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# Recovery of pickling acid solutions by membrane technology:



## The EU REWACEM Project



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ISE Division Solar Thermal and Optics Fraunhofer-Institute for Solar Energy Systems ISE

projects in  
solar energy



Werner Warmuth  
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**EGGA**

European General  
Galvanizers Association

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ASSOCIAZIONE  
ITALIANA ZINCATURA

Assembly 2017 – Corinthia Hotel Prague – 12-15 June 2017



# ReWaCEM



### Project title

Resource recovery from industrial Waste water by Cutting Edge  
Membrane technologies

### Topic

SPIRE-01-2016

Systematic approaches for resource-efficient water management systems in  
process industries

**Grant agreement no.:** 723729

**Project starting date:** 01 October 2016

**Duration in months:** 36

**Call (part) identifier:** H2020-SPIRE-2016

### Co-ordinator:

Dr. Joachim Koschikowski

Fraunhofer-Institute for Solar Energy Systems ISE

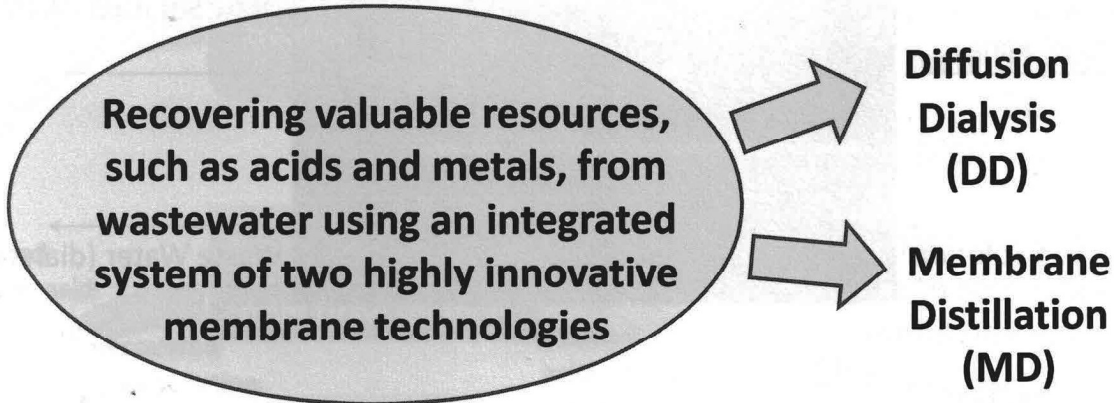
[www.ise.fraunhofer.de](http://www.ise.fraunhofer.de)



# ReWaCEM



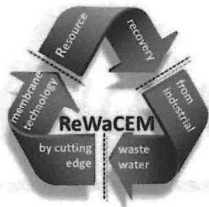
## The project idea



## The target



- Reducing water use
- Reducing wastewater production
- Reducing energy use
- Reducing chemicals consumption



# ReWaCEM



## The technology

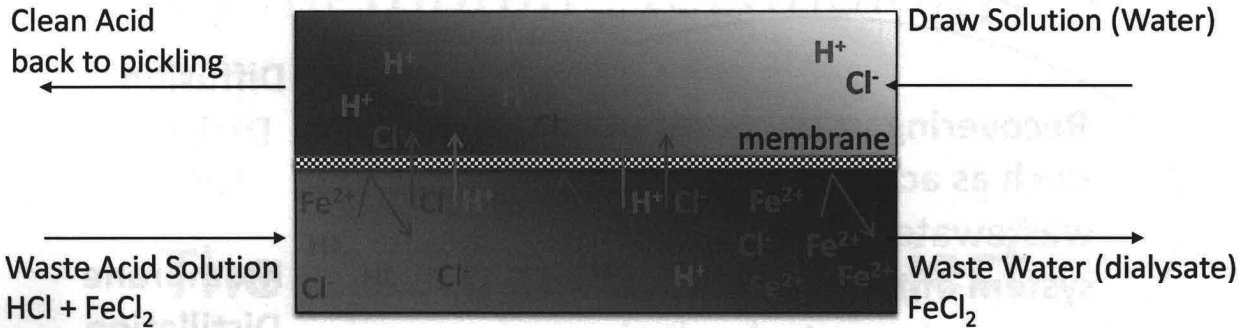
Diffusion Dialysis (DD)

and

Membrane Distillation (MD)

