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
CONTENT

- The Scope of the ReWaCEM Project
- Process design and technology
- Design and construction of demonstration 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 Diffusion Dialysis and Membrane Distillation for acid recovery in steel 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)

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

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

Case 4: Recovery of gold and Palladium in printed circuit board industry (Feed 345 l/h)
Process Design for Acid and Metal Recovery
Combined Membrane Processes and Reactive Precipitation

Core technology for the recovery and concentration of HCl, mixed HNO₃-HF and H₂SO₄

Diluted, metal rich Hydrochloric / Sulfuric/ mixed Nitric – Hydrofluoric waste acid

Pre-treatment

Metal surface treatment process

Waste heat

MD Process separation of acid from draw solution

Recovered draw solution

Mixture acid – draw solution

DD Process Separation of pure acid from acid waste stream

Recovered acid

Water with residuals back to process or dump

Metal rich waste water

Reactive precipitation

Separated metals

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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
Process Design for Acid and Metal Recovery
Membrane Distillation
For Acid Concentration

Temperature and Vapor pressure profile across the membrane

Evaporator channel
Hydrophobic, micro-porous membrane, pore diameter 0.1-0.4 mm (PVDF, PTFE, ...)

Condenser channel
Process Design for Acid and Metal Recovery

Membrane Distillation
For Acid Concentration

Partial pressure of HCl and H₂O

Temperature and Vapor pressure profile across the membrane

Evaporator channel
Condenser channel
Hydrophobic, microporous membrane

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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

Mixture acid – draw solution

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

Metal surface treatment process

Waste heat

Recovered acid

Waste acid

Pre-treatment

Recovered draw solution

Metal surface treatment process

Recovered acid

Waste heat

MD Process
separation of acid from draw solution

Mixture acid – draw solution

Water with residuals back to process or dump

DD Process
Separation of pure acid from acid waste stream

Metal rich waste water
Zink and Iron

Reactive precipitation

Separated metals

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Process Design for Acid and Metal Recovery
Combined Membrane Processes and Reactive Precipitation

Core technology for the recovery of $\text{H}_2\text{SO}_4$ and concentration of $\text{Na}_2\text{SO}_4$ in Cupper electroplating

- Metal surface treatment process
- Reactive precipitation of Cupper with Natrium Hydroxide
- DD Process separation of pure acid from waste stream
- MD Process $\text{N}_2\text{SO}_4$ concentration

Recovered acid

Diluted, metal rich Sulfuric waste acid

Fresh (make up) water as draw solution

Distilled Water

Brine

Waste Heat

NaOH

Reactive precipitation of Cupper with Natrium Hydroxide

Water / Natrium Sulphate

Cupper hydoxide

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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%
Process Flow Diagram
Example Mixed Acid Recovery at DEW

Process flow chart: Example Mixed acid recovery

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Process flow chart: Example Mixed acid recovery

- Treatment capacity: 70 l/h
- Aim: Recovery of acid and concentration by 40%
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
On Site Demonstration - Construction
Building 3 Demonstrators

Demonstration systems for HCl, H₂SO₄ and HF-HNO₃ recovery

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
On Site Demonstration - Construction
Building 3 Demonstrators

Demonstration systems main components

DD Membrane area 10 – 70 m²
(1 or 2 modules)
On Site Demonstration - Construction
Building 3 Demonstrators

Demonstration systems main components

MD membrane area 12 – 25 m²

DD Membrane area 10 – 70 m² (1 or 2 modules)
On Site Demonstration - Construction
Building 3 Demonstrators

Demonstration systems main components

- RP Reactor 20 l
- MD membrane area 12 – 25 m²
- DD Membrane area 10 – 70 m² (1 or 2 modules)
On Site Demonstration - Results
Implementation and Operation Demo A

HCl and Fe recovery from hot dip galvanization at Tecnozinco Sicily

Installation in April 2019
## On Site Demonstration - Results
### Implementation and Operation Demo A

