GESIR - EFFECTIVE USE OF GERMANIUM
RECOVERY OF GERMANIUM FROM GRINDING WASTE WATER

Fraunhofer Center for Silicon Photovoltaics CSP

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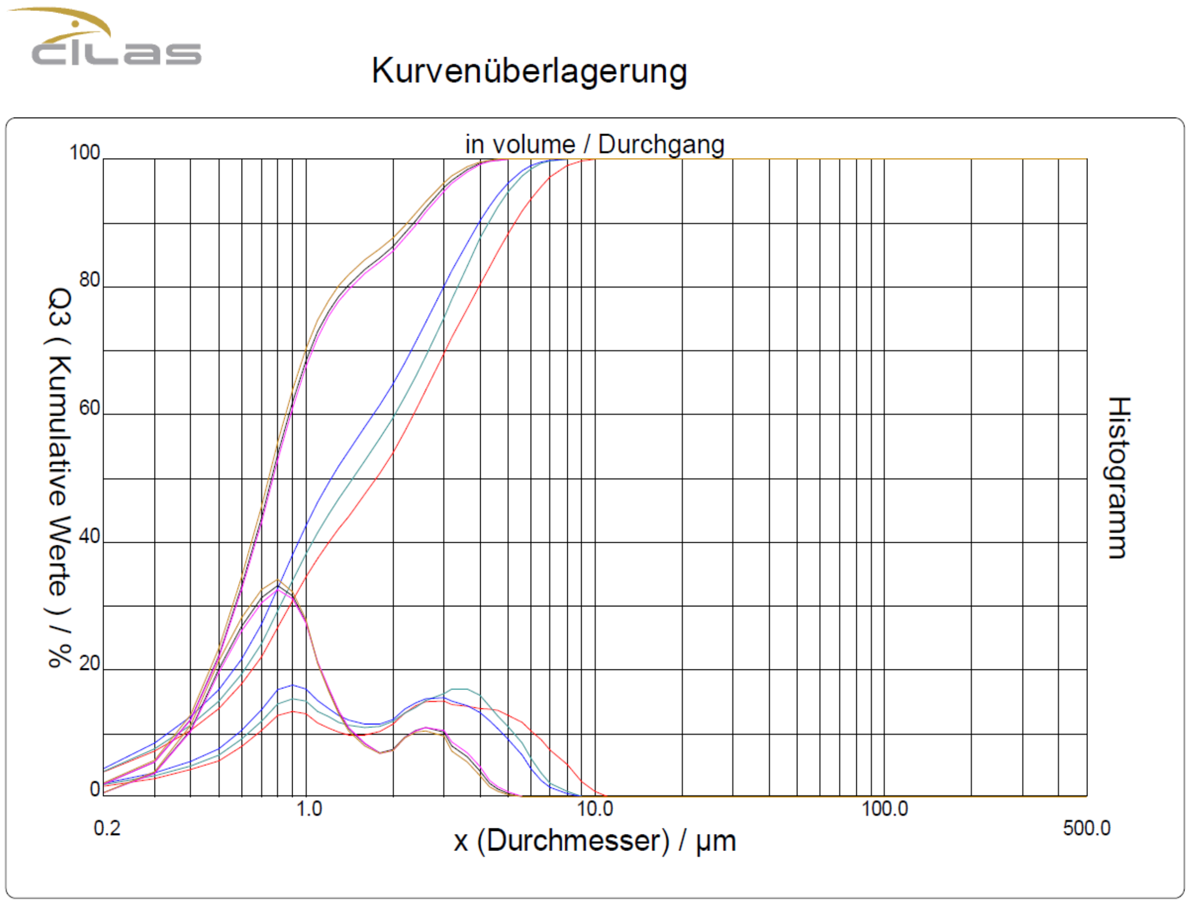
- Motivation
- Concept GeSiR
- Experimental Results
- Discussion / Recommendations

Motivation

- Germanium is a material with a high criticality, high material costs and a high CO_2 footprint for mining (-> mining by burning-off of coal)
- Germanium is used as substrate material for high-efficiency space solar cells.
- Substrates with a certain thickness are needed for the cell manufacturing process; for operation in space, much lower thickness is sufficient.
- After cell manufacturing: grinding-off of excess germanium results in:
  - less weight and
  - germanium is not lost in space after end-of-life.

