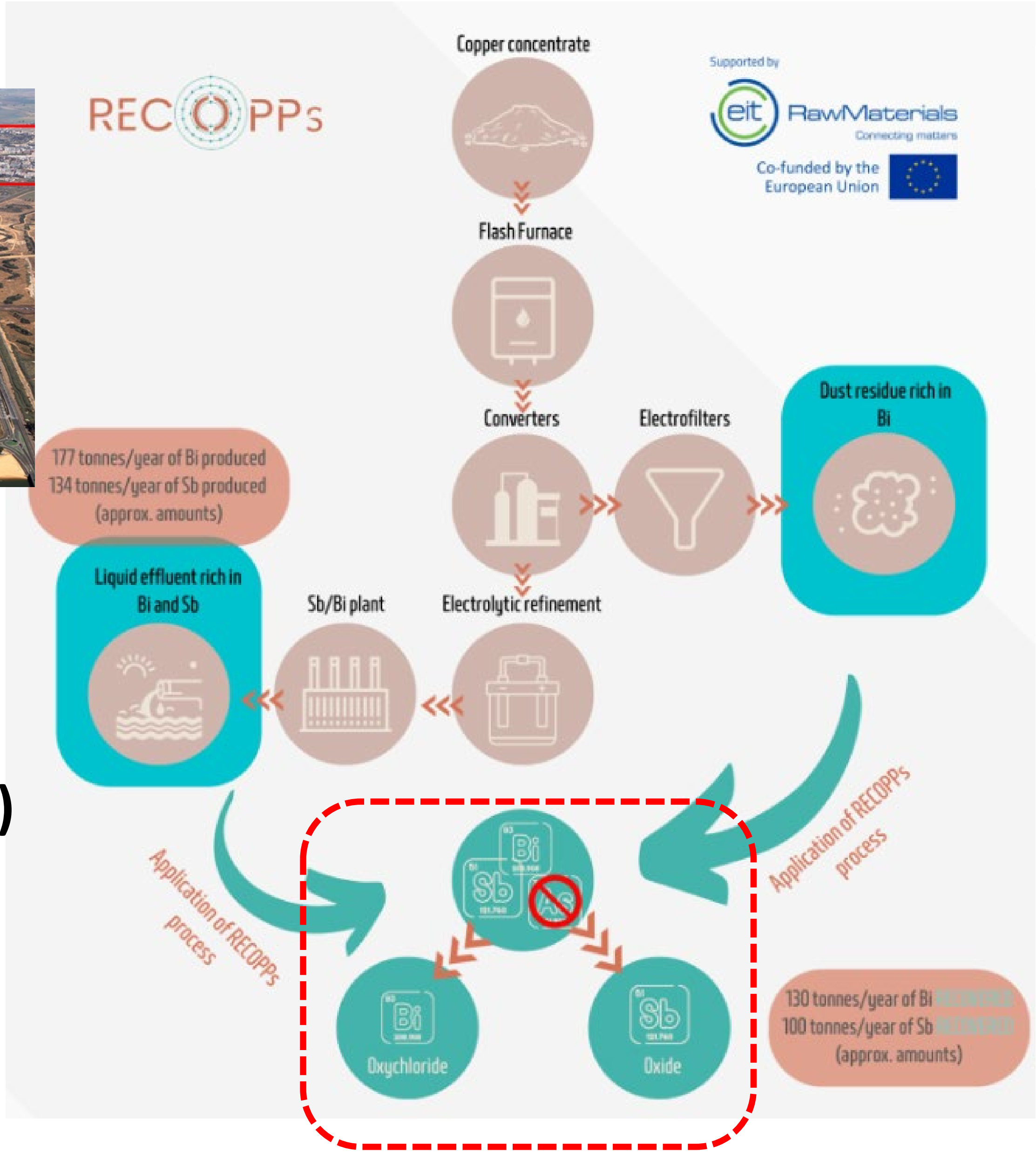
Critic and strategic (2023)

Where are the main process streams for Sb and Bi recovery ?

AC Smelter (Huelva) Flowsheet



Recovery of CRMs (Bi, Sb) in metallurgical process streams (Recopps-EIT-RM-up-scaling)



-RECOPPS

Fast-Track (2018) TRL5

Upscaling(EIT RM PN-19119)

TRL 7-8

Budget: 2.7 M€

Funded by the European Union

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idæa EXCELENCIA SEVERO OCHOA

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ATLANTIC COPPER A Freeport-McMoRan Company

