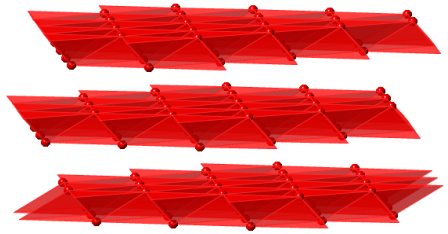
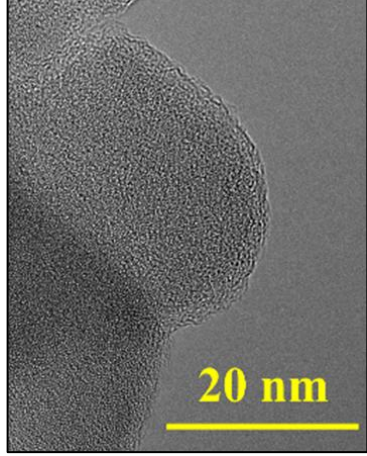
GEUS



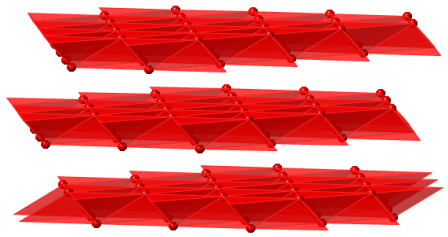


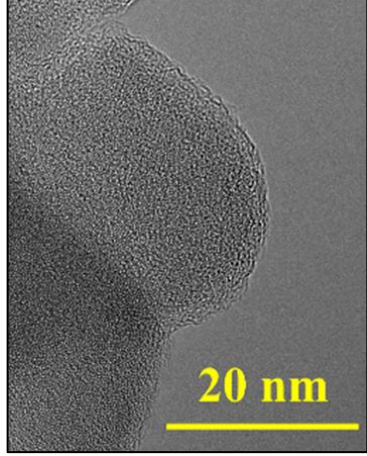
Converting toxic arsenic pollution to high-value functional materials

Case van Genuchten
Senior Researcher
Geological Survey of Denmark and Greenland (GEUS)

Megasites og generationsforureninger
5 November, 2025 13.40 – 14.05
Copenhagen, DK

GEUS





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1B) Background: Arsenic upcycling approach

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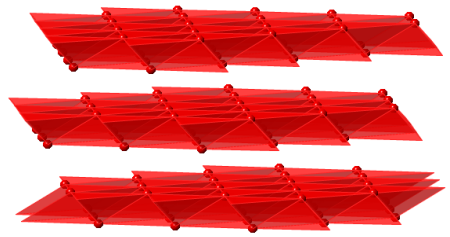
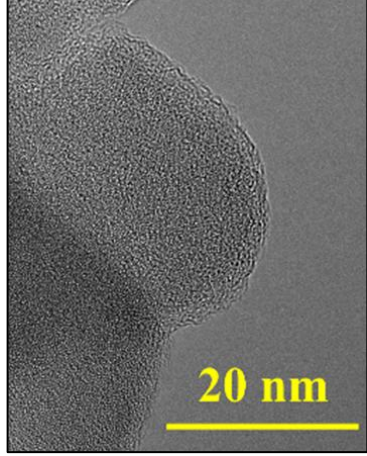
3) Next steps and outlook for megasites with arsenic pollution, including Collstrop

GEUS





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Arsenic is a persistent environmental contaminant …

Collstrop Site Soil Pollution: >100 Tons of Arsenic

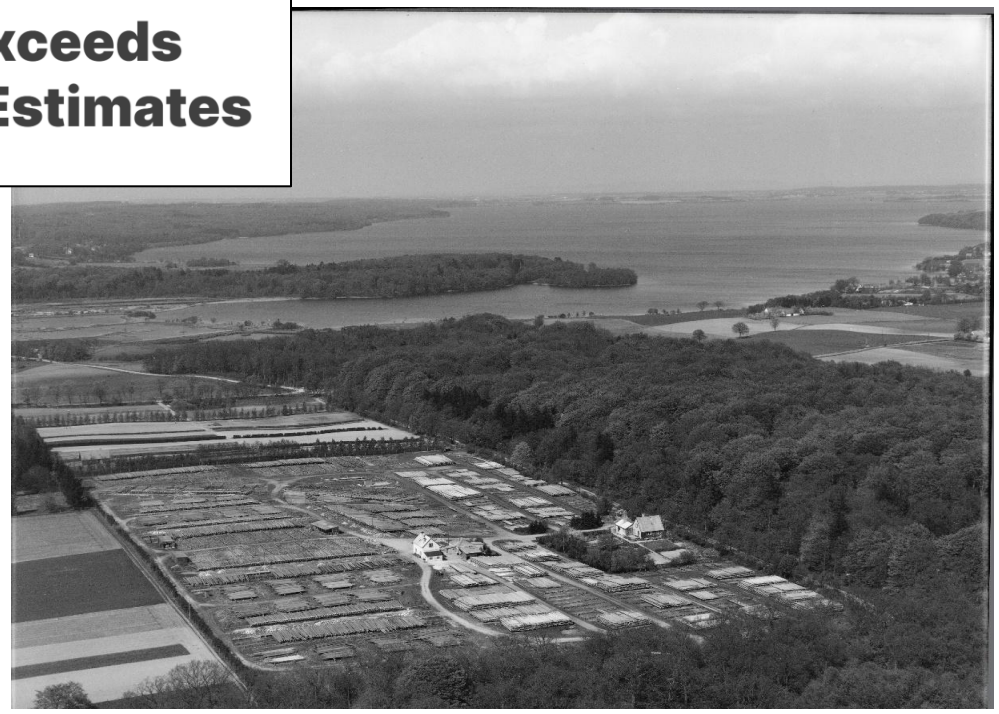
Local National World More Cookie Policy (EU)

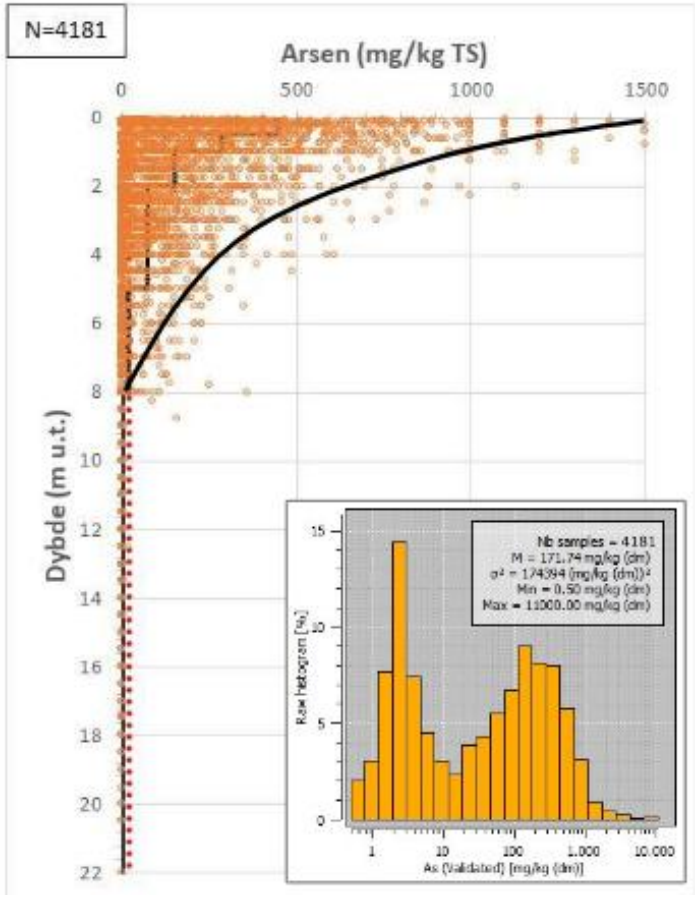
REGIONAL

Arsenic Contamination at Collstrop Site in Hillerød Exceeds Previous Estimates

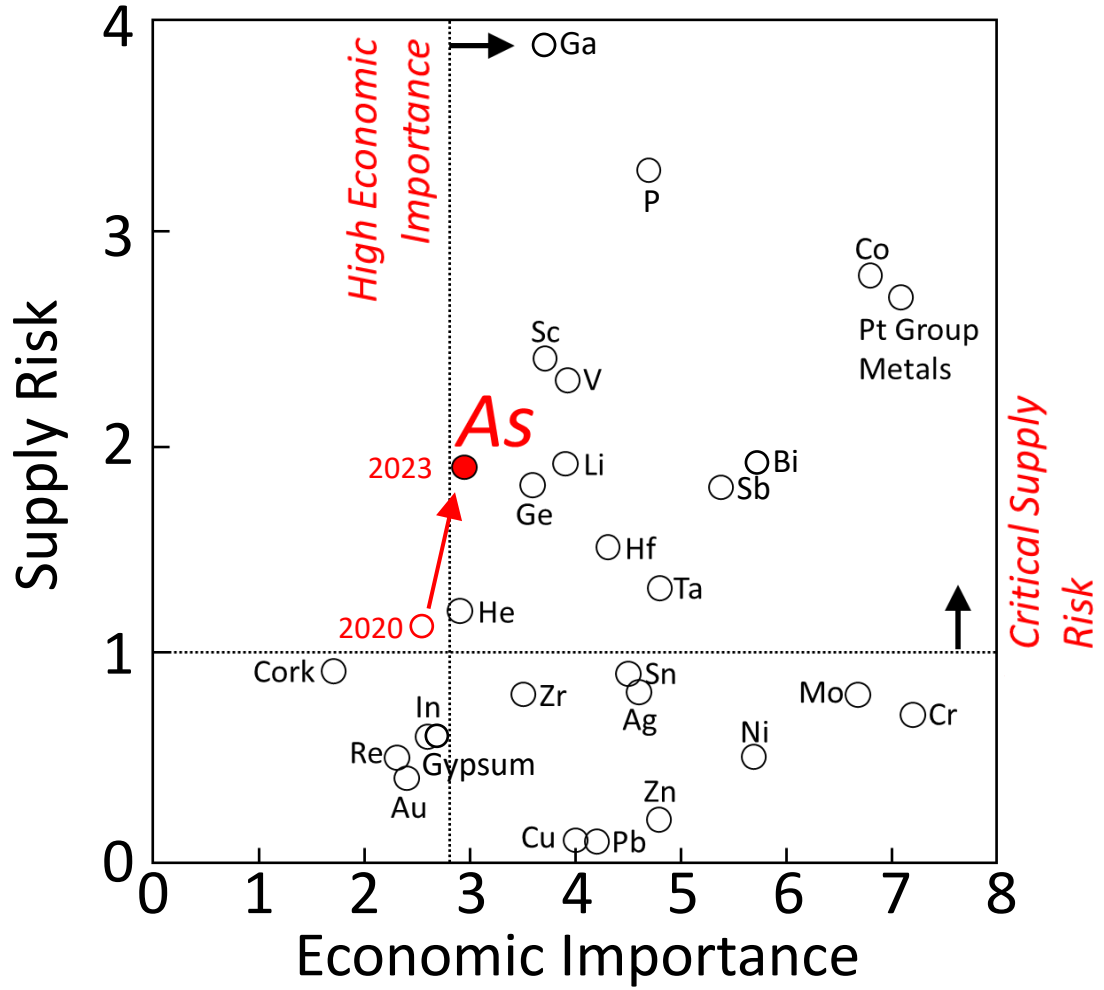
Newsdesk — October 6, 2023

Share





Arsenic is a persistent environmental contaminant …
BUT … Can As also be a valuable resource???



European Commission, ***2023****.*
Study on the EU's List of Critical Raw Materials.

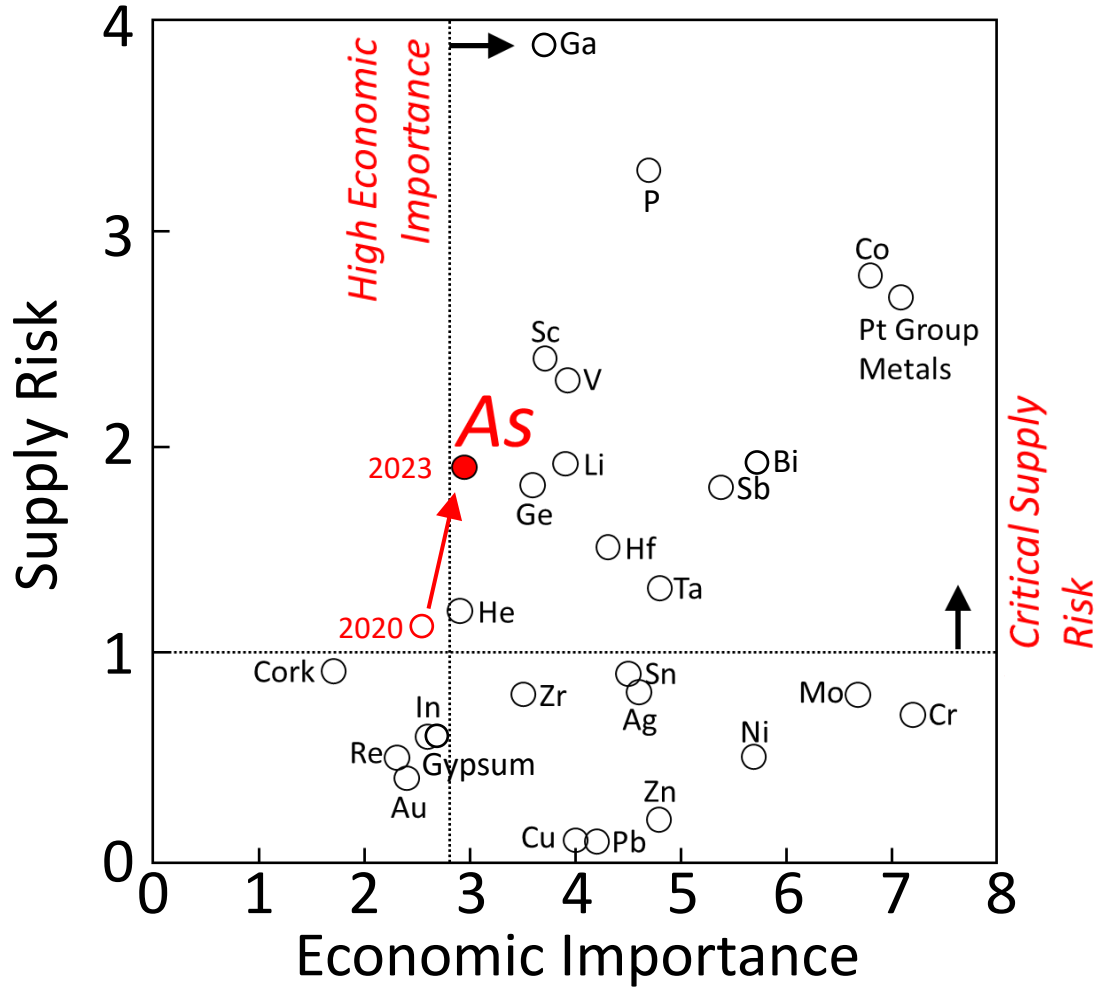
Arsenic is a persistent environmental contaminant …
BUT … Can As also be a valuable resource???

Supply Risk = HHI_{WGI} x $(1-E_0L_{RIR})$ x SI

- HHI = Herfindahl Hirschman Index (proxy for country concentration)
- WGI = scaled World Governance Index (proxy for country governance)
- EOLRIR = End-of-Life Recycling Input Rate
- SI = Substitution Index

Economic Importance = $\sum_s (A_s \times Q_s)$

- A_s = share of demand of a raw material in a megasector
- Q_s = megasector's Gross Value Added



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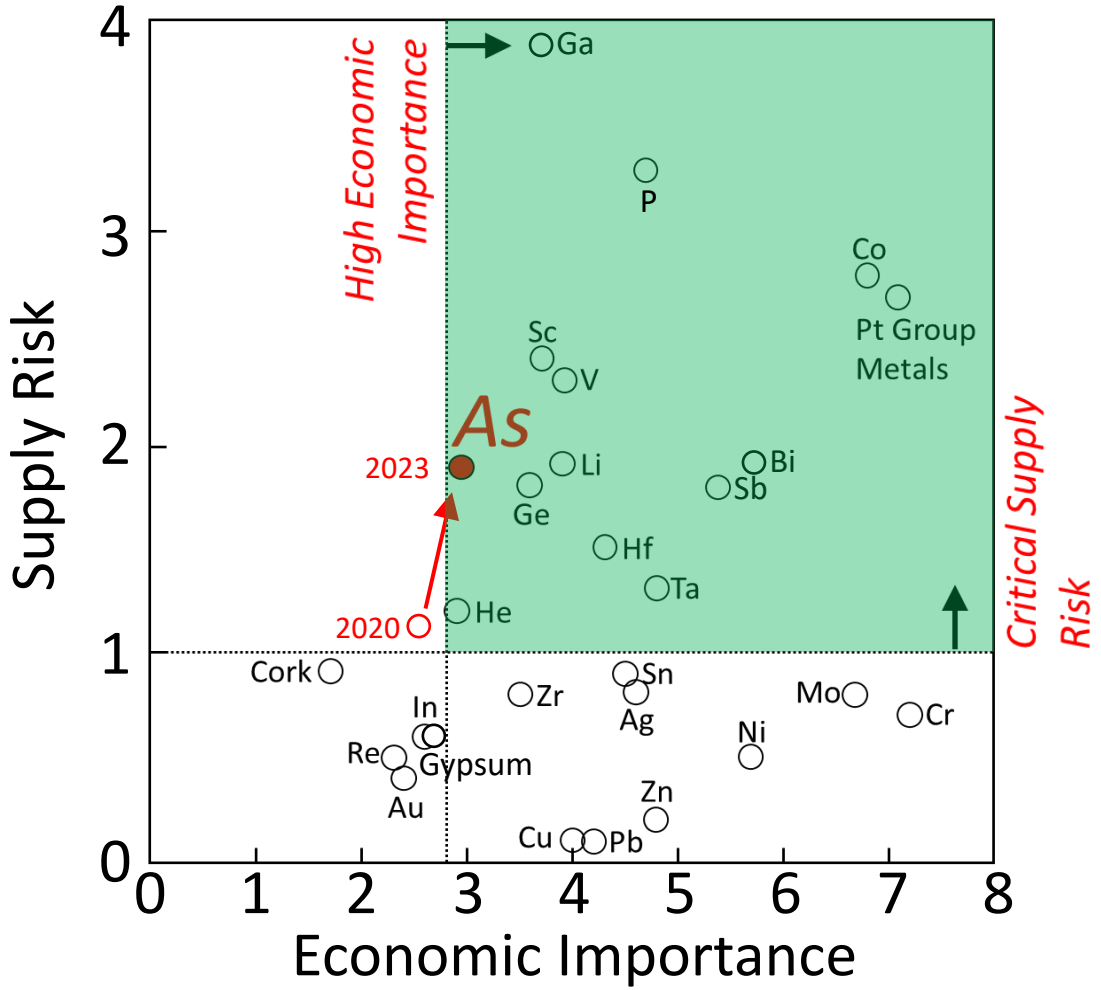
Upper Right Quadrant = **Critical Raw Materials (CRMs, 32 total)**



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Arsenic is a persistent environmental contaminant …
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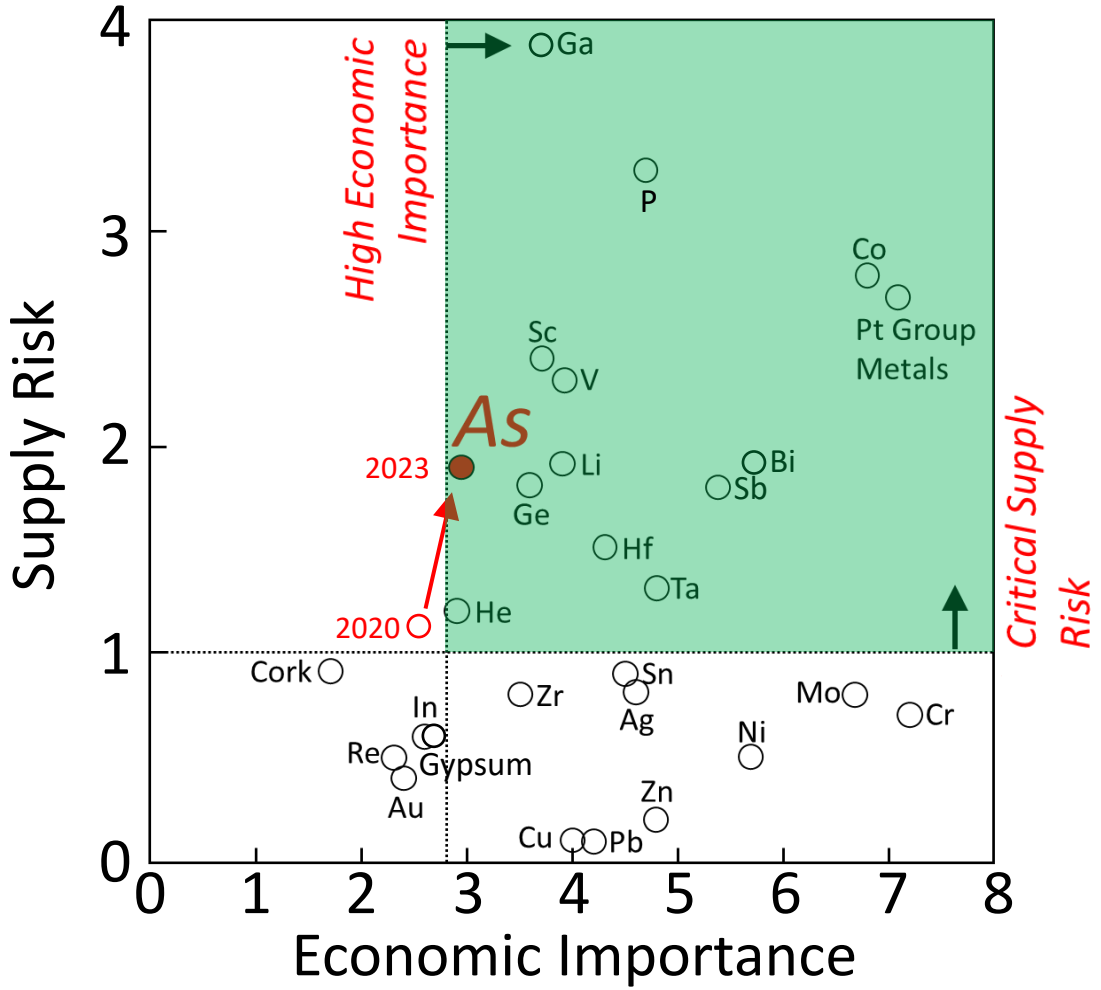
Upper Right Quadrant = **Critical Raw Materials (CRMs, 32 total)**

- What kind of As compound?
  - **- Metallic arsenic (As0)**
  - Used in batteries, alloys and high-speed electronics (**As-bearing semiconductors**)

- As also classified as CRM in the USA
  - Not a single gram of As(0) produced domestically in the US (500 tons consumed annually)



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Where does As(0) metal traditionally come from?

