Recovery of Acids and Metals from Pickling Solutions by Combined Membrane Processes

EU SPIRE Project ReWaCEM

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R&D in Water Treatment

Overview on Skills and Competence

Membrane Technology

- hydrophobic membranes for membrane distillation and related membrane contactors
- electrodialysis membranes and stacks
- scaling and fouling on membranes
- MD module, process and system technology
- liquid-liquid and liquid-gas contactors

Water-Energy Nexus

- PV driven pumping systems
- PV driven reverse osmosis desalination
- PV driven ultrafiltration for purification and disinfection
- solar-, geothermal and waste heat driven membrane distillation (MD) for desalination
- concentrated solar power and multi-effect distillation for desalination

Minerals and Water recovery

- MD for acid recovery in steel plating industry and related processes
- MD for super-concentration of brines before crystallization
- electrodialysis metathesis (EDM) for selective separation of mono and multivalent ions

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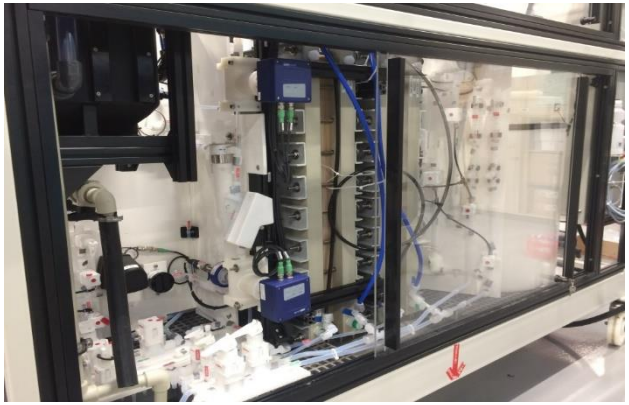
CONTENT

- The Scope of the ReWaCEM Project
- Proces design and technology
- Design and construction of demonstraton systems
- Results and conclusions

Acid and Metal Recovery from Pickling Solutions

Scope of the ReWaCEM Project

Connection of none pressure driven membrane processes for acid, metal salt and water recovery



The scope of the ReWaCEM Project:

- Connection of **D**iffusion **D**ialysis and **M**embrane **D**istillation for acid recovery in steal plating and pickling processes
- Recovery of metal salts by chemical precipitation
- Recovery of fresh water for process reuse
- Total avoidance of liquid discharge

Acid and Metal Recovery from Pickling Solutions

Scope of the ReWaCEM Project

The ReWaCEM Project, 4 Demonstration cases:

Case 1: Recovery of **hydrochloric acid (170g/lt) + metals** from pickling in zinc plating processes **(Feed 13kg/h)**

TecnoZinco
zincatura a caldo
centro lavorazione acciaio

Case 2: Recovery of **sulfuric acid (55g/lt)** from rinsing water in copper coating + Recovery of **water** from precipitation **(Feed 5.6kg/h)**

ELECTRONIQUEL

Case 3: Recovery of **mixed nitric + hydrofluoric acid** (320 / 40 g/lt) **pickling solutions** in the stainless steel industry **(Feed 70kg/h)**

DEUTSCHE EDELSTAHLWERKE

Case 4: Recovery of **gold and Palladium** in printed circuit board industry **(Feed 345 l/h)**

AT&S

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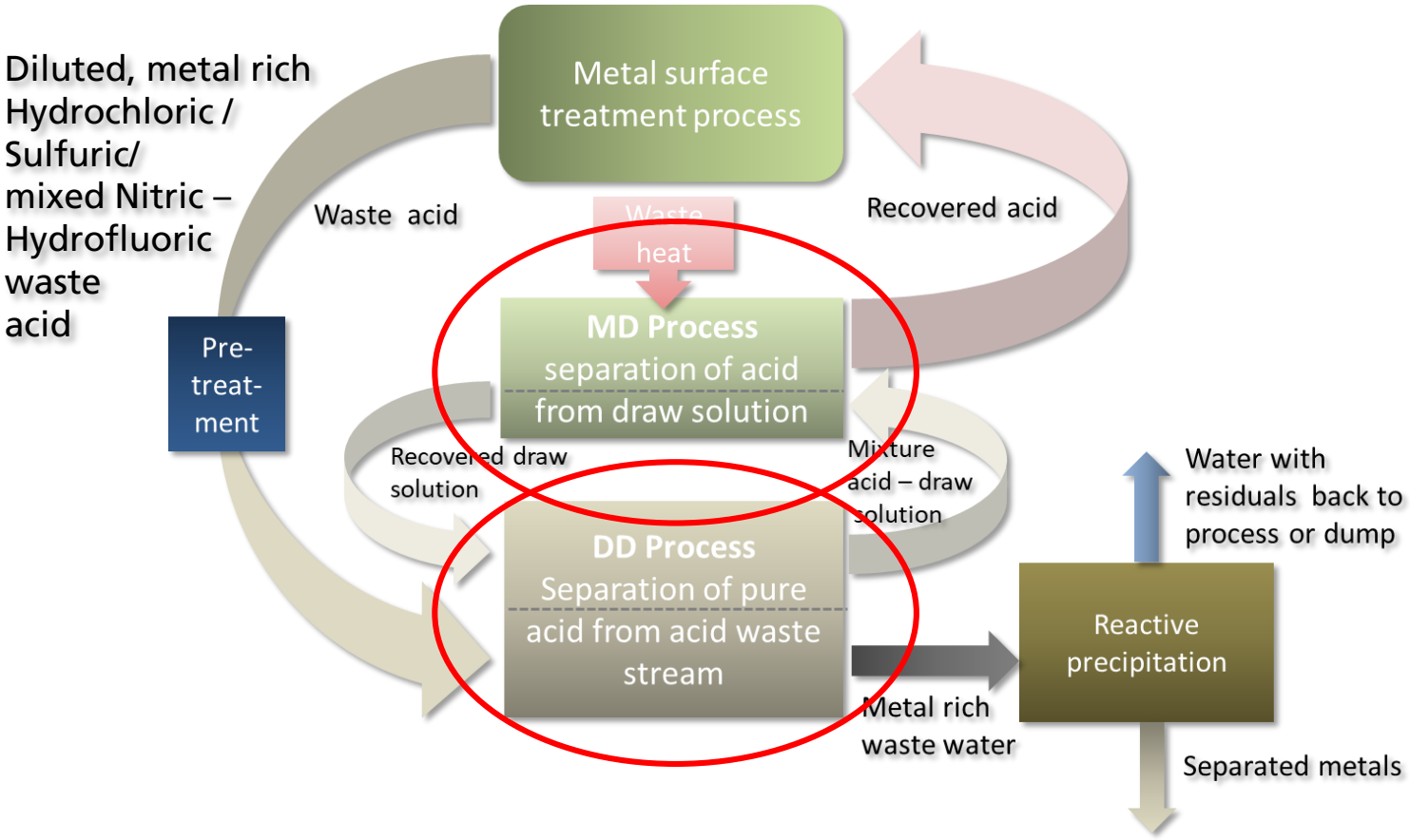
Process Design for Acid and Metal Recovery

Combined Membrane Processes and Reactive Precipitation

Core technology for the recovery and concentration of HCl, mixed HNO_3-HF and H_2SO_4