Łukasiewicz Instytut Metali Nieżelaznych

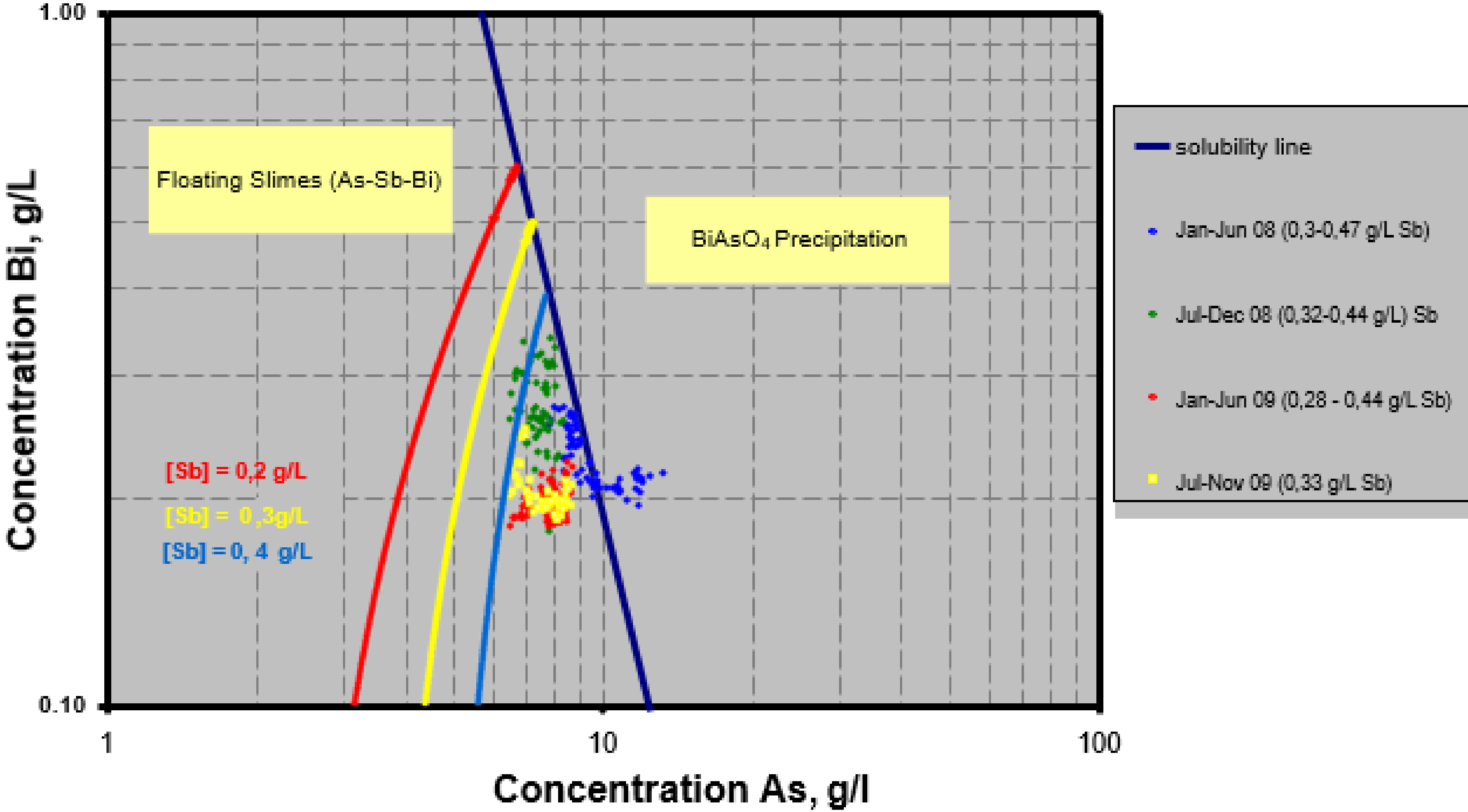
CETAQUA CENTRO TECNOLÓGICO DEL AGUA

eurecat Centre Tecnològic de Catalunya

Where are the main process streams for Sb and Bi recovery ?

