Recycling of valuable components from process and rinsing water in the steel industry

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Stahl

Content

- Valuable components (introduction)
- Separation of particles from process waters in the steel industry
- Recovery of metals from acidic rinsing water streams
- Recovery of acids from pickling process water streams
- Summary

Process and Rinsing Water in Steel Industry

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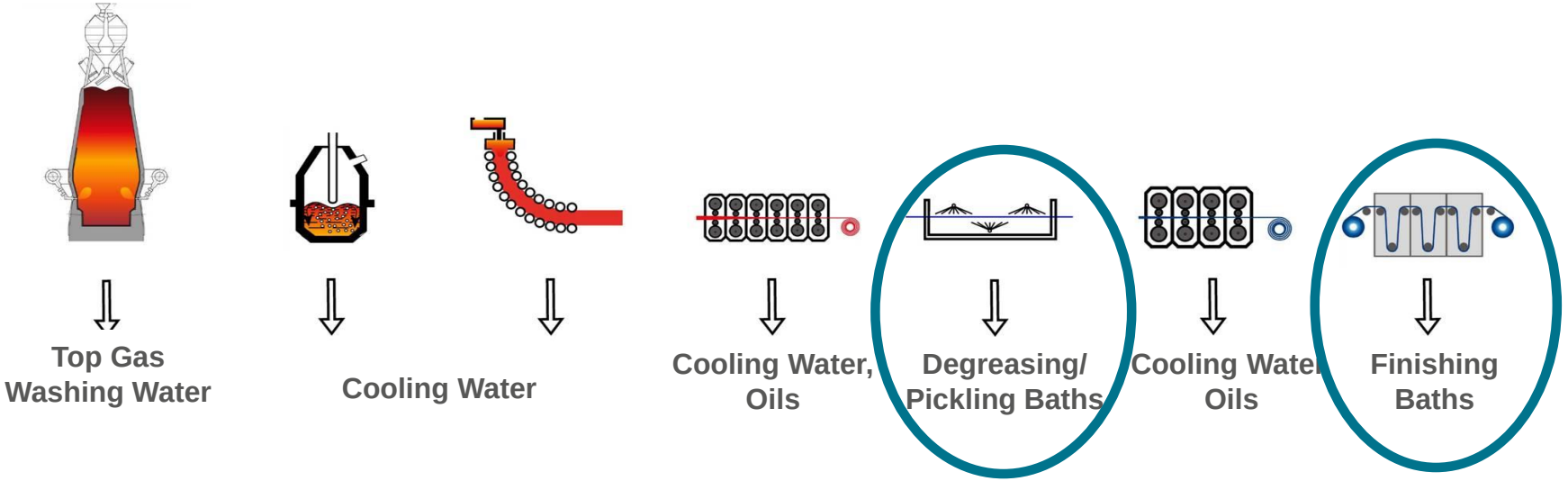
› **Valuable components in process and rinsing water**



- Pickling process: Waste water contains valuable acids (e.g. HCl, H_2SO_4, HF, HNO_3).
- Rinsing after surface treatment: accumulation of particles, metals and acids in liquid media.
- Valuable metals from coating: zinc, tin, nickel, copper …

Process and Rinsing Water in Steel Industry

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› Valuable components in process and rinsing water - costs

Acid components	Costs
H_2SO_4	16 €/m³
HCl	37 €/m³
HF / HNO_3	60 – 70 €/m³

Metals	Costs
Zinc	2.250 €/t
Tin	15.000 €/t
Nickel	14.750 €/t

- Typical volume flows of liquid media containing valuable components are between 100 l/h up to 10 m³/h.
- Costs of valuables especially for metals are strong volatile!

Process and Rinsing Water in Steel Industry

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Technologies for the recycling of valuable components from process and rinsing water in the steel industry

- For **metal** recovery
  - Extraction (chemicals needed)
  - Electrolysis (metal deposition requires high amount of electricity)
  - Membrane technologies
- For **acid** recovery
  - Retardation (with resins – recovery rate 80% possible)
  - Pyrohydrolysis (thermal power and high investment costs – >2.000 m^3/h)
  - Crystallization (thermal power for evaporating or cooling down; H_2SO_4)
  - Membrane technologies
- Discharge limits require innovative water treatment methods.

Membrane technologies are one possibility for creating closed loop systems in steelworks and are suitable for the recovery of valuable metals, salts and acids from process and rinsing water!