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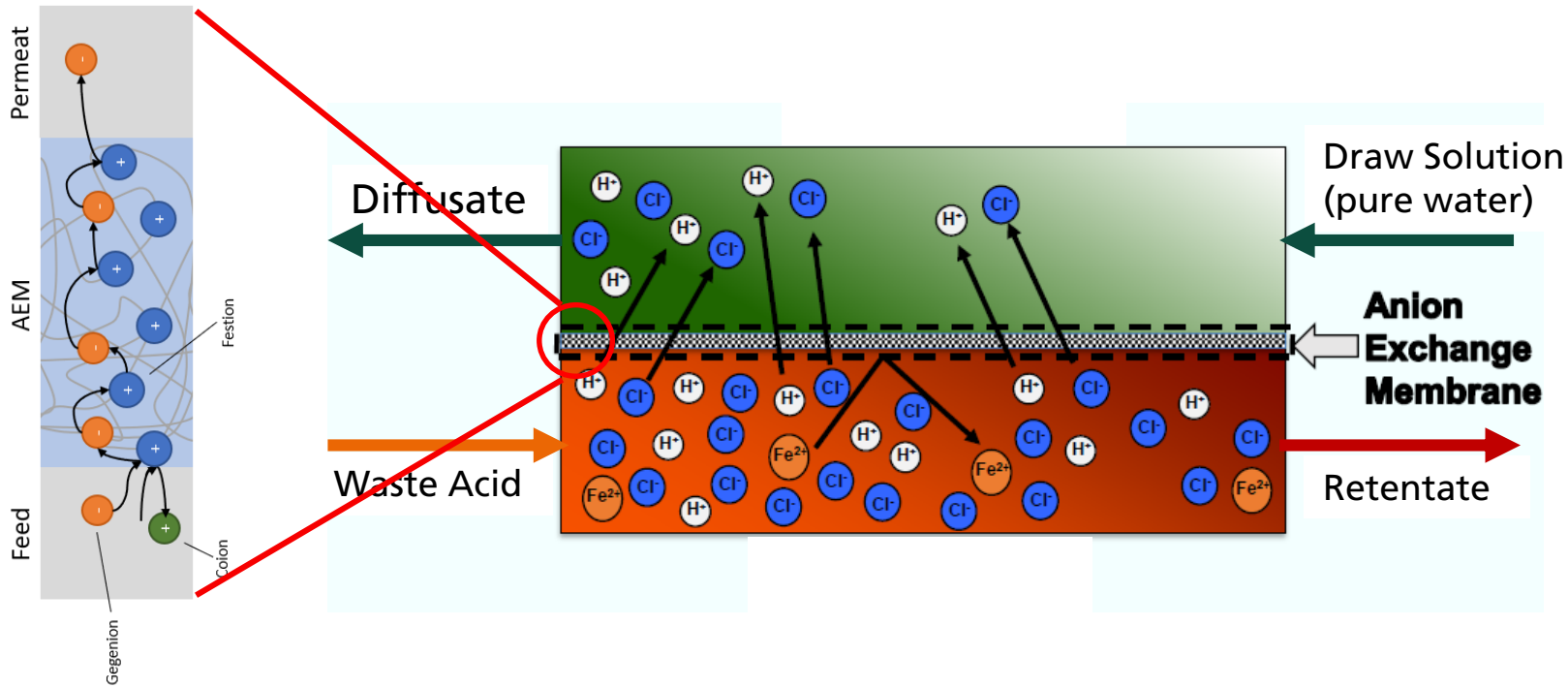
Process Design for Acid and Metal Recovery

Diffusion Dialysis for Acid Recovery

Diffusion Dialysis - Core technology for the recovery of acids



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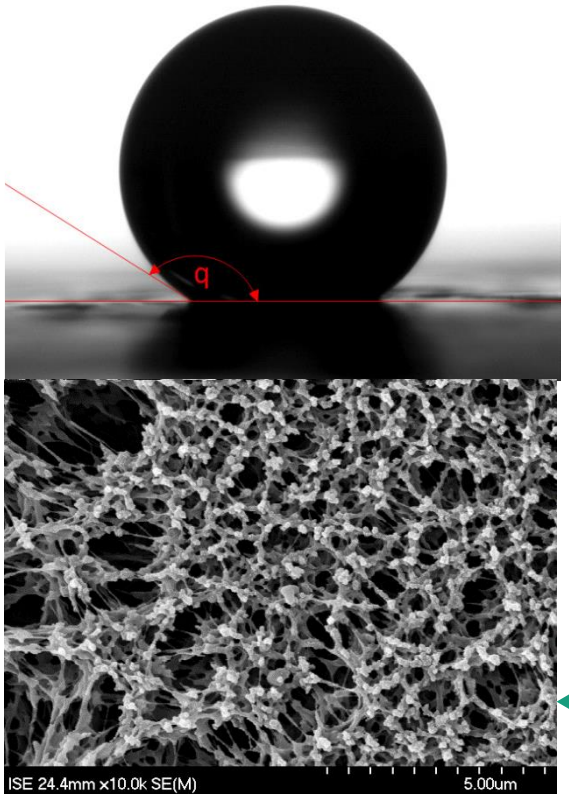
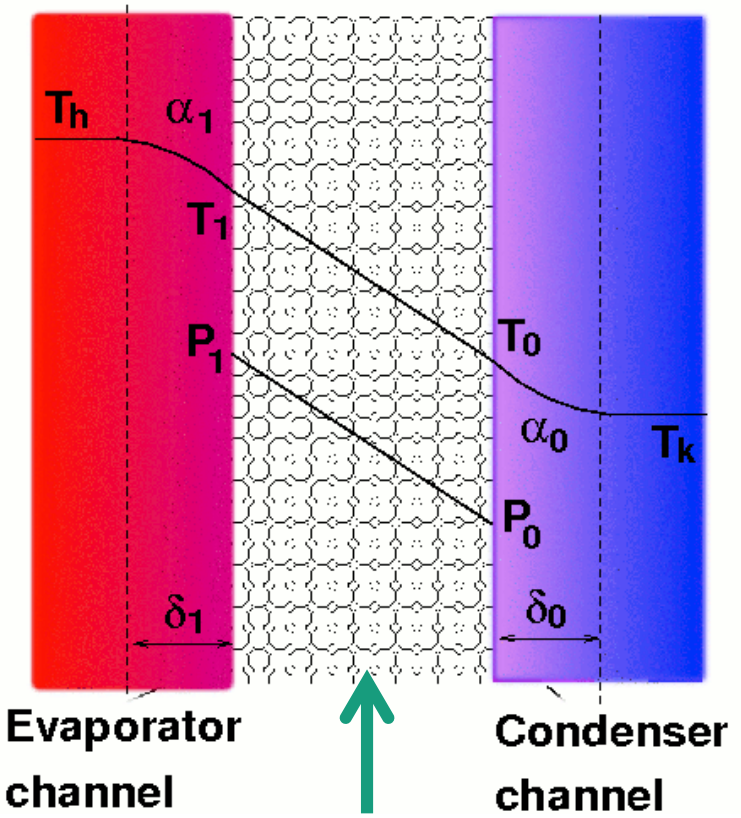
Process Design for Acid and Metal Recovery

Membrane Distillation For Acid Concentration



Temperature and Vapor pressure profile across the membrane



Hydrophobic, micro-porous membrane, pore diameter 0.1-0.4mm (PVDF, PTFE, …)

