The PLATIRUS PGM recycling flowsheet: MW leaching – Ionic liquid solvent extraction – Gas diffusion electrocrystallization

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Outline

- MW-leaching
- Solvent extraction with ionic liquids
- Gas diffusion electrocrystallization
- Integrated PLATIRUS flowsheet

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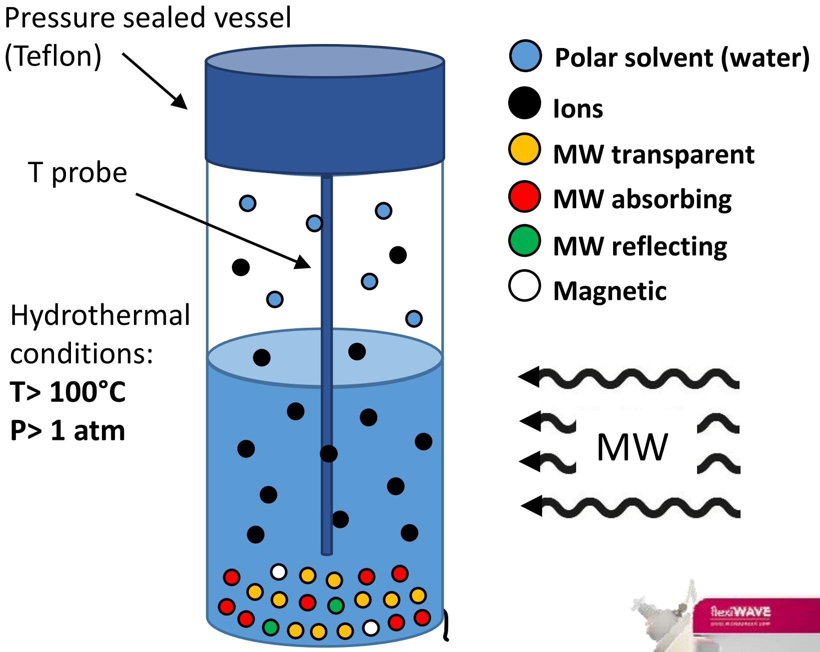
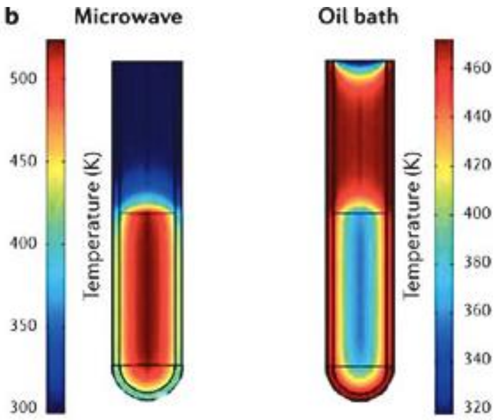
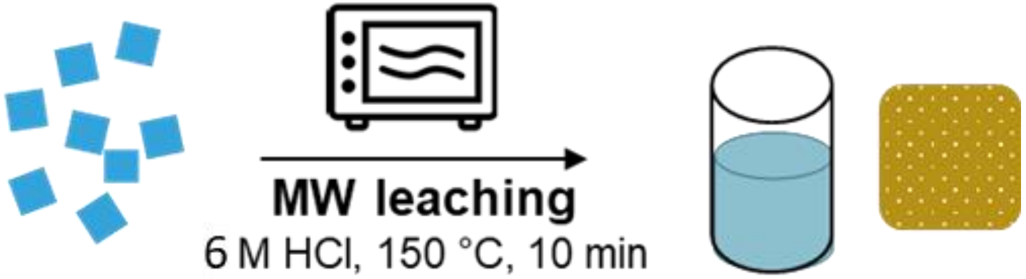
MW-leaching: Technology concept and description



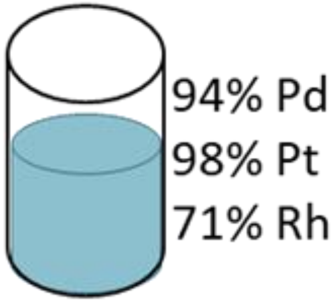


https://www.intechopen.com/books/microwave-heating/microwave-synthesis-a-physical-concept