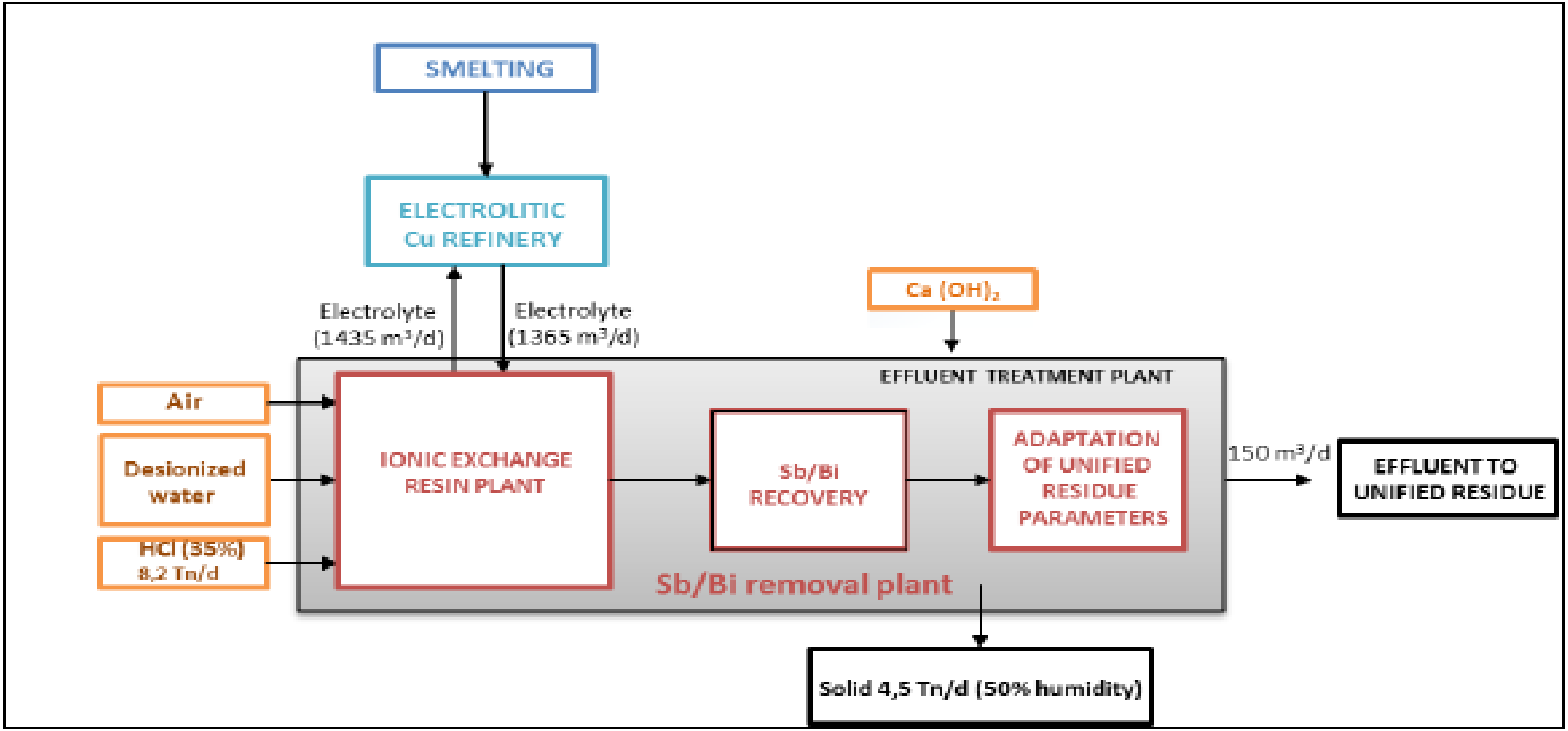
AC Smelter (Huelva) Flowsheet

IX as polishing stage to avoid anode slimes formation



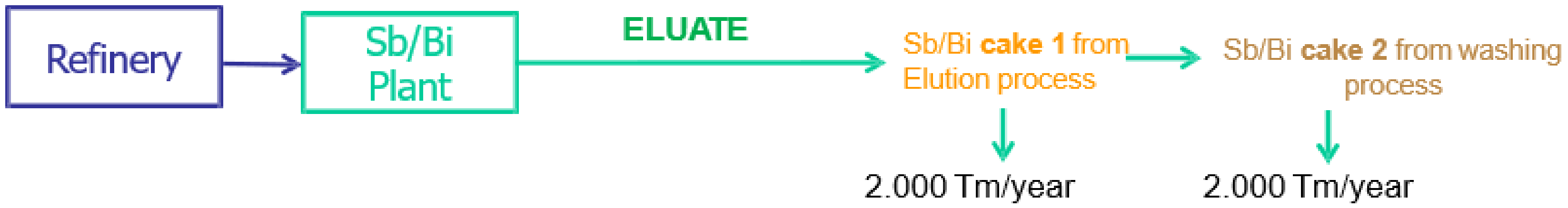
Where are the main process streams for Sb and Bi recovery ?

AC Smelter (Huelva) Flowsheet



Where are the main process streams for Sb and Bi recovery ?

Sb and Bi Removal Plant: Characterization of eluate and cakes



Liming /disposal current treatment

Eluate

Sample	Cl- (g/L)	Fe (mg/L)	Pb (mg/L)	Hg (mg/L	As (mg/L)	S (mg/L)	Sb (mg/L)	Bi (mg/L)
Eluate	166-185	14-16	20-25	1-2	1485	2.300-2700	9.044-10.938	7,525-9.190

The elaute is the working stream

What are the Sb and Bi recovery principles: processing schemes

Target objectives/technological & Scientific challenges

- Sb and Bi recovery as pure as possible (KPI on purity) / No presence of As **(<0.1 %? TBD after market analysis)**
- As removal and stabilization from the stream (**minimizing dilution factor**)
- Potential recovery of HCl (3-5 MHCl): OPEX reduction / on-site process re-use

Main scientific challenges (eluate chemistry)

i) Sb/As speciation control,

ii) Limited thermodynamic data base for Sb/Bi in 3-6 M was limiting the use Chemical Process Modelling Tools to describe and optimize processes involved

Bi, As and Sb speciation issues

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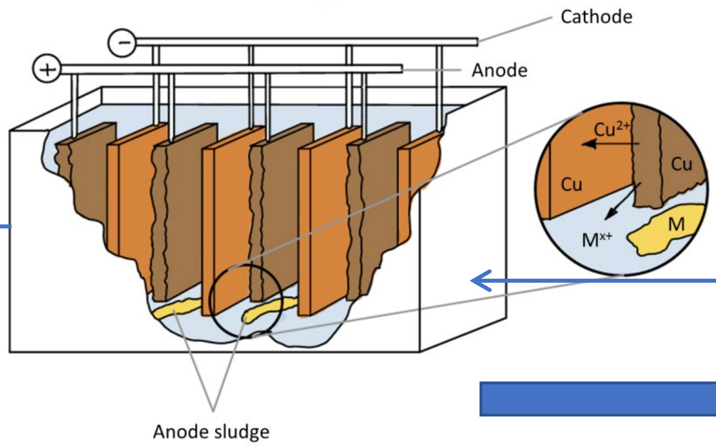
ELECTROREF. UNIT
200-250 g/L H_2SO_4
H_3AsO_3/H_3AsO_4/ Sb(III)/Sb(V)/ Bi(III)



IX PRE-POLISHING
Cu(s)

Objective:
Fe(III) → Fe(II) to extend IX life
What happened to As(V)/As(III) redox par?

STRIPPING SOLUTION
6 M HCl

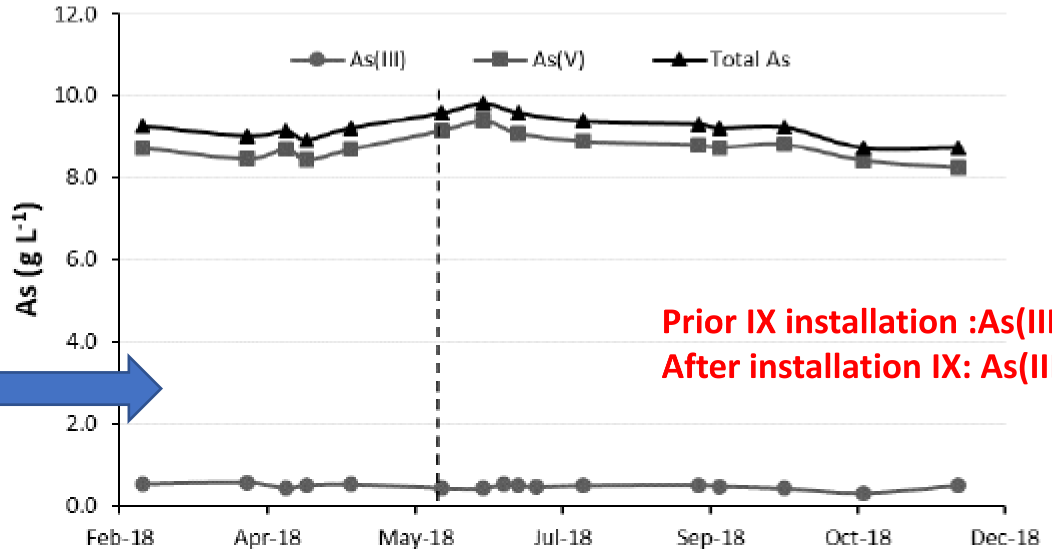
IX STAGE
[Bi^{III}, Sb^{III}]

Un-expected co-extraction of H_3AsO_3/H_3AsO_4/H_2SO_4

ELUATE
3 – 4 M HCl excess, H_2SO_4
$BiCl_4^-$, $SbCl_4^-$ H_3AsO_3/H_3AsO_4
Ca, Cu