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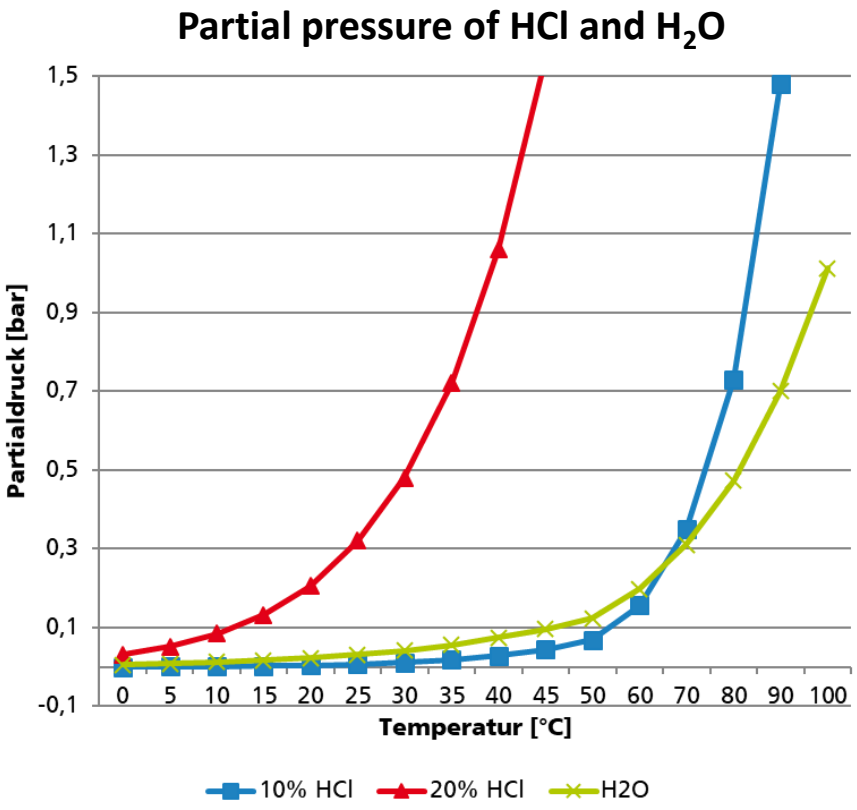
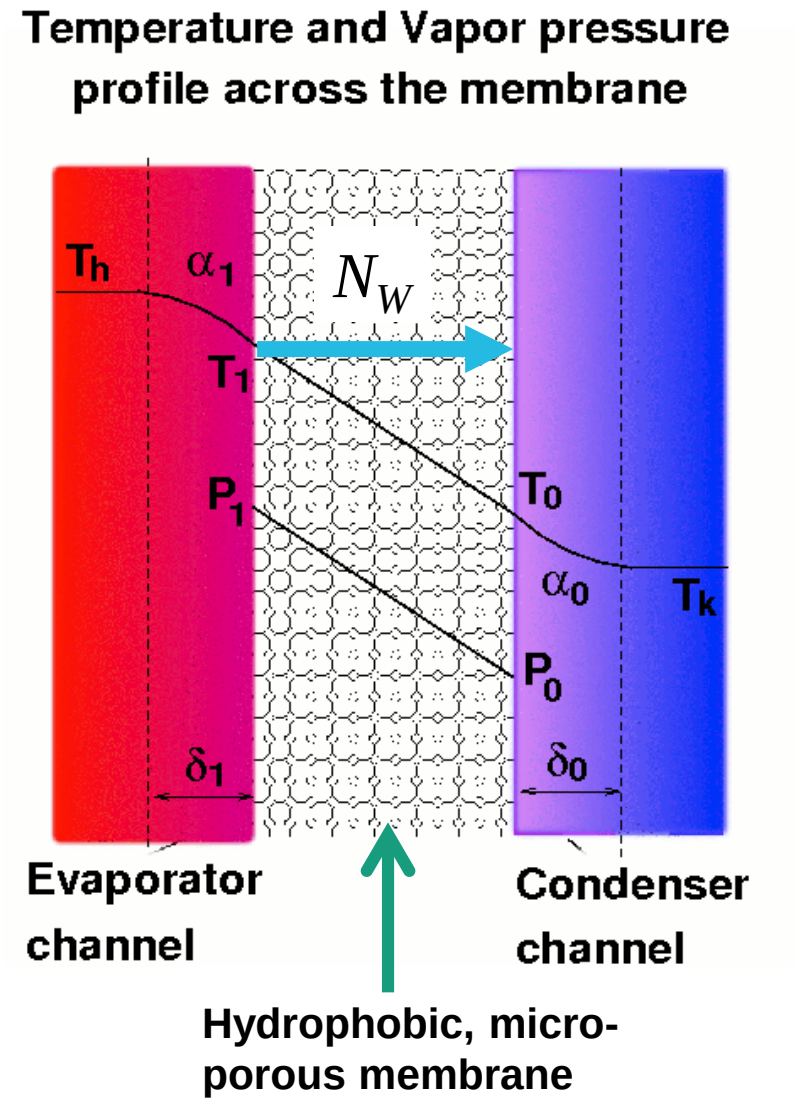
Process Design for Acid and Metal Recovery

Membrane Distillation For Acid Concentration





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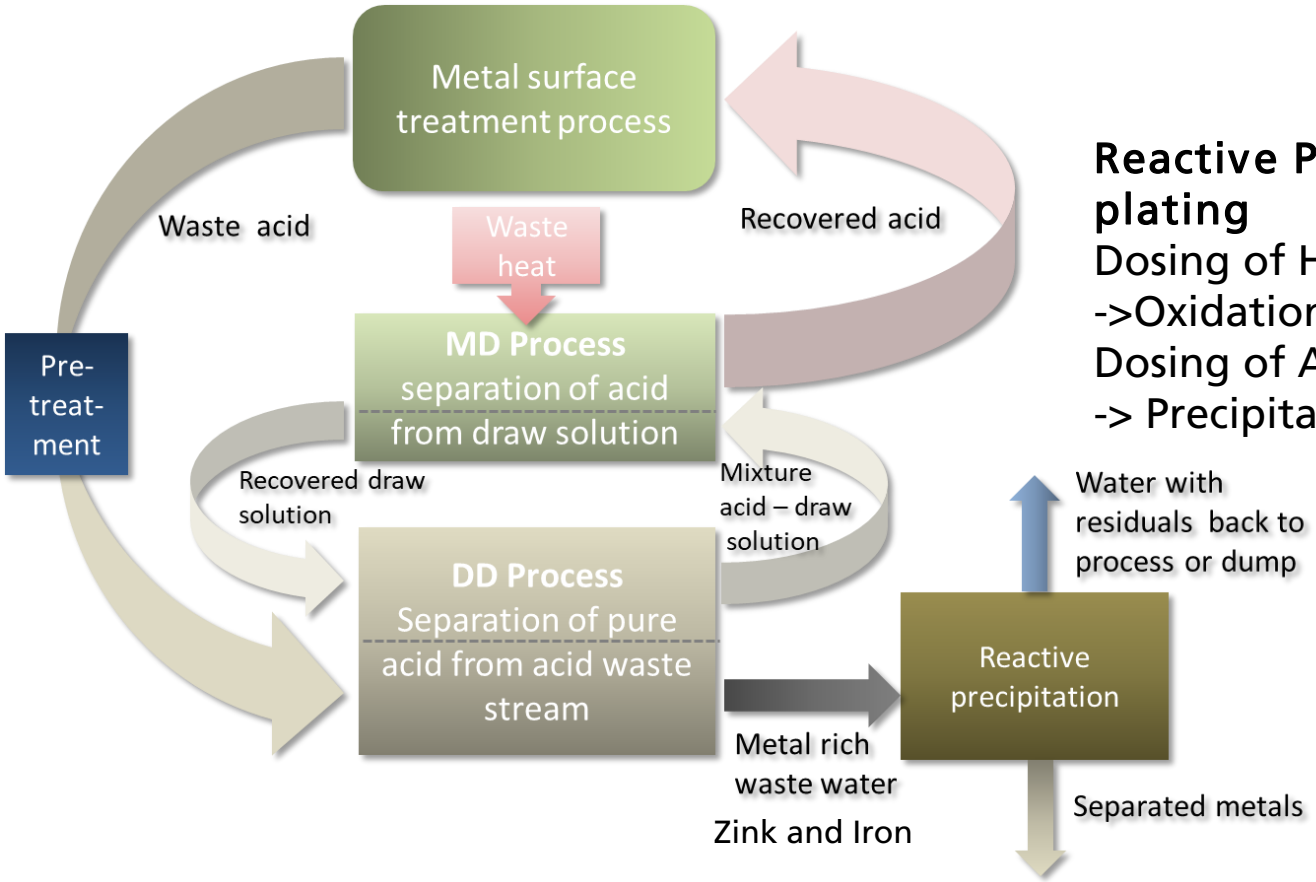
Process Design for Acid and Metal Recovery