HCl and Fe recovery from hot dip galvanization at Tecnozinco Sicily

<table>
<thead>
<tr>
<th></th>
<th>Demo A Recovery HCl / Fe</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed capacity</td>
<td>20 - 40 l/h</td>
<td></td>
</tr>
<tr>
<td><strong>DD</strong> – Acid recovery</td>
<td>80 - 98%</td>
<td>Very high acid recovery is possible</td>
</tr>
<tr>
<td><strong>DD</strong> – Metal rejection</td>
<td>65 - 80%</td>
<td>Far behind expectations, leakages in membrane / sealing are expected</td>
</tr>
<tr>
<td><strong>MD</strong> – Acid concentration factor</td>
<td>1.1 - 1.5</td>
<td>Appropriate for reuse</td>
</tr>
<tr>
<td><strong>MD</strong> – Metal salt rejection</td>
<td>~90%</td>
<td>Too low, reason unclear</td>
</tr>
<tr>
<td><strong>RP</strong> – recovery Fe</td>
<td>~99%</td>
<td>Very good and highly selective</td>
</tr>
</tbody>
</table>
On Site Demonstration - Results
Implementation and Operation Demo B

Demonstration system B for H$_2$SO$_4$ and Cu recovery from electroplating at ELECTRONIQUEL Spain
On Site Demonstration - Results
Implementation and Operation Demo B

H$_2$SO$_4$ and Cu recovery from electro plating at ELECTRONIQUES Spain

<table>
<thead>
<tr>
<th></th>
<th>Demo B Recovery of H$_2$SO$_4$ / Cu / Natrium Sulfate Copper electro plating</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed capacity</td>
<td>5 - 25 l/h</td>
<td></td>
</tr>
<tr>
<td>DD – Acid recovery</td>
<td>70 - 85%</td>
<td>Behind expectations but improvement in progress</td>
</tr>
<tr>
<td>DD – Metal rejection</td>
<td>82%</td>
<td>Lower than expected, reasons may be associated with formation of metal clusters</td>
</tr>
<tr>
<td>MD – Acid / Salt concentration factor</td>
<td>1.6 - 3.8</td>
<td>High concentration ratios can be achieved in both applications</td>
</tr>
<tr>
<td>MD – Acid / Salt rejection</td>
<td>100%</td>
<td>Works very well</td>
</tr>
<tr>
<td>RP – Recovery ratio Copper</td>
<td>80 - 85 %</td>
<td>Acceptable can also be improved</td>
</tr>
</tbody>
</table>
On Site Demonstration - Results
Implementation and Operation Demo C

HF-HNO₃ recovery from stainless steel pickling line at DEW Germany

Source:DEW
## On Site Demonstration - Results
### Implementation and Operation Demo C

**HF-HNO₃ recovery from stainless steel pickling line at DEW Germany**

<table>
<thead>
<tr>
<th></th>
<th>Demo C Recovery of HNO₃ / HF in stainless steel pickling</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed capacity</td>
<td>35-100 l/h</td>
<td></td>
</tr>
<tr>
<td><strong>DD – Acid recovery</strong></td>
<td></td>
<td>Very good recovery of acid by DD possible but MD distillate as draw solution has lower driving force through HF contamination</td>
</tr>
<tr>
<td>DD – Metal rejection</td>
<td>90-95%</td>
<td>Metal rejection is good</td>
</tr>
<tr>
<td><strong>MD – Acid concentration factor</strong></td>
<td>1.2</td>
<td>Concentration of acid by MD is lower than expected → HNO₃ mainly, HF is not concentrated → too volatile and passes the membrane</td>
</tr>
<tr>
<td><strong>MD – Metal salt rejection</strong></td>
<td>100%</td>
<td>Very good</td>
</tr>
<tr>
<td>Operation experience</td>
<td>~600h</td>
<td>No damages, fully atomized operation</td>
</tr>
</tbody>
</table>
Thank you for your attention

ReWaCem project team visits DEW Hagen

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