Joint Workshop on Scale-up of Pd Membrane Technology
20 November 2014, ECN – Petten, NT

Plant for the recovery of metallic supports from membranes used in ultra-pure hydrogen production

KT Kinetics Technology

High Tech Recycling HTR
SAPIENZA
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ECO Recycling

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Hydrogen Applications:

- Reagent in hydrogenation processes in the petrochemical industry
- Reagent for the removal of oxidizing agents in metallurgy
- Coolant or fuel
- Energetic carrier

→ **GREEN ECONOMY**

Hydrogen Production Methods:

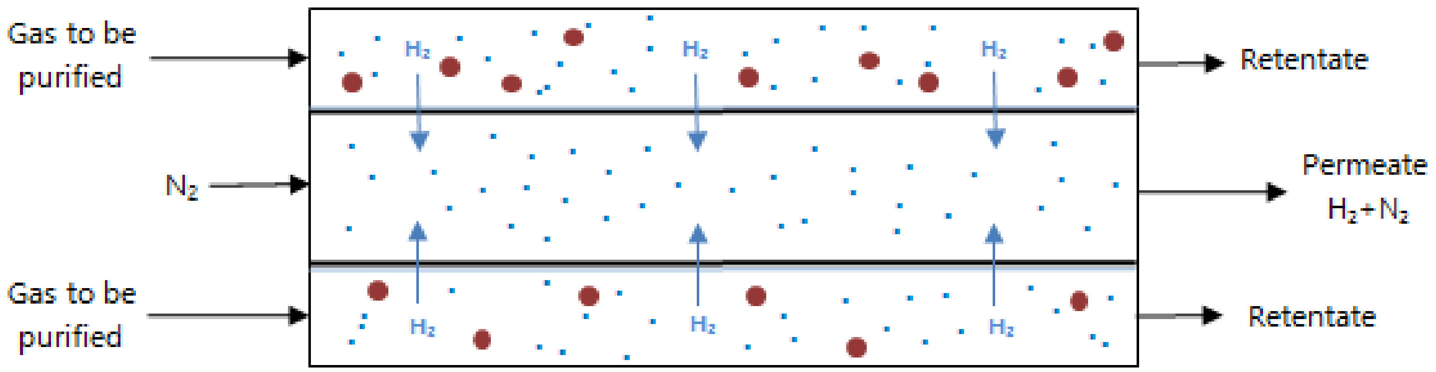
- Electrolysis of water
- Non-catalytic partial oxidation of hydrocarbons
- Coal gasification
- Reforming of hydrocarbons, especially methane