Combined Membrane Processes and Reactive Precipitation

Core technology for the recovery and concentration of HCl and Iron recovery in Zinc plating



Reactive Precipitation in zinc plating

Dosing of Hydrogen Peroxide
->Oxidation Fe(II) -> Fe(III)
Dosing of Ammonia Bicarbonate
-> Precipitation Fe(III)-Hydroxide

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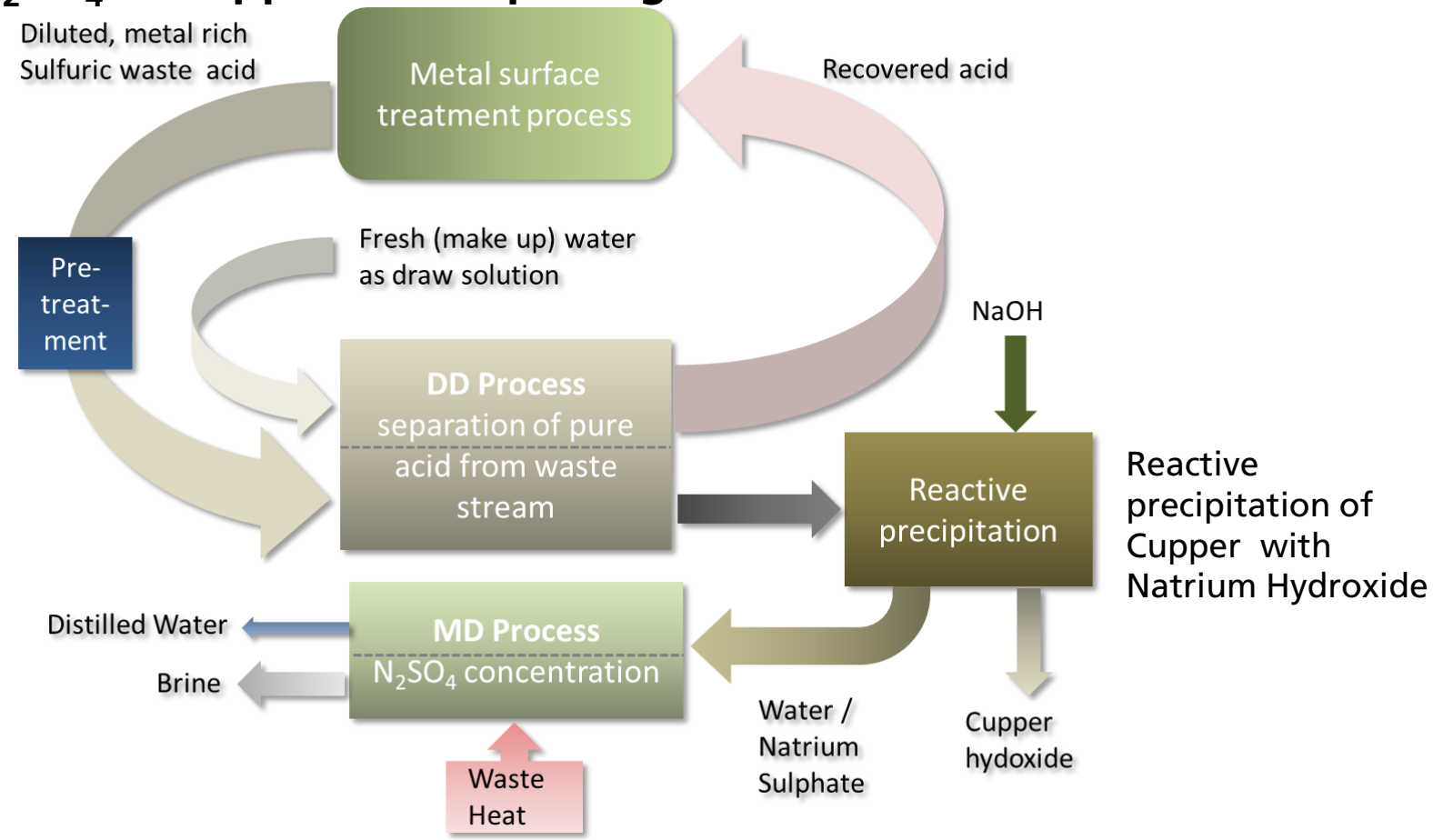
Process Design for Acid and Metal Recovery

Combined Membrane Processes and Reactive Precipitation

Core technology for the recovery of H_2SO_4 and concentration of Na_2SO_4 in Cupper electroplating



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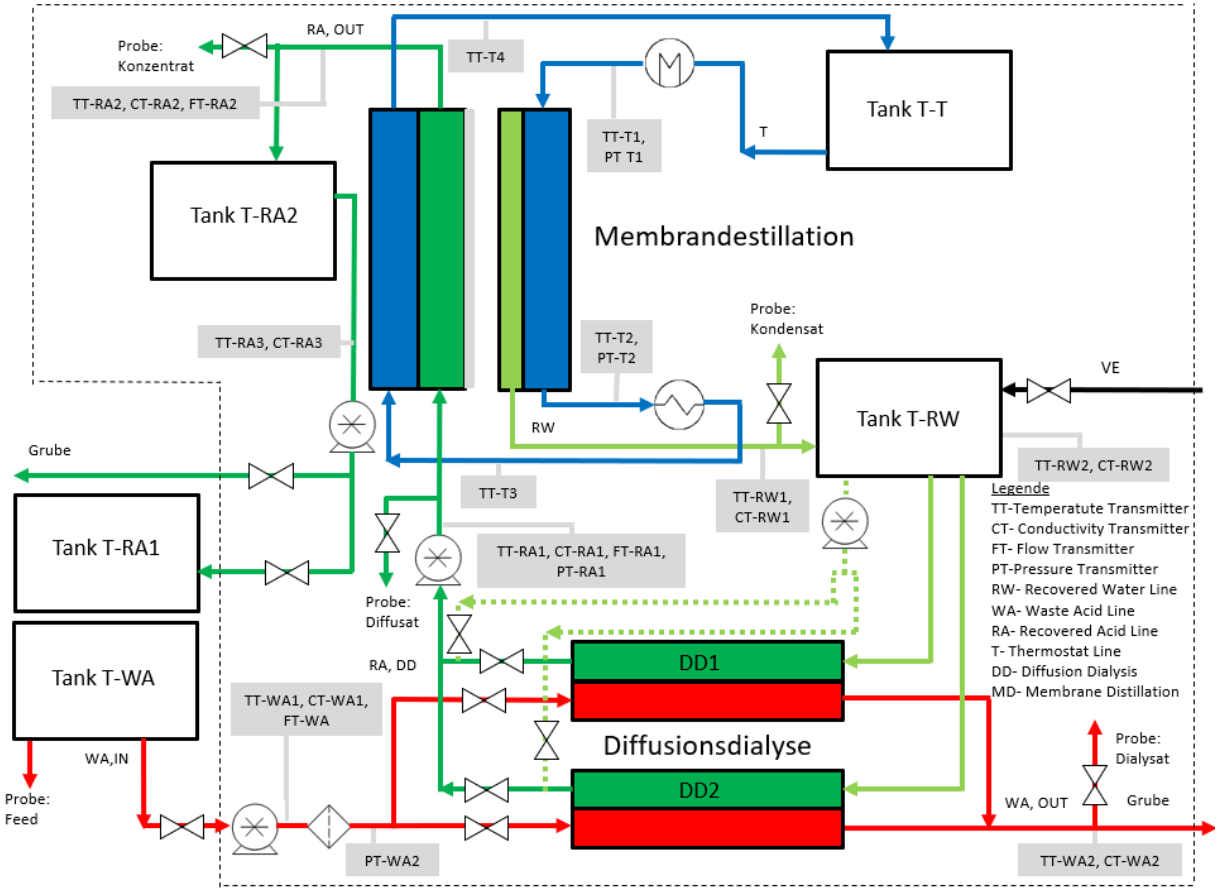
Process Flow Diagram
Example Mixed Acid Recovery