Process and Rinsing Water in Steel Industry

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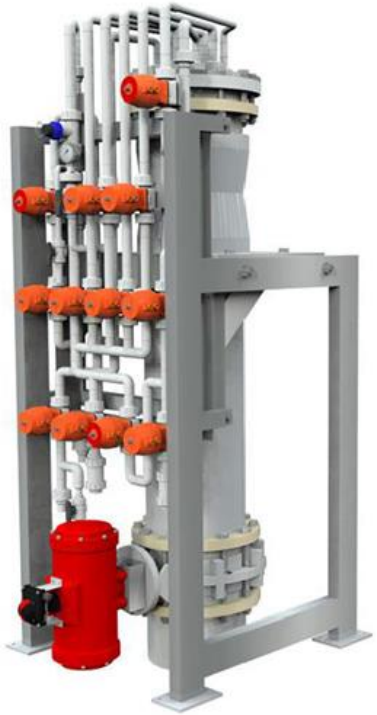
- **Pressure driven membrane technologies:**
  - Microfiltration (MF)
  - Ultrafiltration (UF)
  - Nanofiltration (NF)
  - Reverse Osmosis (RO)

- **Concentration driven membrane technologies:**
  - Diffusion Dialysis (DD)
  - Membrane Contactors

- **Electrodialysis**

Particle Separation (as pretreatment step)

- Nearly all process water streams in the steel industry contain particles!
- Filtration technologies are necessary before further treatment, e.g. for mixed acids: Filter cartridge (dead-end filtration with backflush)



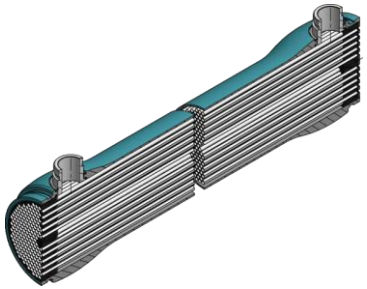
Source: Scanacon

Filtration vessel

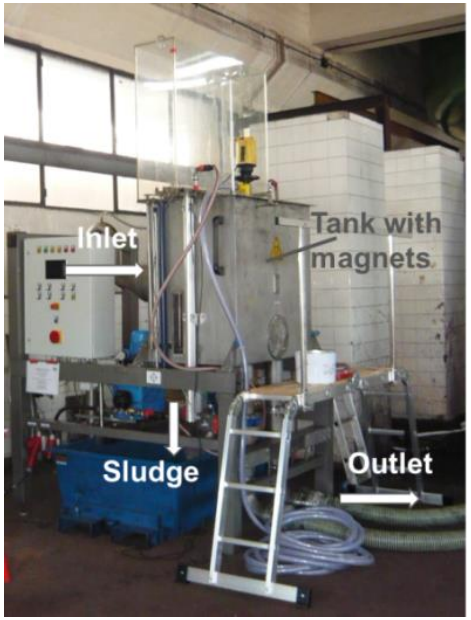
Filtration sludge storage tank

Particle Separation Technologies (as pretreatment step)

- Microfiltration (e.g. with cross-flow modules – operation continuously)
- Magnetic Separation (especially for iron particles)



Microfiltration



Magnetic separation

(e.g. for iron recovery)

Recycling of Liquid Media (metal recovery)