→ **FLUE GAS AND FOSSIL CONSUPTION**

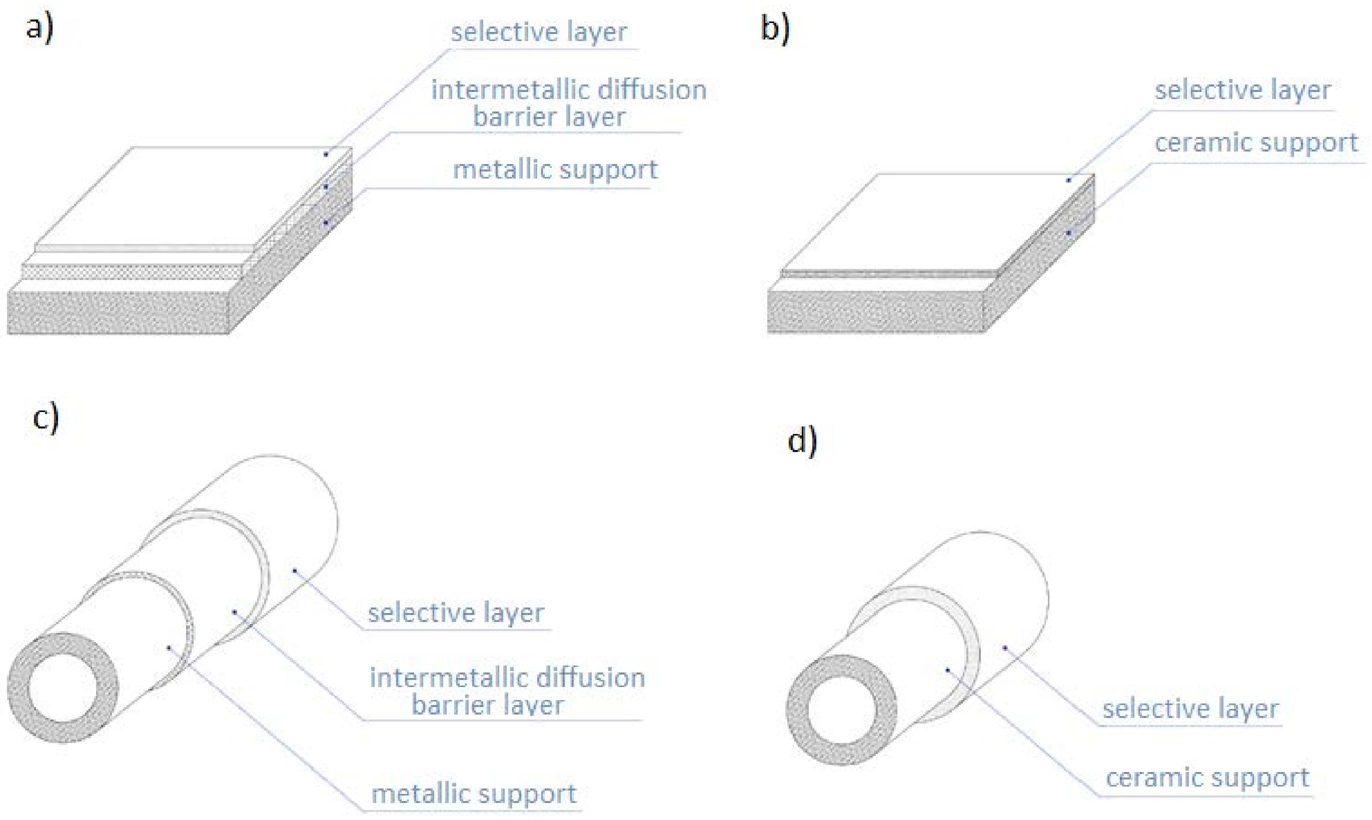
H_2 separation requirements:

- Purity
- Versatility
- Cheapness

MEMBRANE REACTOR



Gas permeation through a membrane



- *Membrane module cost:* 3000-10000 €/m^2
- *Selective layer:* Pd or Pd/Ag (23%wt)
- *Substrates:*
  - Ceramic layer
  - Asymmetric stainless steel layer + intermetallic diffusion barrier

Selective layer: Pd-Ag

Support: AISI 316 L

Intermetallic barrier: TiN

Structure: tubular

Job Purpose

- Membrane's support recovery
- Palladium and silver recovery from leaching solution
- Identify possible improvements in membranes' production cycle to simplify the recovery/recycling of various membranes' components
- Pilot plant building

Activity

- 'State of the art' analysis of hydrometallurgical extraction of Pd and Ag
- Samples characterization, experimental leaching tests and results analysis (AAS e SEM)
- Pilot plant design

Palladium Leaching

Article	Support	Reagents	Concentration	T (°C)	t (h)	Recovery Pd %
1	Waste printed circuit boards (WPCB)	1step: thiourea-Fe^{+3}-H_2SO_4	20g/L-6g/L-10g/L	25	3	2,13
		2step: NaClO-HCl-H_2O_2	10%v-5M-1%v	63	3	97,87
2	Automotive catalyst residue	HCl-H_2O_2	11,6mol/L-1%vol	65	3	100
		NaClO-HCl-H_2O_2	3%vol-5Kmol/m^3-1%vol	65	3	98,7
		NaClO-HCl	3%vol-5Kmol/m^3	65	3	96,6
3	Spent automotive catalysts	HCl-$AlCl_3$-ag.ox	15%w/w-0,33%w/w-ag.ox	90	1,5	99
4	Spent catalytic converters	HCl-CuCl·$2H_2O$	6M-0,3M [Cu^{+2}]	80	4	95
5	Car catalytic converters	HCl-HNO_3-H_2SO_4-NH_4F	12M-15M-18M	90	6	>95 (PGM)
		HCl-H_2O_2-H_2SO_4-NH_4F	12M-110vol-18M	90	6	>95 (PGM)