Where does As(0) metal traditionally come from?
Mining arsenic sulfide mineral ore, with devastating consequences

Reuters

World Business Markets Sustainability Legal Breakingviews Technology Investigations

Environment

Arsenic pollution sows despair in Chinese cancer village

A sealed mine entrance is seen at a closed realgar mining plant. REUTERS/Jason Lee

The Guardian

News Opinion Sport Culture Lifestyle

Arsenic poisoning in rural China - in pictures

Mines and chemical plants mushroomed in the realgar-rich area around Heshan from the 1950s. Shut down in 2011 due to the pollution they caused, dust and run-off plagues the village to this day, destroying crops and poisoning people

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SCIENCE

Arsenic Pollution Has Decimated This Village In China And Cursed The Population With Cancer [PHOTOS]

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Environmental Science & Technology

Article

pubs.acs.org/est

Anthropogenic Cycles of Arsenic in Mainland China: 1990–2010

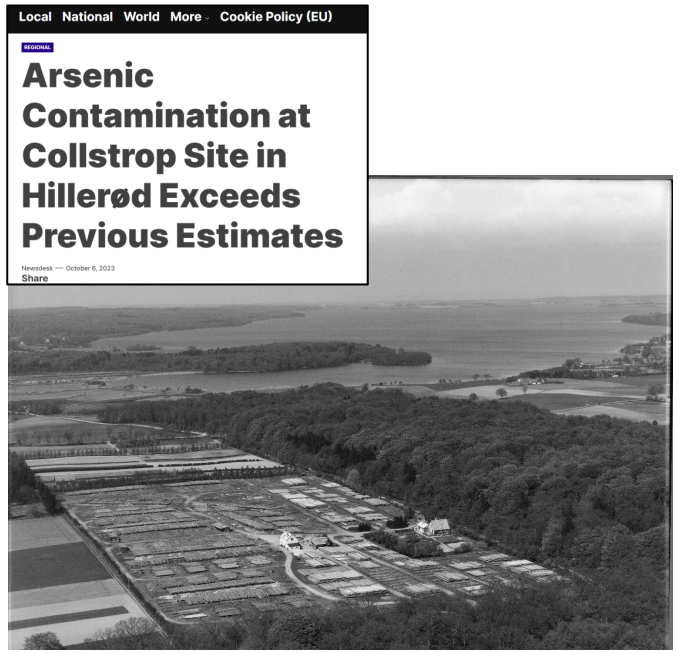
Ya-Lan Shi,[†,‡] Wei-Qiang Chen,[*,‡] Shi-Liang Wu,[§,∥] and Yong-Guan Zhu[‡]

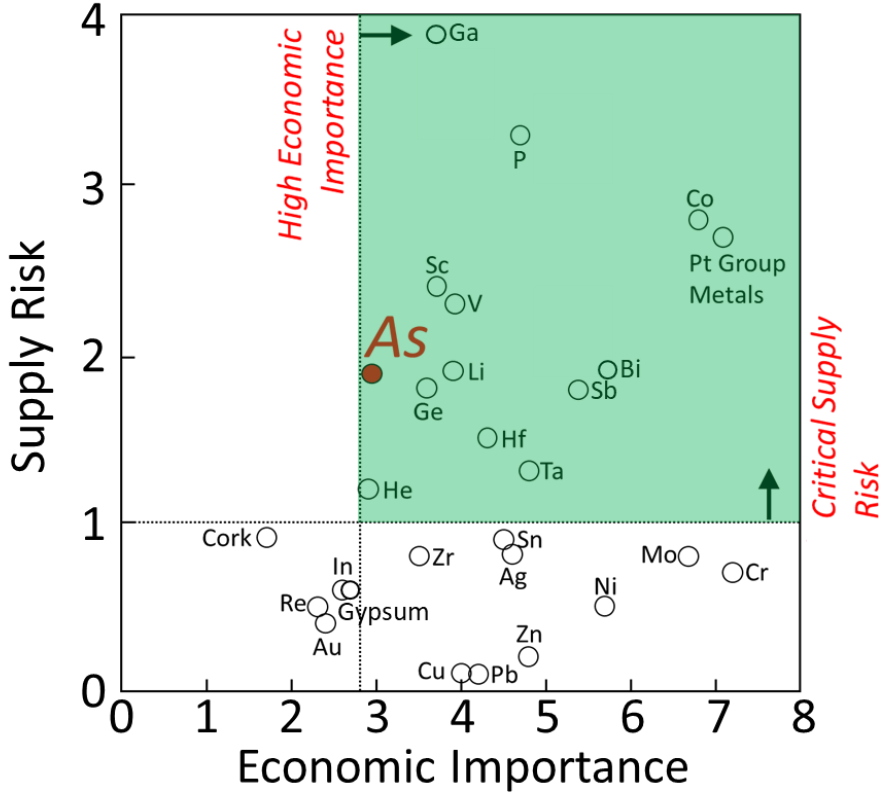
"China has been a net exporter of … arsenic metalloid, thus suffering from the environmental burdens of producing arsenic products for other economies"

Arsenic pollution is an environmental problem

AND

As(0) is a Critical Raw Material





Can Arsenic Pollution be a Source of CRMs?

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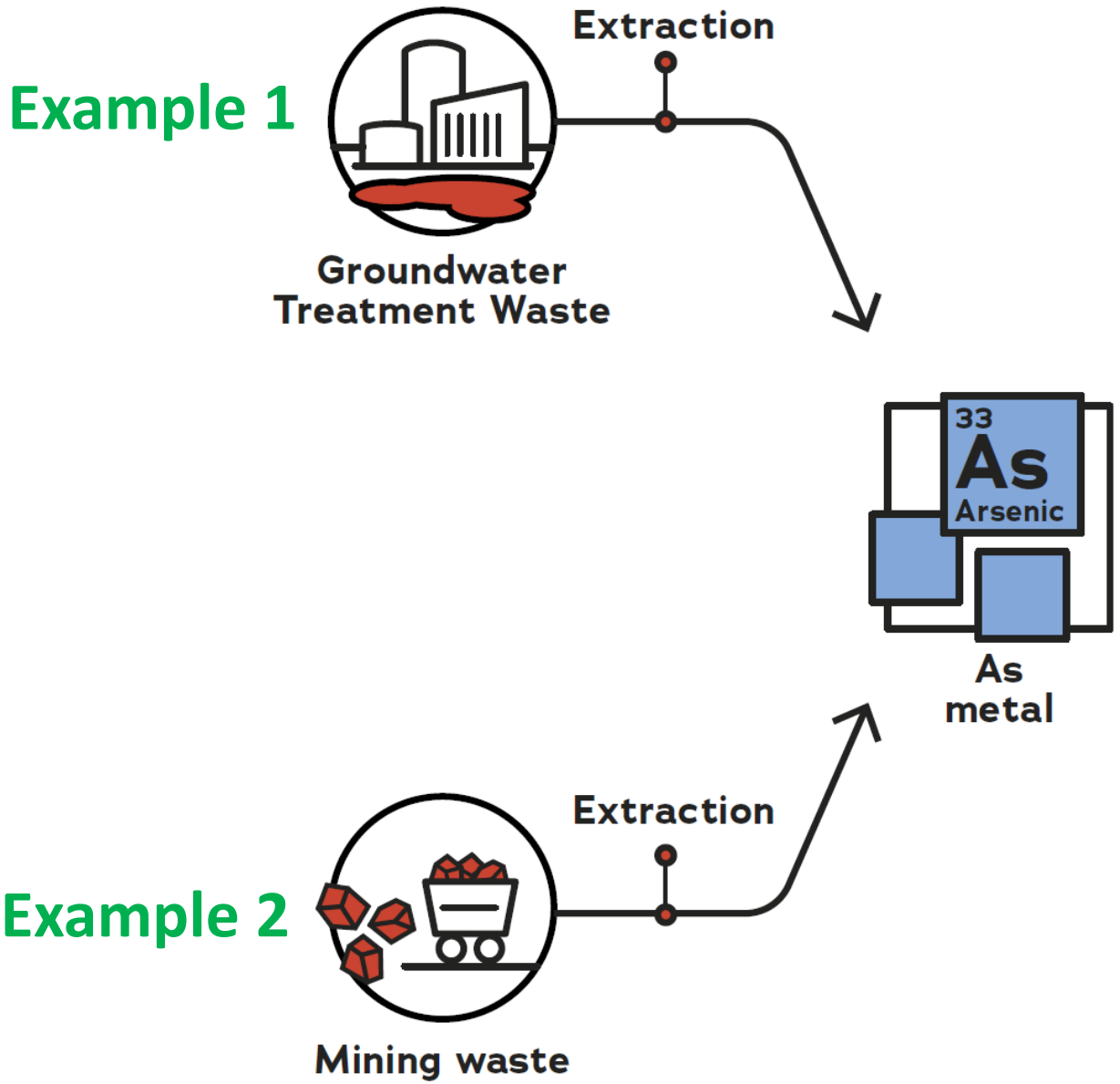

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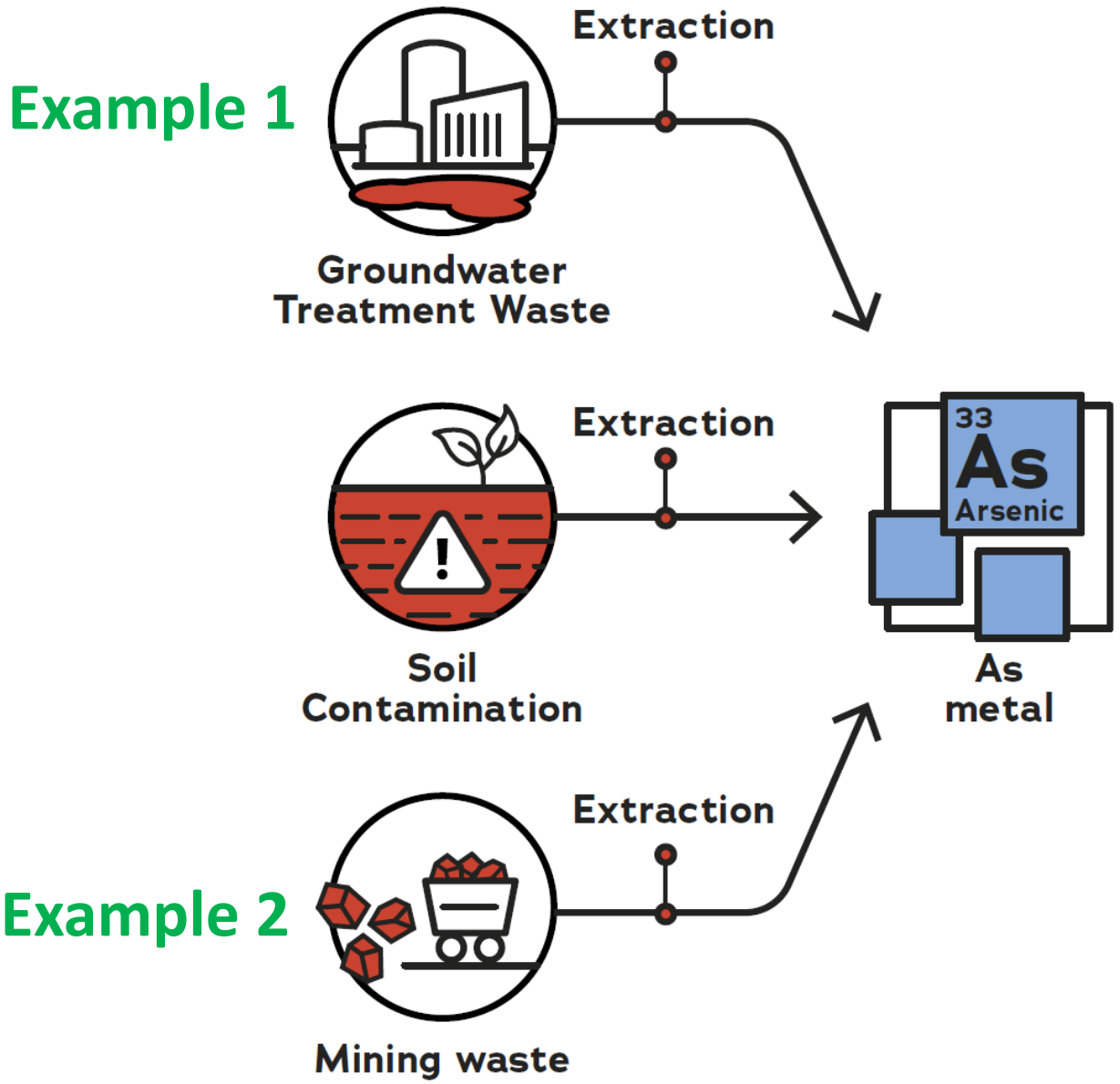

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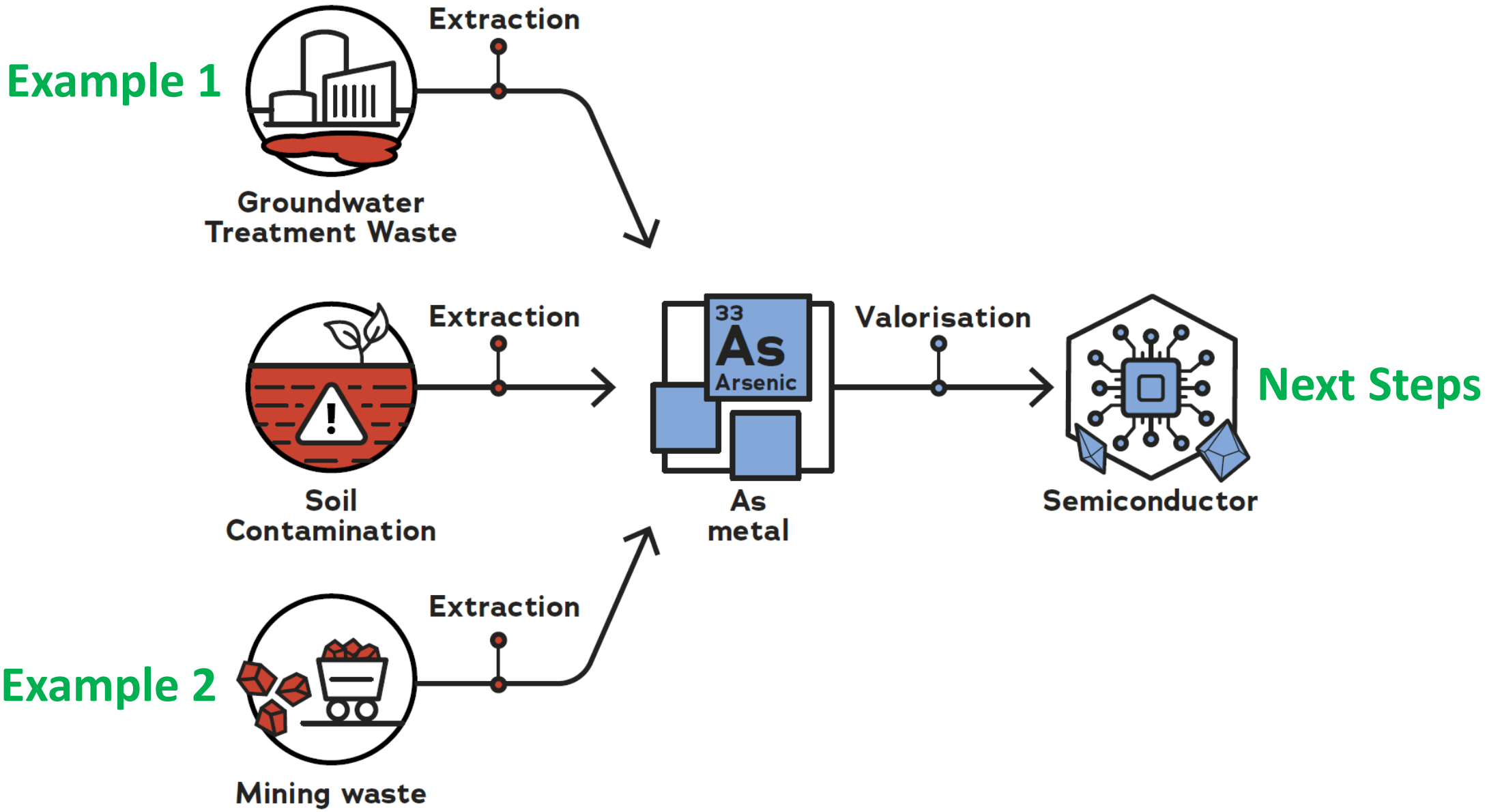


Upcycling Approach: As(0) from As-laden Groundwater Treatment Waste

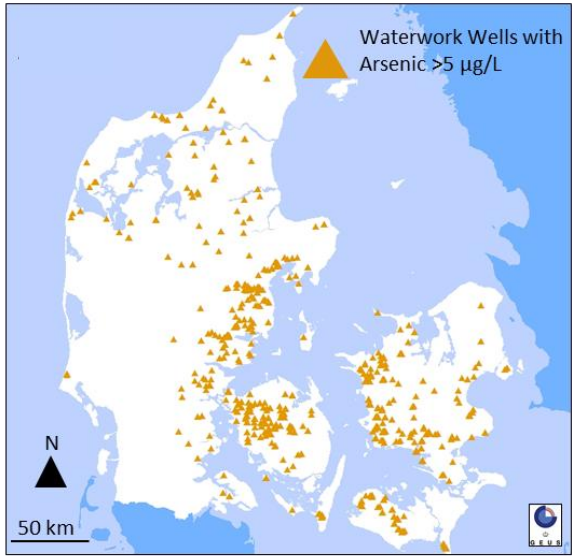
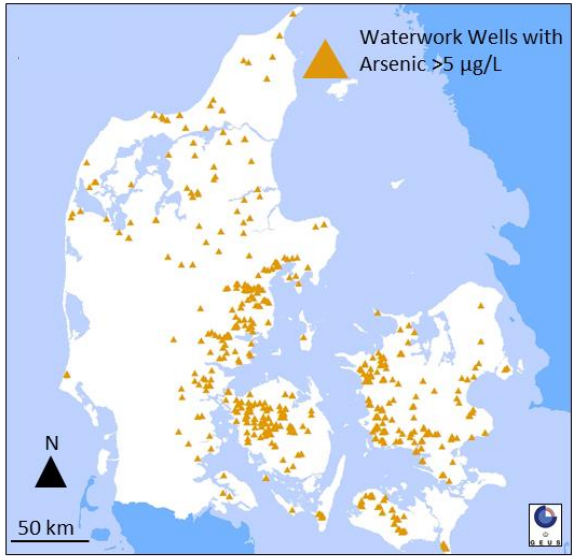


Photo: A. Ahmad

Upcycling Approach: As(0) from As-laden Groundwater Treatment Waste



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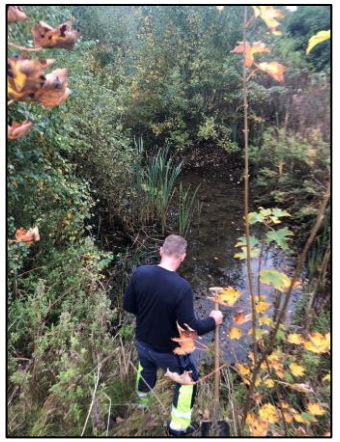
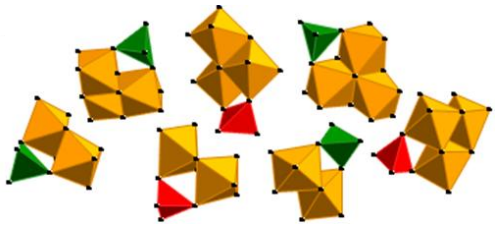


Disposal/Storage Pond
Kerte, Denmark

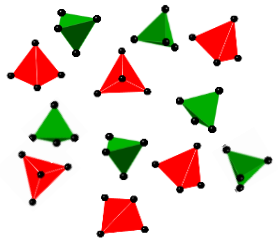
Upcycling Approach: As(0) from As-laden Groundwater Treatment Waste

1) Characterization — **2) Extraction** — **3) Selective As Reduction** — **4) Recovery of Other CRMs?**