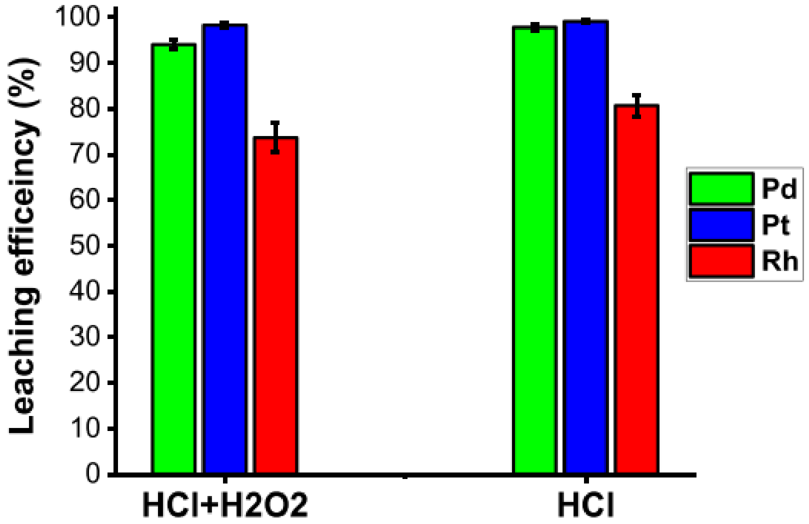


Cordierite ($Mg_2Al_4Si_5O_{18}$)
Wash coat (CeO_2, ZrO_2)
PGMs (Pd, Pt, Rh)

Cordierite ($Mg_2Al_4Si_5O_{18}$)
Mullite (Al-silicate)



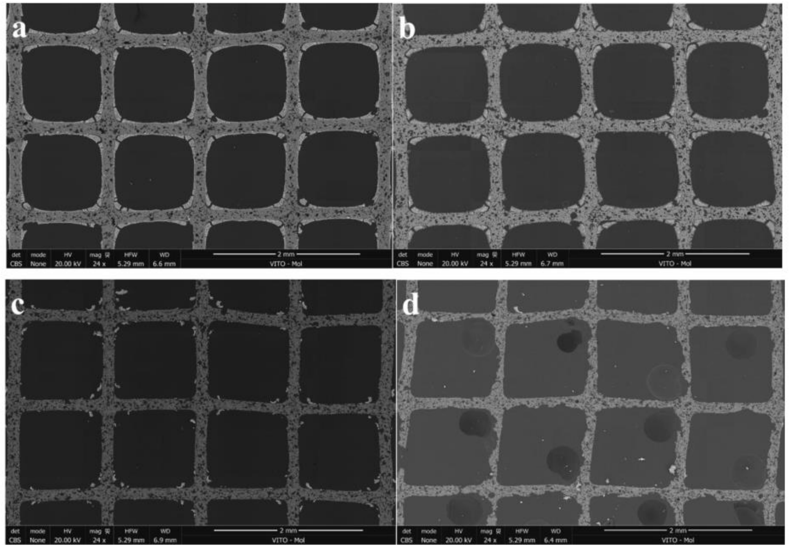
MW-leaching: Main achievements



MW leaching of milled ceramic catalysts:

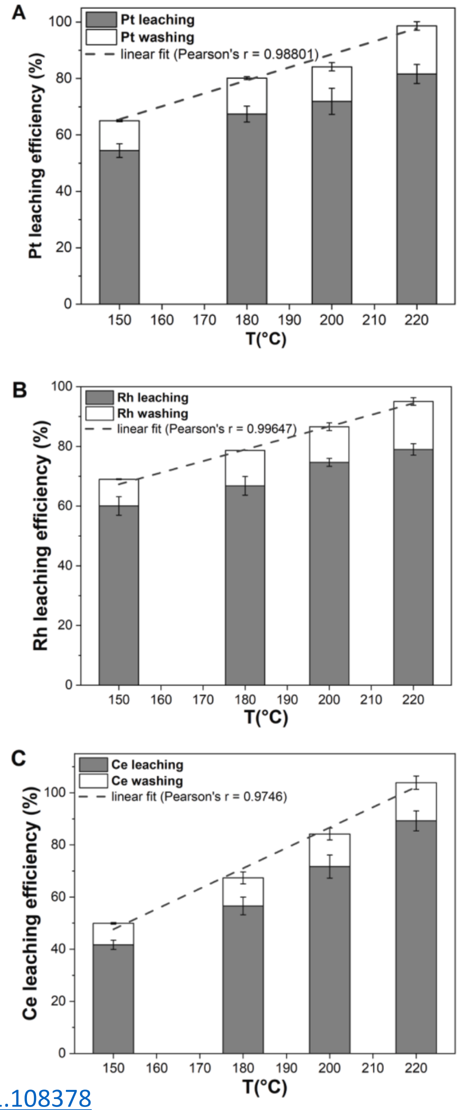
- Fast: 10 min leaching (150 °C)
- Less chemicals required:
  - 6 M HCl (vs. 12 M HCl)
  - No oxidation agent needed!