1) Process development for recovery of copper and precious metals from waste printed circuit bards with emphasize on palladium and gold leaching and precipitation. ***Behnamfard, 2013***
2) Leaching of Pt, Pd and Rh from Automotive Catalyst Residue in Various Chloride Based Solutions. ***Sri Harjanto, 2006***
3) Microfluidic solvent extraction of platinum and palladium from a chloride leach solution using Alamine 336. ***Chun-Yang Yin, 2012***
4) Oxidative leaching process with cupric ion in hydrochloric acid media for recovery of Pd and Rh from spent catalytic converters. ***C.A. Nogueiraa, 2014***
5) Recovery by hydrometallurgical extraction of the platinum-group metals from car catalytic converters. ***D. Jimenez de Aberasturi, 2011***

Silver Leaching

Article	Support	Reagents	Concentration	T (°C)	t (h)	Recovery Ag %
1	Waste printed circuit boards (WPCB)	1step: H_2SO_4-H_2O_2	2M-20v%(35%)	25	3	0.86
		2step: H_2SO_4-H_2O_2	2M-20v%(35%)	25	3	11,37
		3step: thiourea-Fe^{+3}-H_2SO_4	20g/L-6g/L-10g/L	25	3	71,36
2	Lead/zinc flotation tailings	Thiosulfate-$CuSO_4$	0,15M-0,076M	-	2	60
3	Copper anode slime	HNO_3	4M	90	3	96,25
4	PCB of waste mobile phones	Thiourea-Fe^{+3}-H_2SO_4	24g/L-0,6%-0,5M	25	2	50
5	Ag_2S	$(NH_4)_2S_2O_3$-$(NH4)_2SO_4^-$-$CuSO_4$	0,125M-tot.amm.0,35M-10mM	35	24	Ag
6	Ag	$(NH_4)_2S_2O_3$-$CuSO_4$+$(NH_4)_2SO_4$-EDTA	0,1M-0,05M-0,6M-$1,25 \cdot 10^{-4}$M	25	0,3	≈100
7	PCB of waste mobile phones	$(NH4)_2S_2O_3$-$CuSO_4$-$(NH_4)^+$	0,12M-20mM-0,2M	25	2	98 Au
8	WPCB	Thiourea-Fe^{+3}-H_2SO_4	20g/L-6g/L-10g/L	25	3,5	69 Au
	Pins 30%wt Au	Thiourea-Fe^{+3}-H_2SO_4	20g/L-6g/L-10g/L	25	3,5	82,1 Au