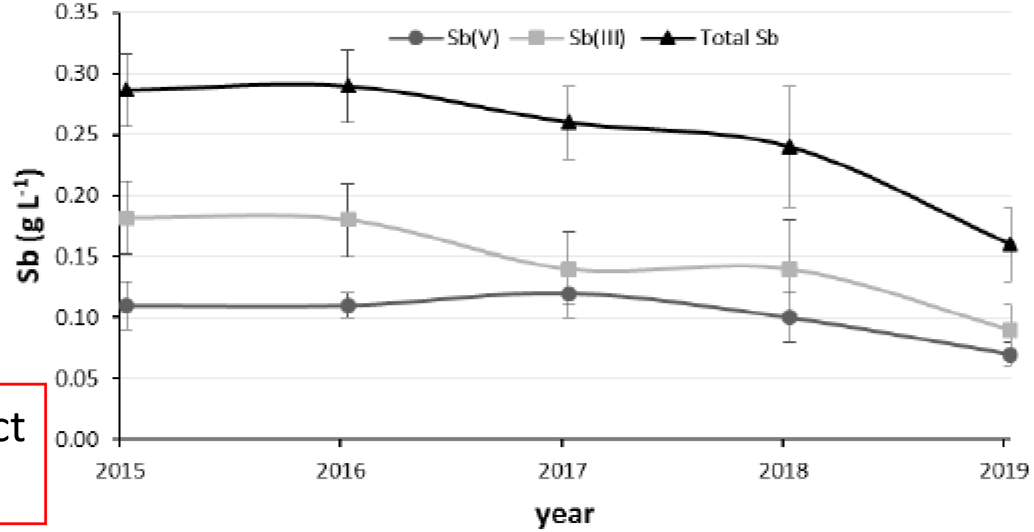
Bi and Sb recovery project [RECOPP]

SPECIATION ON THE ELECTROREFINING REACTOR



As(V): 94%
As(III): 6%

Prior IX installation :As(III): 0.51, As(V): 8.60 g/L
After installation IX: As(III) 0.46 As(VI) 8.71 g/L



Electrolyte:
57 Sb(III)
43% Sb(V)

What are the Sb and Bi recovery principles: processing schemes

ELUATE

HCl (3-6 M),
H_2SO_4(0.1-0.3M)

Bi(III): $BiCl_4^-$ (0.02-0.09 M)
Sb(III): $SbCl_4^-$
Sb(V): $SbCl_6^-$ (0.02-0.07 M)

As(III): H_3AsO_3
As(V): H_3AsO_4 (0.01-0.04 M)

M(II): Ca(II), Cu(II), Zn(II), Fe(II)…(0.001-0.01 M)

Acidic organophosphorous extractants (BASF)

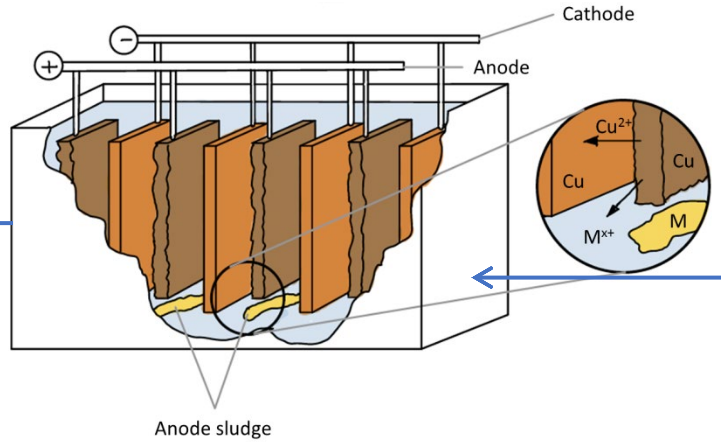
Solvating organophosphorous extractants (Solvay)

Potential separation / Recovery processes

- Solvent Extraction (SX) route taking benefit of extractant selectivity

Bi, As and Sb speciation issues (industrial site)

ELECTROREF. UNIT
200-250 g/L H_2SO_4
H_3AsO_3/H_3AsO_4/ Sb(III)/Sb(V)/ Bi(III)



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6 M HCl

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[Bi^{III}, Sb^{III}]

Un-expected co-extraction of H_3AsO_3/H_3AsO_4/H_2SO_4

ELUATE
3 – 4 M HCl excess, H_2SO_4
$BiCl_4^-$, $SbCl_4^-$ H_3AsO_3/H_3AsO_4
Ca, Cu

	Initial Electrolyte
	mean ± sd
Sb(V)	0.09 ± 0.01
Sb(III)	0.12 ± 0.01
Total Sb	0.21 ± 0.01
Fe(II)	0.85 ± 0.03
Fe(III)	0.06 ± 0.02
Total Fe	0.91 ± 0.03

Electrolyte:
57 Sb(III)
43% Sb(V)

	Electrolyte + Cu Shavings
	mean ± sd
Sb(V)	0.07 ± 0.01
Sb(III)	0.14 ± 0.04
Total Sb	0.21 ± 0.03
Fe(II)	0.86 ± 0.02
Fe(III)	0.05 ± 0.02
Total Fe	0.91 ± 0.03

Electrolyte:
67 Sb(III)
33% Sb(V)