Abo Atia, T., et al., *Resour. Conserv. Recy.* ***2021, 166***, 105349**.**
10.1016/j.resconrec.2020.105349



MW leaching of non-milled ceramic catalysts:

- Very fast: 3 min leaching (220 °C)
- Less chemicals required:
  - 6 M HCl (vs. 12 M HCl)
  - No oxidation agent needed!
- No stirring needed, filtration facilitated



Abo Atia, T.; Spooren, J., *Chem. Eng. Process.* ***2021, 164***, 108378**.** 10.1016/j.cep.2021.108378

MW-leaching: Main achievements

~50g/batch(1L)

TRL 5

Metallic foil catalysts
WEEE (capacitors)
Anode slime
→ 1st leaching step → 2nd MW-leaching step (150 °C) → PGM rich leachate

Feed	1st leaching step		2nd leaching step			
	Leaching conditions	Removed main impurities	Leaching conditions	Metal recovery (%)		
				Rh	**Pd**	**Pt**
Metallic foil catalyst	MW-leaching in dilute acid	**Fe**, Al, Ca, Ce, Cr, Ni, Zn	6 M HCl + H_2O_2	**73.2±0.8**	**90±1**	**91±3**
WEEE (capacitors)	MW-leaching in dilute acid	Ba, Fe, Ni, Pb, Sn, Ti, Zn	6 M HCl + H_2O_2	**/**	**95±1**	**/**
Anode slime	Room-temperature alkaline leaching	**As**, Cu, Pb, Sn	6 M HCl	**77**	**96**	**84**

Future work:

- Scaling up of microwave assisted leaching
- Further reduce the HCl concentration
- (Re)cycling of leachates

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- Solvent extraction with ionic liquids
- Gas diffusion electrocrystallization
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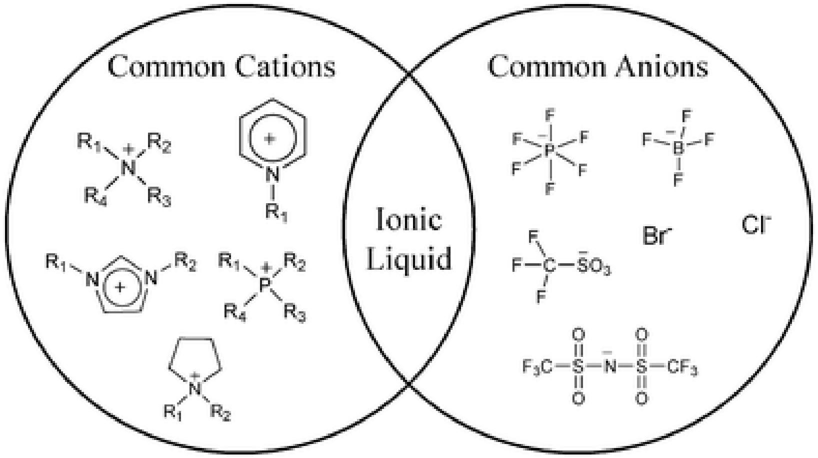
IL solvent extraction: Technology concept and description

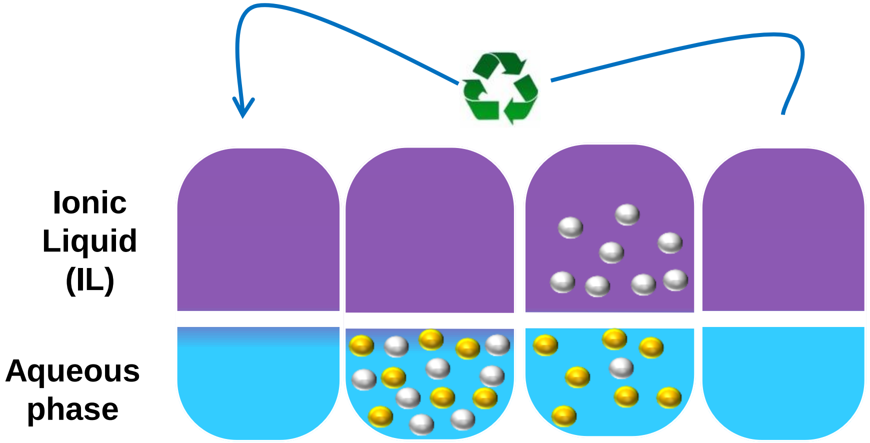
IONIC LIQUIDS

Ionic Liquids (IL) are organic salts which consist entirely of ions

METAL SOLVENT EXTRACTION

A method to separate metal complexes, based on their chemical properties, using an extractant and two immiscible liquids