=> Concept for recovery of germanium from grinding process-waste water is needed.

Concept
Analysis of Grinding Waste Water



- Particle size distribution is in the **lower micrometer / sub-micrometer range**.
- Germanium is present as **solid particles** (micrometer, sub-micrometer range) **together with dissolved GeO_2** in aqueous solution
- Germanium concentration is in the range of **50 - 100 g/m³ (50 to 100 ppm).**

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Concept
Analysis of Grinding Waste Water

Table II: Germanium etch rate for aqueous oxidative chemistries.

	Etch rate (nm/min)
H_2O with O_2 bubbling	0.005
H_2O with O_3 bubbling	4
H_2O/H_2O_2 (9/1)	40

A Study of the Influence of Typical Wet Chemical Treatments on the germanium Wafer Surface

B. Onsia[1, 2, a], T. Conard[1], S. De Gendt[1, 2], M. Heyns[1], I. Hoflijk[1], P. Mertens[1], M. Meuris[1], G. Raskin[3], S. Sioncke[1], I. Teerlinck[1], A. Theuwis[3] J. Van Steenbergen[1] and C. Vinckier[2]

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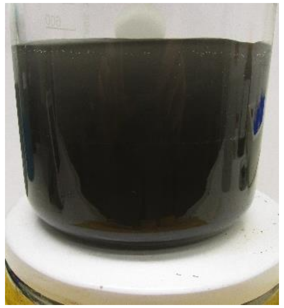
- Maximum solubility of germanium in water:
  - 4 g/l @ RT
  - Around 10 g/l @ T_b
- Dissolution in water:
  - Lack of oxygen: slow
  - Oxidizing agent: fast (up to 1 µm in diameter within 10 minutes)