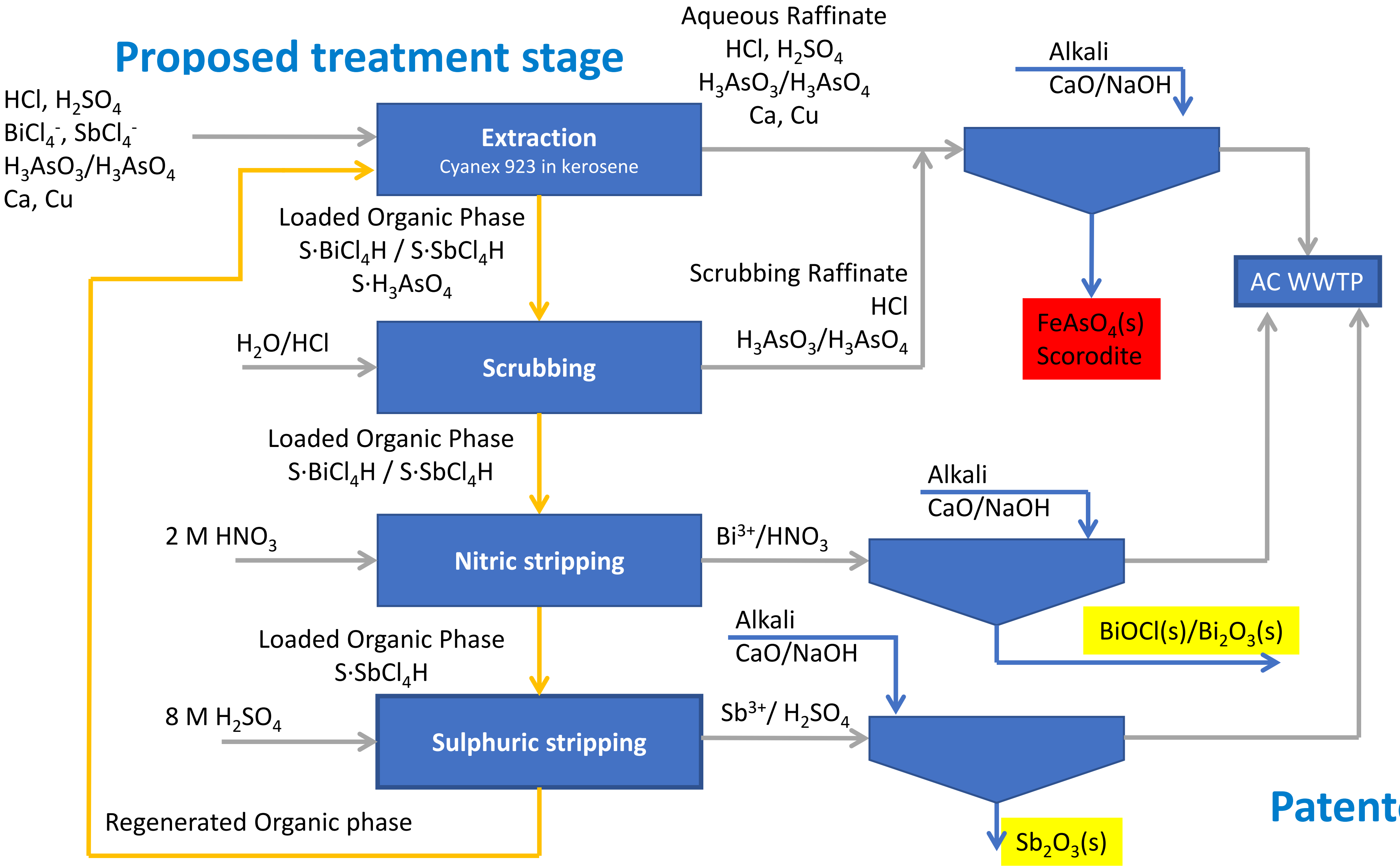
	Electrolyte + Cu Shavings + Ion Exchange Resin
	mean ± sd
Sb(V)	0.04 ± 0.00
Sb(III)	0.00 ± 0.00
Total Sb	0.04 ± 0.00
Fe(II)	0.86 ± 0.05
Fe(III)	0.05 ± 0.01
Total Fe	0.91 ± 0.04

IX stage
100% extraction Sb(III)
57% extraction Sb(V)

Bi and Sb recovery project [RECOPP]

82% Sb(III)
18% Sb(V)

RECOPP recovery schemes: *Selective Separation route using Solvent extraction*



Patented, 2020

Routes to recover Sb and Bi avoiding the precipitation of As

WORKING HYPOTHESIS: REDOX CONTROL OF MAIN COMPONENTS As and Sb

Eluate composition shown mixed redox states : As(III),As(V) (94%)/Sb(III) (82%), Sd(V):

Not redox control is applied: Formation of $SbAsO_4$(s), $SbSbO_4$(s) and BiAsO4(s) in Cu-electro-refining cells has been widely described, but also described for As(III)(6%)/Sb(V) (18%): AsSbO4(s), BiSbO4(s)

Option 1.

Redox control is applied to have As(V)/Sb(V) to precipitate Sb_2O_5(s)

but what about the interferences of Bi(III) to form BiAsO4(s) and BiSbO4(s)?

H_2O_2
Cl_2 (g)
O_3 (g)

Option 2.

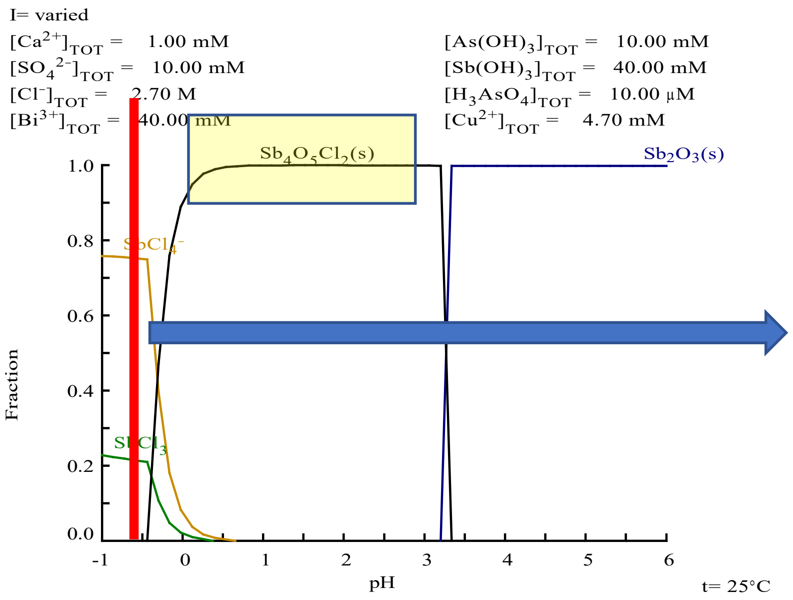
Redox control is applied to As(III)/Sb(III) to form oxychlorides (e.g. SbOCl(s), Sb4Cl2O4(s)) but it has been described the formation of solid solutions (As,Sb)2O3(s) however non equilibrium data of this mineral phases are available

Fe powder
NaH_2PO_2
Cu powder
$NaHSO_3$
SO_2(g)

ELUATE SOLUTION CHEMISTRY: review of the Sb and Bi geochemical data bases for minerals identified on the electrolyte circuits (modelling predictions)