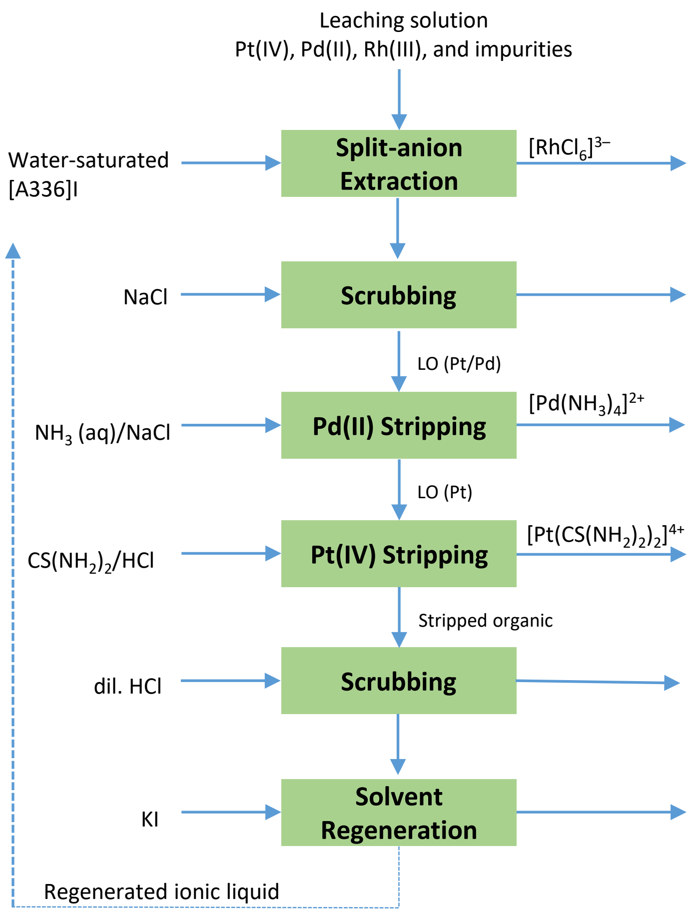


- Negligible vapor pressure
- High thermal stability
- Do not accumulate static electricity
- Selective and efficient in solvent extraction
- Sometimes greener and safer than molecular solvents

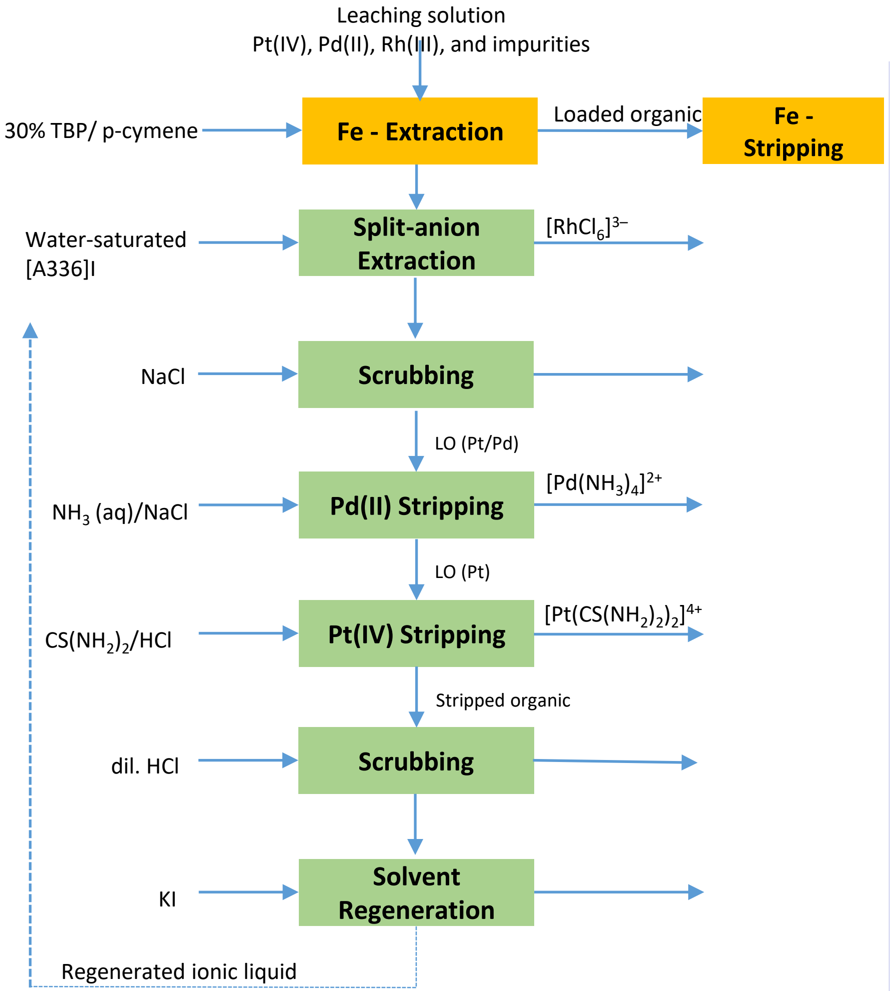
- Capability to separate even very similar elements: several different extractants are available
- Low energy consumption
- Easy continuous operation
- Large production capacity
- High selectivity