Concept
Analysis of Grinding Waste Water

With stirrer

0,5l Ge-grinding water (P1200, 0,13 g/l – 130 ppm)
20 drops of H_2O_2 (50%),

0 min

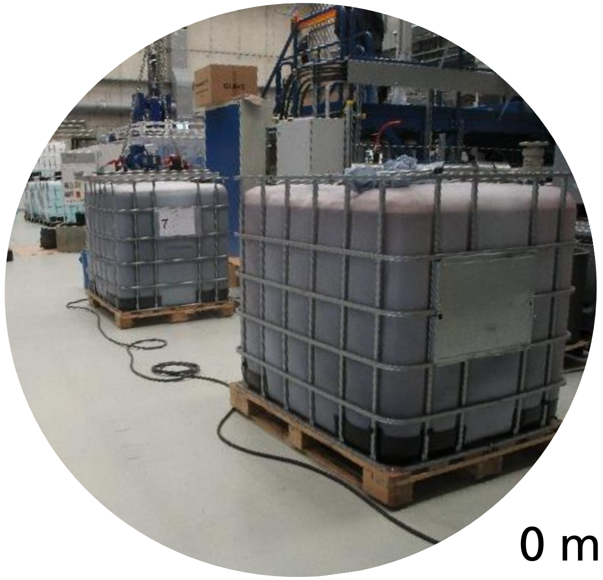


5 min

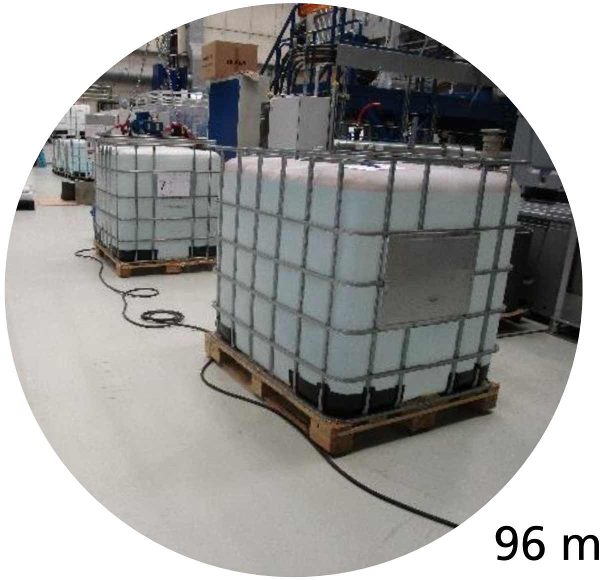
10 min

15 min

Without stirrer



0 min



96 min

Recovery of Germanium from Process Water

Basic Recycling Concepts: Boundary Conditions

Recycling Concepts

- **Osmosis**
  - Membrane selection
  - Single or cascade set-up
  - Prevention of Ge-particles

  Fast; No particles allowed; low energy consumption; Ge-concentr. below 3 g/l

- **Evaporation**
  - Vacuum vrs. normal pressure
  - Energy consumption
  - Corrosion

  High Ge-concentration required

- **Ion exchanger**
  - Definition of column
  - Desorption method
  - Removal of additional cations & anions

  Fast; No particles Regeneration of exchanger resin

- **Precipitation**
  - Flocculant / precipitant
  - Extraction of Ge
  - Ratio of precipitated Ge

  Fast; Extraction of Ge might be difficult

Recovery of Germanium from Process Water

Basic Recycling Concepts: Boundary Conditions

Grinding water:

Mix of dissolved GeO_2 / very small particles and larger particles

Complete recovery of Ge

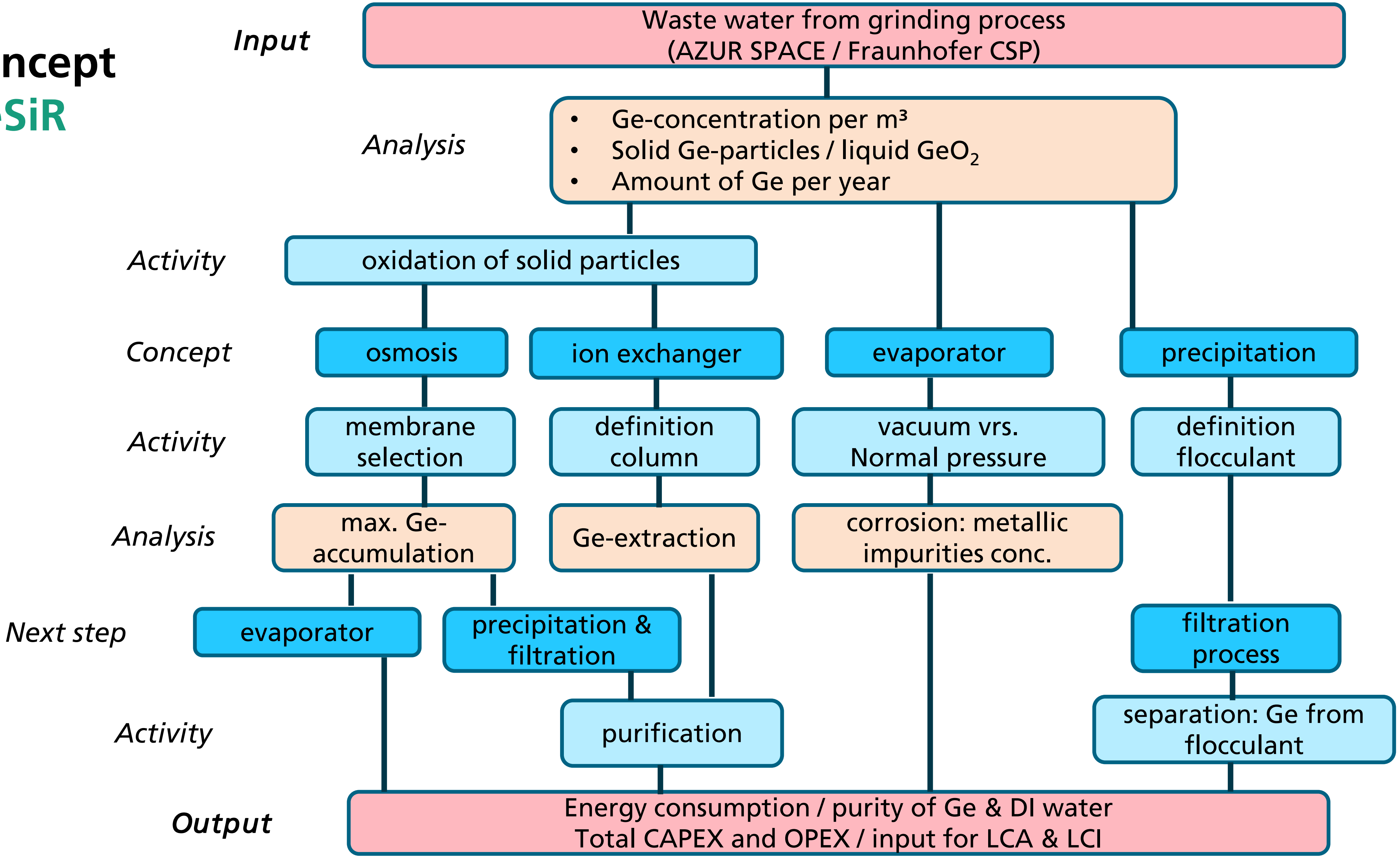
-> oxidation with H_2O_2 + recovery of dissolved GeO_2