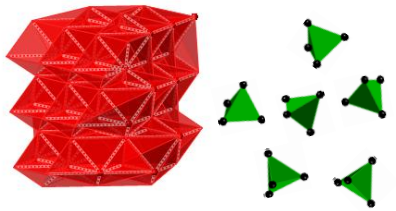
Groundwater Treatment Sludge



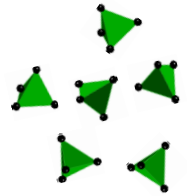
As & P Release

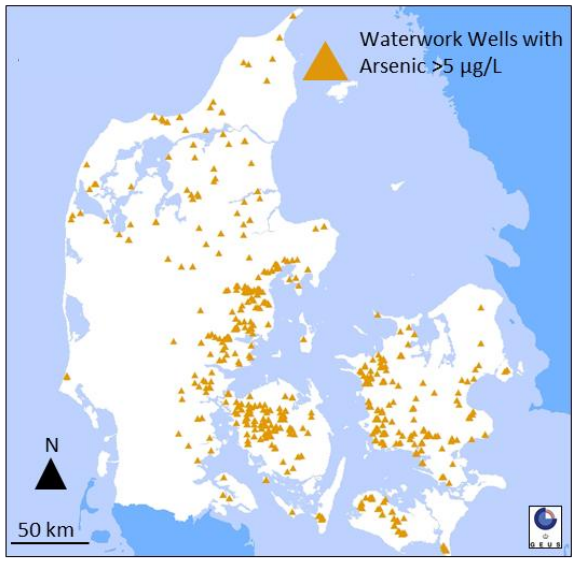


As^0 Formation



As^0 Separation





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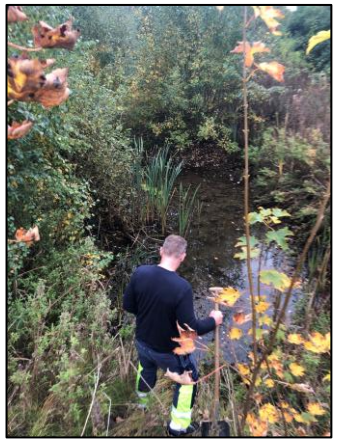
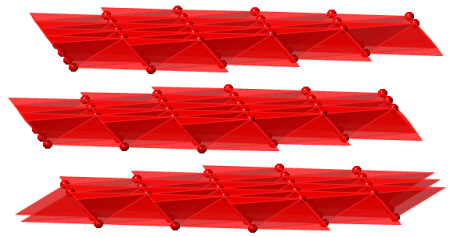
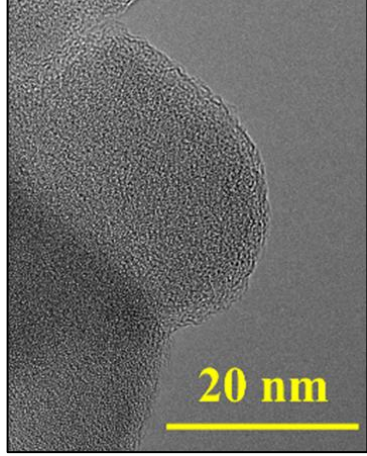


Disposal/Storage Pond
Kerte, Denmark

GEUS





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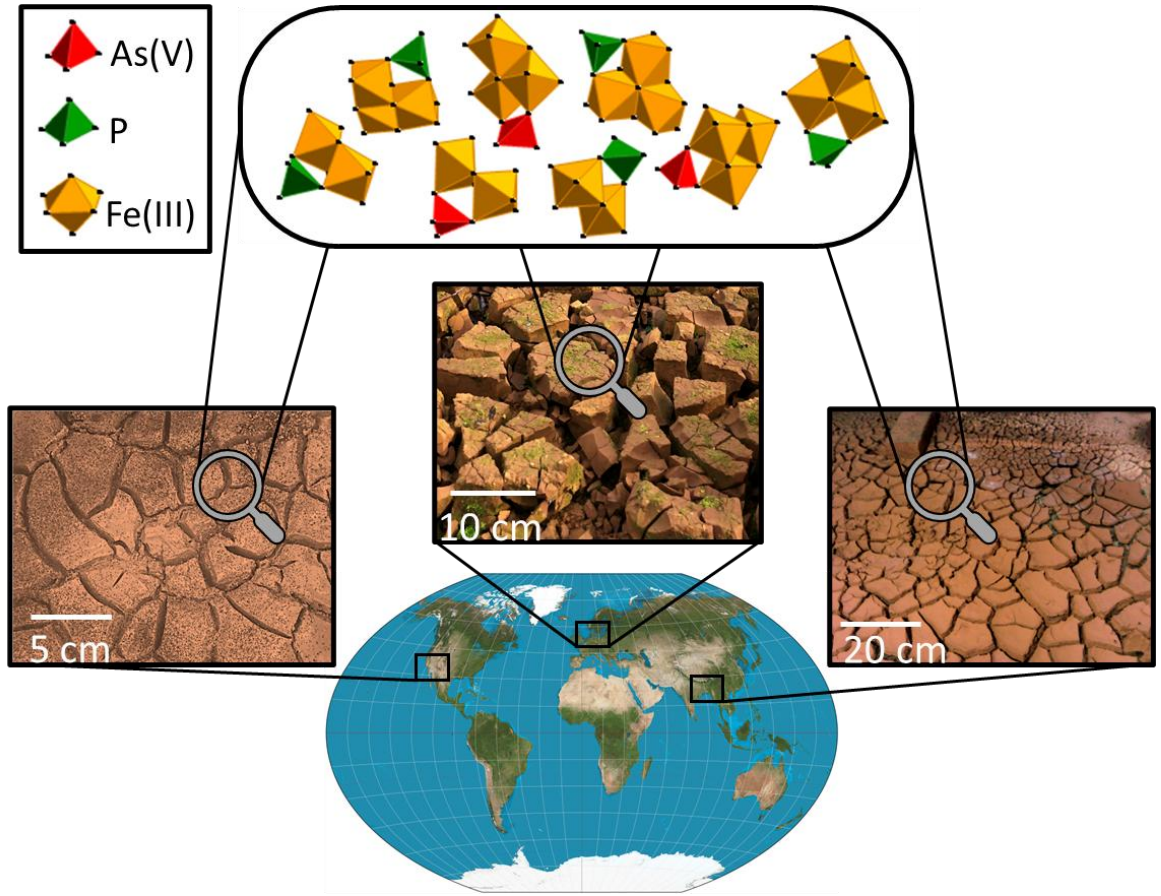
Groundwater Treatment Sludge Collection

Sludge collected from several treatment plants selected to span:

- Geographic Location
  -North America, Europe, Asia
- Treatment plant capacity
- Groundwater composition
- Treatment mechanism



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Molecular-scale characterization of groundwater treatment sludge from around the world: Implications for potential arsenic recovery

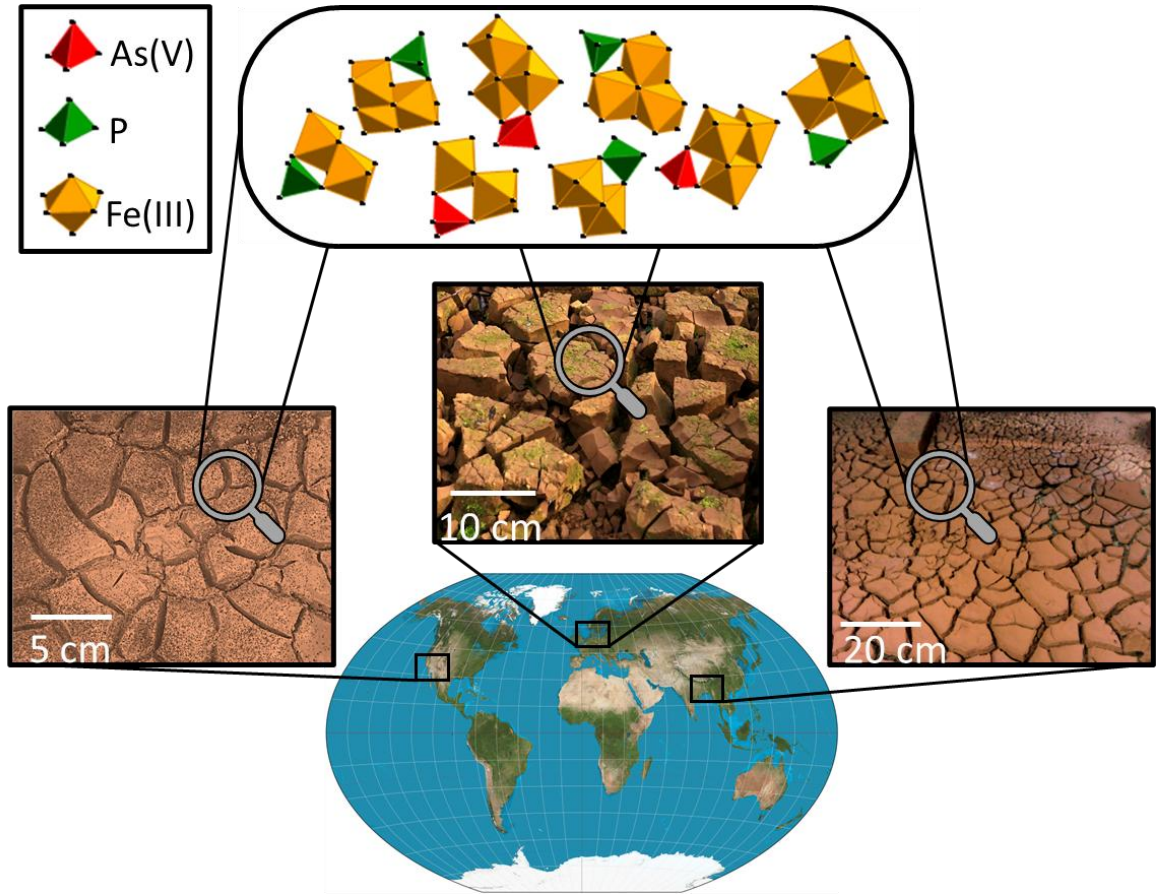
K. Wang [a], P.E. Holm [b], U. Brinkmann Trettenes [c], S.R.S. Bandaru [d], D. van Halem [e], C.M. van Genuchten [a,*]

Sludge composition

As content as high as **2070 mg/kg**

P content as high as **20 g/kg**

Treatment Plant Location	As (mg/kg)	P (g/kg)
Kværndrup, Denmark	**2070±100**	16.4±0.1
Kerte, Denmark	1200±30	17.0±0.5
Holmehave (HH), Denmark	940±20	**20.0±2.5**
Allensworth, California, USA	870±50	ND
Dhapdhapi, West Bengal, India	790±50	4.9±0.4
Mol, Belgium	630±40	16.5±0.9
Lunde, Denmark	220±80	14.4±0.6



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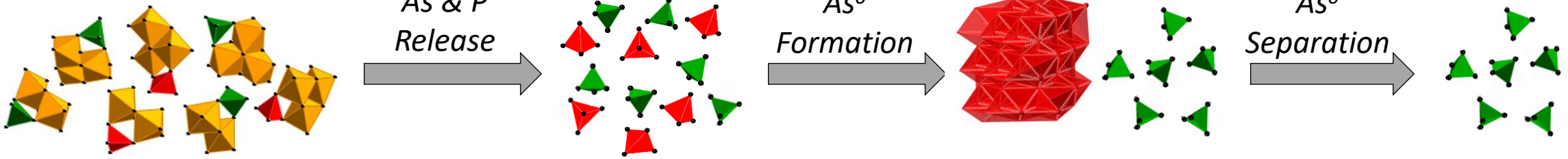
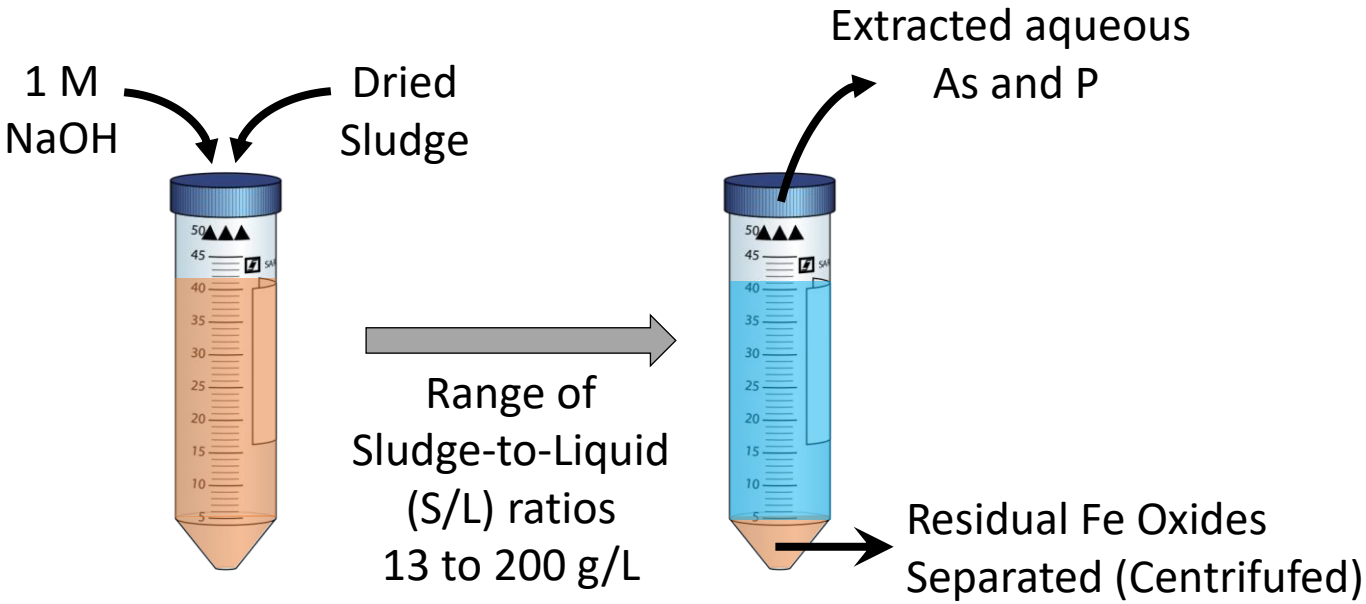
Road Map: Converting As in Groundwater Treatment Waste to As(0)

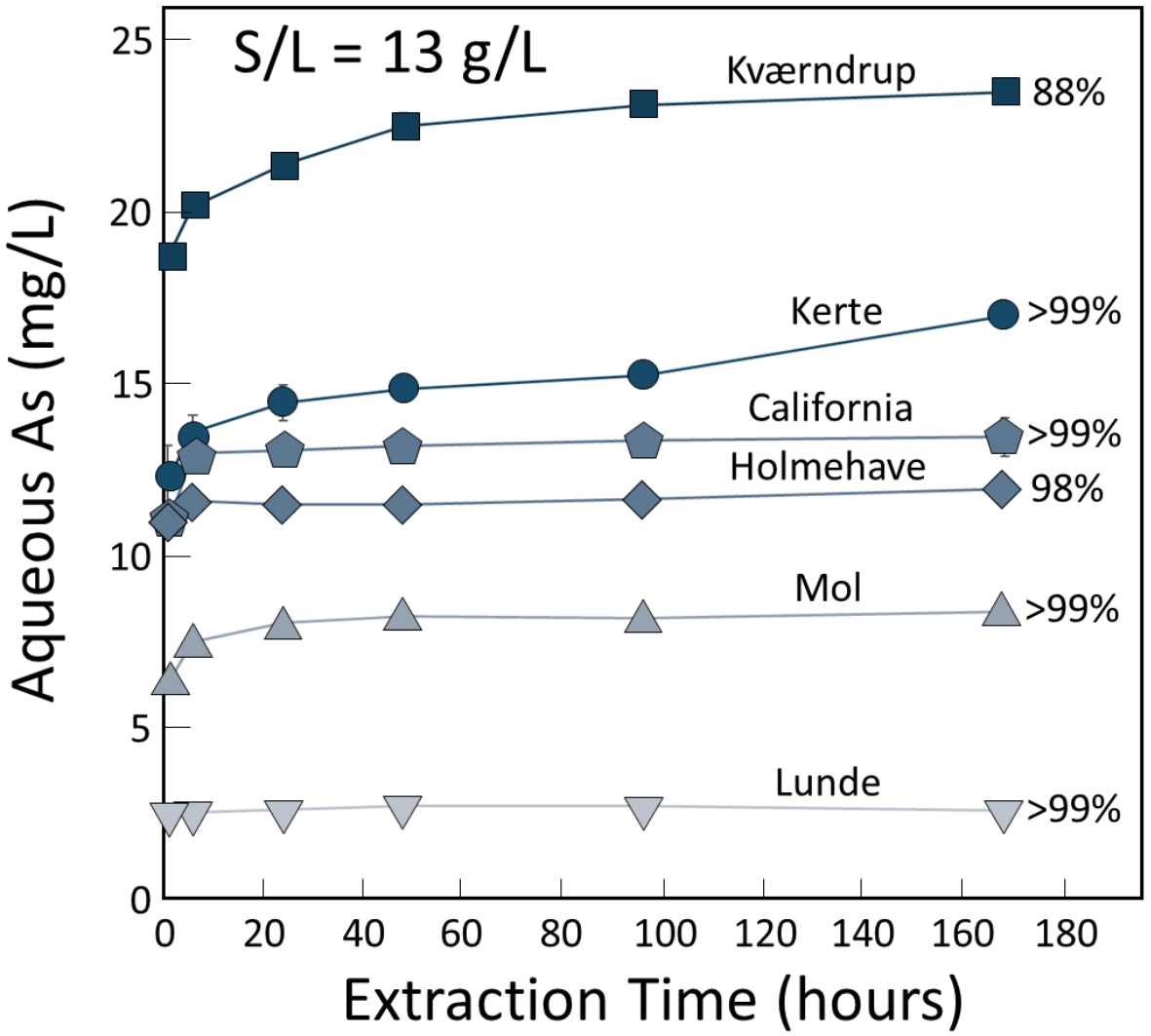
Characterization — **1) Extraction** — **2) Selective As Reduction** — **3) Recovery of Aqueous P?**

Groundwater Treatment Sludge





Results 1: Extraction of As in 1 M NaOH



Shade of color scales with sludge As mass fraction

Total As released given in %

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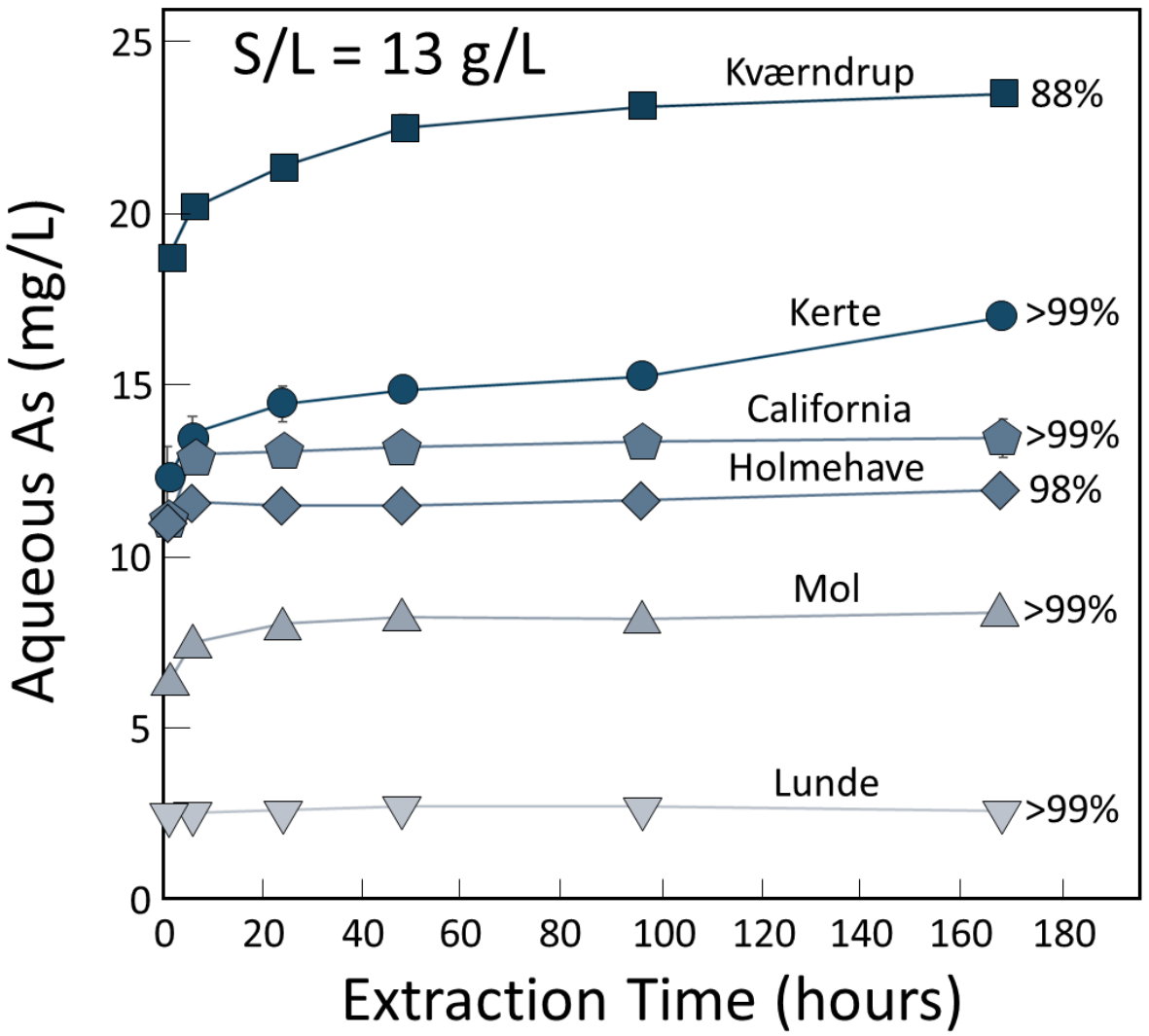