IL solvent extraction: Main achievements

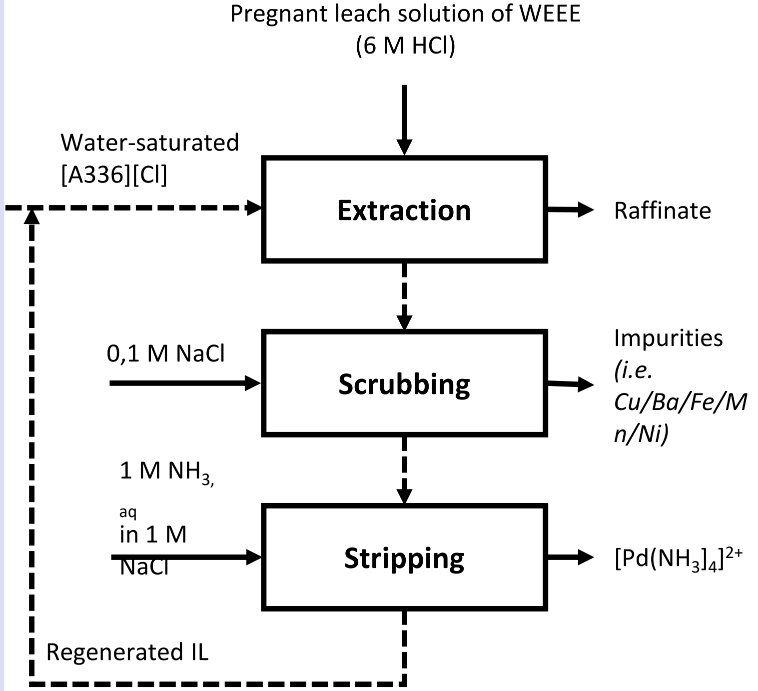
Ceramic catalyst



Metallic foil catalyst



WEEE



IL solvent extraction: Main achievements

Solvent extraction with ionic liquids: application on different feeds

Feed	Number of steps	Metal recovery (%)			Main impurites in output solutions		
		Rh	Pd	Pt	Raffinate	Stripping-Pd	Stripping-Pt
Ceramic	4	**54**	**81**	**62**	Al, Ce, Mg, and Zr	Zn	Ca, Al (< 1.0 ppm)
Metallic foil	5	**77**	**95**	**79**	Al, Ba, Ce, Cr, La, and Nd	As, Cu, and Zn	Al, Ca and Zn (< 10 ppm)
WEEE	3	**n/a**	**94**	**n/a**	Ba, Ca, Cu, La, Nd, Ni, Ti, and Zr	As and Zn	n/a

- It is possible to purify Rh, Pd and Pt
- **Pd and Pt can particularly be stripped with high purity**
- Rh purity could be improved if the pregnant leach solution comes more concentrated
- **The process can be run in continuous mode using mixer-settlers**
- **Only one extractant is needed, the separation is mainly based on scrubbing and selective strippings**
- The ionic liquid is stable and can be recycled
- Further optimization in pilot plant is required to bring the technology closer to the market

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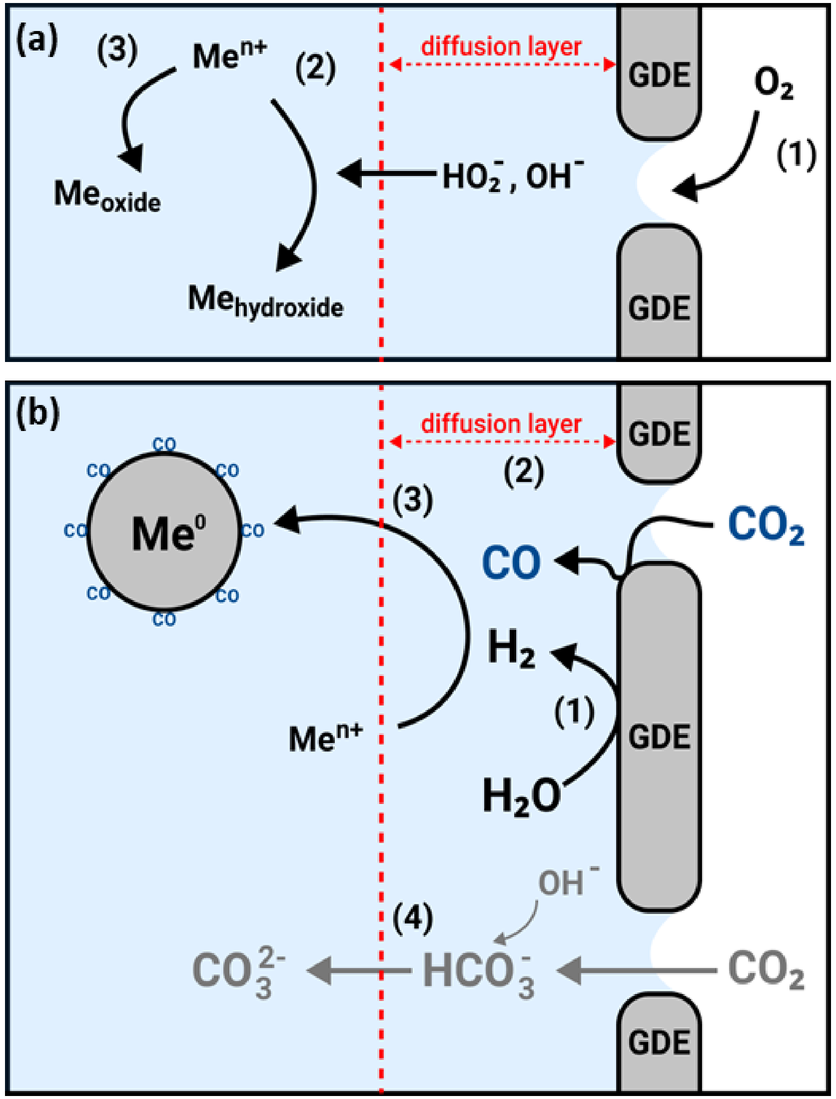
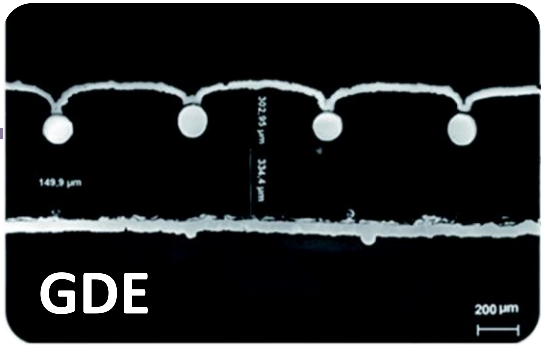
GDEx: Technology concept and description