-> filtration of particles + recovery of dissolved GeO_2

Partial recovery of Ge

-> filtration of particles

Concept
GeSiR



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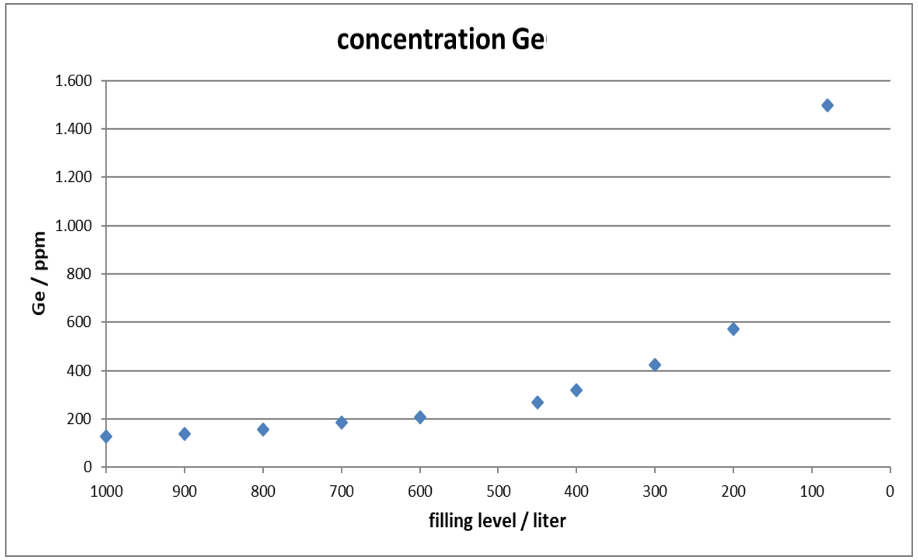
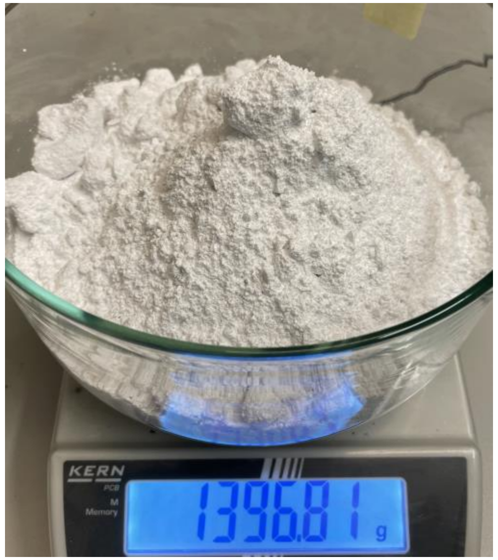
Results I
Osmosis and evaporation