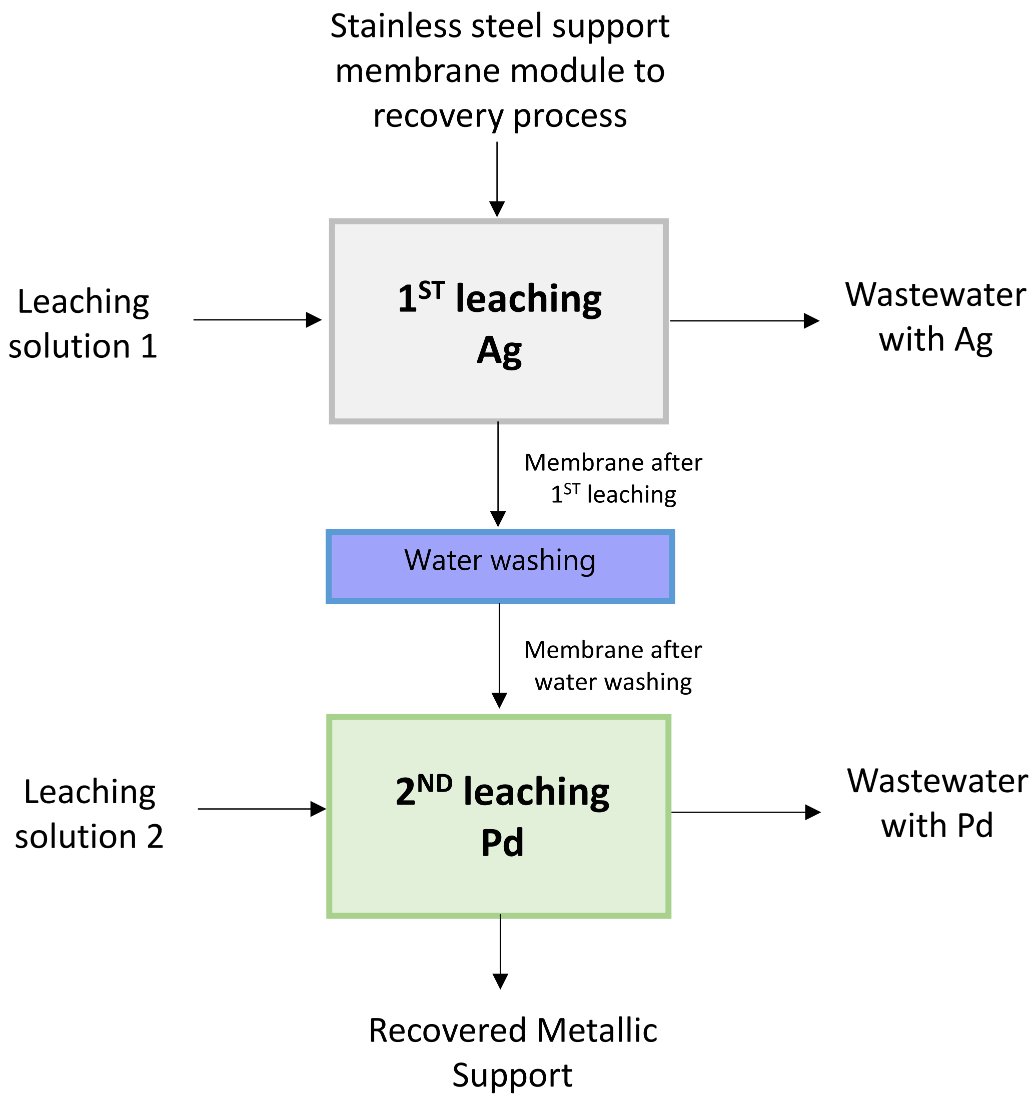
1) Process development for recovery of copper and precious metals from waste printed circuit bards with emphasize on palladium and gold leaching and precipitation. ***Behnamfard, 2013***
2) Recovery of silver from lead/zinc flotation tailings by thiosulfate leaching. ***Chieng, Pau, 2006***
3) Ag recovery from copper anode slime by acid leaching at atmospheric pressure to synthesize silver nanoparticles. ***Atefeh Khaleghi, 2013***
4) Thiourea leaching gold and silver from the printed circuit boards of waste mobile phones. ***Li Jing-ying, 2011***
5) Silver sulfide leaching with thiosulfate in the presence of additives: Copper-Ammonia. ***Deutsch, 2013***
6) A kinetic–thermodynamic study of silver leaching in thiosulfate–copper–ammonia–EDTA solutions. ***Puente-Siller, 2012***
7) Thiosulphate leaching of gold from waste mobile phones. ***Vinh Hung Ha, 2009***
8) Study on the influence of various factors in the hydromettallurgical processing of waste printed circuit boards for copper and gold recovery. ***Birloaga, 2012***

** Leaching solution 1:*

- $(NH_2)_2CS$=24 g/l
  Fe_2SO_4=0,6 %
  H_2SO_4=0,5 M
  H_2O dist.
- $(NH_4)_2S_2O_3$=0,1 M
  $CuSO_4$=0,05 M
  $(NH_4)_2SO_4$=0,6 M
  H_2O dist.

** Leaching solution 2:*

- HCl=12 M
  H_2O2 (30%v)= 1%v
- HCl=12 M
  NaClO=3%v
  H_2O_2(30%v)= 1%v
  H_2O dist.



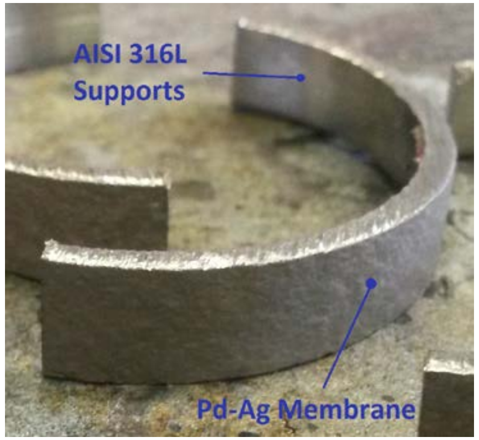
** Process variables:*

- **Leaching 1:**
  - T=25°C
  - P=1 atm
  - pH=10,2
  - τ=30 min
- **Leaching 2**
  - T=60 °C
  - P=1 atm
  - pH=1,2
  - τ=180 min

*** Literature conditions to be tested in laboratory**

Materials

- *Characteristics of samples:*
  - Metallic support: porous AISI 316L
  - Intermetallic barrier: TiN, thickness 2 µm
  - Selective layer: Pd/Ag, thickness 3 µm
- *Preparation of samples:*
  - Epoxy resin layer on membrane support