- Process of reactive precipitation of metals in solution with intermediaries issued from the electrochemical reduction of gases, at GDEs
- Fast, economical, efficient and sustainable technology for the removal and recovery of dilute metals and metalloids from fluids (wastewater, brines, leachates, … , solvents)
- Tackles unique challenges that no unique BAT can deal with effectively and economically
    - Optimal for dilute metal concentrations
    - < 10 g L-1, preferably at ppm level
- Selective recovery from complex matrices
- GDEx meets discharge limits & effectively recovers the targeted metals into products that can be integrated within existing processing chains

GDEx: Qualitative benchmark vs BAT

Criteria	Technologies					
	Coagulation and flocculation	Precipitation (e.g., pellet crystallization)	Electrocoagulation and electroflotation	Membrane electrolysis	Electrodeposition or electrowinning	GDEx
Chemical addition	Essential (high)	Essential (high)	No	No	Sometimes	No
Sludge formation	High	Medium to low	Medium to low	No	No	No
Selectivity	High	Medium to high	Low	Possible to high	Possible to high	Possible to high
Investment	Low	Medium to high	Medium	Medium	Medium to high	Medium to low
Operational costs	Very high	Very high	Very high	Medium to high**	Medium to low**	Low
High volumes	Discouraged	Yes	Discouraged	Discouraged	Yes	Yes
Metal concentration	High	Medium to high	High	Medium to very low	Medium to high	Medium to very low
Complex and varying matrices	No	Possible to yes	No	Possible to yes	Possible to yes	Possible to yes
Pre-treatment needed	pH correction	pH correction	Conductivity corr.	Conductivity & pH corr.	Not significant	Not significant
Expected effectiveness	>60%	>90%	Below 60%	>90%	>90%	>90%
Product can be valorized	No	Sometimes	No	Sometimes	Yes	Yes
Environmental issues	Yes (polluted sludge)*	No	Yes (sludge, but easier)*	Yes (chlorine)	Yes (toxic products)	Sometimes (chlorine)
Complexity	High	Medium to low	High (complexation)	High	Medium	Medium
Automation	Possible	Possible	Possible	Possible	Possible	Possible
Component replacement	No	Yes (seeding material)	Sporadic	High (membranes)	Sporadic	Sporadic