- By removing high purity water from the system, GeO_2 is accumulated in the solution/concentrate.
- GeO_2 is accumulated from 0,1 g/l up to a concentration of about 2 g/l, i.e. increase of the Ge-concentration by a factor of 10 to 20.
- Vacuum evaporator: GeO_2 sludge
- Heat chamber: solid GeO_2 (high purity)

	sample	level [L]	XRD intensity	Ge-conc. / ppm	GeO_2-conc. / ppm
Konzentrat	IBC CSP	1000	3.611	126	182
		900	4.018	139	200
		800	4.584	156	225
		700	5.550	186	268
		600	6.254	208	299
		450	8.173	267	384
		400	9.819	317	457
		300	13.219	422	608
		200	18.130	573	826
		80	48.125	1.497	2156





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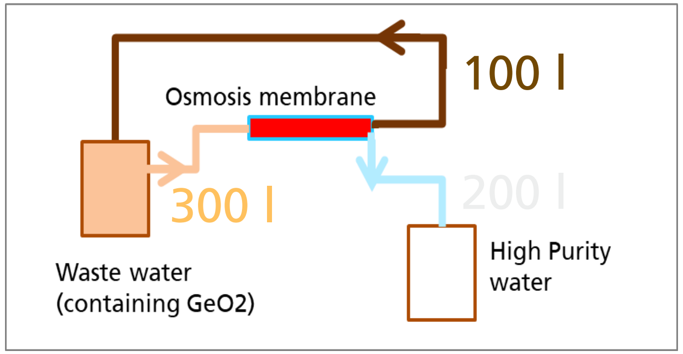
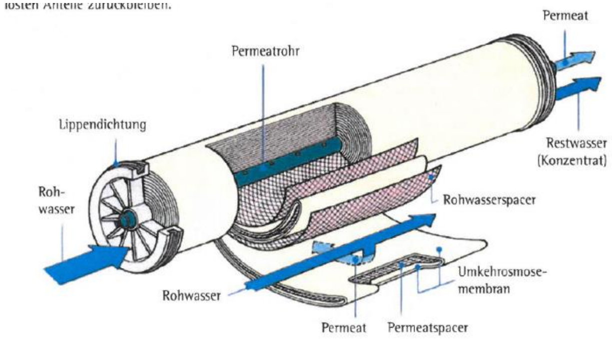
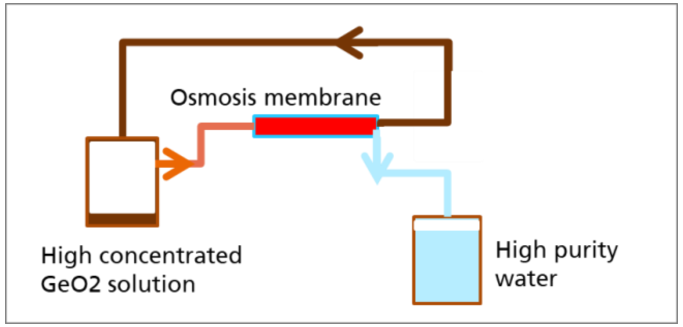
Recycling Concept
Osmosis

- A membrane was connected to a water pump, flow meters and a 5 µm filter.
- The concentration in the concentrate increases by a factor of 2-3 with each cycle.