Shade of color scales with sludge As mass fraction

Total As released given in %

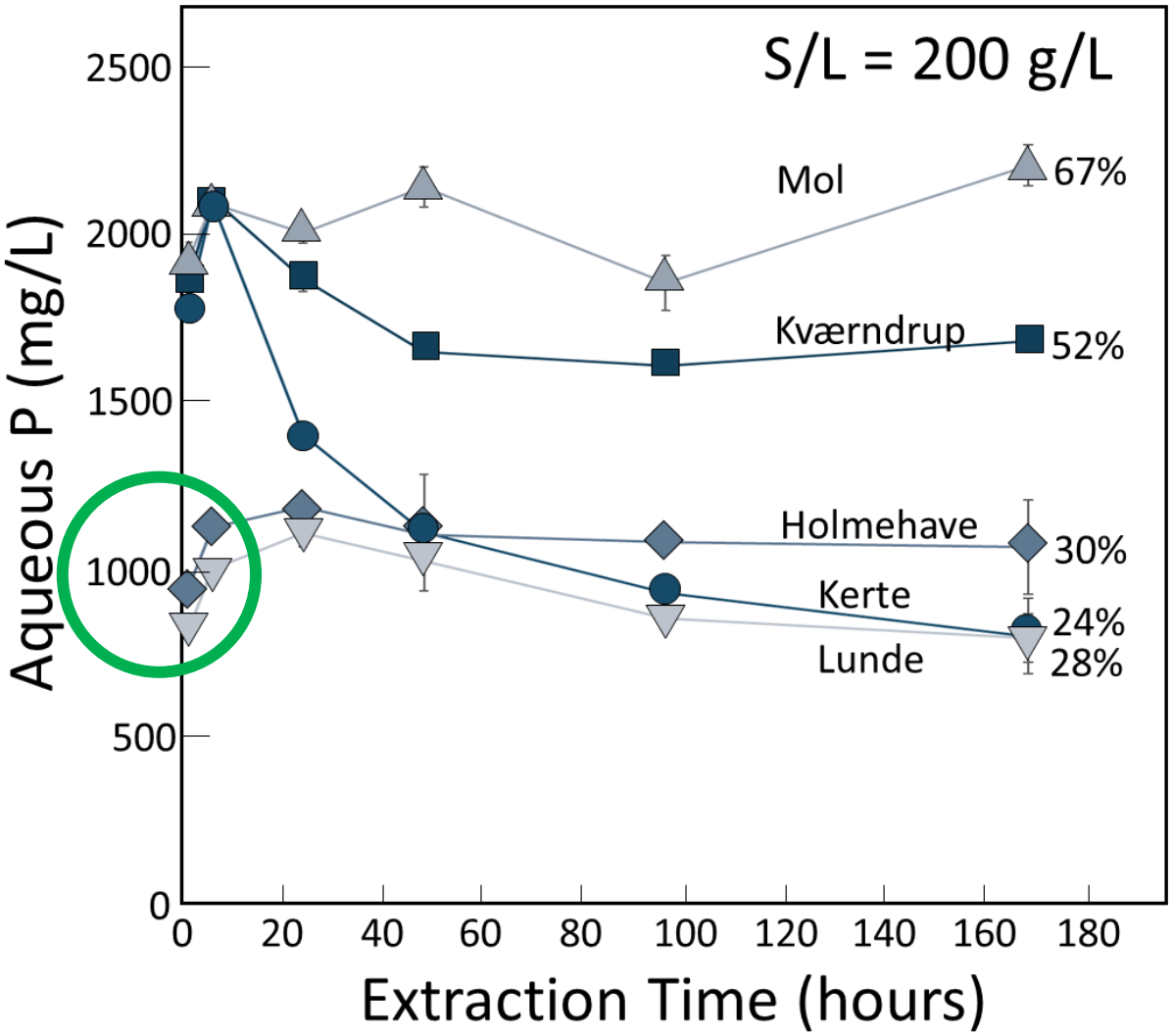
Key Results:

- Highly effective As release: > 99% extracted for most samples)
  - Important for reuse of the Fe oxides as sorbents and/or soil amendment

- Fraction of As released to solution increases with extraction time (up to 7 days)

- Extracted As concentration increases with initial As mass fraction in the sludge

Results 1: Extraction of P in 1 M NaOH



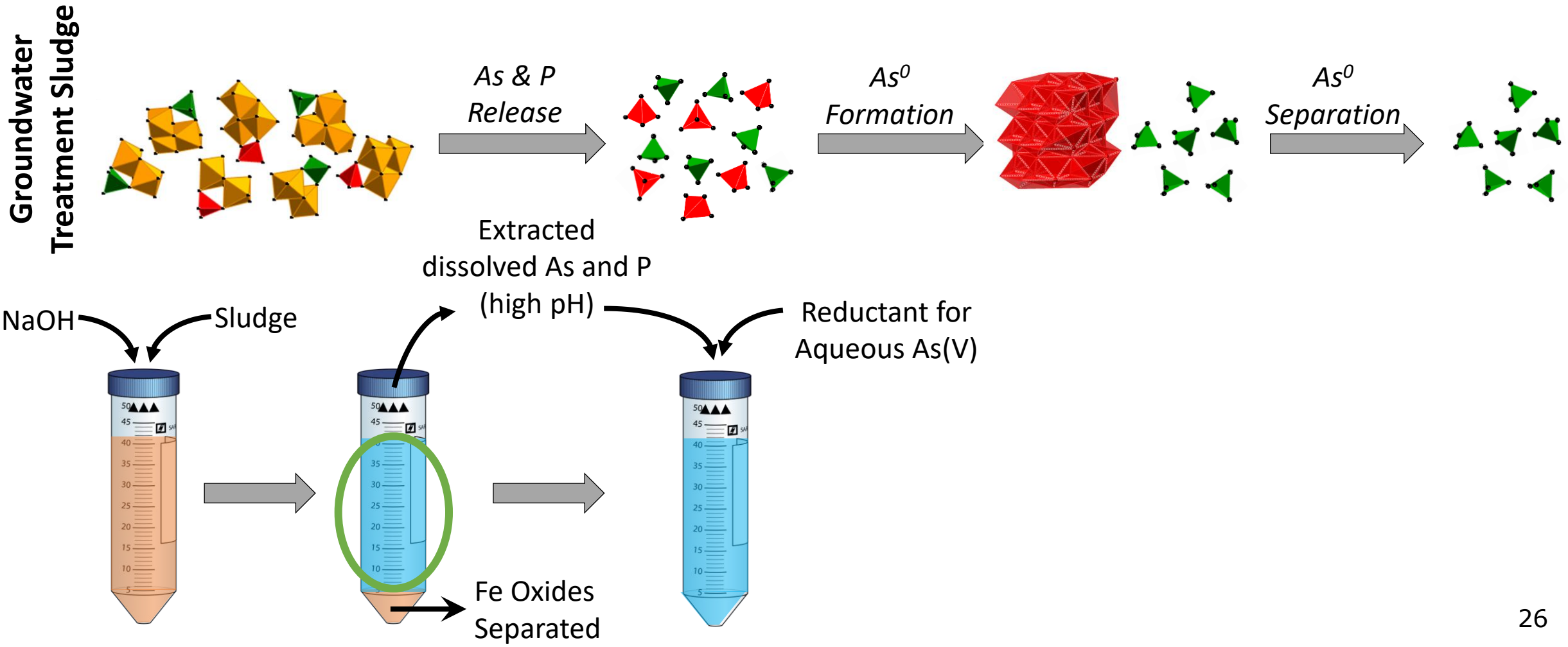
Key Results:

- Co-extraction of **high** concentrations of P
  - 1000 to 2000 mg/L

- Opportunity for P and As co-recovery

Road Map: Converting As in Groundwater Treatment Waste to As(0)

Characterization | **1) Extraction** | **2) Selective As Reduction** | **3) Recovery of Aqueous P?**



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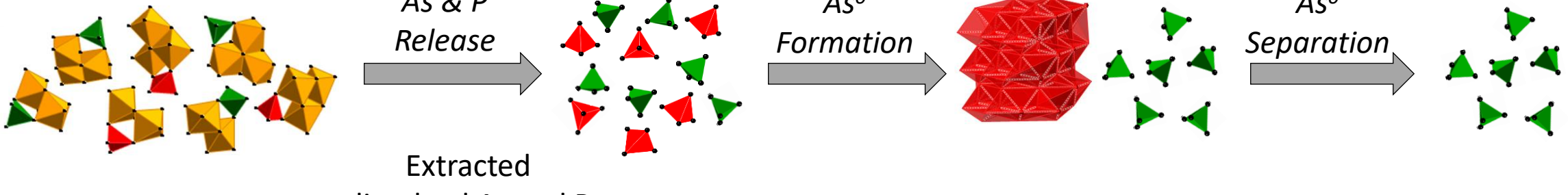
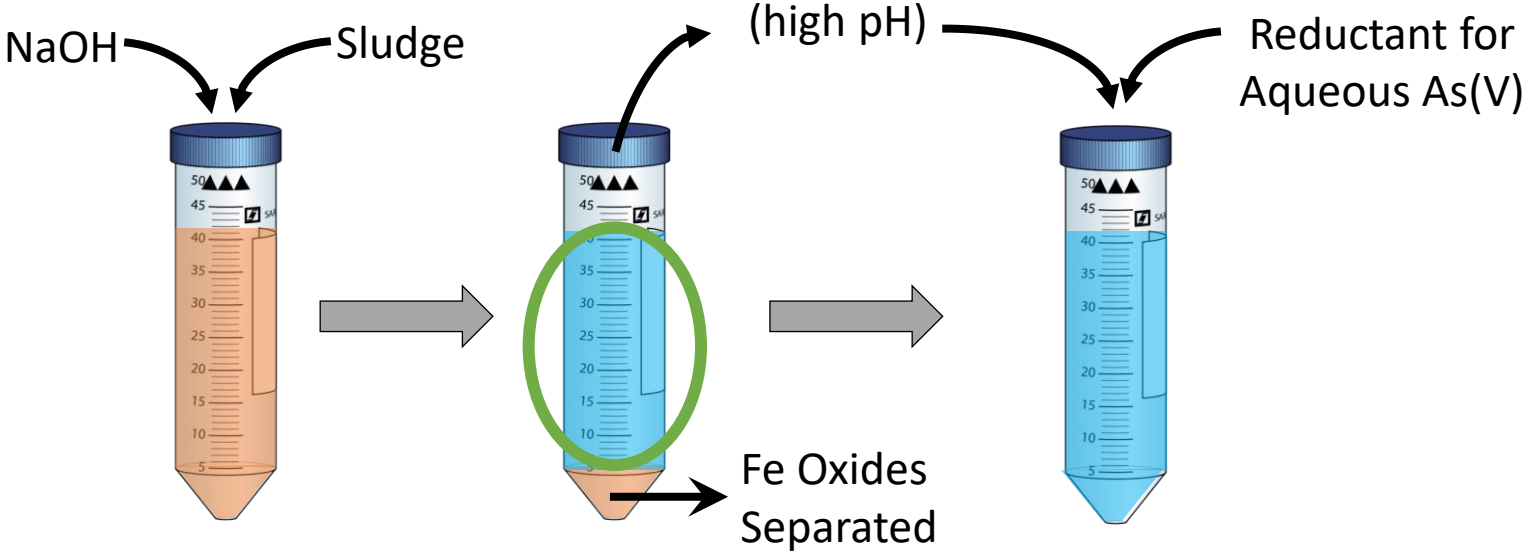
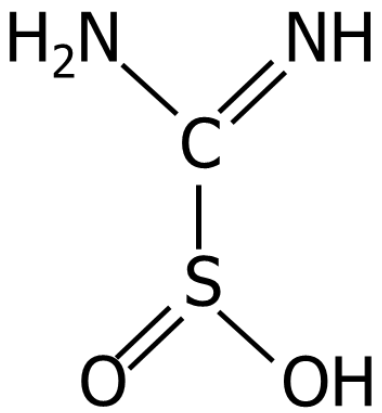


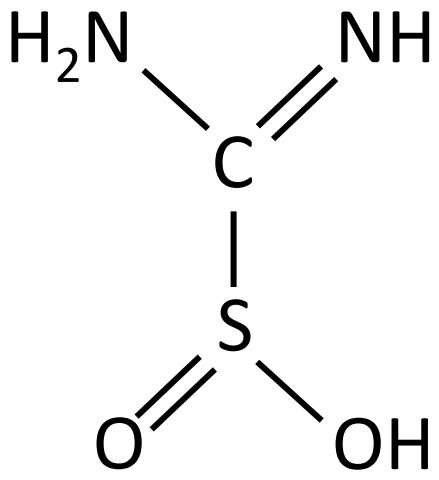


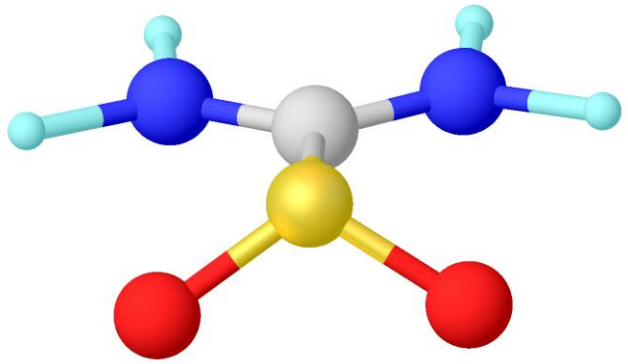
Thiourea Dioxide (TDO)



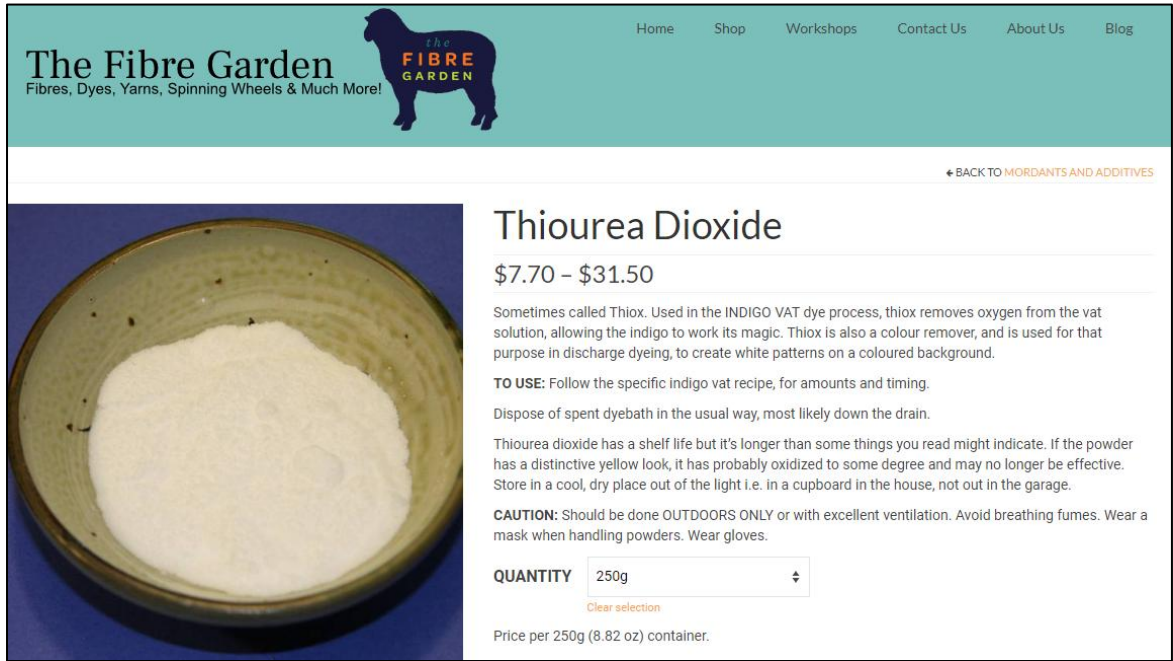
Road Map: Converting As in Groundwater Treatment Waste to As(0)

Thiourea Dioxide (TDO)





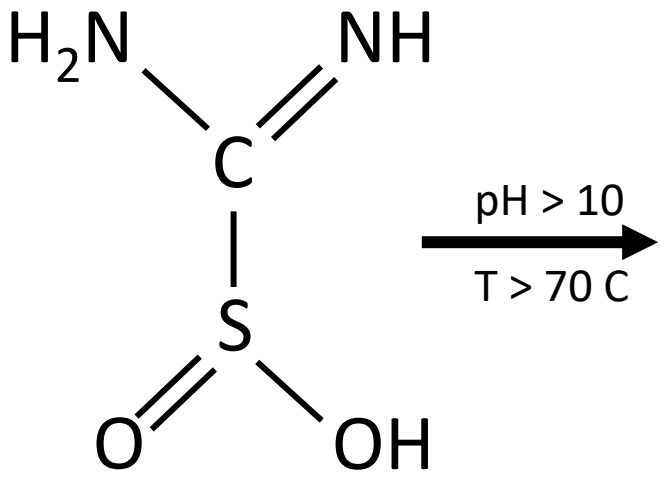
- Used in garment and textile industry as a bleaching agent
- Stable and has low toxicity
  - “store in a cupboard in the house”
  - “dispose down the drain”
- Relatively cheap (3 USD/kg in bulk)



Road Map: Converting As in Groundwater Treatment Waste to As(0)

Thiourea Dioxide (TDO)

Figure 5, Makarov et al. 2014
"Recent developments in the Chemistry of Thiourea Dioxide". Chem. Eur. J.



- Used in garment and textile industry as a bleaching agent
- Stable and has low toxicity
  - "store in a cupboard in the house"
  - "dispose down the drain"
- Relatively cheap (3 USD/kg in bulk)
- **Reduction efficiency increases with increasing pH and temperature**

Road Map: Converting As in Groundwater Treatment Waste to As(0)

Thiourea Dioxide (TDO)

Figure 5, Makarov et al. 2014
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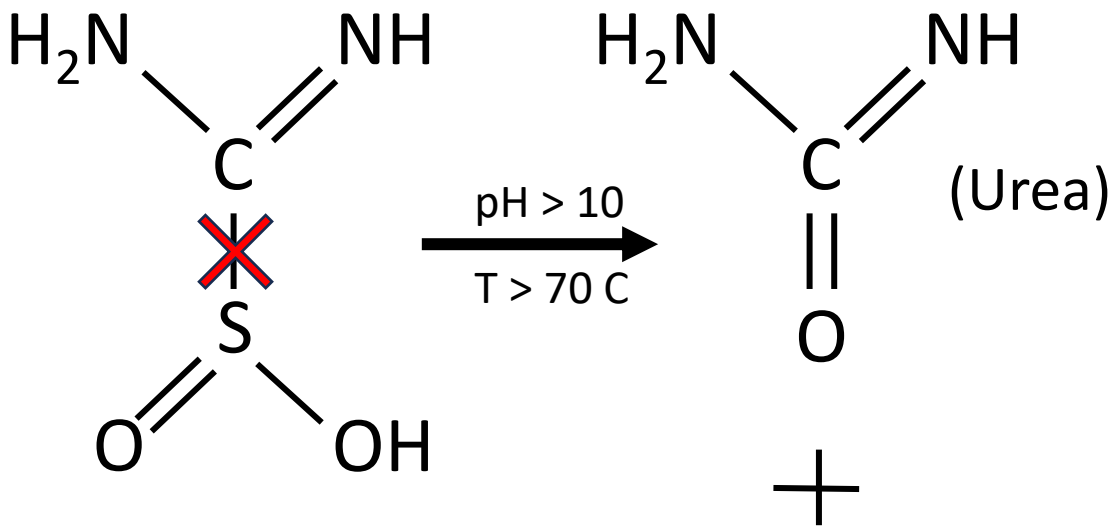