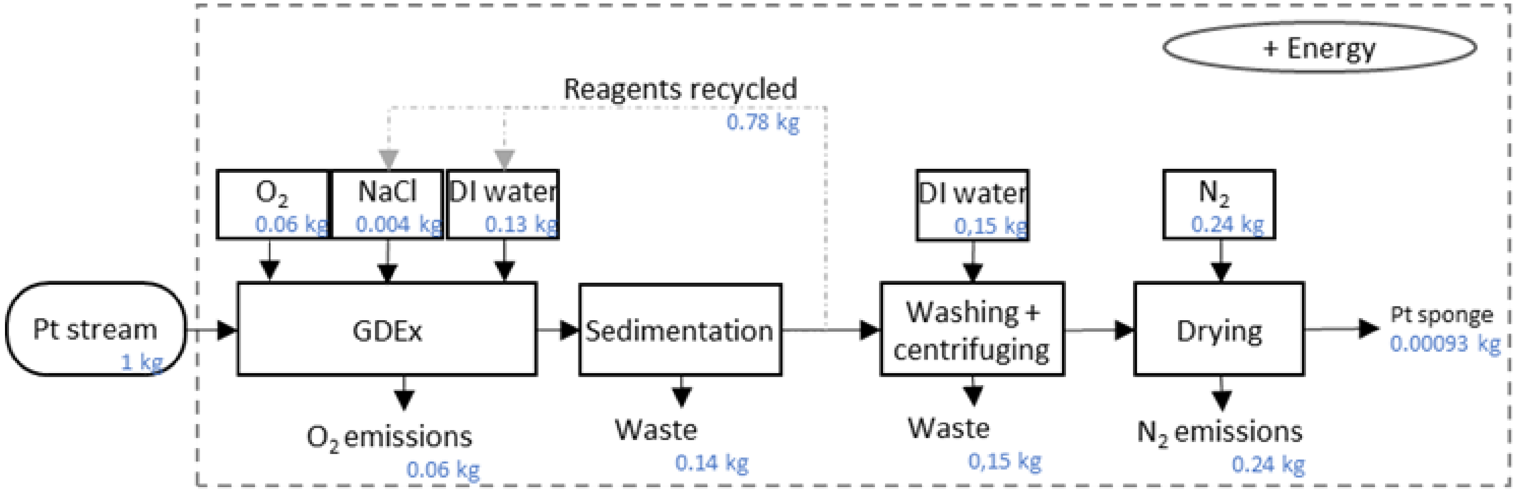
Flemish Knowledge Centre for Best Available Techniques[1], WASS (water treatment selection system)[2] → decision support tool

→ Diverse BAT physicochemical treatments *vs* new electrochemical methods *vs* GDEx