- In our case, 200 l/h high purity water / 100 l/h concentrate is obtained, i.e. about 4.5 h is needed for one IBC.

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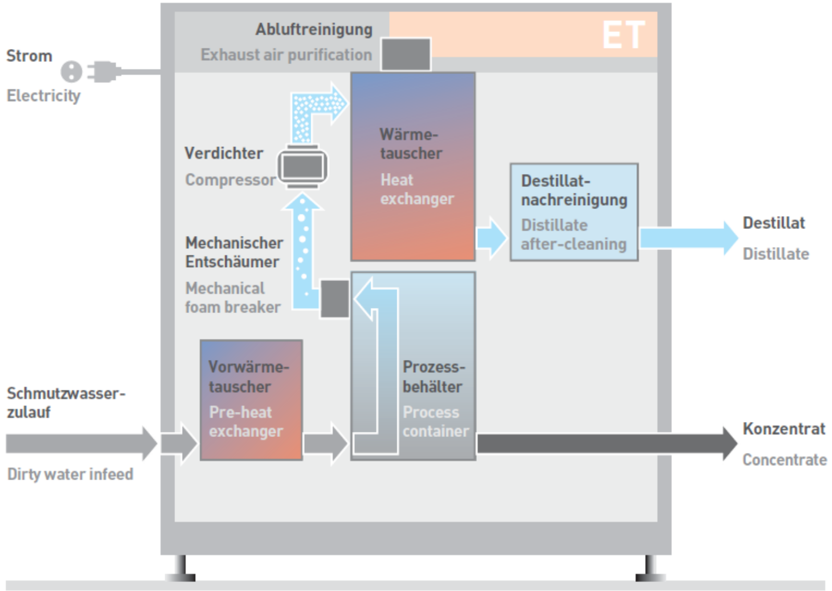
Recycling Concept

Evaluation (boiling – condensating / normal pressure)

- Industrial size evaporator: capable of up to 1500 l/h; tested @ the company site
- Capex is rather high:
  - ET 1000 (1m³/h): 200 – 250 k€
  - ET-100 (100 l/h): 70 k€



Typ	Nennleistung l/h Rated capacity l/h	Energiebedarf kWh/m³ Energy demand kWh/m³	Maße L x B x H mm Dimensions L x W x H mm
ET 50	50	75	1800 x 1100 x 2350
ET 75	75	68	1800 x 1100 x 2350
ET 100	100	60	2450 x 1400 x 2600
ET 150	150	60	2450 x 1400 x 2600
ET 250	250	55	2900 x 1550 x 2600
ET 350	350	40	2900 x 1550 x 2600
ET 500	500	40	4400 x 1950 x 3100
ET 750	750	40	4400 x 1950 x 3100
ET 1000	1000	37	4400 x 2400 x 3100
ET 1500	1500	35	4400 x 2400 x 3100

Recycling Concept

Evaporation (Vacuum Evaporator): Fraunhofer CSP

- Lab/pilot-scale evaporator: 170 l/d
- Energy consumption: 3 kW/h
- Output: GeO_2 sludge

Parameter	Einheit	R 150V3 --1
Elektrische Versorgung	-	230 [V] **50** [Hz] 1F
Max. Destillaterzeugung (Wasser)	[l/24h]	170 ± 10%
Leistungsaufnahme bei Dauerbetrieb	[kW]	2,6 ± 10%
Spezifischer elektrischer Energiebedarf pro Liter Destillat	[Wh/l]	380 ± 10%

Results II
Filtration

- Using a chamber filter, the coarse particles are removed by forming a filter cake.
- The filtered solution is still turbid (easily cleared up by H_2O_2).
- Solution used for osmosis / ion-exchanger
  - Osmosis: limited advantage, same amount of liquid has to be handled
  - Ion-exchanger: longer operating time of the exchanger resin.