Process flow chart: Example Mixed acid recovery

- Treatment capacity: 70 l/h
- Aim: Recovery of acid and concentration by 40%



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Process Flow Diagram
Example Mixed Acid Recovery at DEW

Process flow chart:
Example Mixed acid recovery

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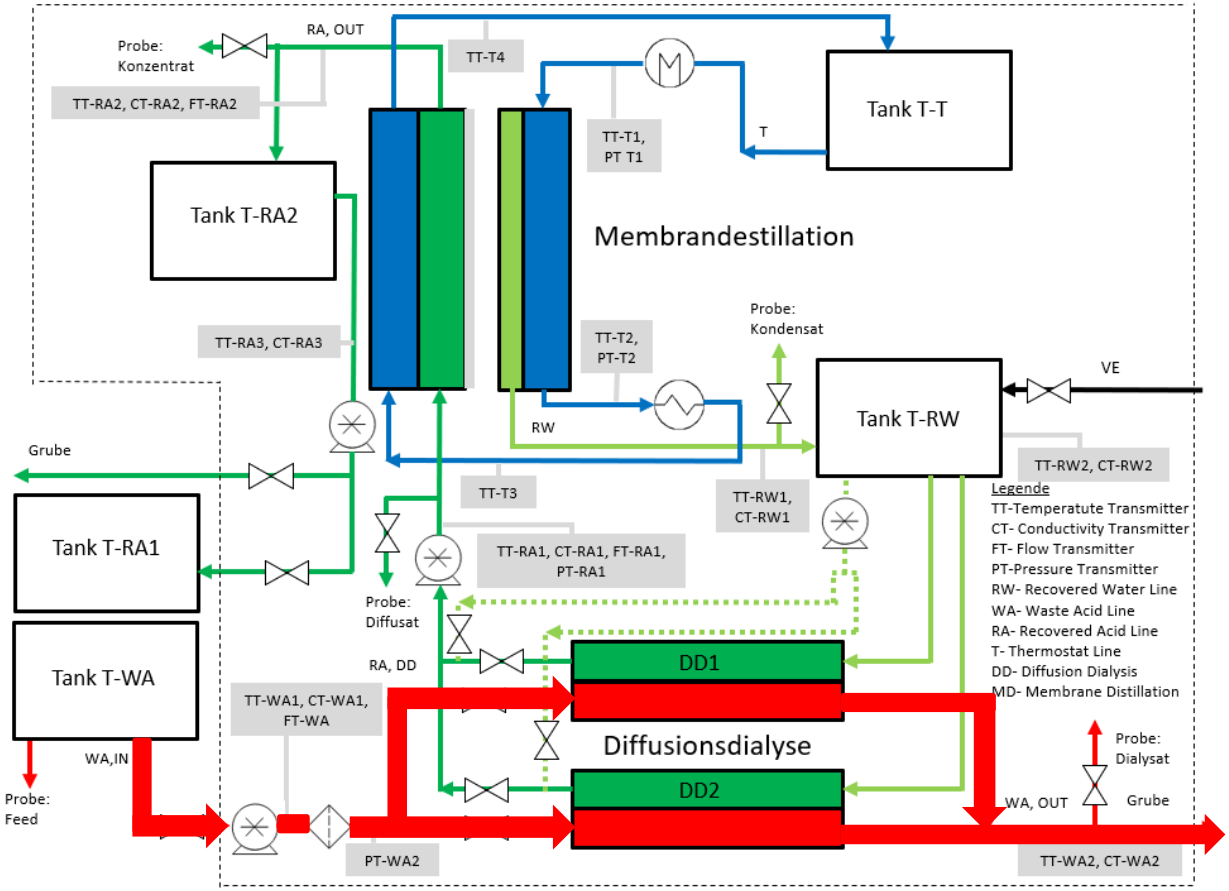

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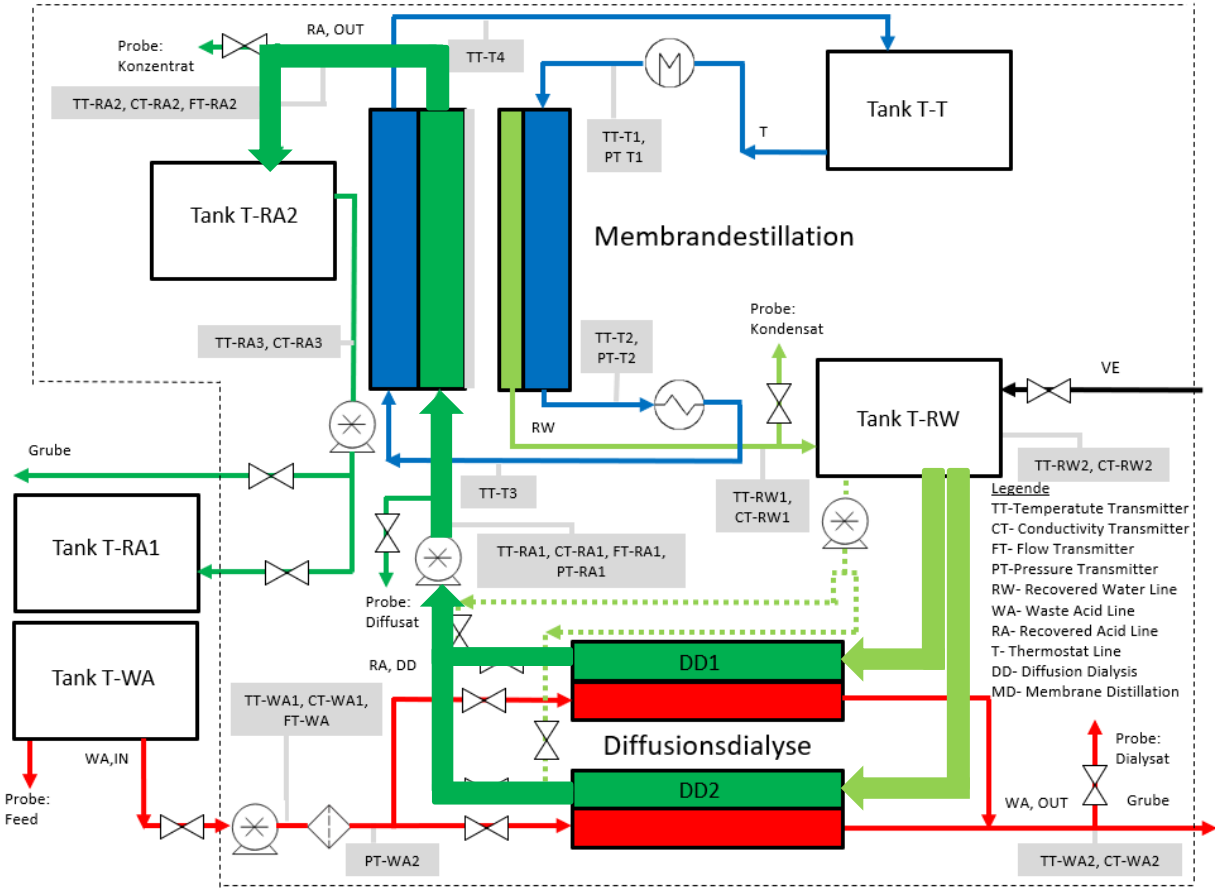