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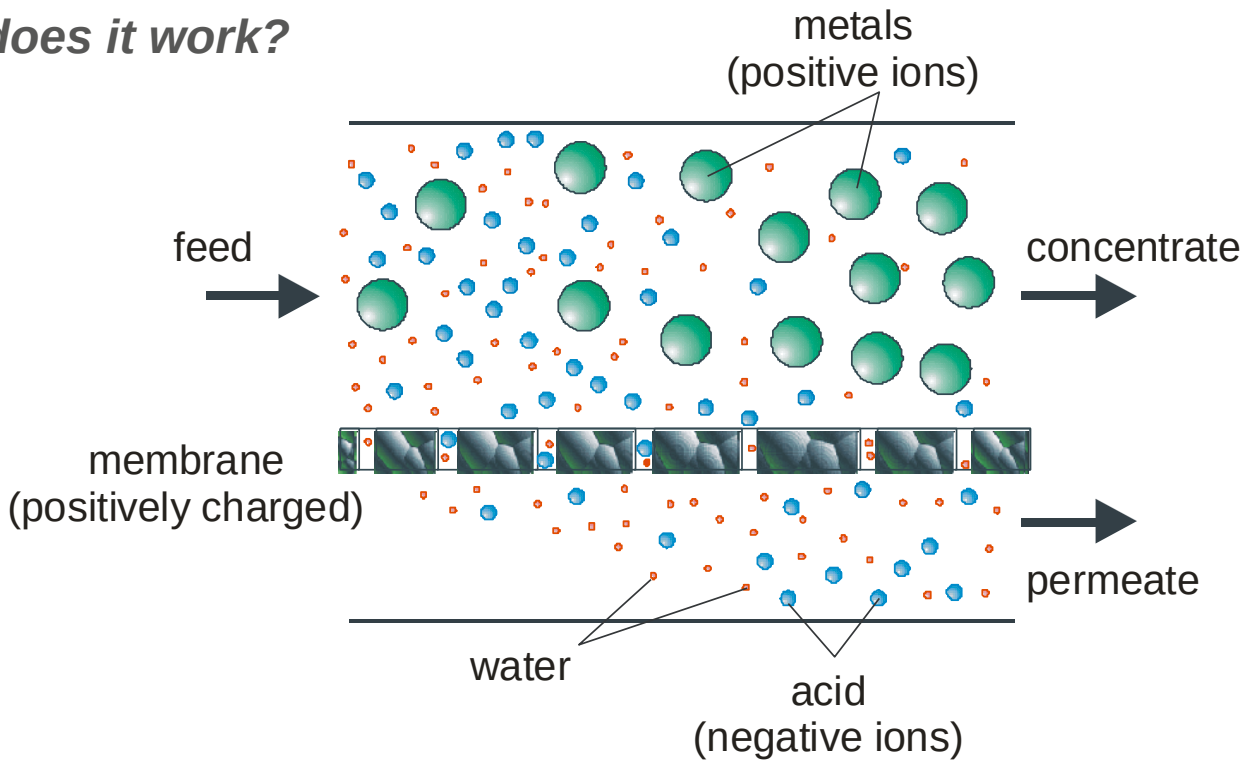
Recovery of metal ions (e.g. by nanofiltration)

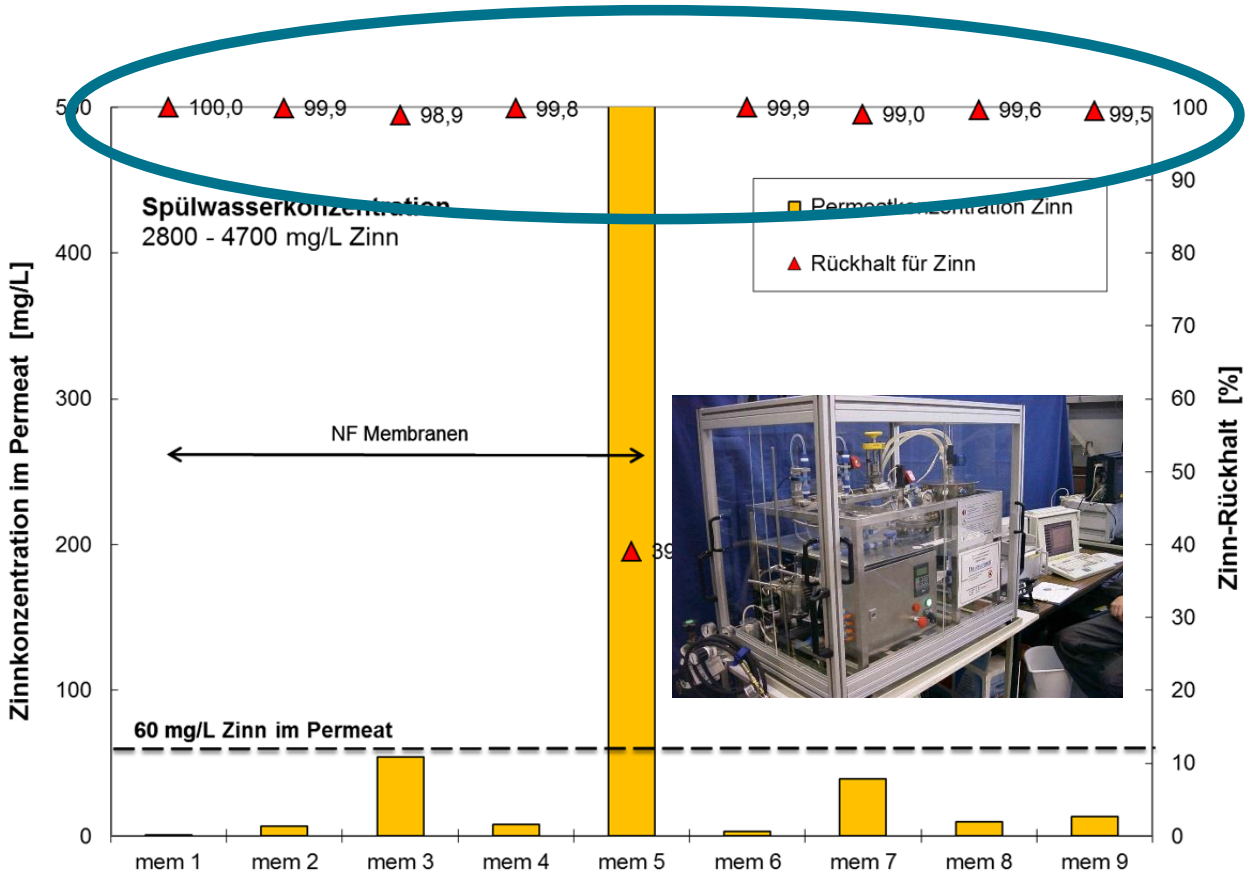
How does it work?