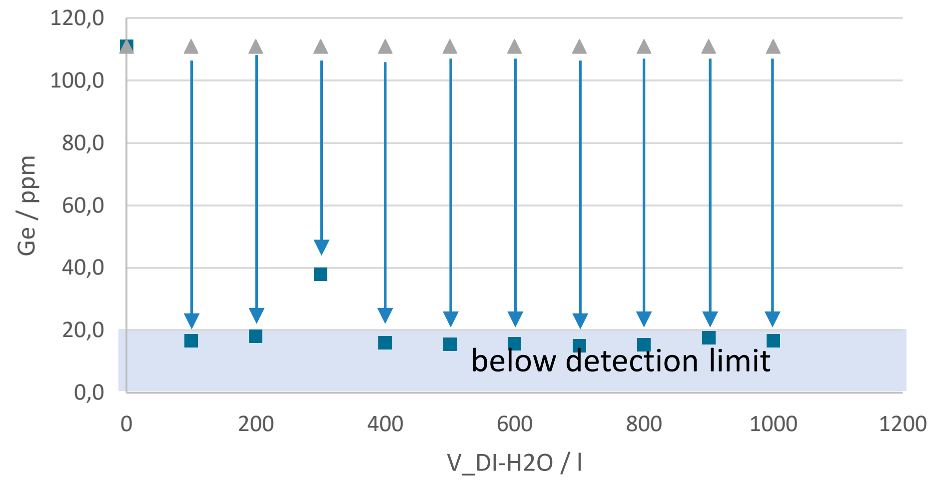
Left: lab scale chamber filter; middle: input solution (100 ppm), right: filtered solution (45 ppm). Total volume: 100 liter.

Results III

Ion Exchanger (mixed bed)

- Test with an IBC of 1,000 liter with a GeO_2 concentration of 110 ppm, Flow rate: 300 l/h.
- Solid particles had been oxidized prior to the ion-exchanger using H_2O_2.
- Several ion-exchanger are now available at the CSP, the resin can be exchanged easily.
- Ge-concentration outlet: below detection limit (LOD=20ppm).
- A 20 l exchanger (which is still a rather small one) could extract 1 kg of germanium / could handle 10.000 liter of grinding water.