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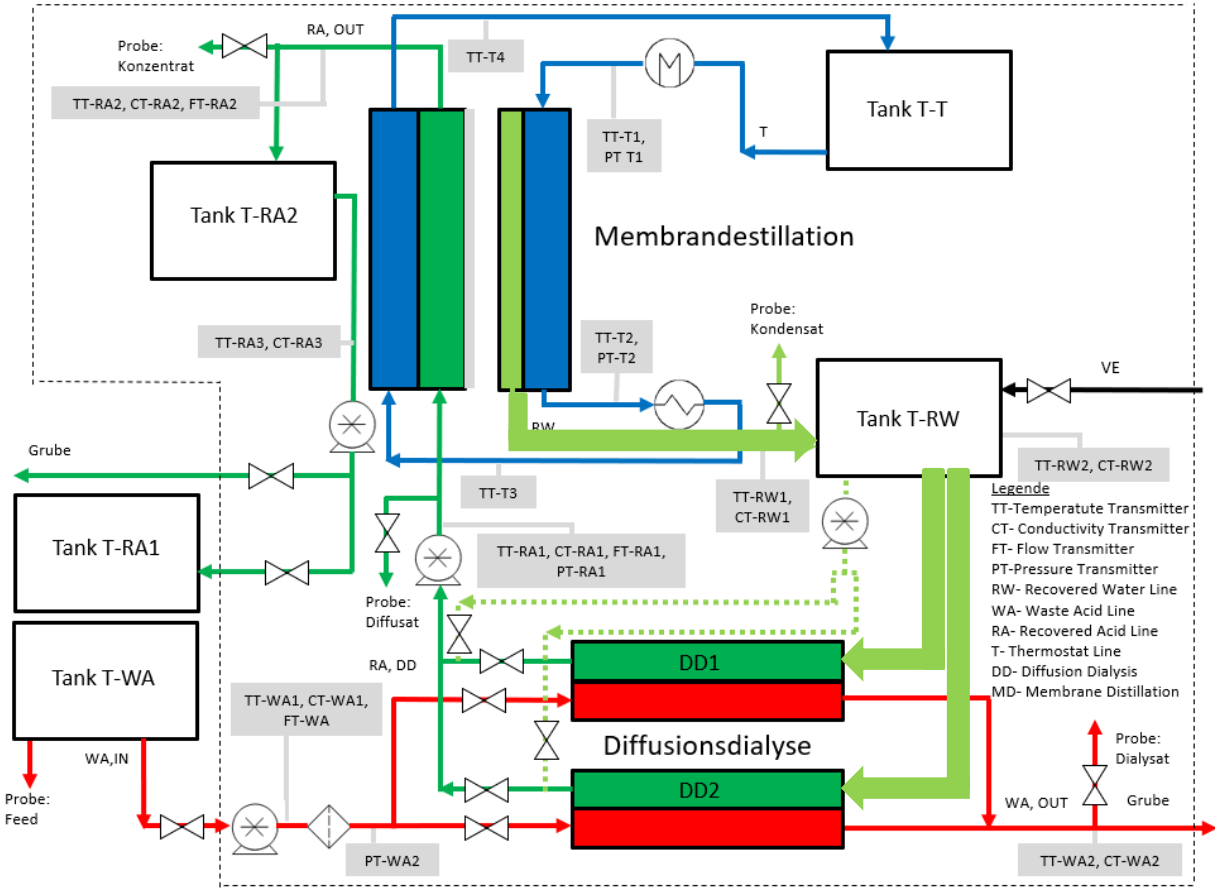

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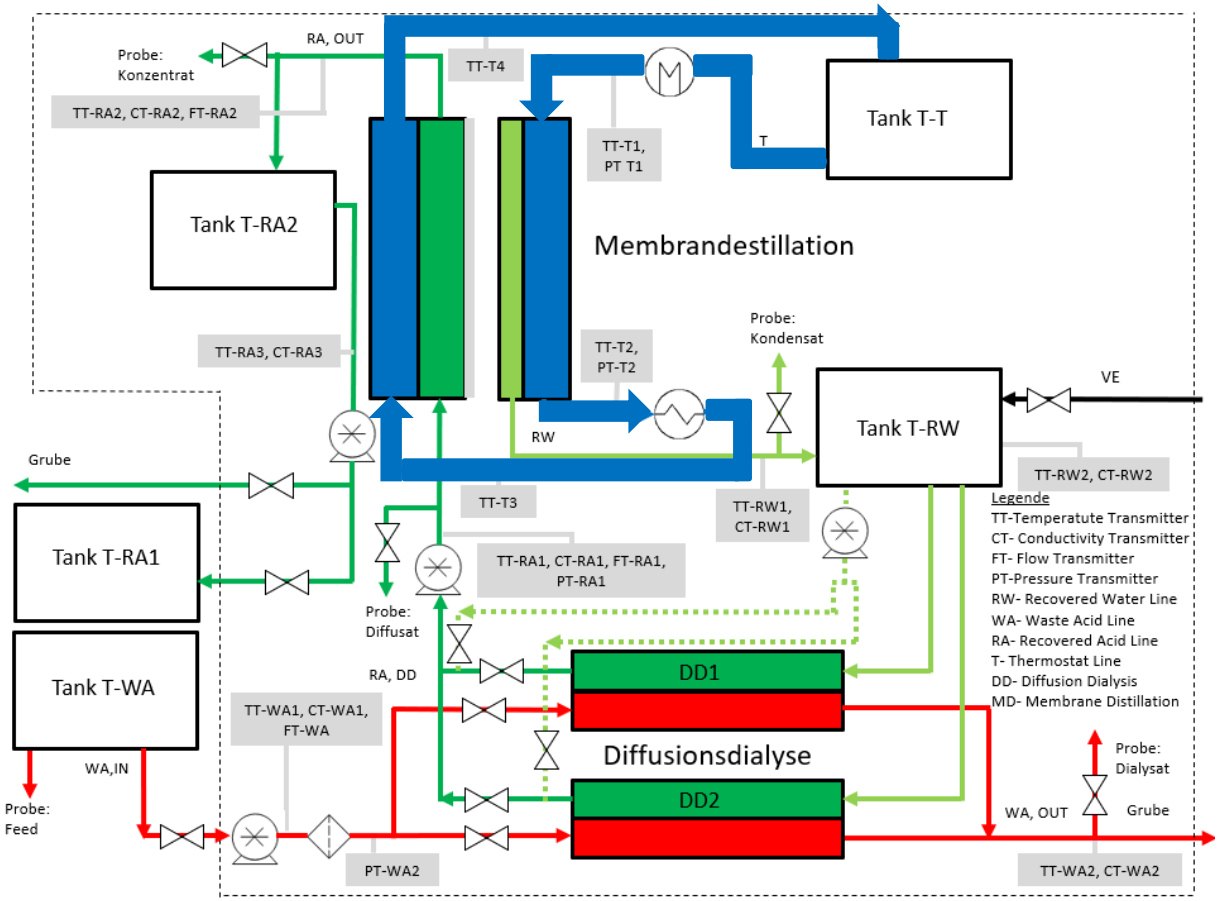