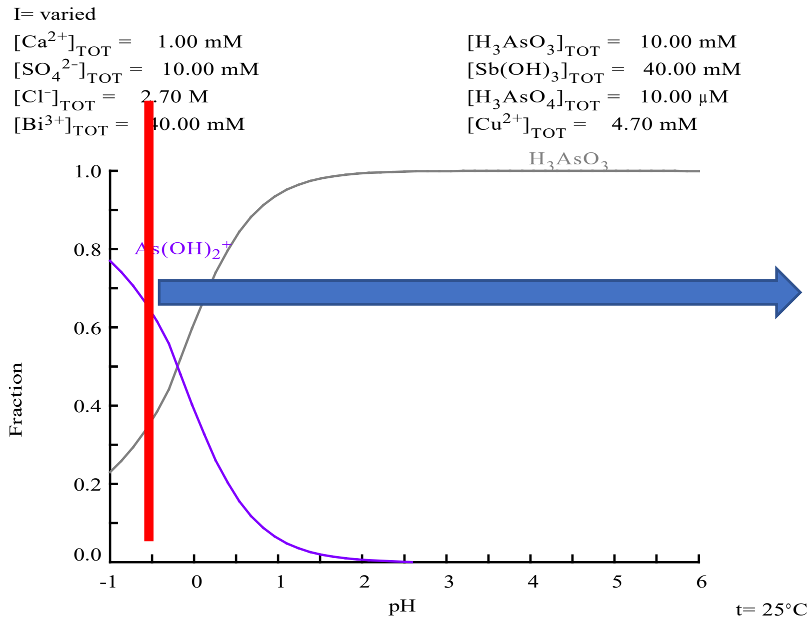
Eluate

pH=-0.5



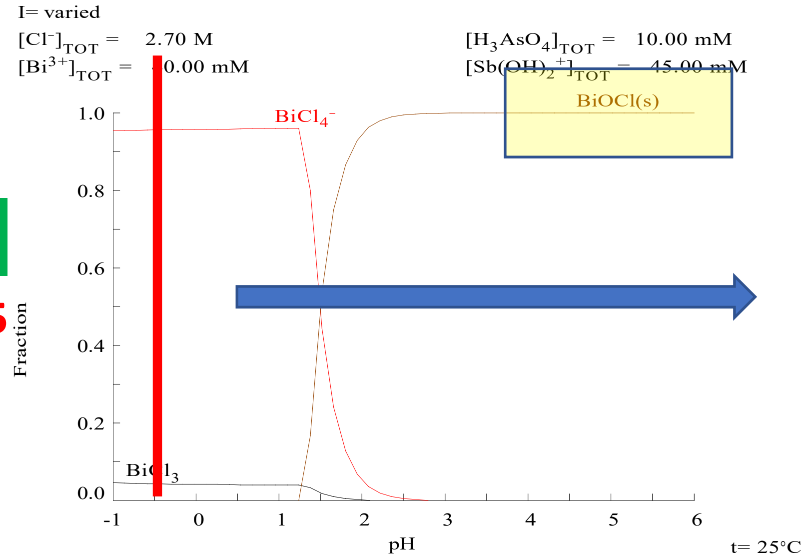
Eluate

pH=-0.5

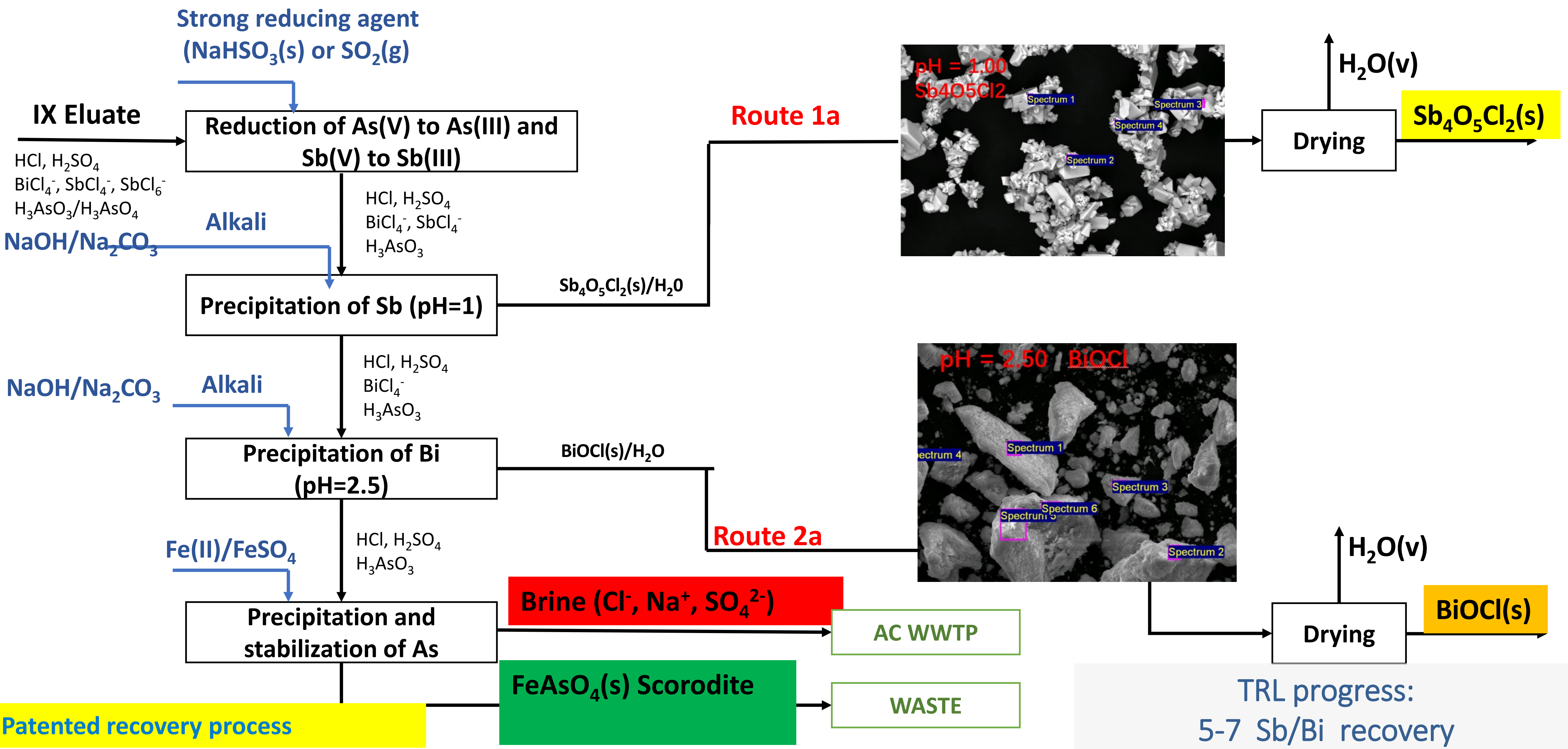


Eluate

pH=-0.5



Sb and Bi recovery protocol to oxychloride forms (routes 1a and 2a)