Sample

Methods

- *Mineralization (different solvents)*
- *Leaching:*
  - Jacketed reactor magnetically agitated
  - Thermostat
  - Sample fastened to a support via a nylon wire
  - Solutions are characterize with atomic absorption technique and solid by SEM analysis

Leaching test

Mineralization:

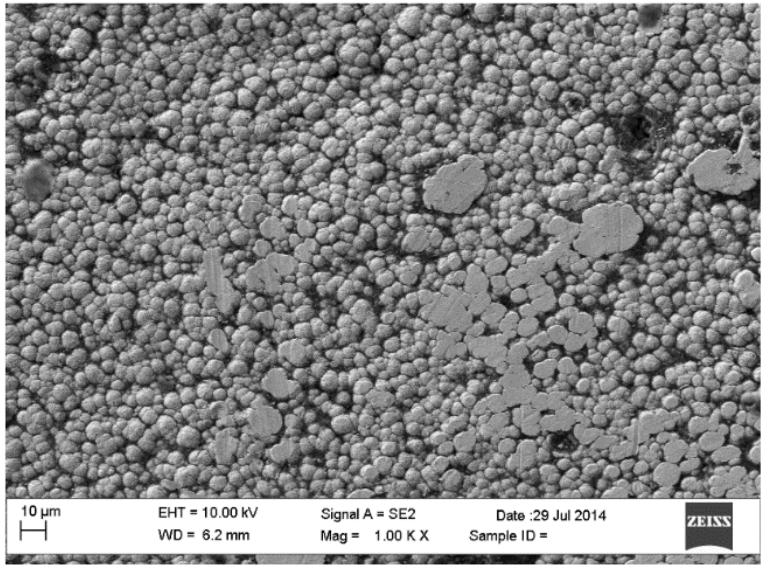
Test	Solvent
Min. I	HNO_3
Min .II	Aqua Regia
Min. III	H_2SO_4

PALLADIUM: 1,2 mg_{Pd}/g_{Sample}

SILVER: 0,3 mg_{Ag}/g_{Sample}

Morphological characterization of the Pd-Ag membrane:

Element	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error [wt.%]
C	24,29	25,75	75,49	3,25
Pd	58,24	61,74	20,42	2,06
Ag	11,8	12,51	4,08	0,5