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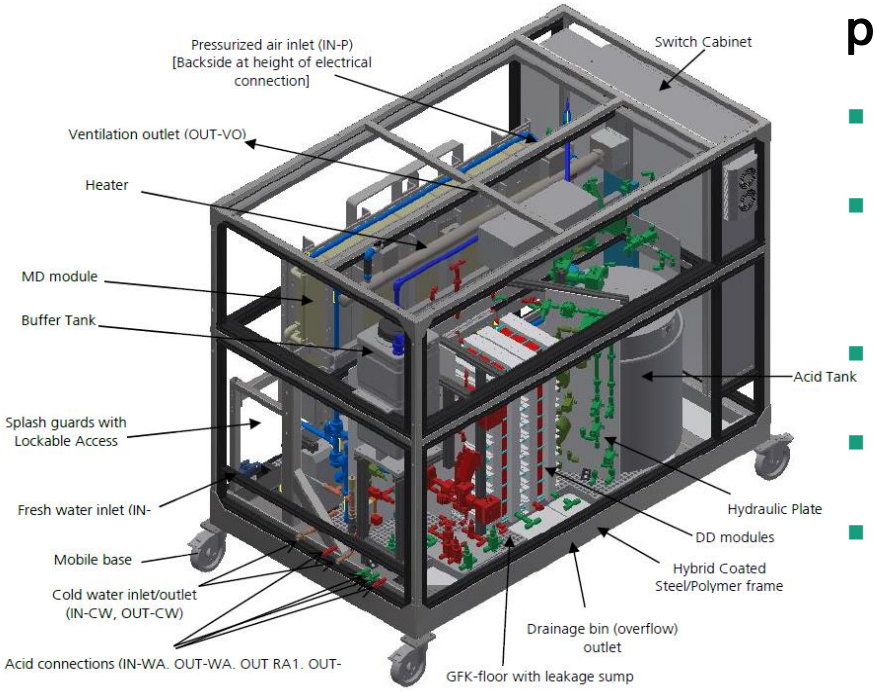
On Site Demonstration - Construction

Building 3 Demonstrators

Demonstration system for HF-HNO_3 recovery from pickling solutions in stainless steel production



Demonstration systems, technical properties:

- Treatment capacity 10 – 100 l/h
- All components are made from acid resistant polymers (PVDF, PTFE,…)
- Completely encapsulated and exhausted
- Fully self controlled by SPS system
- CE certified for operation in industrial environment

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On Site Demonstration - Construction

Building 3 Demonstrators

Demonstration systems for HCl, H_2SO_4 and HF-HNO_3 recovery

Demonstration systems, technical properties:

- Treatment capacity 10 – 100 l/h
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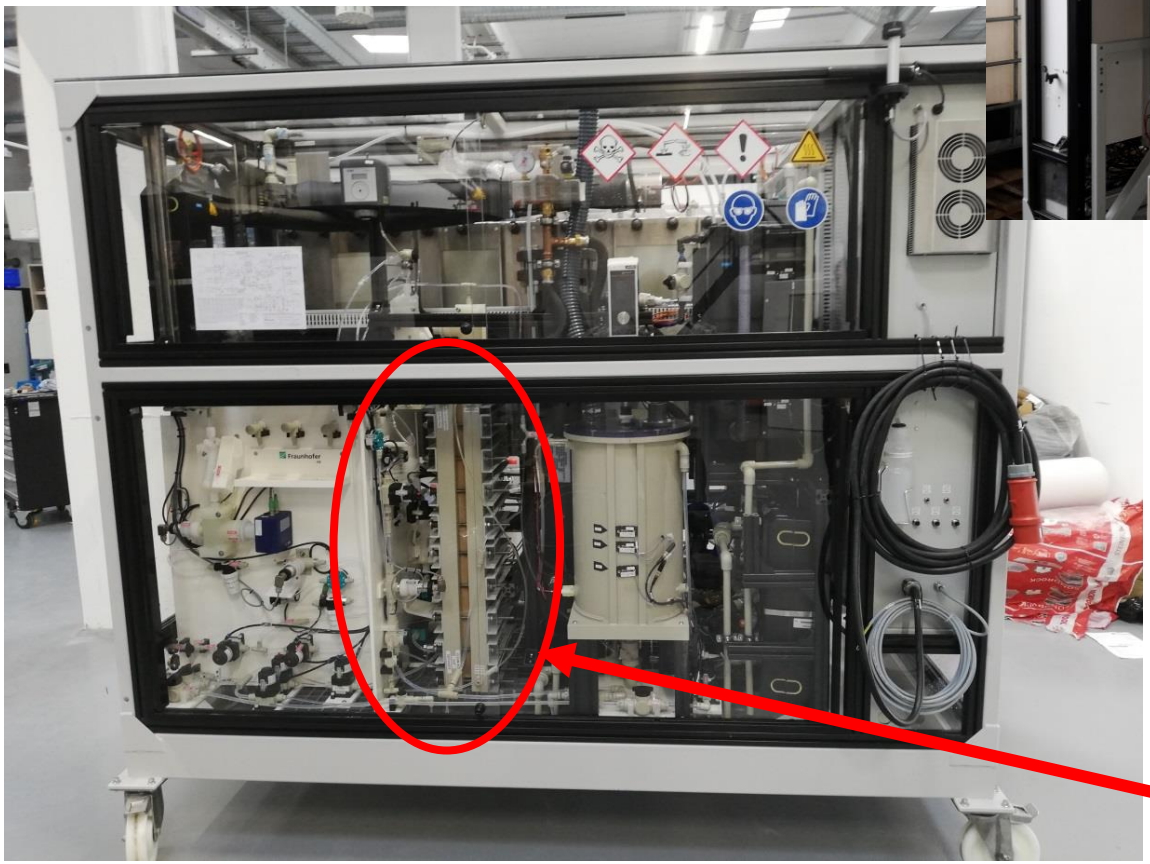
On Site Demonstration - Construction

Building 3 Demonstrators

Demonstration systems main components



DD Membrane
area 10 – 70 m²
(1 or 2 modules)

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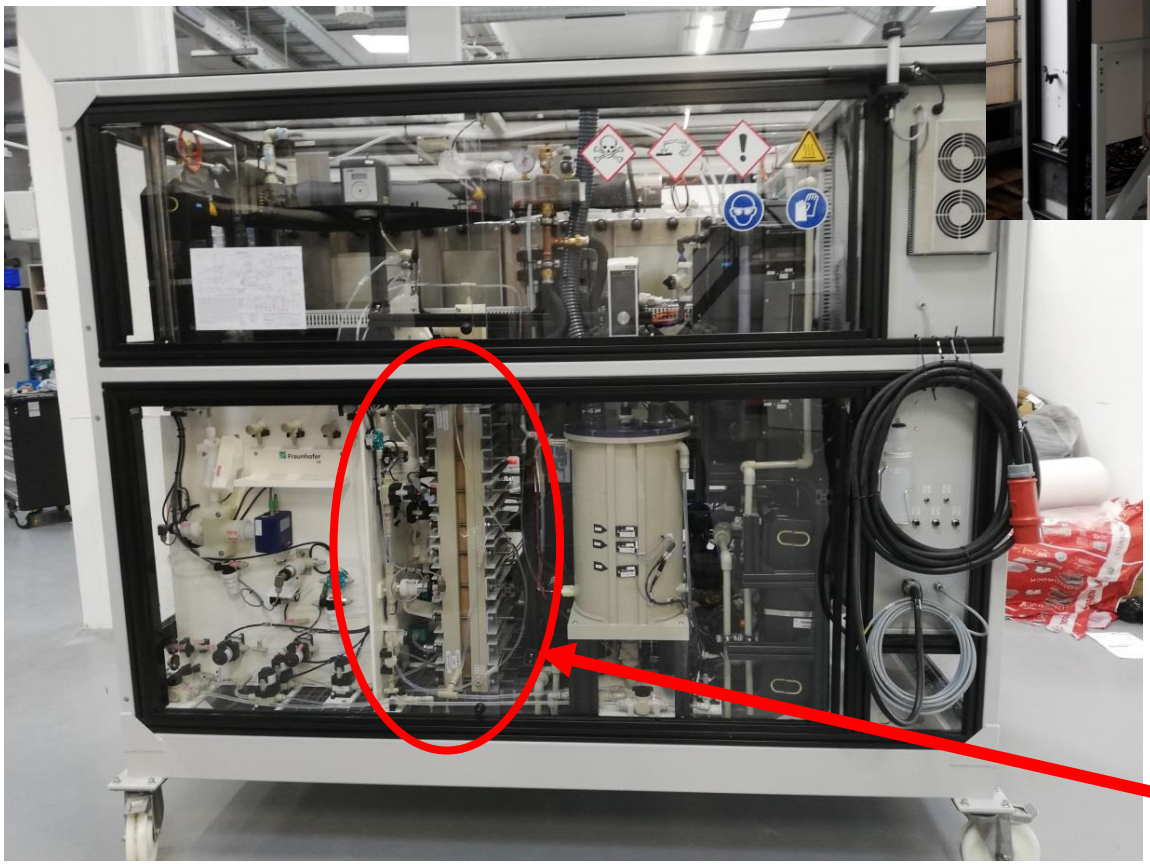
On Site Demonstration - Construction