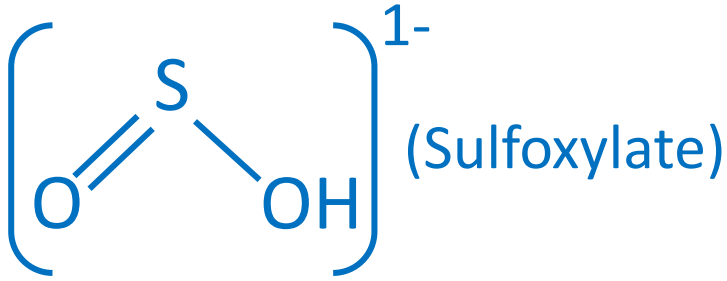

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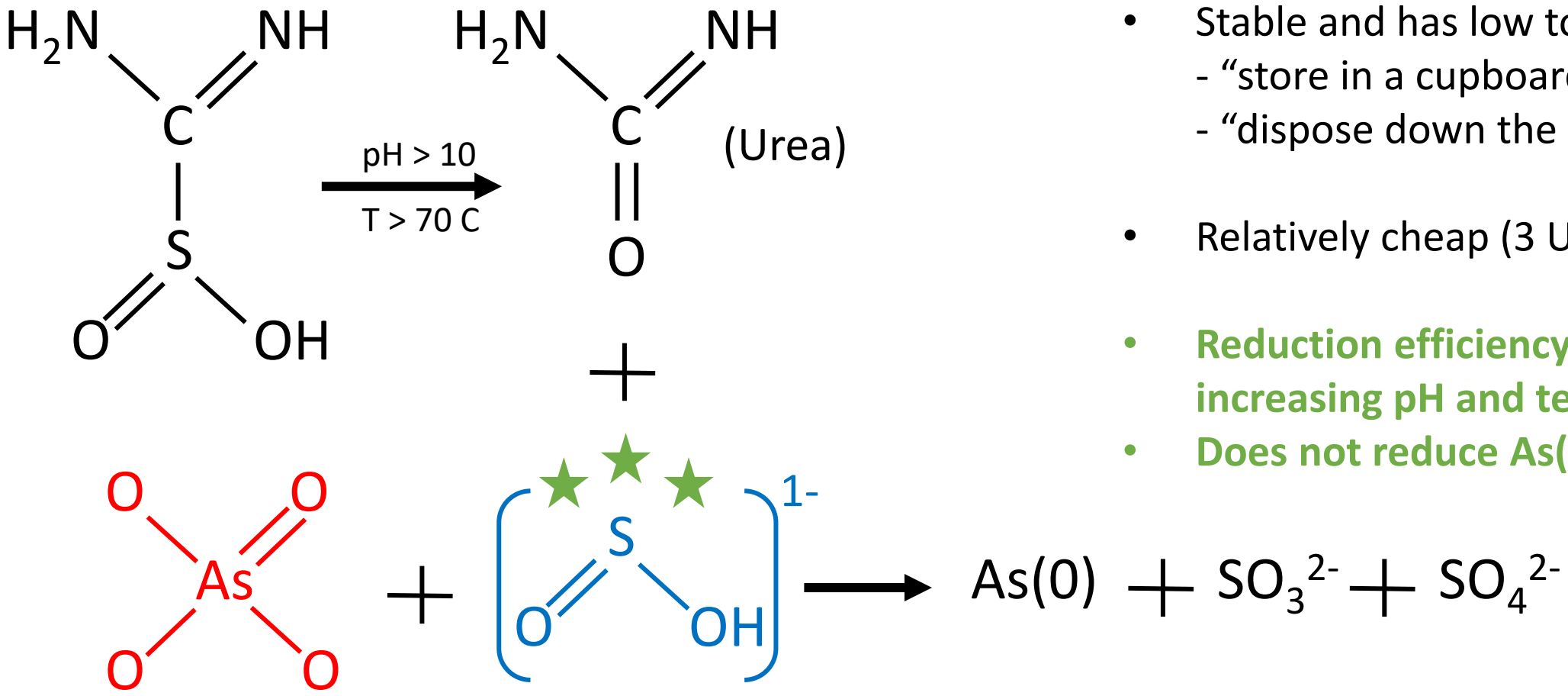
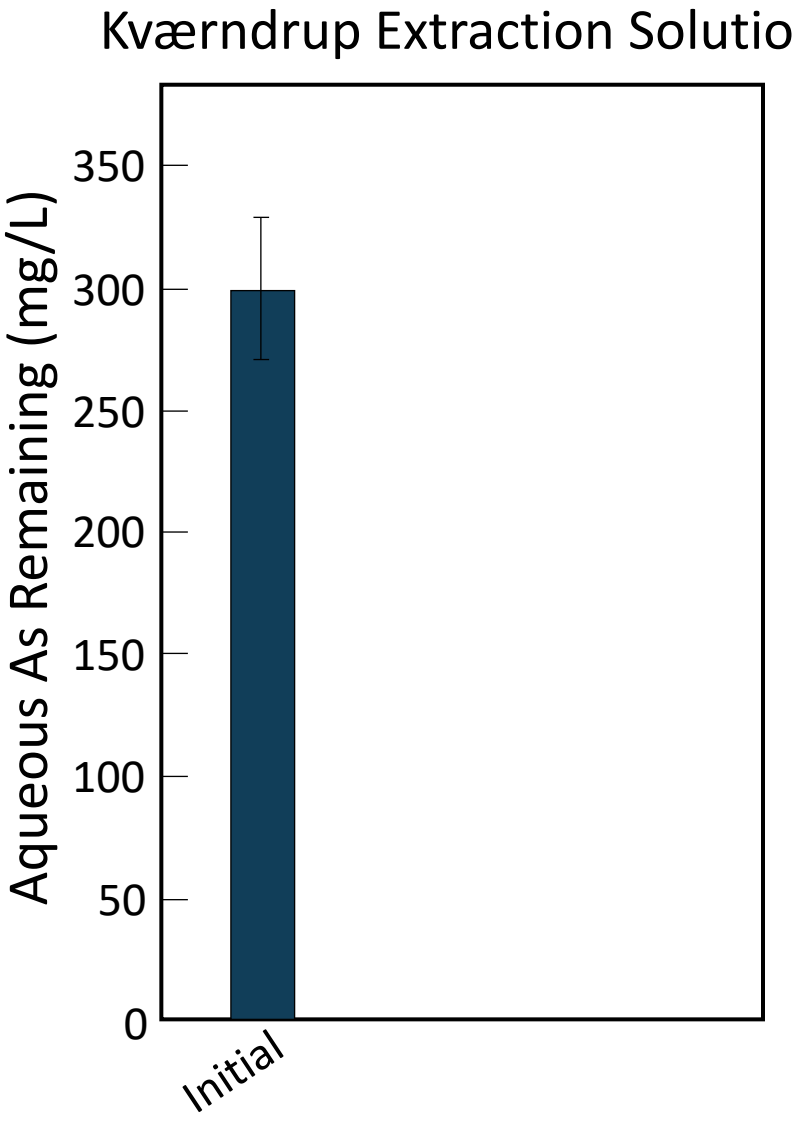
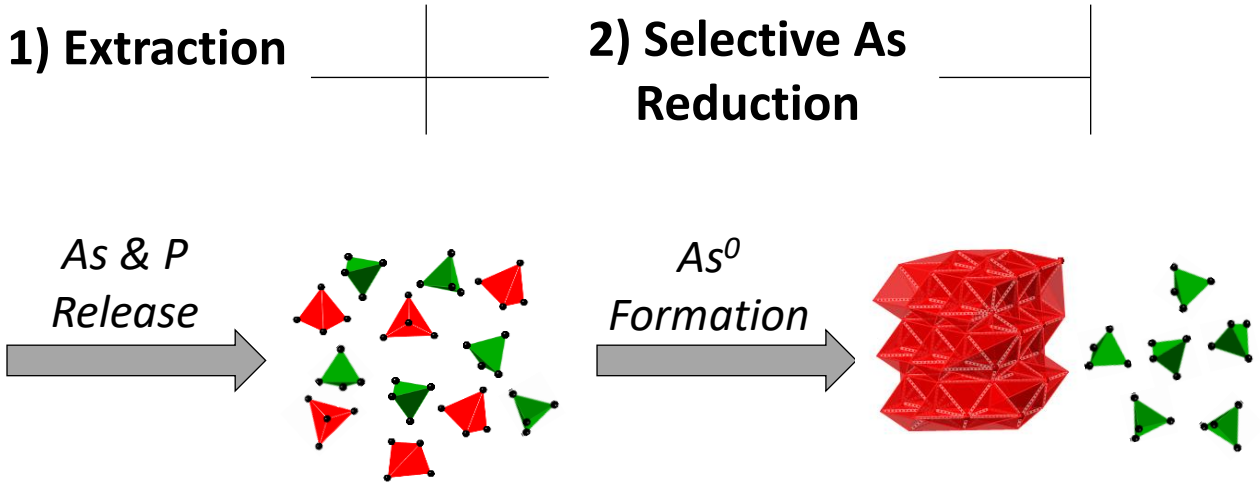


- Used in garment and textile industry as a bleaching agent
- Stable and has low toxicity
  - "store in a cupboard in the house"
  - "dispose down the drain"
- Relatively cheap (3 USD/kg in bulk)
- **Reduction efficiency increases with increasing pH and temperature**
- **Does not reduce As(III,V) to H_3As**

Results 2: Reductive precipitation of As(0) from extracted aqueous As





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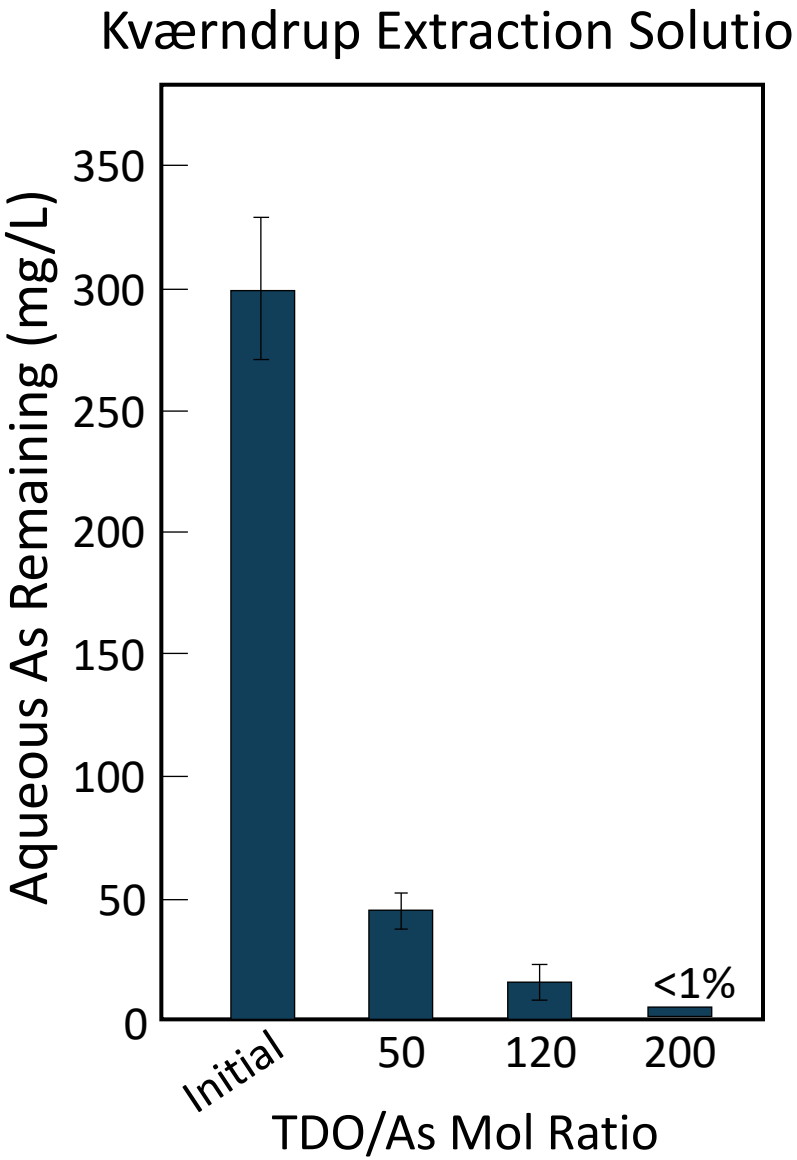
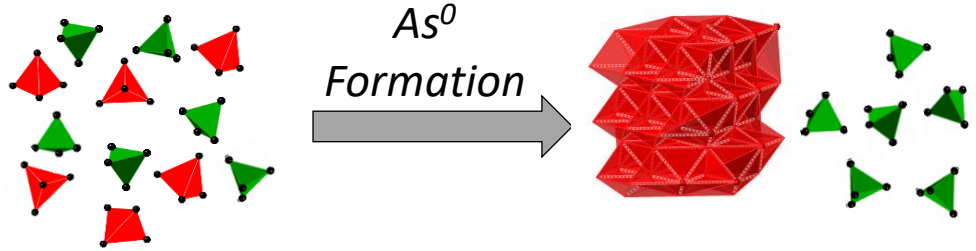


1) Extraction

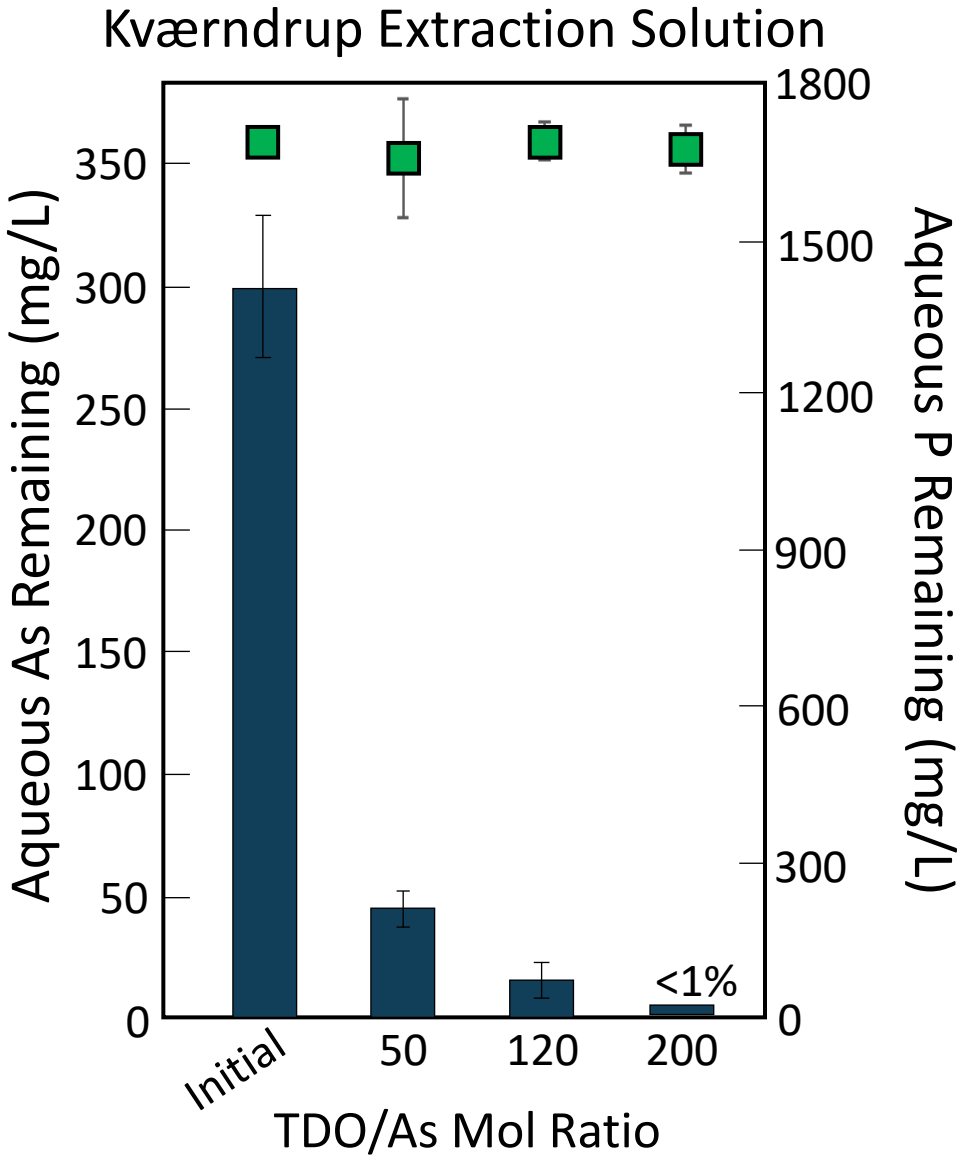
2) Selective As Reduction

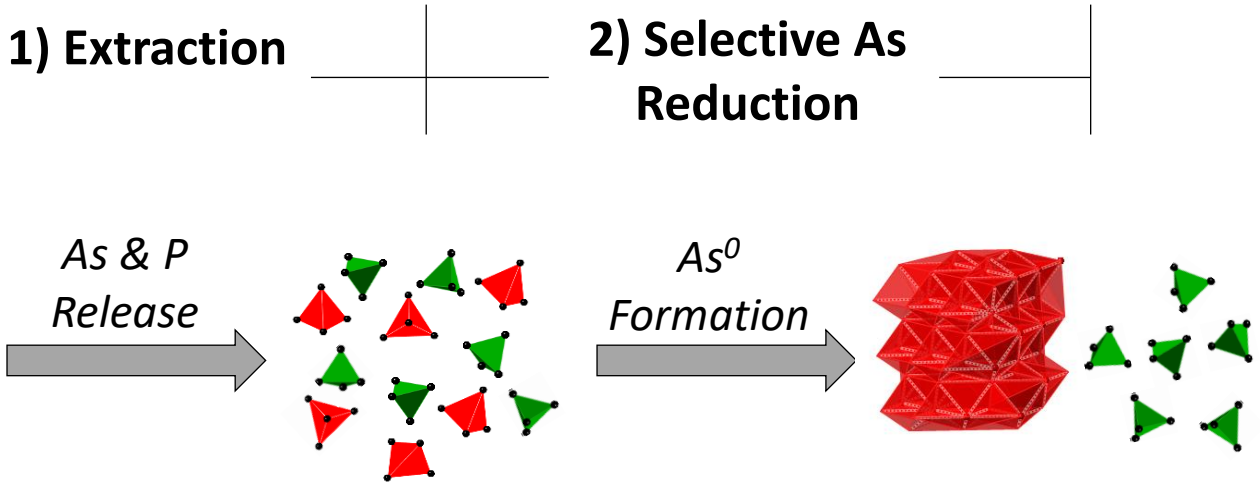
As & P Release

As^0 Formation

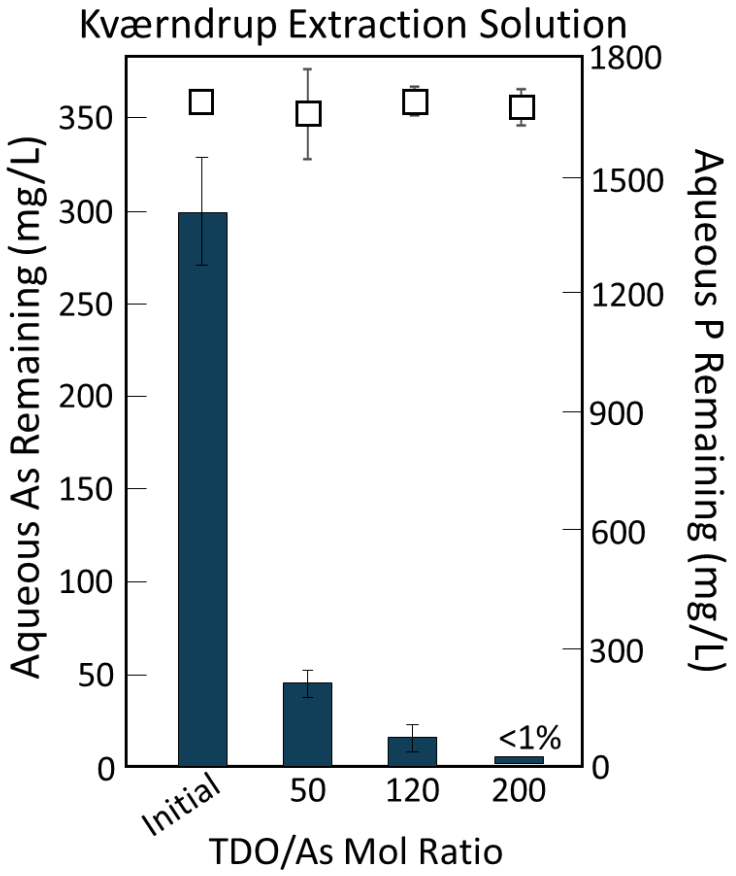


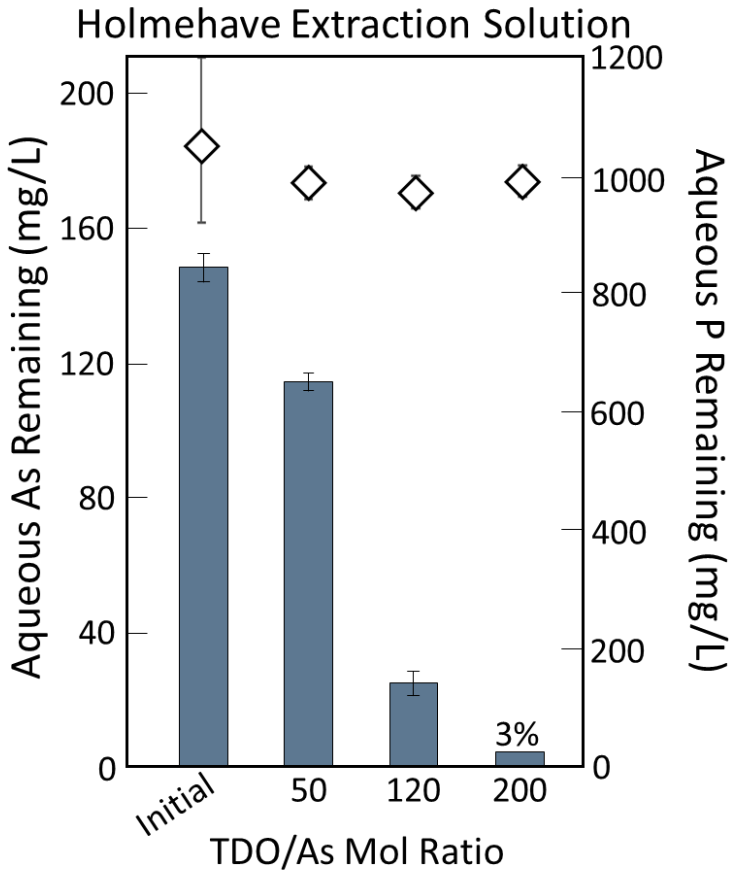
High aqueous P concentration remains!
Co-recovery of As and P (ongoing PhD student project)

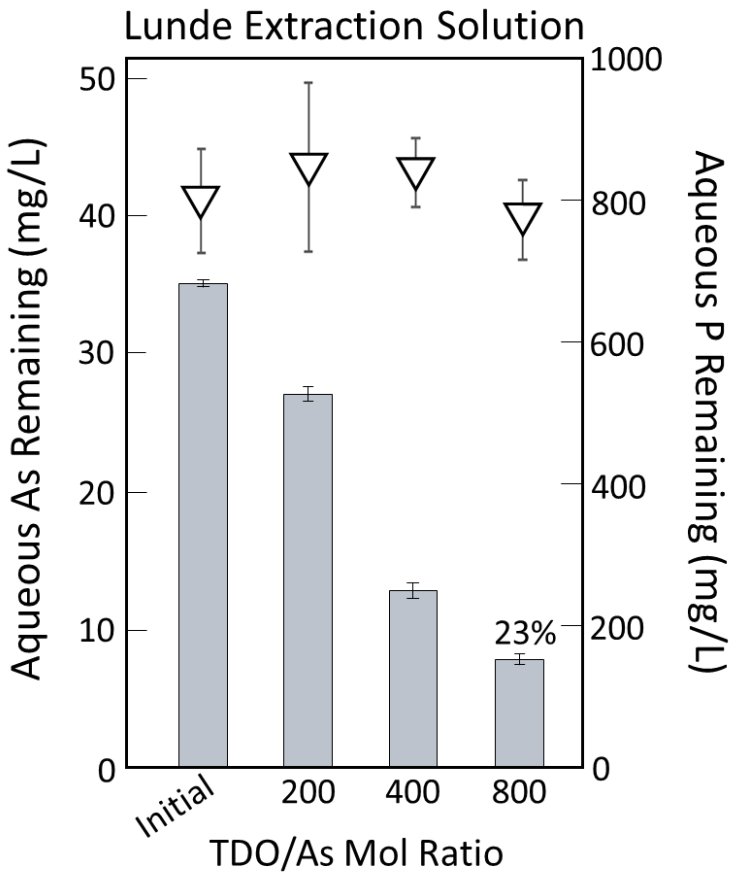




Results 2: Reductive precipitation of As(0) from extracted aqueous As
Impact of sludge composition