Patented recovery process

TRL progress:
5-7 Sb/Bi recovery

Sb and Bi recovery protocol to oxychloride forms (routes 1a and 2a

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ACS APPLIED MATERIALS & INTERFACES — Research Article
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Electrochemical Performance of $Sb_4O_5Cl_2$ as a New Anode Material in Aqueous Chloride-Ion Battery

Xiaoqiao Hu,† Fuming Chen,*,† Shaofeng Wang,† Qiang Ru,† Benli Chu,† Chengyan Wei,‡ Yumeng Shi,§ Zhicheng Ye,∥ Yanxu Chu,∥ Xianhua Hou,*,† and Linfeng Sun*,⊥

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Supporting Information

Deciphering the $Sb_4O_5Cl_2$−MXene Hybrid as a Material for Advanced Potassium-Ion Batterie

Yanqin Shi, Dan Zhou, Tianli Wu, and Zhubing Xiao*

Cite This: ACS Appl. Mater. Interfaces 2022, 14, 29905−29915 Read Online

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ABSTRACT: Potassium-ion batteries (PIBs) possess great potential in new-generation large-scale energy storage. However, their applications are plagued by large volume change and sluggish reaction kinetics of the electrode materials during the repeated charge/discharge processes. Guided by computerization modeling, we, herein, report the atomic-scale interfacial regulation of $Sb_4O_5Cl_2$ coupled with structural engineering for the robust anode material of PIBs via simple MXene hybridization using a microwave-assisted hydrothermal method. Benefiting from the ostensive interfacial interplay between $Sb_4O_5Cl_2$ and Ti_3C_2, MXene hybridization induces a favorable variation in spin polarization densities and the coordination of Sb atoms in $Sb_4O_5Cl_2$, which are effective in optimizing the K^+ ion diffusion path, thus resulting in a significantly reduced K^+ ion diffusion barrier and promoted K^+ insertion/extraction kinetics. The as-prepared $Sb_4O_5Cl_2$−MXene anodes exhibit a highly reversible discharge capacity and decent cyclability, in addition to the low discharge plateau and promising full cell performance. This work is pivotal for not only paving the way for the exploratio PIBs but also shedding light on the fundamental research on K^+ ion storage in antimon

KEYWORDS: potassium ion batteries, MXene, spin polarization densities, antimony oxychl

Photoswitchable Chlorine Vacancies in Ultrathi Selective CO_2 Photoreduction

Xian Shi, Xing'an Dong, Ye He, Ping Yan, Shihan Zhang, and Fan Don

Cite This: ACS Catal. 2022, 12, 3965−3973 Read Online

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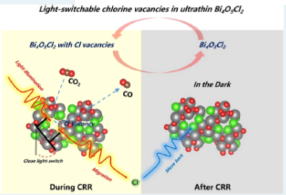
ABSTRACT: CO_2 photoreduction currently faces two challenges: low photoreduction efficiency and poor product selectivity. Ultrathin two-dimensional bismuth oxyhalide, with a large number of surface vacancies (active sites), is an ideal material for regulating CO_2 photoconversion. However, surface vacancies in this catalyst are easily deactivated during the reaction. CO_2 photoreduction relies on sufficient active sites; hence, we synthesized ultrathin $Bi_4O_5Cl_2$ nanoplates via a water-assisted self-assembly process with sufficient photoswitchable surface Cl vacancies for solar-driven CO_2-to-CO reduction. The surface Cl vacancies were generated under light irradiation and filled again with migrated Cl^- under an O_2 atmosphere after turning off the irradiation. These photoswitchable vacancies enabled $Bi_4O_5Cl_2$ to produce 58.49 μmol g^{-1} CO after 4 h of irradiation with high stability and lowered the energy barriers of the rate-determining (CO_2-to-$COOH^-$) and selectivity-determining steps ($COOH^-$-to-CO), enabling 100% product selectivity. The reversible, photoswitchable Cl vacancies have a higher potential as active sites for CO_2 photoreduction than synthetically introduced static surface vacancies, which could provide a feasible strategy for the creation of highly dynamic, active-defective catalysts for solar-energy conversion.



KEYWORDS: photoswitchable Cl vacancy, $Bi_4O_5Cl_2$, active sites, CO_2 photoreduction, product selectivity

OPEN

th and antimony-based oxyhalides and chalcohalides as ial optoelectronic materials

njiang Wang[1], Yuwei Li[2], Dongwen Yang[1], Xin-Gang Zhao[1], Koushik Biswas[3], David J. Singh[2] and Lijun Zhang[1]

Synthesis, Functional Modifications, and Diversified Applications of Hybrid BiOCl-Based Heterogeneous Photocatalysts: A Review

Xiaoli Yang, Shaodong Sun,* Jie Cui, Man Yang, Yongguang Luo, and Shuhua Liang*

Cite This: Cryst. Growth Des. 2021, 21, 6576−6618 Read Online

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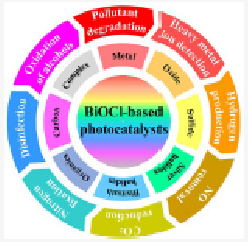
nd regulation of heterogeneous interfaces are beneficial to and photocharge separation of hybrid BiOCl-based d to the synergistic effects that originate from the integrated omponents. With the rapid development of synthetic d micro-/nanostructures with diversified components, en well prepared. Moreover, hybrid BiOCl-based photo- ytic applications, such as O_2 reduction, heavy metal Previously, several review methods, morphological d micro-/nanostructures. and the corresponding catalytic mechanisms has refore, a comprehensive understanding of the basic theory and e. This review aims to provide an overview of the important s, including metal/BiOCl, metal oxide/BiOCl, metal sulfide/ Cl, organics/BiOCl, carbon/BiOCl, and other BiOCl-based , modification strategies, relationships between interfacial n some typical examples. Additionally, some scientific issues ill provide a useful reference for researchers currently focusing