** *very high for very low metal concentrations*

GDEx: Main achievements

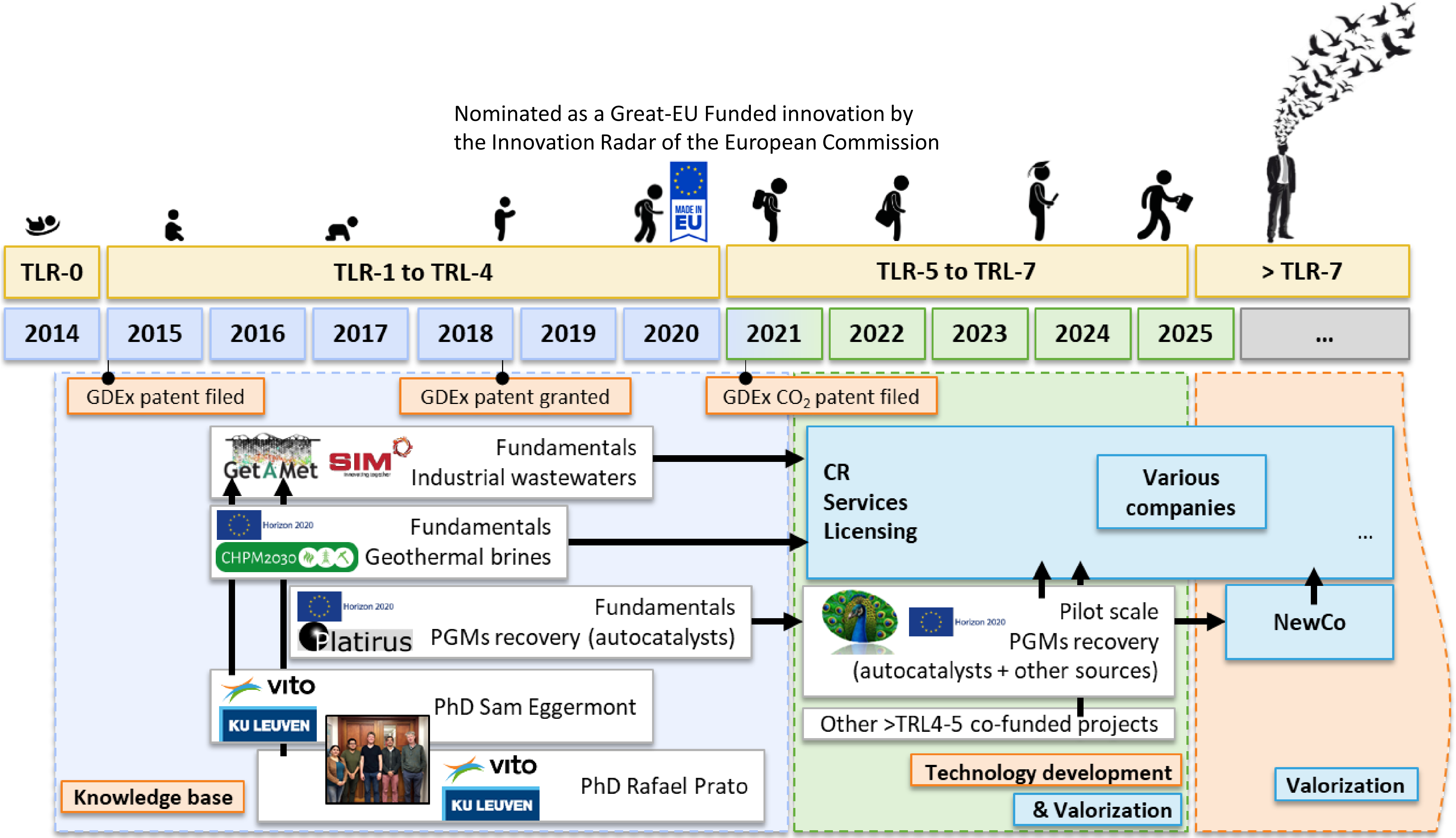
- Processing of Batch A



- GDEx (fed with CO_2) attained a recovery of ~70 ± 1% of Pd from the KU Leuven strip sample.
- Pd was recovered with a purity of 91–93%, with Pt, Rh and Al as the major impurities, and additional minor impurities of Ba, Fe, Mg, Co and Cu.
- The Pd^0 sponge generated by GDEx was redissolved to Pd nitrate for ultimate recycling on the remanufacturing of catalytic converters, which despite the small impurities performed better than the conventional ones.

- 1 publication accepted, 2 in preparation
- The key GDEx patent EP3242963B1 has been granted in Europe in the course of Platirus (priority 2015)
- A patent has been filled within the Platirus project: EP21165681 Recovery of PGMs & preparation of PGM nanoparticles with GDEx fed by CO_2

GDEx: Research & valorization roadmap for metal recovery



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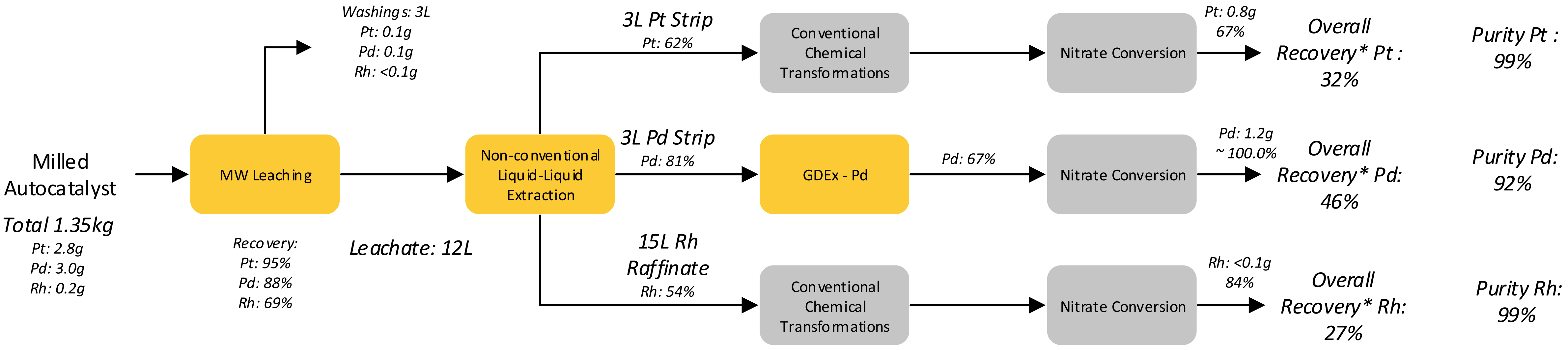
Integrated PLATIRUS process



Nicol, G.; *et al.*, Platinum Group Metals Recovery Using Secondary Raw Materials (PLATIRUS): Project Overview with a Focus on Processing Spent Autocatalyst. *Johnson Matthey Technolo. Rev.* ***2021, 65 (1), 127-147.*** https://doi.org/10.1595/205651321X16057842276133

Conclusions

- The selected PLATIRUS process was tested in cascade on milled spent ceramic catalyst material, and consists of:
  - **MW-assisted leaching**:
    Overall ~1.35 kg material was leached in 6 M HCl
  - **IL solvent extraction**:
    12 L of leachate processed by a continuous solvent extraction demonstrator, using multi-stage mixer-settlers
  - **Gas diffusion electrocrystallization**:
    Recovered ~70% of Pd from the strip sample with a purity of 91-93%

- Each individual technology reached TRL 5, whereas the overall PLATIRUS flowsheet was tested at TRL 4

- Further optimization and upscaling of all 3 processing steps is planned

Main Contacts

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