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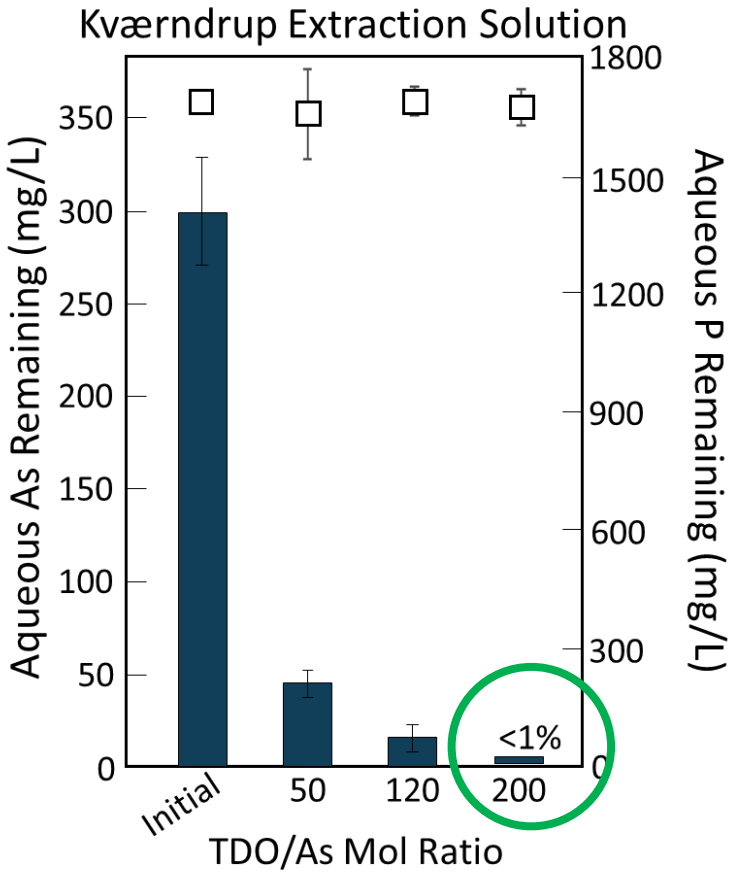
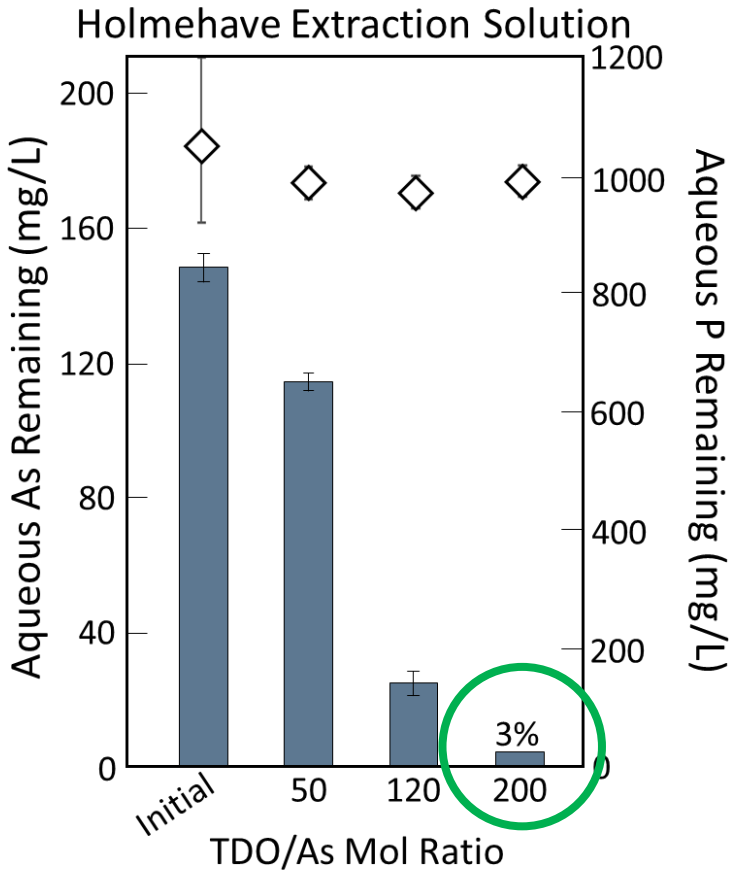
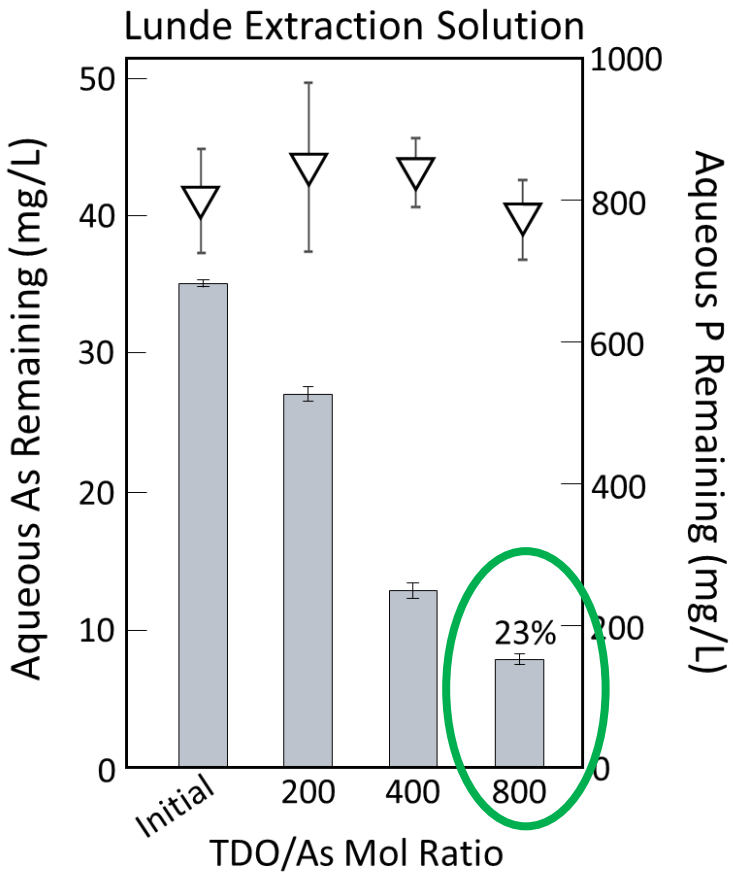




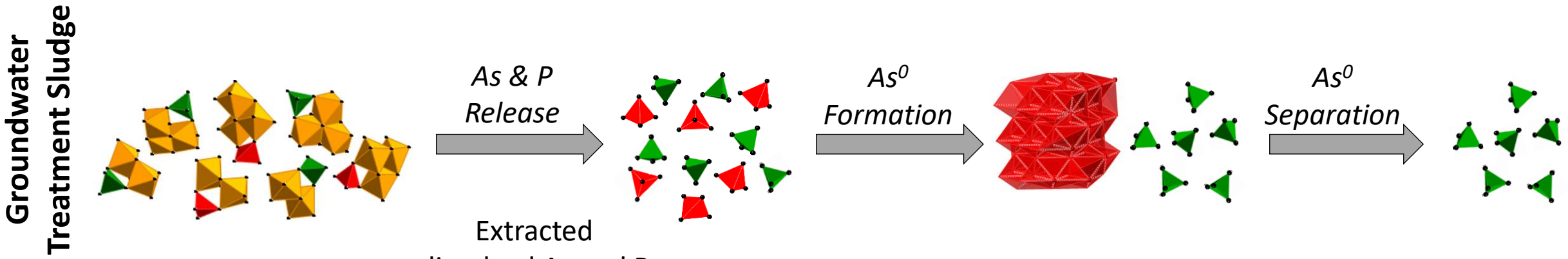


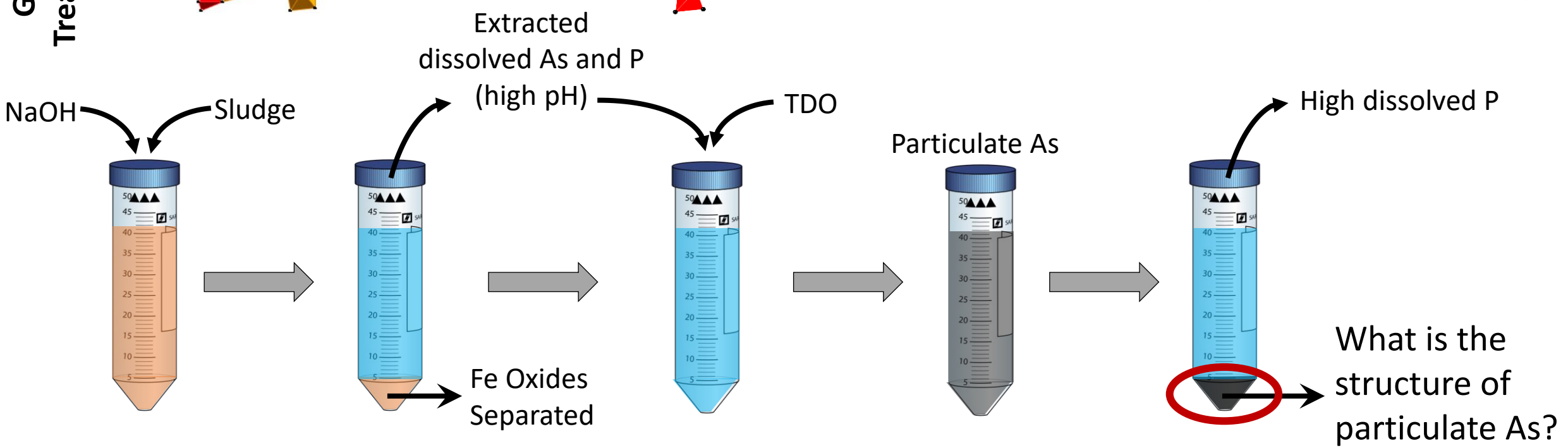
Reductive removal efficiency increases with increasing extracted As concentration

More effective As reduction for waste with high As mass fractions!

Road Map: Converting As in Groundwater Treatment Waste to As(0)

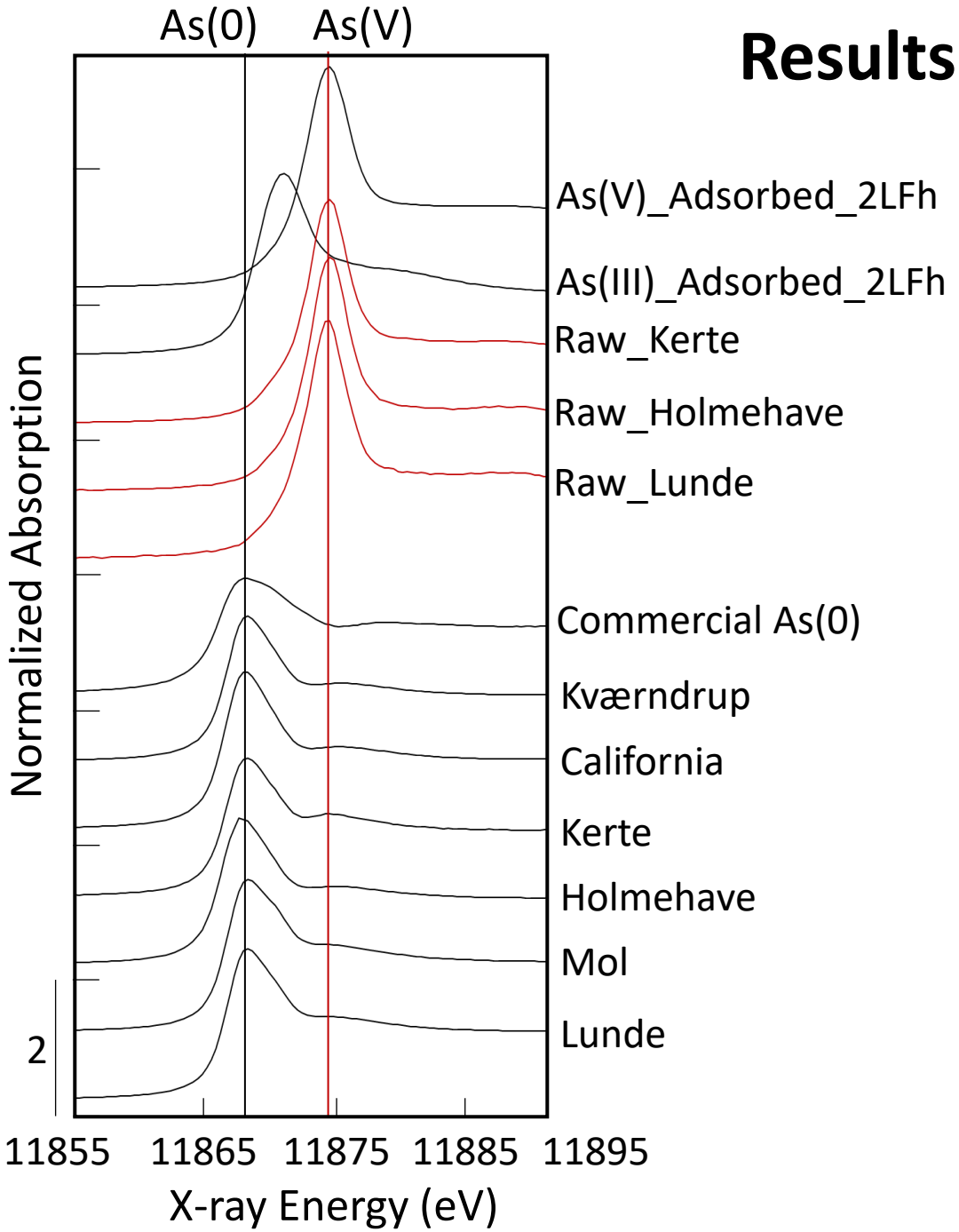
Characterization | **1) Extraction** | **2) Selective As Reduction** | **3) Recovery of Aqueous P?**





Results 4: Unique Structure of Upcycled As(0)

As K-edge XANES Spectra



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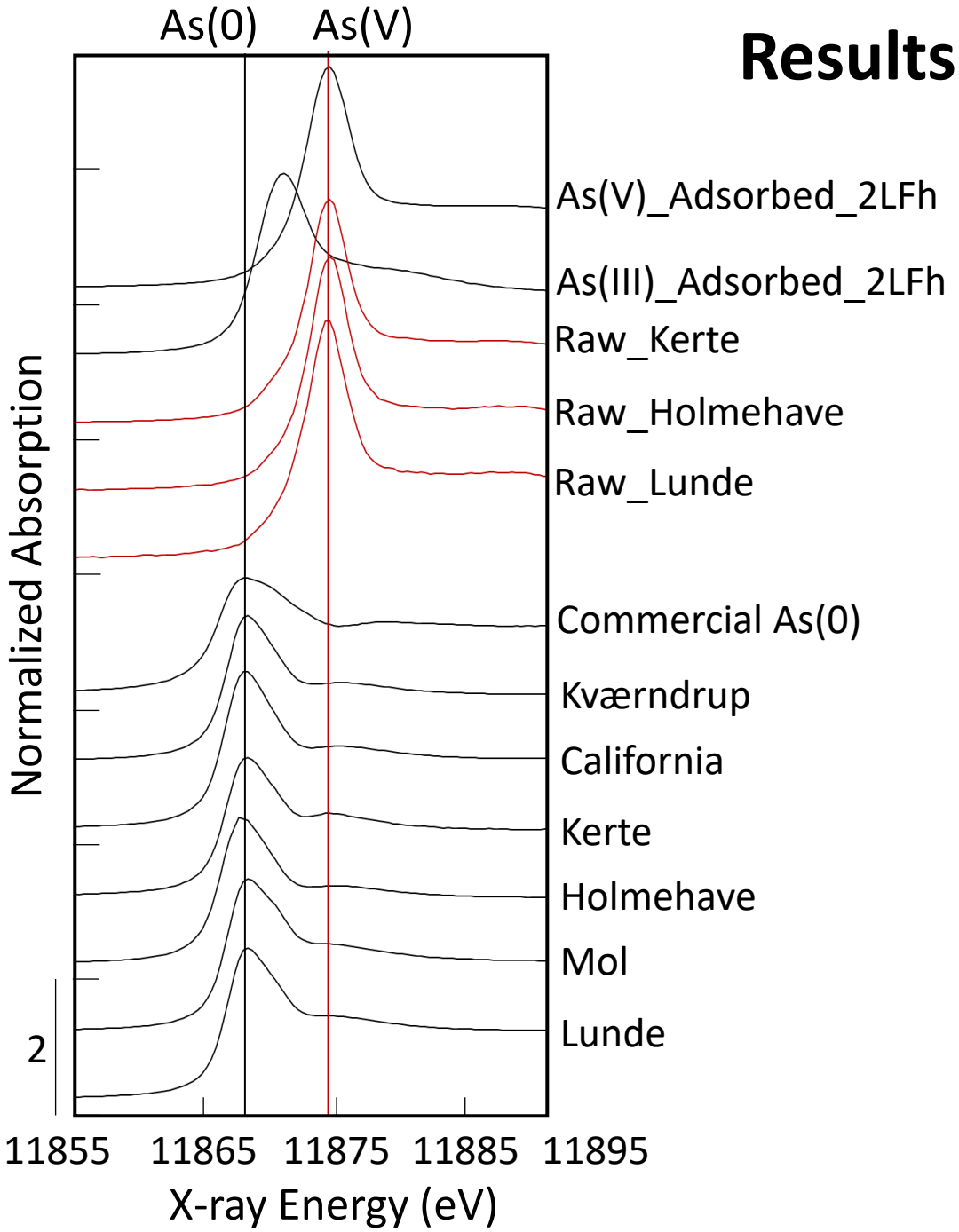


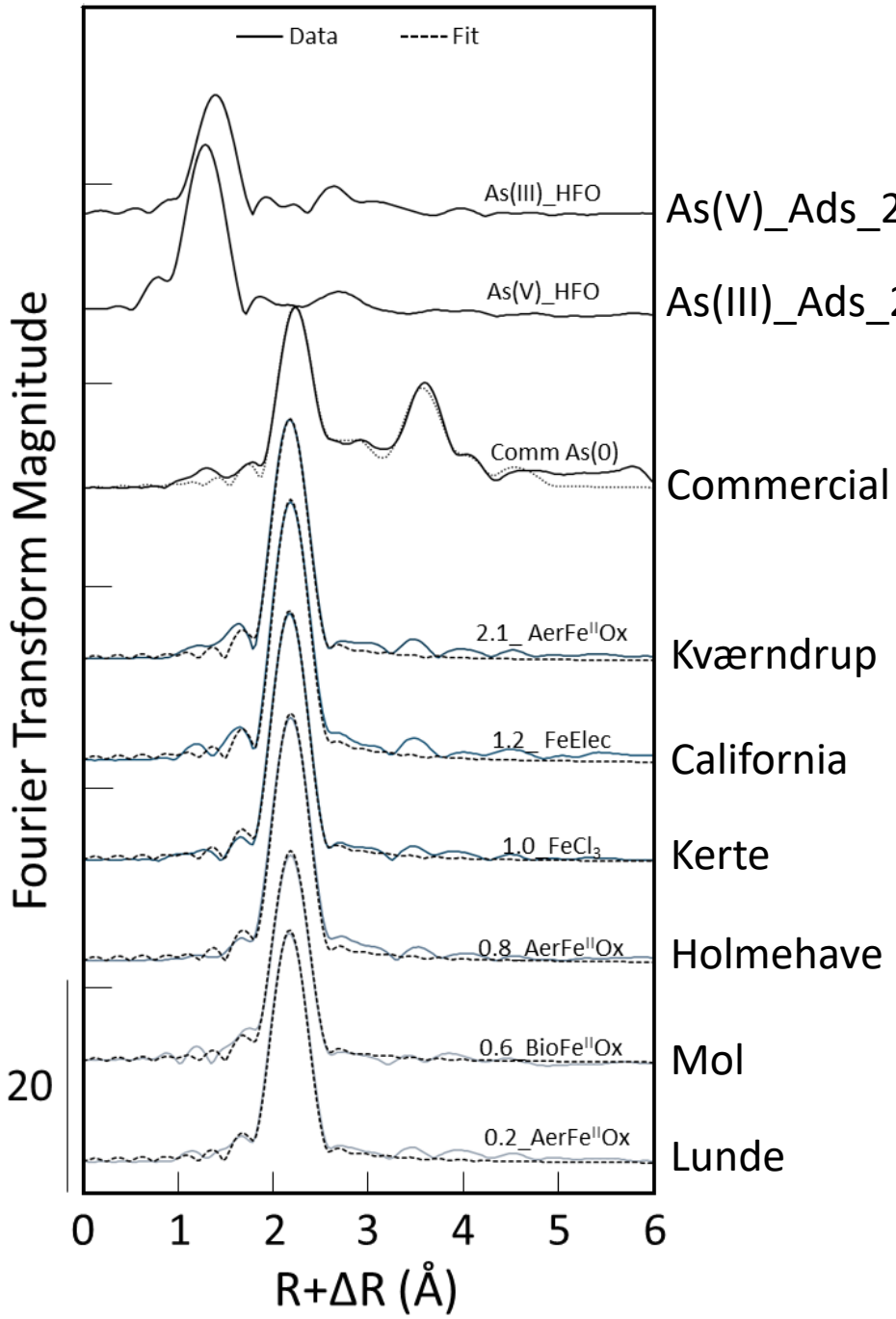
As K-edge XANES Spectra

Key Results:

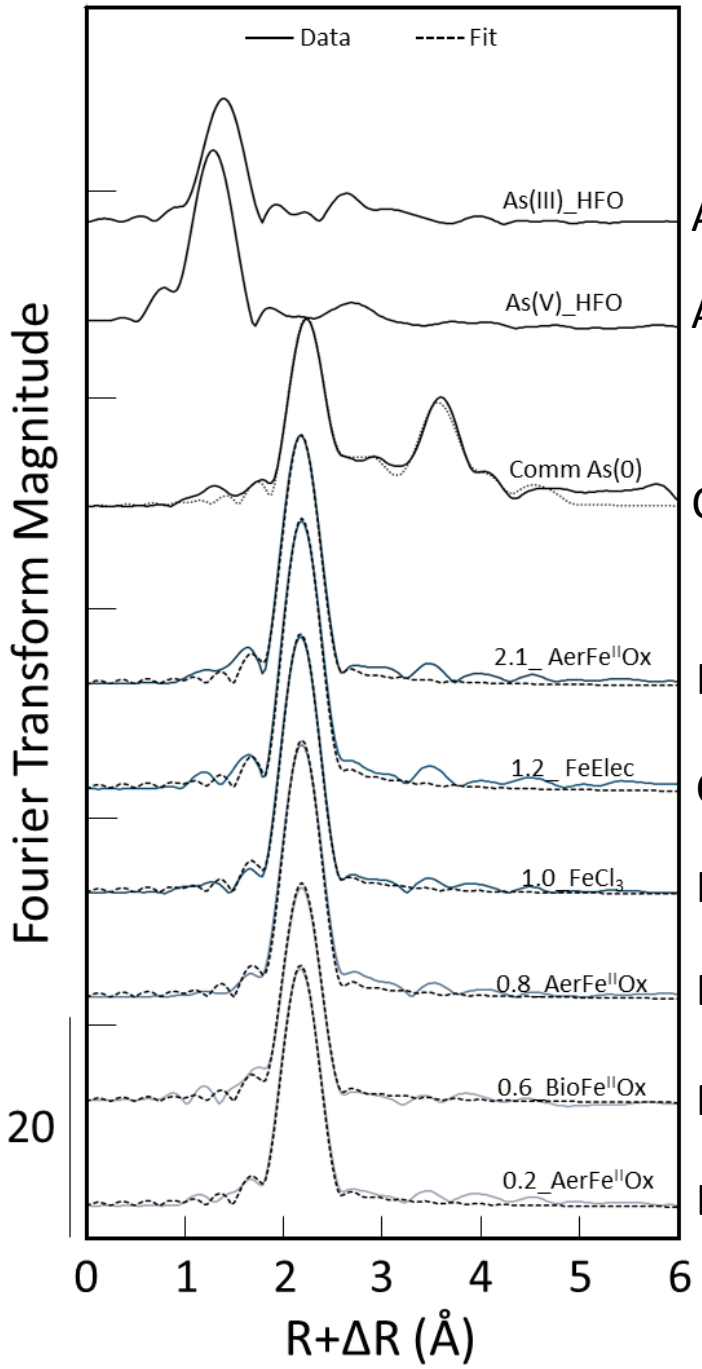
- Upcycled As(0) solids have absorption maximum that matches commercial As(0) reference spectrum
- All upcycled As solids have similar XANES spectra regardless of initial As content in the sludge

Results 4: Unique Structure of Upcycled As(0)

FT As K-edge EXAFS Spectra



Results 4: Unique Structure of Upcycled As(0)



As(V)_Ads_2LFh

As(III)_Ads_2LFh

Commercial As(0)

Kværndrup

California

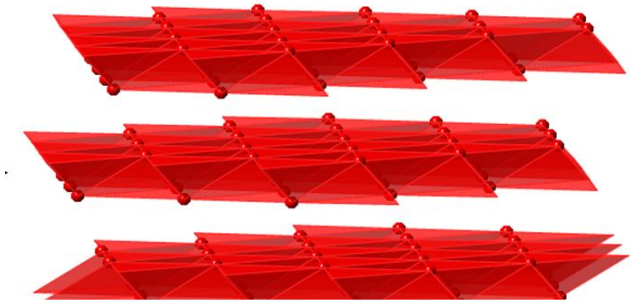
Kerte

Holmehave

Mol

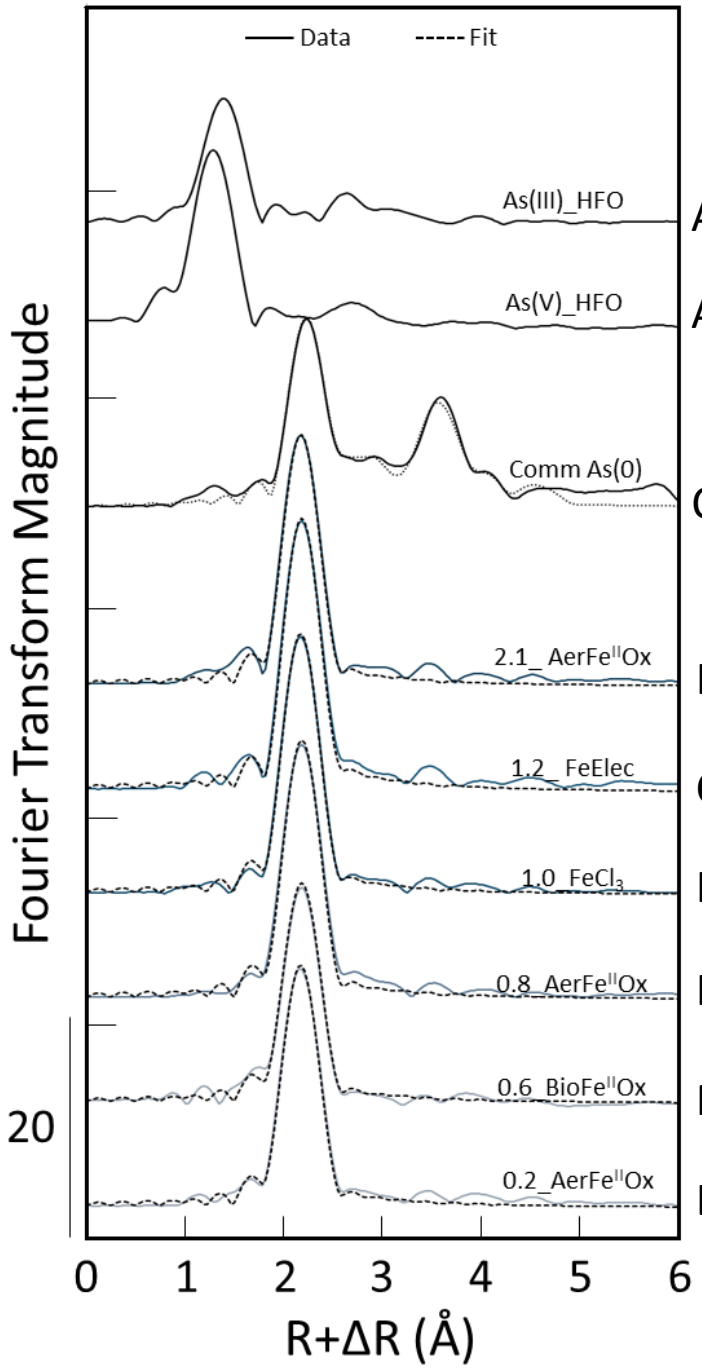
Lunde

FT As K-edge EXAFS Spectra



Crystalline As(0)
(α-As)

Results 4: Unique Structure of Upcycled As(0)



As(V)_Ads_2LFh

As(III)_Ads_2LFh

Commercial As(0)

Kværndrup

California

Kerte

Holmehave

Mol

Lunde

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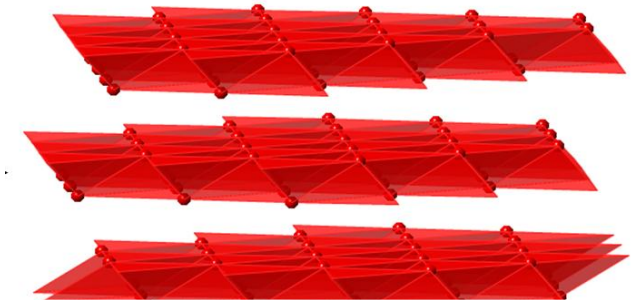
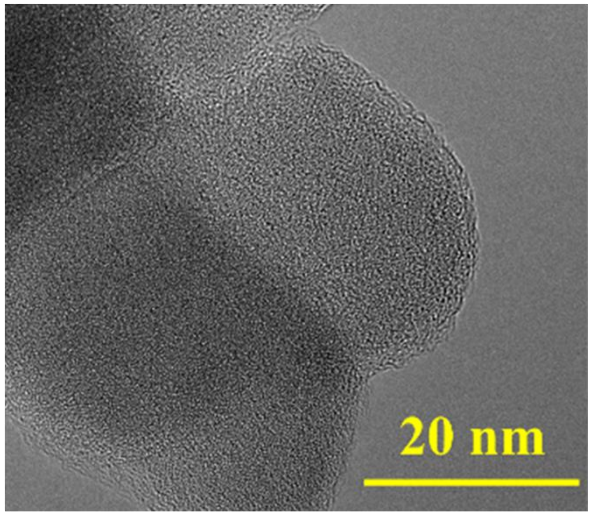


Crystalline As(0)
(α-As)

Transmission Electron Microscopy



Upcycled As(0)
(amorphous)

High purity
(>99% As)

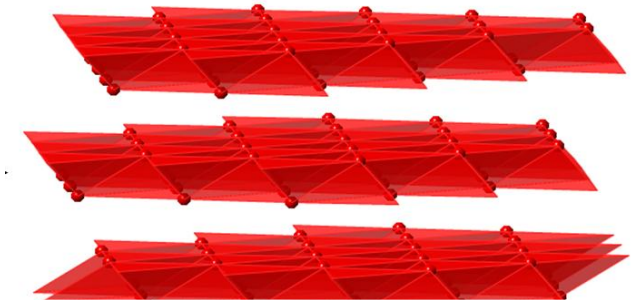
Upcycled As(0) is **amorphous**

SCIENCE ADVANCES | RESEARCH ARTICLE

ENVIRONMENTAL STUDIES

Commodifying a carcinogen: Critical raw materials from arsenic-laden groundwater

Kaifeng Wang and Case M. van Genuchten*



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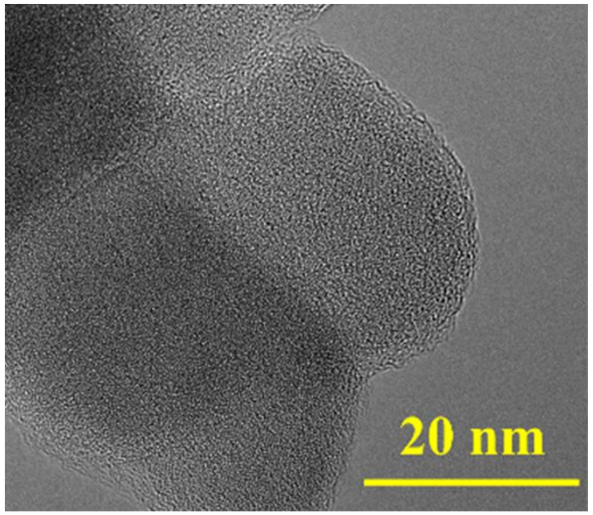

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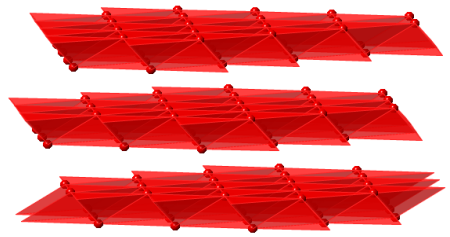
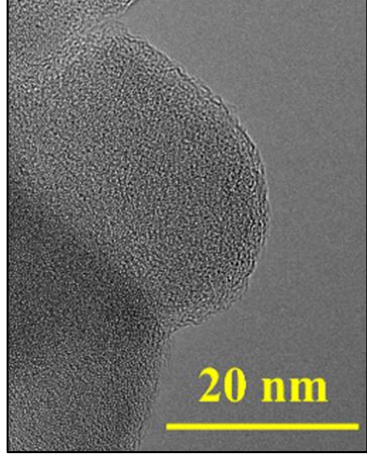
GEUS





Outline

~~1A) Background: Arsenic as a resource~~

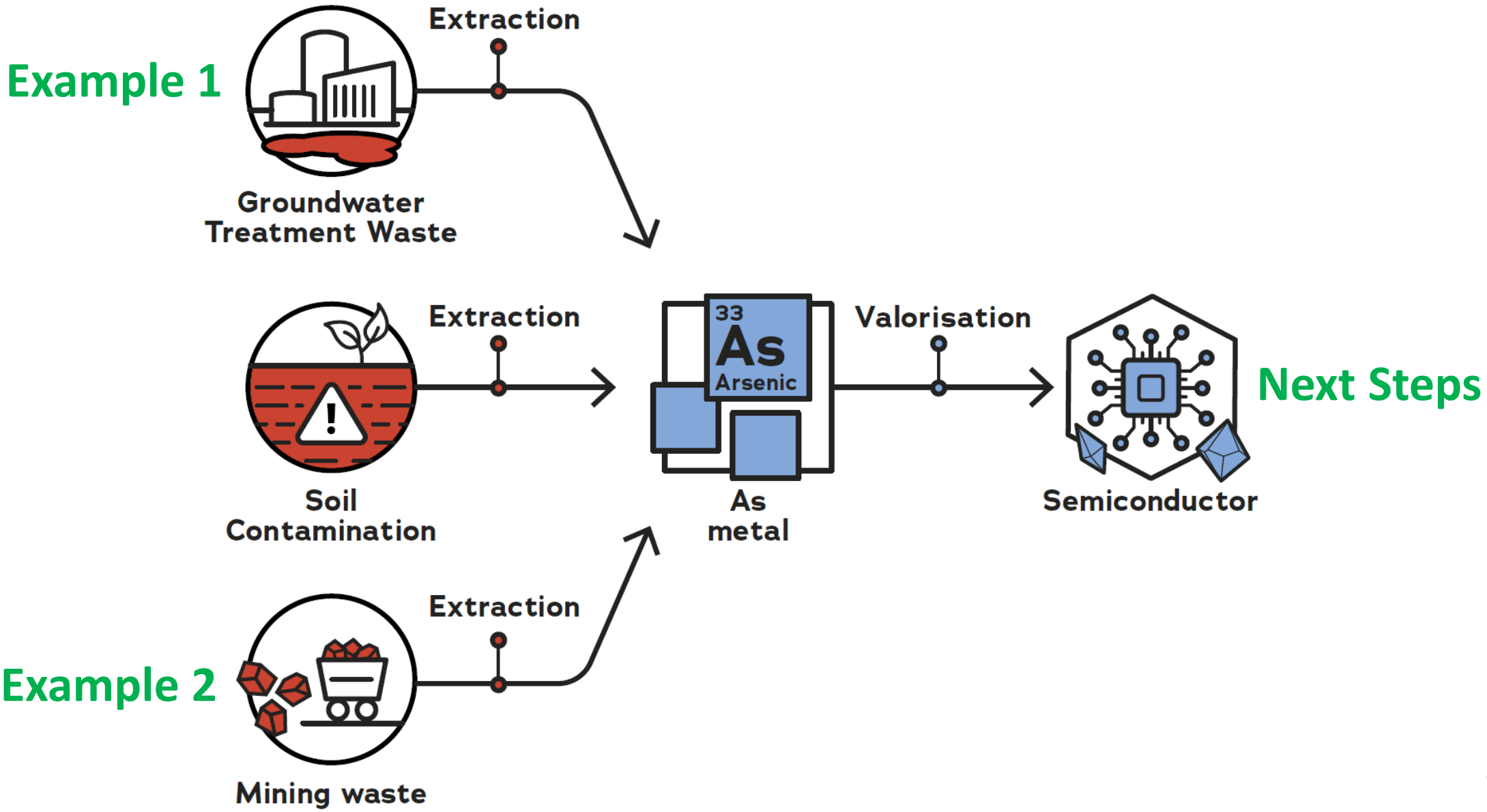
~~1B) Background: Arsenic upcycling approach~~

~~2A) Results: Upcycling arsenic-laden groundwater treatment residues~~

~~2B) Results: Upcycling mining waste~~

3) Next steps and outlook for megasites with arsenic pollution, including Collstrop

Can Arsenic Pollution be a Source of CRMs?



Can Arsenic Pollution be a Source of CRMs?

goodfellow ADVANCED MATERIALS

Search

Materials | Forms | Services | Sectors | Resources

Home > Arsenic Pellets

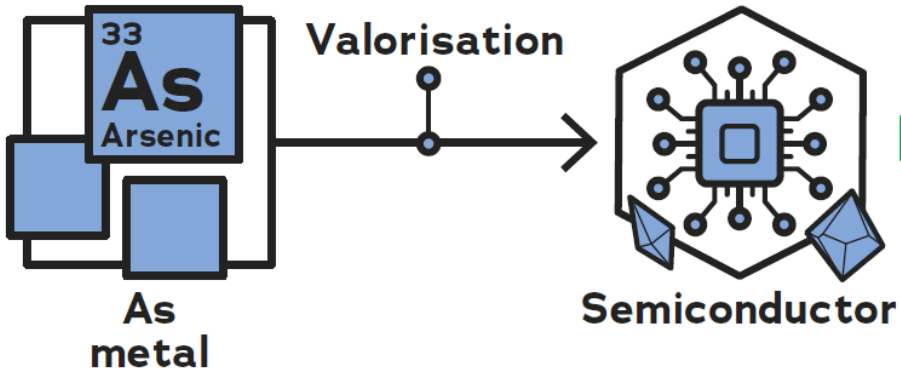
Images are for guidance only and might not represent the final product.

Arsenic Pellets

Formula: As
Form: Pellet/Lump
Material: Arsenic
CAS Number: 7440-38-2
Commodity: Metals
Maximum Lump Size: 20mm
Hazard Pictogram: GHS06, GHS09

TECHNICAL DATA SHEET

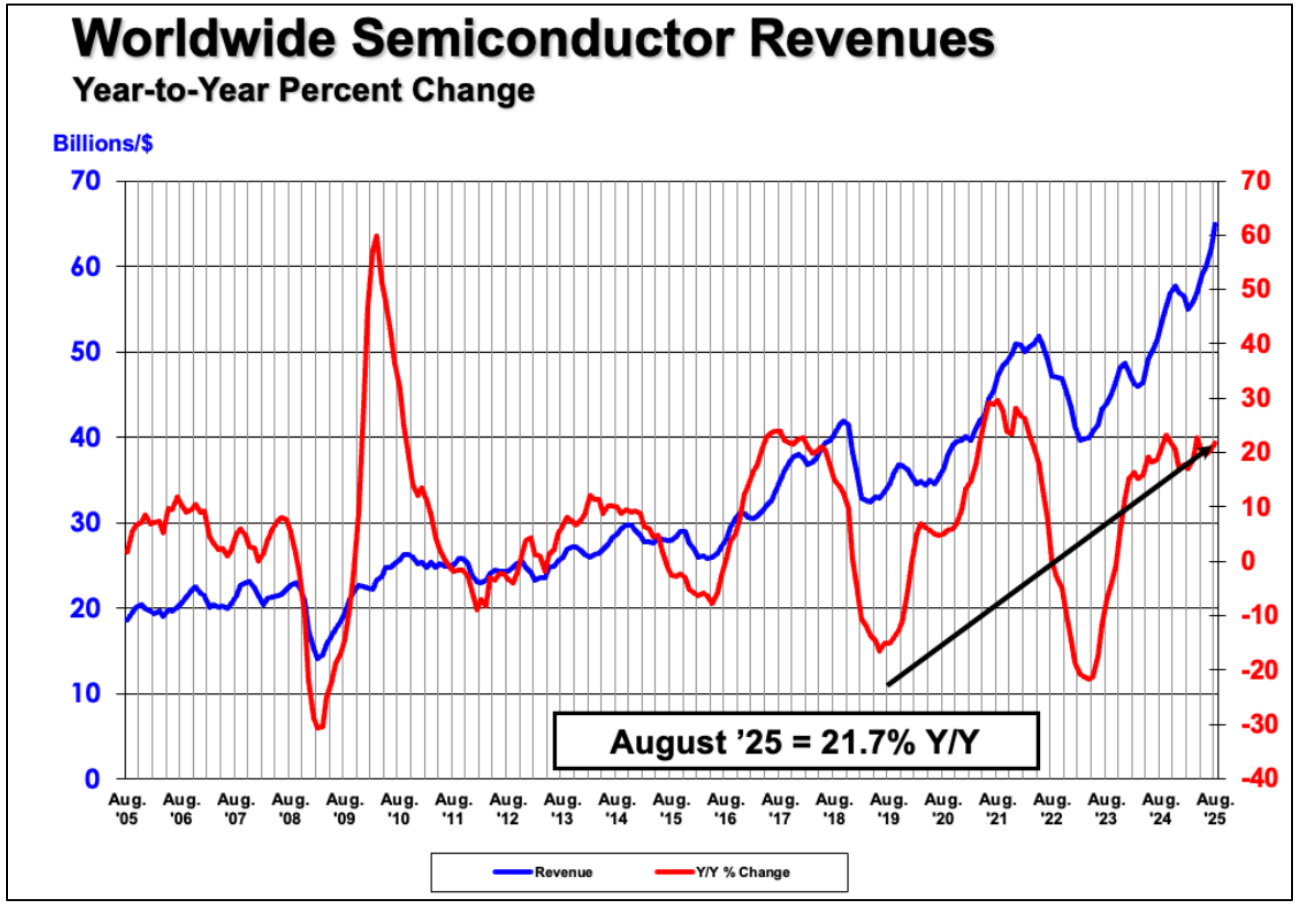
1000030265	99.99%	1000g	€2,459.76



Next Steps

Is there a market for high purity As(0)?