Sb and Bi oxychlorides applications for new K,Cl-batteries, optoelectronics, photocatalys…

ed Bismuth Oxyhalides for

a Christudas Beena, and Sara E. Skrabalak*

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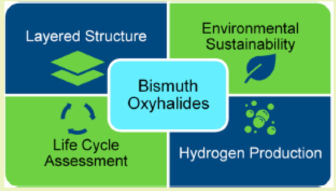
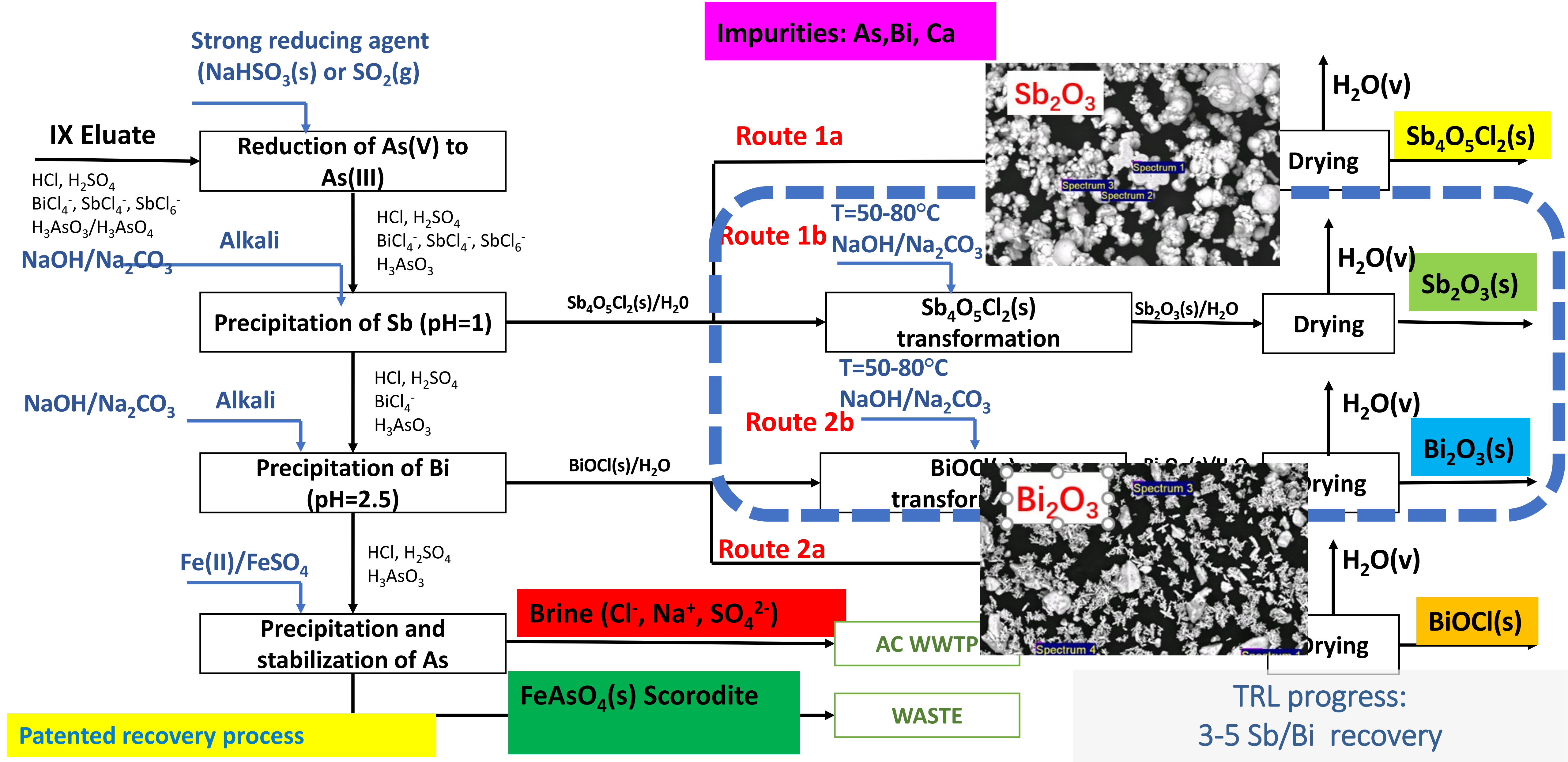
ABSTRACT: Bismuth oxyhalides ($Bi_xO_yX_z$ X = Cl, Br, I) are promising layered photocatalysts that can produce H_2 using solar light. The layered crystal structures minimize electron−hole recombinations in these materials and provide compositional flexibilities that allow for band gap tuning. Current literature highlights developments in synthetic routes and improved performance metrics; however, an analysis of the sustainability of these compounds is missing. In this Perspective, we use the life cycle assessment framework as a guide to evaluate the sustainability of each stage of the bismuth oxyhalide life cycle, from raw material extraction (mining, refinement, purification) all the way through the end of the material's life and consider ways to recycle and/or reuse the spent photocatalyst. Here, we gather and unite information from the bismuth oxyhalide field with information from the sustainability literature in the first attempt to evaluate the sustainabilities of these materials as photocatalysts for H_2 production. We present our own perspective on the future of the field and make recommendations for researchers interested in this class of materials and photocatalysts more broadly.



KEYWORDS: bismuth oxyhalides, life cycle assessment, layered nanomaterials, hydrogen production, sustainability

Sb and Bi recovery protocol to oxyde forms (routes 1b and 2b) (reducing the levels of impurities As)



Recopps piloting at IMN (2023)

TRL progress:
5-7 Sb/Bi recovery

Outlook

- Potential recovery scheme to recover oxychloride by-products or oxides forms depending on the quality requirements and expected quality parameters.
- Products quality is depending on the molar ratios of the three elements (Sb, Bi and As).
- Finalizing the quality assessment of end-users or final refiners to achieve market requirements

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-RECOPPS (Recovery of added-value elements from Copper primary production) EIT RM PN-19119)

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IMN Team (Mateusz Ciszewski)

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