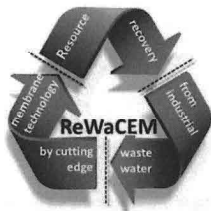


# Diffusion Dialysis (DD)

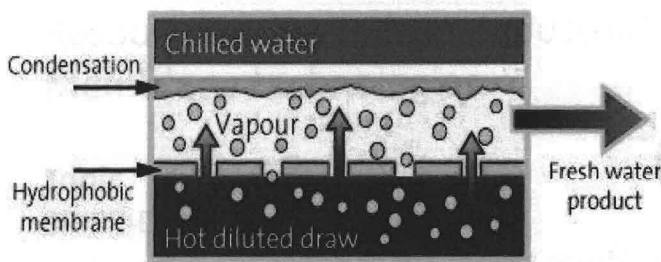


### Main advantages:

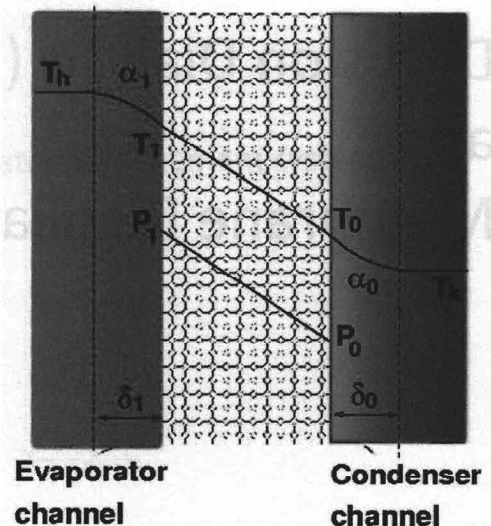
- High efficiency in wastewater treatment
- Low energetic consumption
- Low installation and executive costs
- Environment friendly



# Membrane Distillation (MD)

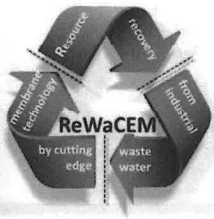


Temperature and Vapor pressure profile across the membrane

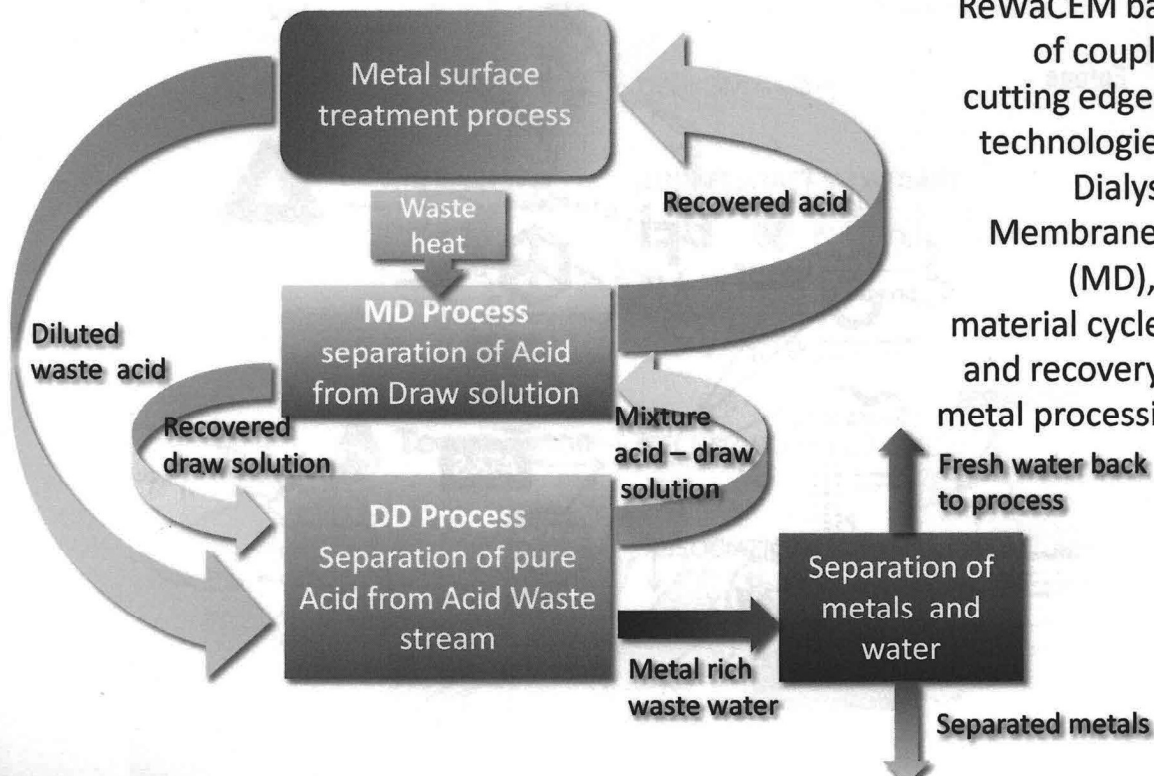


### Main advantages:

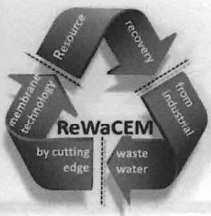
- Low working temperature and pressure
- Low energy cost
- Low stringent mechanical properties
- Operational simplicity
- Simple up-scaling