- Membranes form a **selective barrier** for separating and concentrating
- Membranes allows some components (here: water, acids) to pass through and stops others (metals)

Recycling of Liquid Media (metal recovery)

Membrane Screening: Recovery of metals (example metal tin)

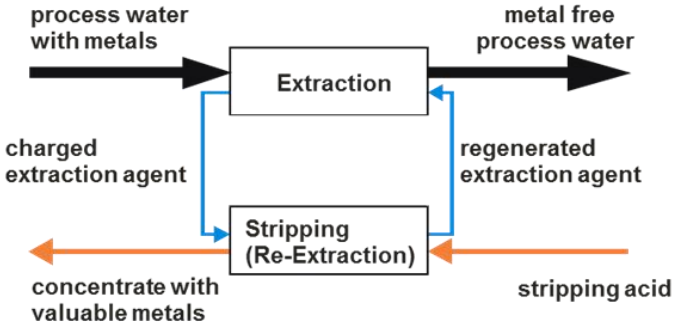


High metal recovery

› High recovery rates for metal ions (e.g. for rinsing water after coating)

Recycling of Liquid Media (metal recovery)

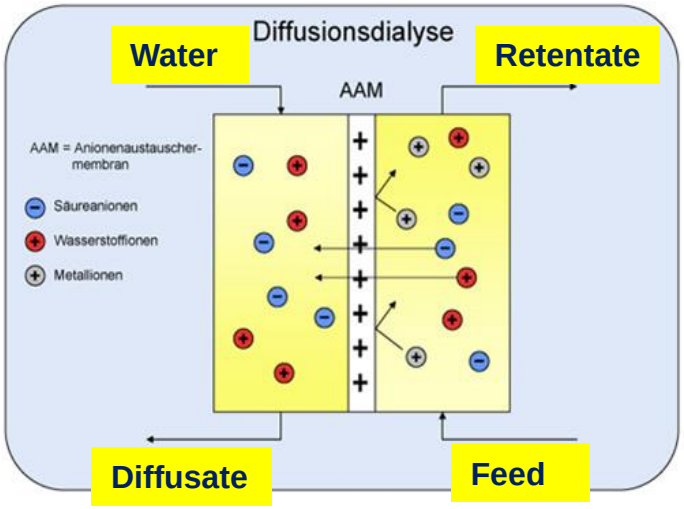
Recovery of valuable metals with membrane contactors



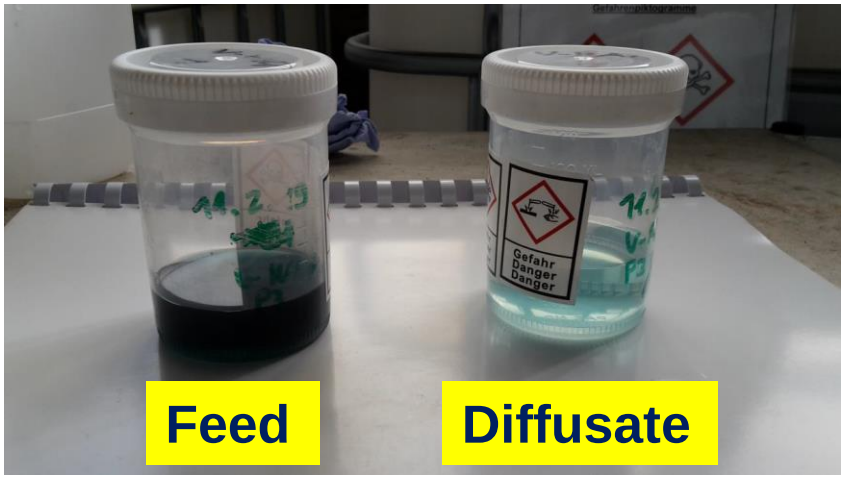
› **Membrane contactor** plant (8 m² membrane area) for recovery of valuable metals using **extraction media** - e.g. for nickel, zinc, manganese from phosphating process water; advantages: very large interface area and no mixing of bath and extracting agent (no phase separation).