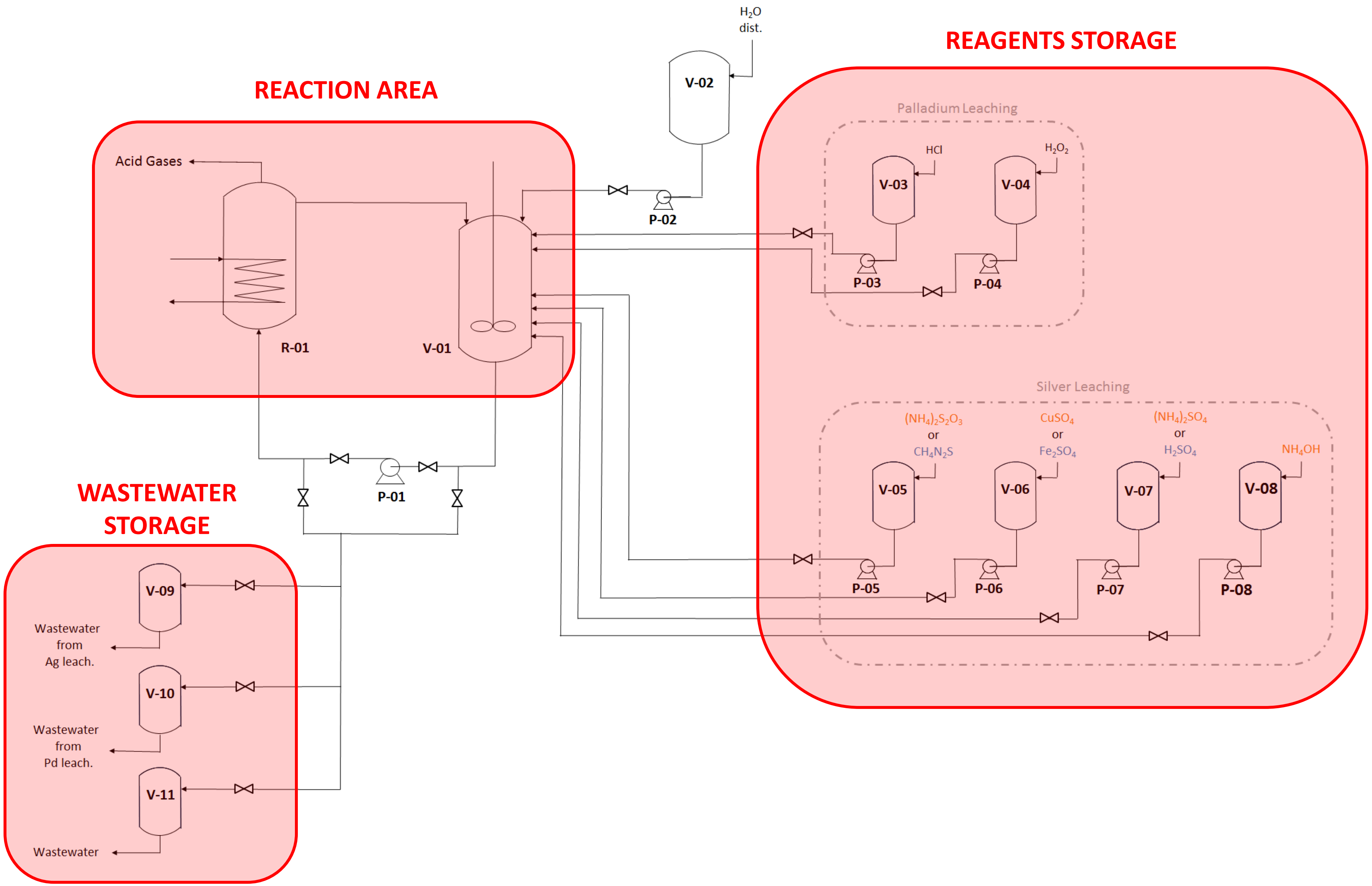


Leaching test

Experiment	Reagents	Pd %	Ag %	Notes
Leaching I	HCl - H_2O_2	n.p.	-	No epoxy resin on sample
Leaching II	HCl - H_2O_2	n.p.	n.p.	No dissolution of targets, Ti traces on the sample surfaces (SEM)
Leaching III	CH_4N_2S - $Fe_2(SO_4)$ - H_2SO_4	-	3,9	Ti traces on the sample surfaces (SEM)
Leaching IV	$(NH_4)_2S_2O_3$ - $(NH_4)_2SO_4$ - $CuSO_4$ - NH_4OH	-	11,7	Precipitates in solution
Leaching V	HCl - H_2O_2	2,1	-	Detachement of Pd-Ag e TiN
Leaching VI	CH_4N_2S - $Fe_2(SO_4)$ - H_2SO_4	-	2,4	Precipitates in solution, Ti traces on the sample surface (SEM)
Leaching VII	$(NH_4)_2S_2O_3$ - $(NH_4)_2SO_4$ - $CuSO_4$ - NH_4OH	-	n.p.	-
Leaching VIII	HCl - H_2O_2	1,9	n.p.	Detachment of Pd-Ag e TiN

Conclusion measurements of metals in solution and SEM analysis:

- Coating detachment with the most aggressive solution (Leaching V, VIII)
- Detachment of both Pd-Ag membrane and interdiffusion barrier TiN
- Membrane was not leached by the silver leaching solution


REACTION AREA
REAGENTS STORAGE
WASTEWATER STORAGE
Acid Gases
R-01
V-01
H2O dist.
V-02
P-02
Palladium Leaching
HCl
H2O2
V-03
V-04
P-03
P-04
Silver Leaching
(NH4)2S2O3 or CH4N2S
CuSO4 or Fe2SO4
(NH4)2SO4 or H2SO4
NH4OH
V-05
V-06
V-07
V-08
P-05
P-06
P-07
P-08
P-01
V-09
Wastewater from Ag leach.
V-10
Wastewater from Pd leach.
V-11
Wastewater

- Establish the leaching reagent that increase the target metals dissolution rate
- Testing Pd-Ag extraction process at different temperature and reagent concentrations
- Design the process for palladium and silver recovery from wastewater
- Pilot plant optimization