Ge-concentration in DI-H2O after passing the ion exchanger

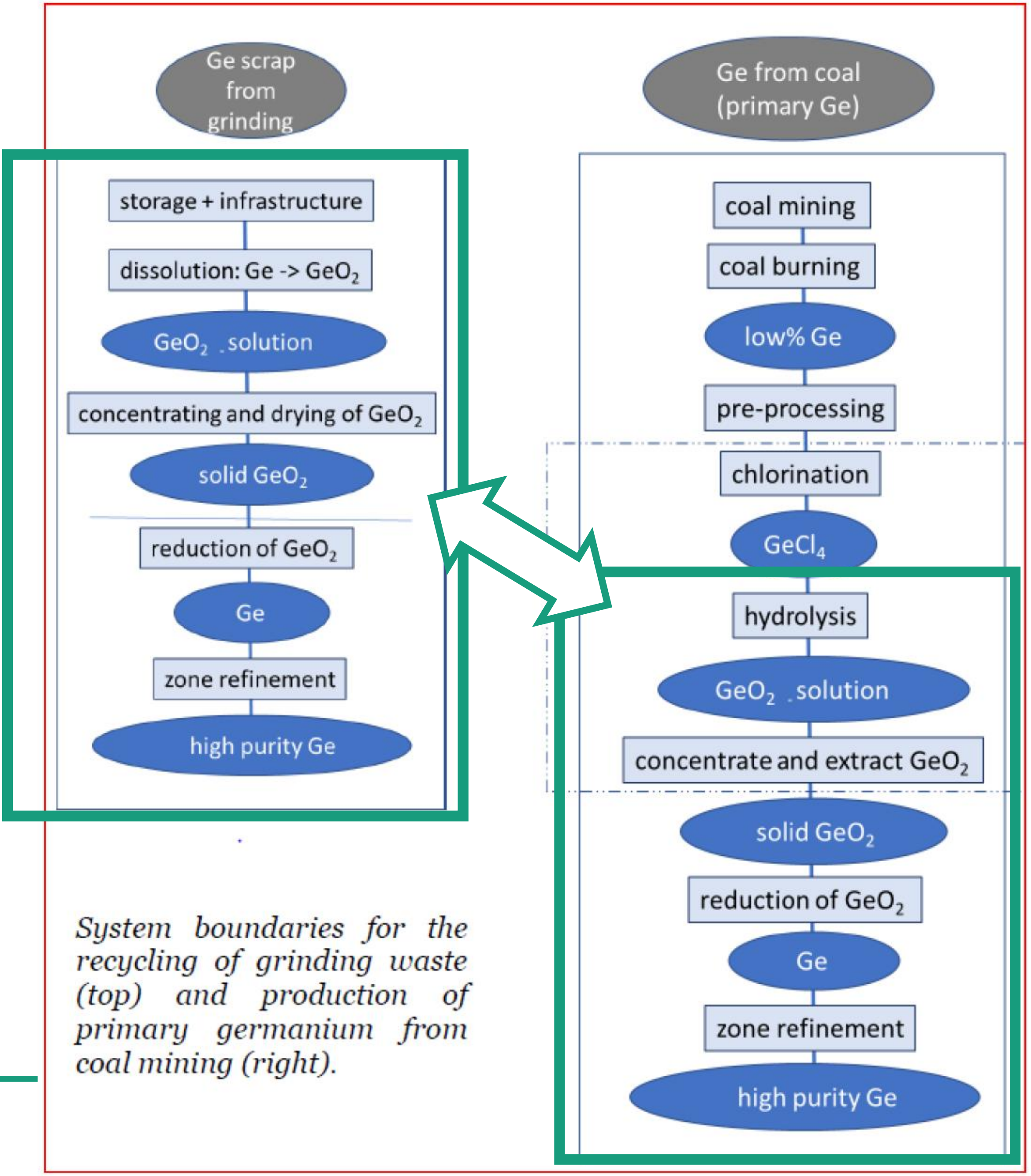


GeSiR
LCA

- The data from Fraunhofer CSP will set in comparision to the work of *B. Robertz et al.: The primary and secondary production of germanium: a life-cycle assessment of different process alternatives.*

- Our recycling concept is equivalent to the part following "hydrolysis" in the Ge exploitation of primary germanium.

Figure 1: Schematic process description



System boundaries for the recycling of grinding waste (top) and production of primary germanium from coal mining (right).

Recommendations

100% germanium recovery:

- Option 1: Filtration/Oxidation + Osmosis + evaporation + drying: DI-water + solid GeO_2
  - Osmosis: CAPEX and OPEX is low; evaporator: CAPEX and OPEX rather high
- Option 2: Filtration/Oxidation + Ion-exchanger
  - Ion-exchanger: CAPEX and OPEX is low; regeneration requires skills

Limited germanium recovery:

- Filtration / Ultrafiltration (loosing dissolved GeO_2 and very fine particles)

Summary

- Recovery of germanium from grinding waste water is possible using existing technologies.
- For most processes, CAPEX / OPEX / energy consumption is rather low.
- Combining certain extraction technologies (osmosis + evaporator / filtration + ion exchanger), complete extraction of germanium is possible (together with DI-water).
- DI-water can be re-used for the grinding process.
- The results might be transferred to waste stream from other germanium manufacturing processes.