Building 3 Demonstrators

Demonstration systems main components

MD membrane
area 12 – 25 m²



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On Site Demonstration - Construction

Building 3 Demonstrators

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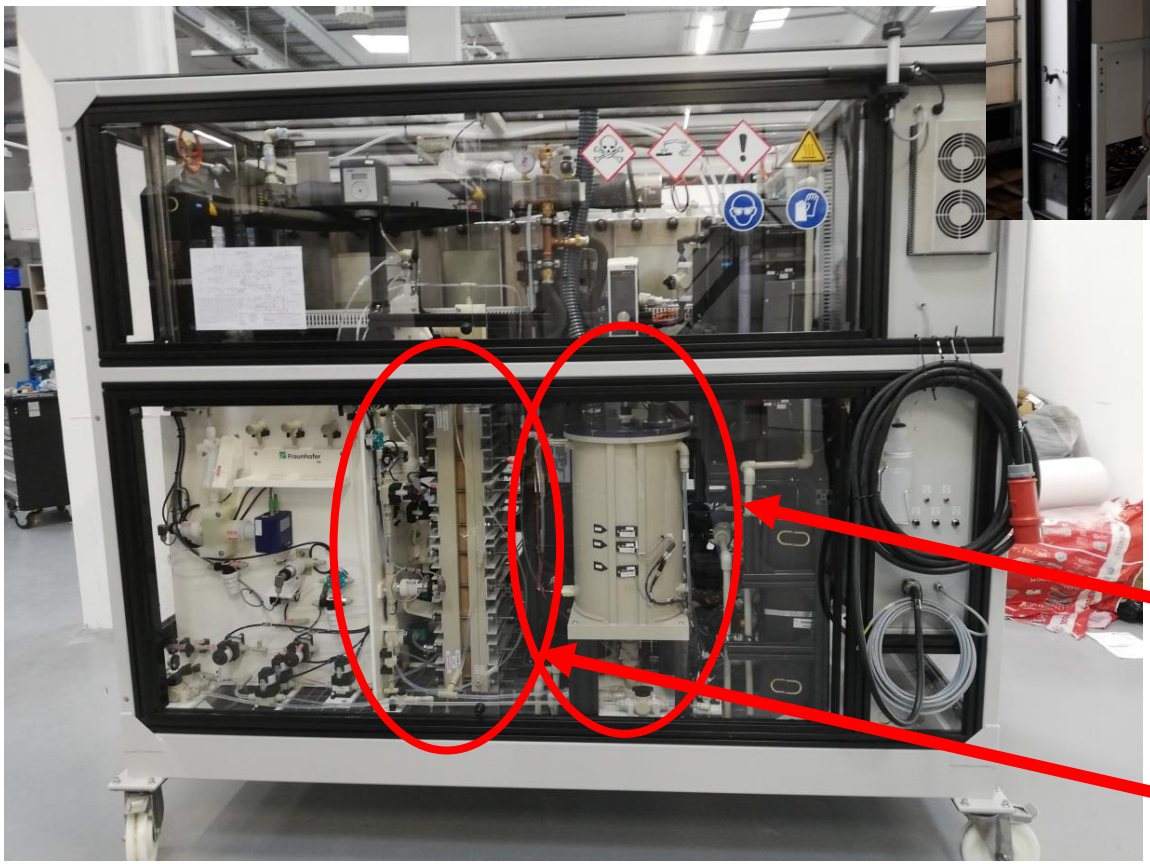

RP Reactor 20 l

DD Membrane
area 10 – 70 m²
(1 or 2 modules)

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On Site Demonstration - Results

Implementation and Operation Demo A

HCl and Fe recovery from hot dip galvanization at Tecnozinco Sicily

Installation in April 2019

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On Site Demonstration - Results

Implementation and Operation Demo A

HCl and Fe recovery from hot dip galvanization at Tecnozinco Sicily

	Demo A Recovery HCl / Fe	Comment
Feed capacity	20 - 40 l/h	
DD – Acid recovery	80 - 98%	Very high acid recovery is possible
DD – Metal rejection	65 - 80%	Far behind expectations, leakages in membrane / sealing are expected
MD – Acid concentration factor	1.1 - 1.5	Appropriate for reuse
MD – Metal salt rejection	~90%	Too low, reason unclear
RP – recovery Fe	~99%	Very good and highly selective

On Site Demonstration - Results

Implementation and Operation Demo B

Demonstration system B for H_2SO_4 and Cu recovery from electro plating at ELECTRONIQUEL Spain

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On Site Demonstration - Results

Implementation and Operation Demo B

H_2SO_4 and Cu recovery from electro plating at ELECTRONIQUEL Spain

	Demo B Recovery of H_2SO_4 / Cu / Natrium Sulfate Cupper electro plating	Comment
Feed capacity	5 - 25 l/h	
DD – Acid recovery	70 - 85%	Behind expectations but improvement in progress
DD – Metal rejection	82%	Lower than expected, reasons may be associated with formation of metal clusters
MD – Acid / Salt concentration factor	1.6 - 3.8	High concentration ratios can be achieved in both applications
MD – Acid / Salt rejection	100%	Works very well
RP – Recovery ratio Cupper	80 - 85 %	Acceptable can also be improved

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On Site Demonstration - Results

Implementation and Operation Demo C

HF-HNO_3 recovery from stainless steel pickling line at DEW Germany

Source:DEW

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On Site Demonstration - Results

Implementation and Operation Demo C

HF-HNO_3 recovery from stainless steel pickling line at DEW Germany

	Demo C Recovery of HNO_3 / HF in stainless steel pickling	Comment
Feed capacity	35-100 l/h	
DD – Acid recovery	80-90% DD only 80 - 90% DD – MD open loop 65% with DD - MD closed loop	Very good recovery of acid by DD possible but MD distillate as draw solution has lower driving force through HF contamination
DD – Metal rejection	90-95%	Metal rejection is good
MD – Acid concentration factor	1.2	Concentration of acid by MD is lower than expected →HNO_3 mainly, HF is not concentrated → too volatile and passes the membrane
MD – Metal salt rejection	100%	Very good
Operation experience	~600h	No damages, fully atomized operation

Thank you for your attention

ReWaCem project team visits DEW Hagen

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