Can Arsenic Pollution be a Source of Semiconductors?



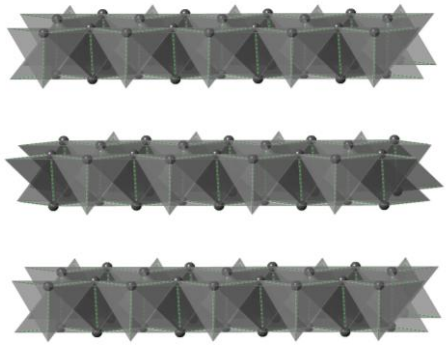
Source: World Semiconductor Trade Statistics (WSTS)

Foundation of modern electronics

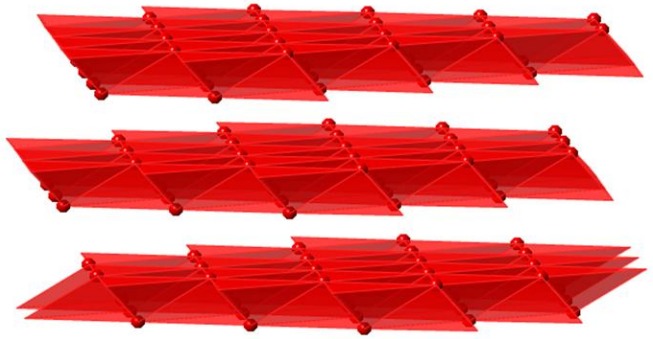
Semiconductor

Next Steps

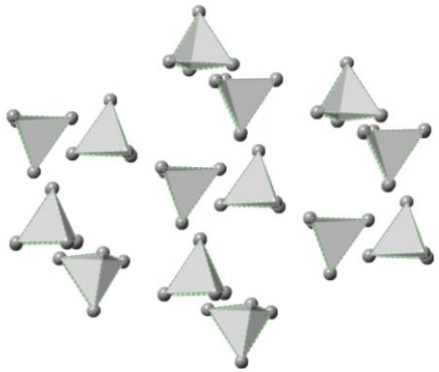
Potential benefits of amorphous material



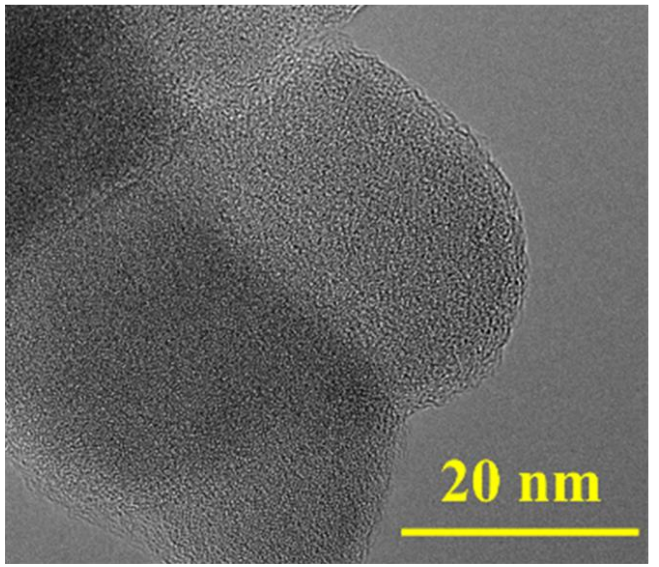
Black phosphorous
Graphite-like structure
Melting point >500 °C



Crystalline As(0)
(α-As)



White phosphorous
Amorphous
Melting point < 50 °C

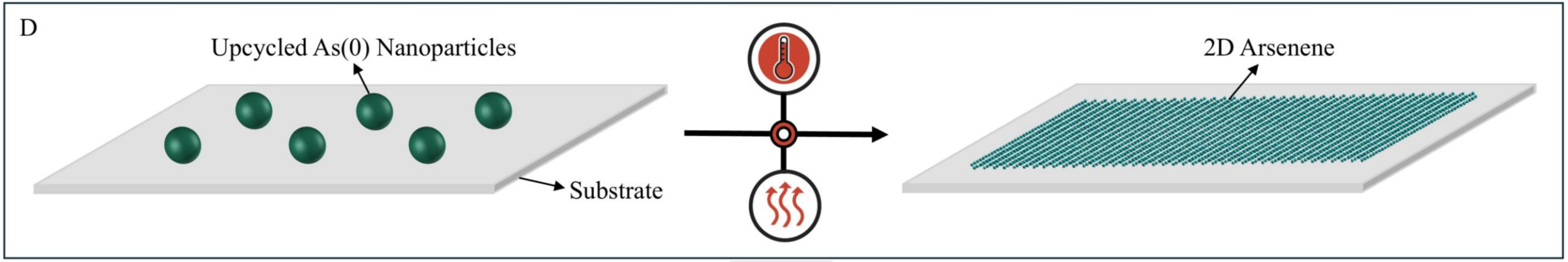


Upcycled As(0)
(amorphous)

High purity (>99% As)

Different fundamental properties than crystalline analogs

Amorphous As(0) better for semiconductor production?



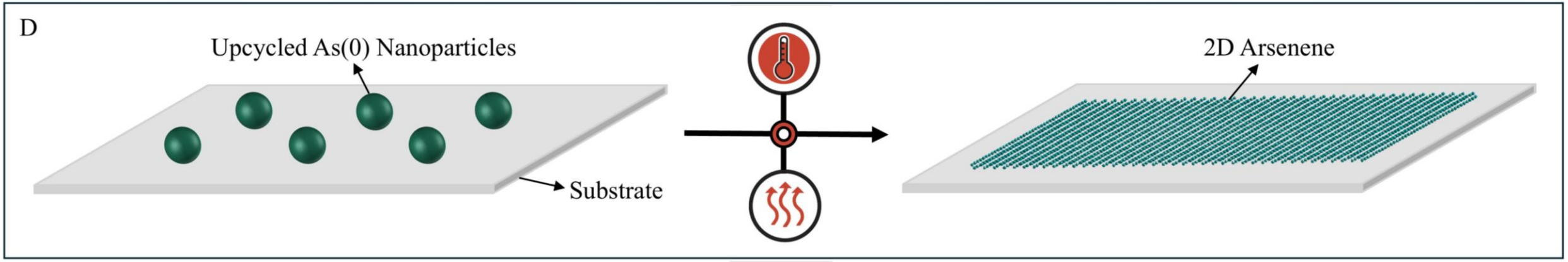
PAPER

Experimental evidence of monolayer arsenene: an exotic 2D semiconducting material

J Shah[1], W Wang[1,2], H M Sohail[1] and R I G Uhrberg[1]

[1] Department of Physics, Chemistry, and Biology, Linköping University, S-581 83 Linköping, Sweden
[2] MAX IV Laboratory, Lund University, Box 118, SE-221 00 Lund, Sweden

Amorphous As(0) better for semiconductor production?



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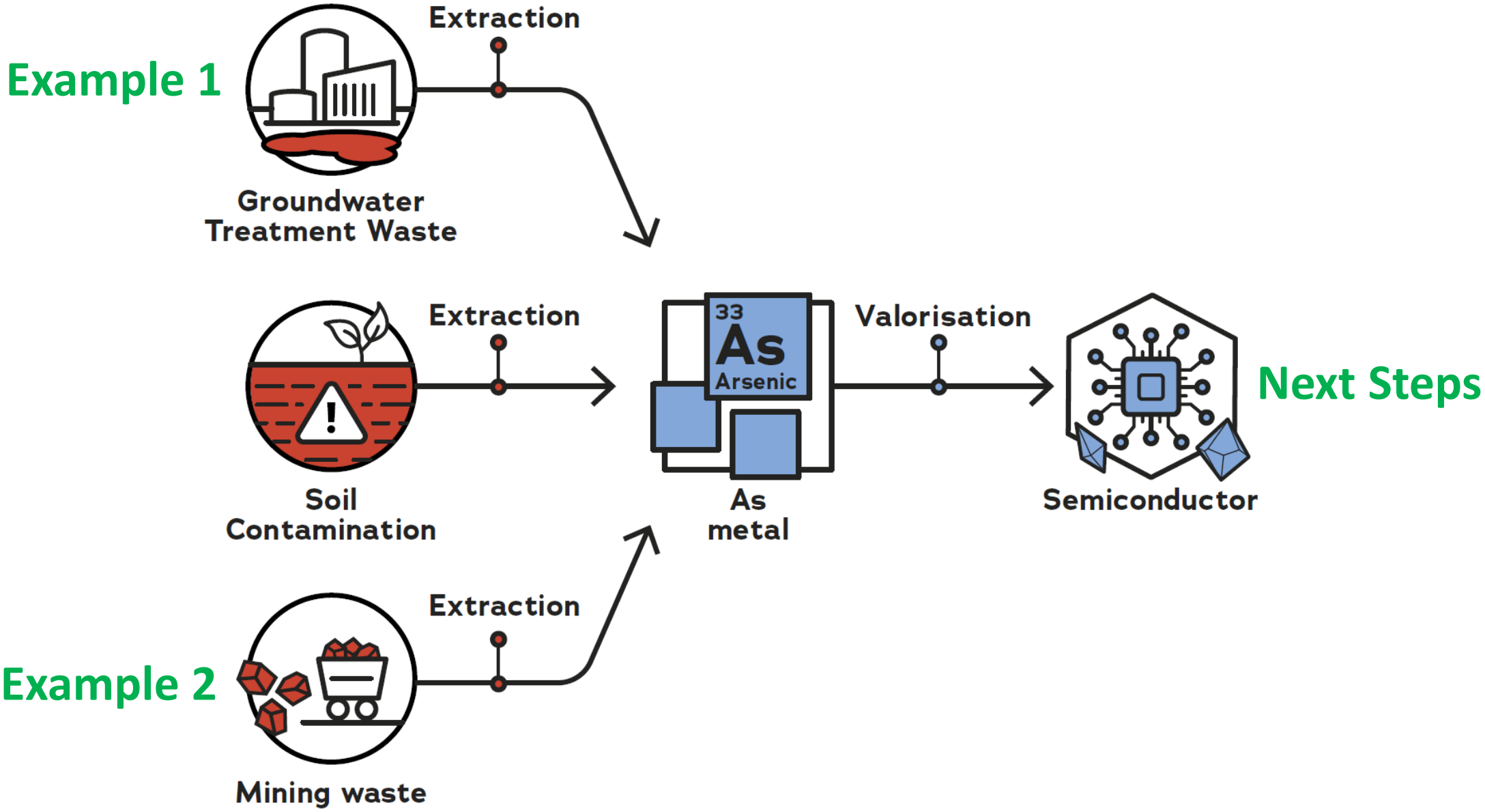
[1] Department of Physics, Chemistry, and Biology, Linköping University, S-581 83 Linköping, Sweden
[2] MAX IV Laboratory, Lund University, Box 118, SE-221 00 Lund, Sweden

Successful semiconductor experiments already in progress

Can Arsenic Pollution be a Source of CRMs?



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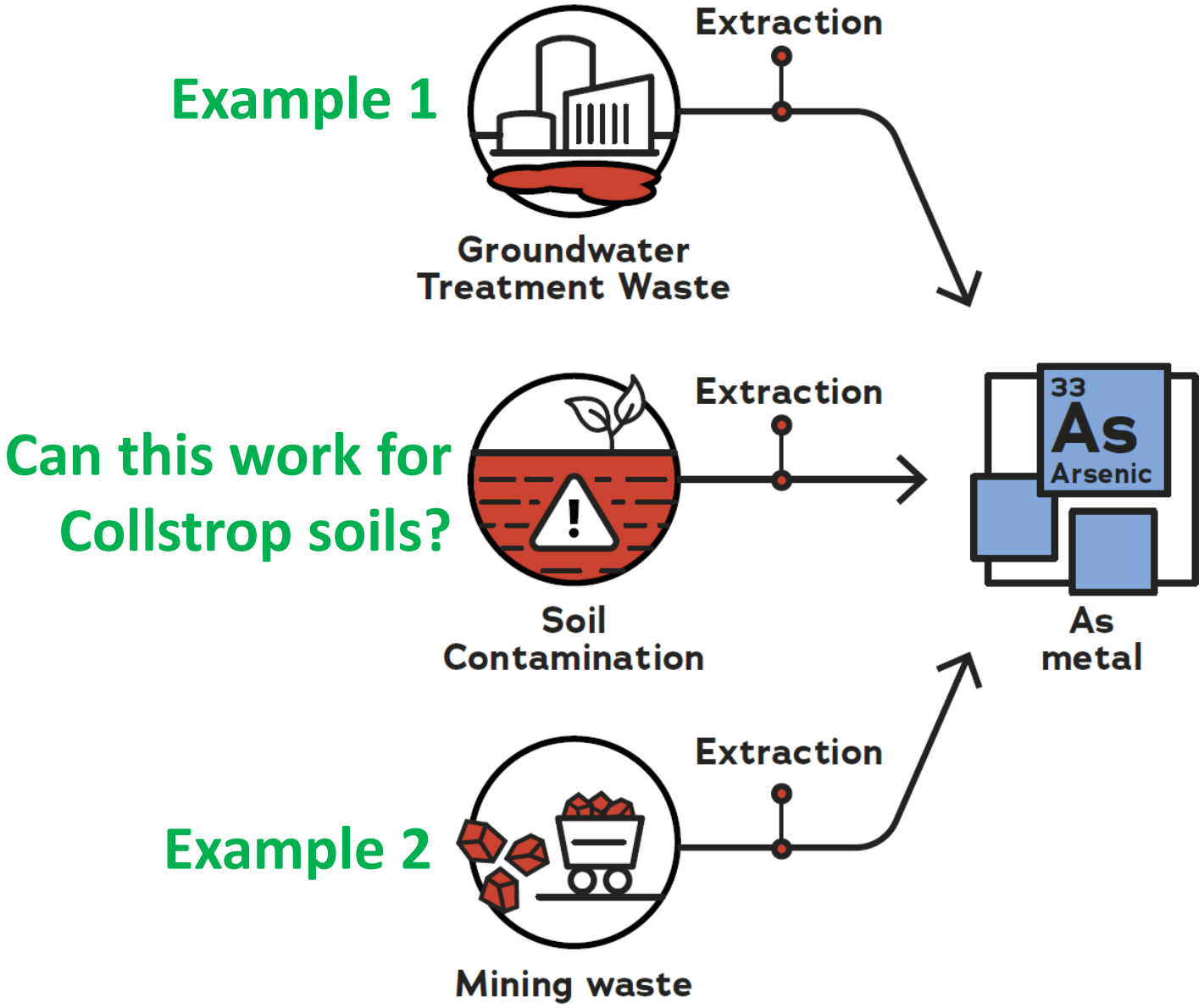
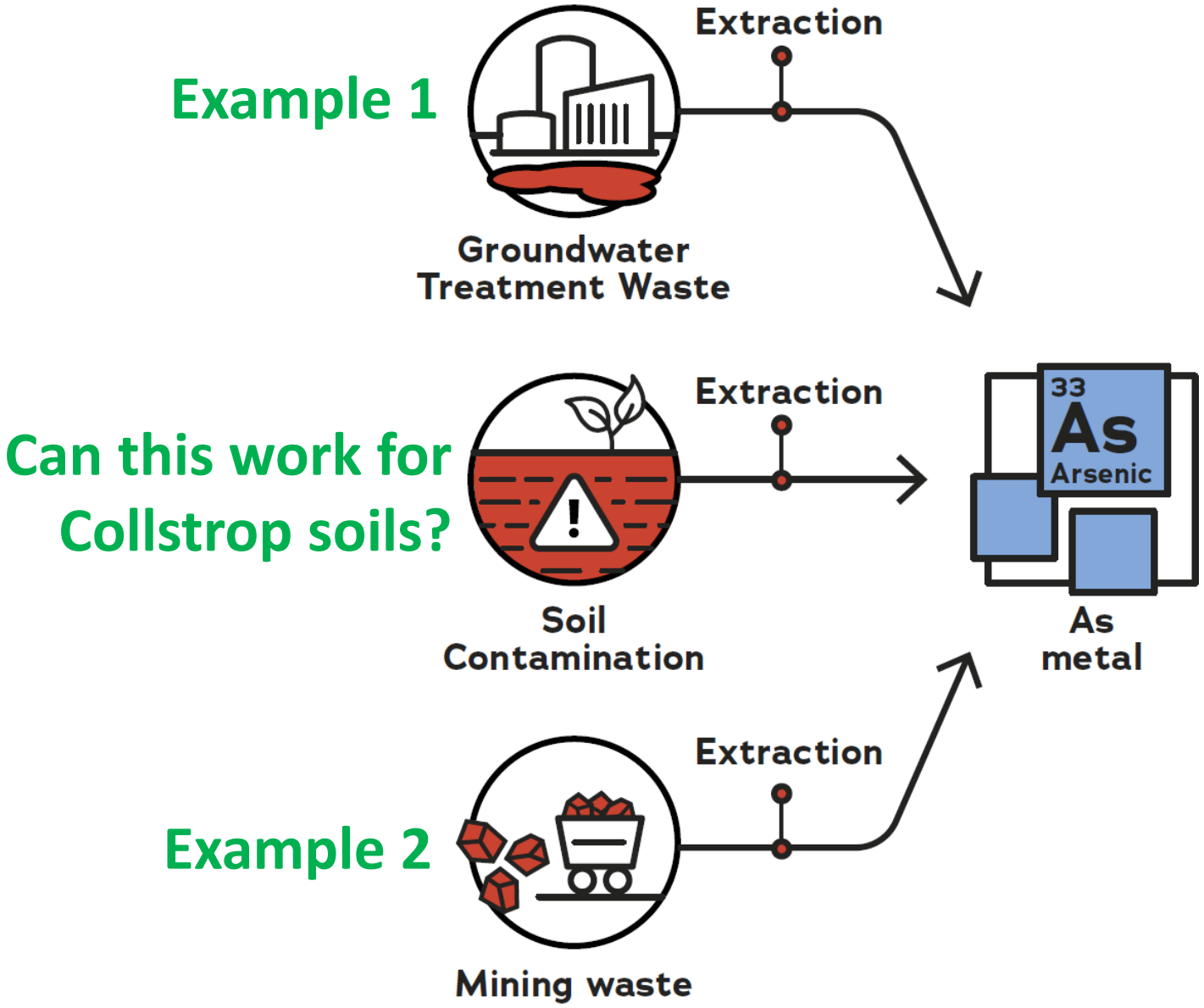


Taking a Step Back…

- This is not like mining for gold, arsenic has low price but high economic importance
- Major benefit is environmental (at the moment at least)
- Arsenic waste upcycling is a very early stage (immature) method

Can Arsenic Pollution be a Source of CRMs?



Many Remaining Questions

- What conditions are best for upcycling soil As pollution?
- Are there co-recoverable species at Collstrop (Cu?)
- What is the best end-use of upcycled As(0)?
- Does the environmental and economic benefits of upcycling outweigh costs of upcycling?
- Role of regulatory frameworks?
- How can this be coordinated with other remediation strategies for optimum results?

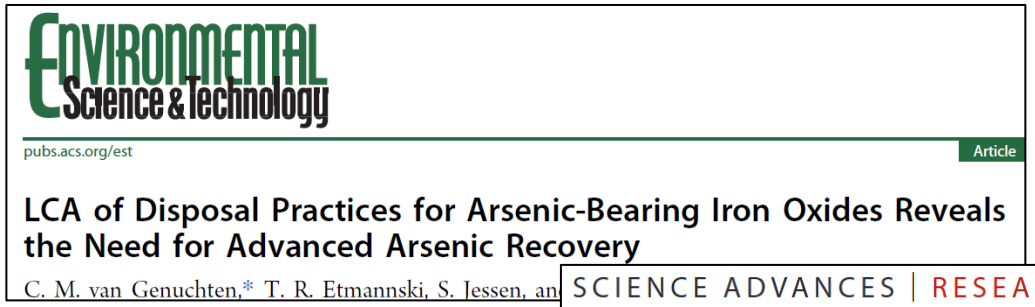
Thanks and Questions?

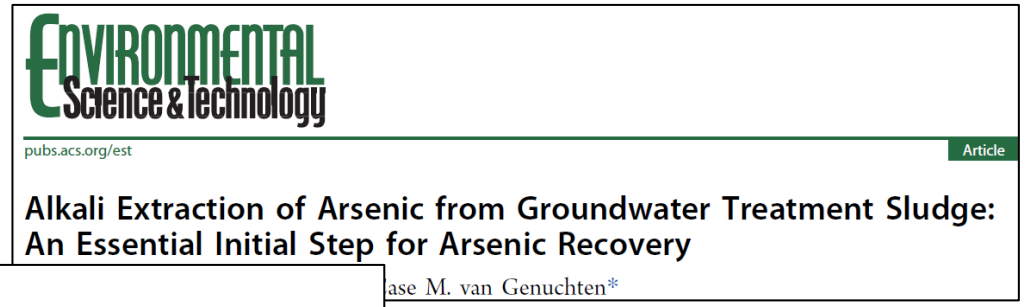
Interested in As-rich sludge upcycling?

Producing As-rich waste that must be managed?

cvg@geus.dk

cmvangenuchten@lbl.gov





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INDEPENDENT RESEARCH FUND DENMARK

Water4All
Water security for the planet