Recovery of acids by Diffusion Dialysis

How does it work?



Feed (WA) and diffusate sample (after DD)



› Concentration difference between feed side (waste acid) and diffusate (recovered acid) as driving force using a selective anion exchange membrane.

› Separation of metals (high rejection) from acids (high passage through AAM)

Recycling of Liquid Media (acid recovery)

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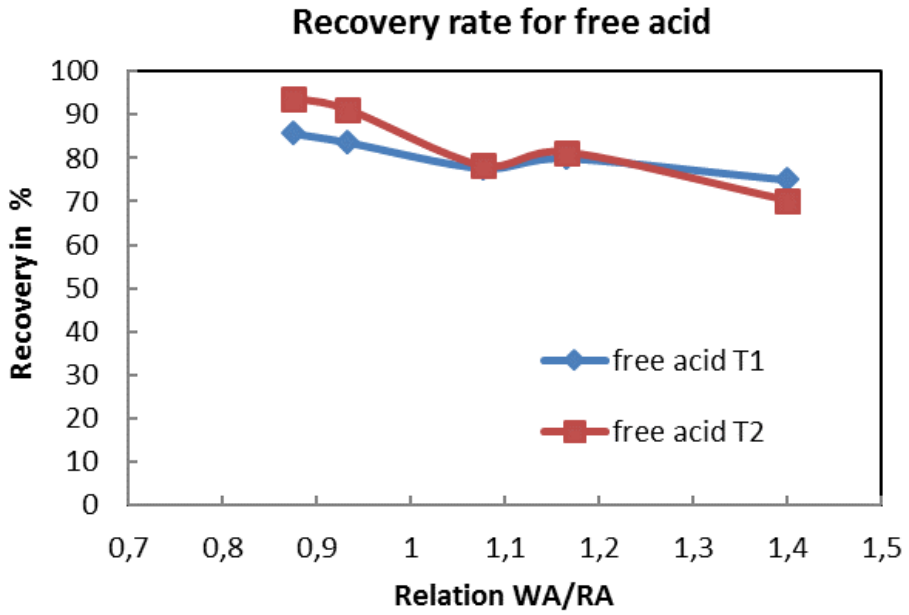
Recovery of mixed acids by DD/MD (HF/HNO3)

Installation of **ReWaCEM** Demo plant DD/MD for mixed acid recovery (DEW)

Funding:

European Commission

Results of recovery of acids by DD (HF/HNO3)



Recovery rate for free acid in diffusate:

› Highest recovery rate for free acid for WA/RA < 1

› Recovery rate of **80 – 90 %** for free acid possible

Development of acid resistant tubular RO-membranes

Innovative tubular RO-membranes

Advantages for industrial partners:

› Recycling of fresh water (ZLD)

› Suitable for small water volume flows

› Low particle content in feed is permitted

› Acid-resistant membranes for pH > 1.5

Actual results show:

› High metal retention

› Low electrical conductivity in permeate (high reduction of acids achieved)

Summary

Recycling of valuable components from process and rinsing water in the steel industry

- Waste water contains often valuable acids (HCl, H_2SO_4, HF, HNO_3) or valuable metals from coating processes (zinc, tin, nickel ...).
  Treatment and recycling of rinsing and process water is necessary for cost savings and for reaching regulating discharge limits.
- Accumulation of particles occur in nearly all process and rinsing water flows. A pretreatment method for particles is almost necessary.
- Membranes enable a selective separation of valuable components from process, rinsing and waste water streams. They are suitable for metal and acid recovery as well as for desalting (mono- and multivalent ions) in many applications of the steel industry.
- Most recycling methods require thermal energy, current or chemicals. Membrane technologies (e.g. DD, NF, RO) need in general pump energy: Reduction of the amount of waste water or chemicals used in subsequent treatment plants and therefore saving of costs for dumping are realized!


Thank you for your attention!