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Thank you

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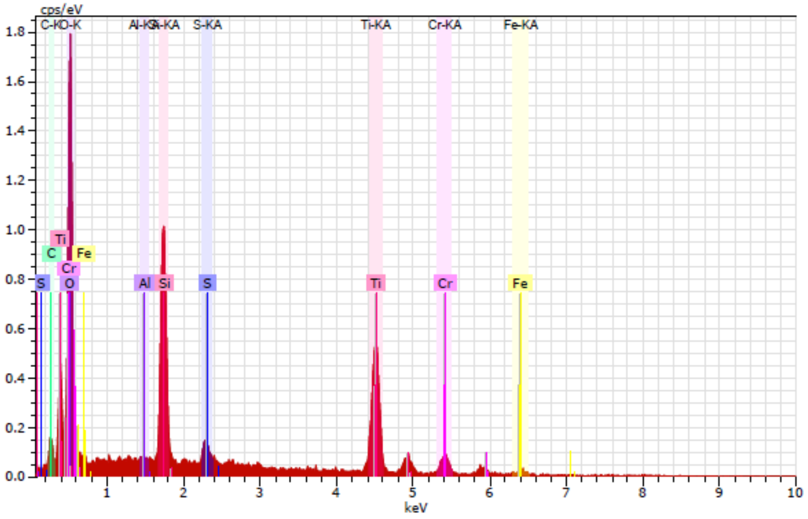
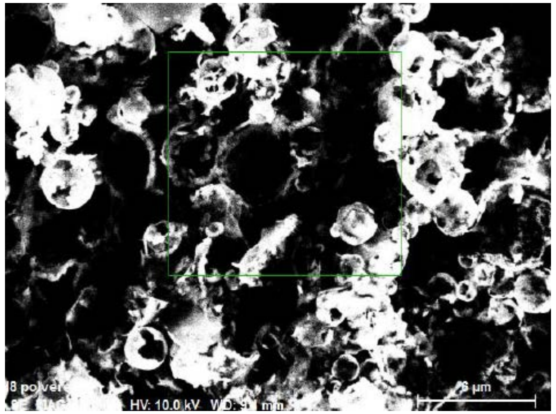
Leaching VIII substrate

El	AN	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
O	8	K-series	29.19	35.26	56.06	3.77
Fe	26	K-series	26.31	31.78	14.48	1.41
C	6	K-series	5.57	6.73	14.25	1.10
Cr	24	K-series	9.06	10.95	5.36	0.47
Cl	17	K-series	4.97	6.00	4.31	0.22
Si	14	K-series	2.79	3.37	3.05	0.16
Ni	28	L-series	2.19	2.65	1.15	0.53
Mo	42	L-series	1.95	2.35	0.62	0.13
Ca	20	K-series	0.41	0.50	0.32	0.06
Mg	12	K-series	0.23	0.28	0.29	0.05
Al	13	K-series	0.10	0.13	0.12	0.04
		Total:	82.77	100.00	100.00	

Leaching VIII detachment





Leaching III - Thiourea

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Oxygen	K-series	22.37	29.18	37.83	3.04
Carbon	K-series	16.96	22.12	38.20	2.35
Palladium	L-series	15.14	19.74	3.85	0.57
Sulfur	K-series	4.49	5.86	3.79	0.20
Silicon	K-series	6.41	8.36	6.17	0.31
Magnesium	K-series	3.26	4.26	3.63	0.21
Silver	L-series	3.45	4.50	0.87	0.17
Aluminium	K-series	0.31	0.40	0.31	0.05
Iron	K-series	1.44	1.88	0.70	0.21
Nitrogen	K-series	2.17	2.84	4.20	0.57
Calcium	K-series	0.65	0.85	0.44	0.07
	Total:	76.66	100.00	100.00	

Leaching VIII - Thiosulfate

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (1 Sigma) [wt.%]
Oxygen	K-series	27.33	32.83	41.03	3.64
Carbon	K-series	19.87	23.87	39.74	2.76
Silicon	K-series	6.69	8.03	5.72	0.32
Palladium	L-series	12.12	14.57	2.74	0.47
Sulfur	K-series	4.44	5.34	3.33	0.20
Magnesium	K-series	3.94	4.73	3.89	0.24
Calcium	K-series	1.56	1.88	0.94	0.12
Aluminium	K-series	0.49	0.58	0.43	0.06
Silver	L-series	2.49	3.00	0.56	0.14
Copper	L-series	4.03	4.84	1.52	0.76
Iron	K-series	0.27	0.33	0.12	0.10
	Total:	83.22	100.00	100.00	