## Coupling of DD and MD



ReWaCEM basic scheme of coupling the two cutting edge membrane technologies, Diffusion Dialysis (DD) and Membrane Distillation (MD), as a closed material cycles approach and recovery concept in metal processing industry



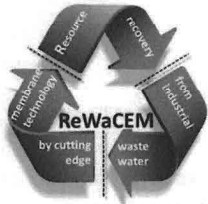
## Coupling of DD and MD

**Recovery of acid in pickling solutions used in the plating hot-dip galvanizing and stainless steel industry**

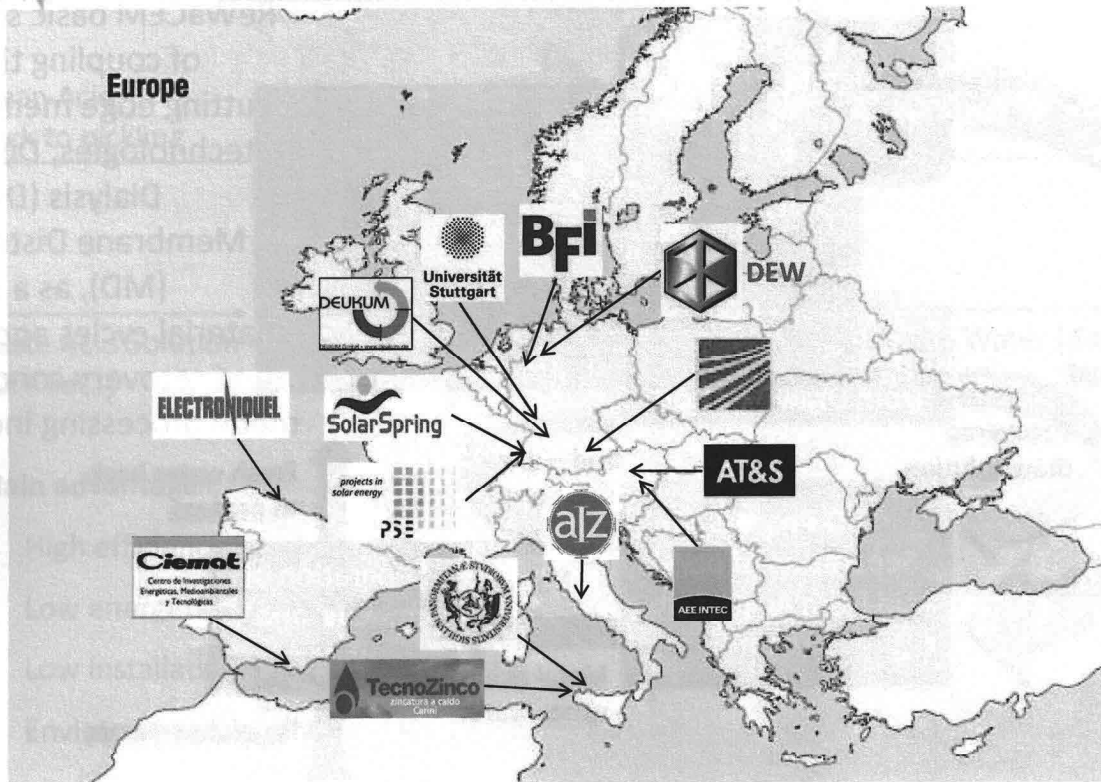
The innovation in ReWaCEM is to combine both technologies which allows:

- the separation of metallic ions from the acid molecules (DD) AND
- the recovery of acid solution to be reused after a concentration step (MD)



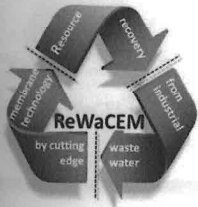


# The ReWaCEM project Consortium

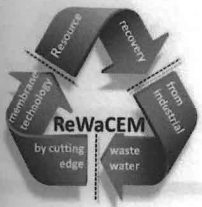


# The ReWaCEM project Consortium

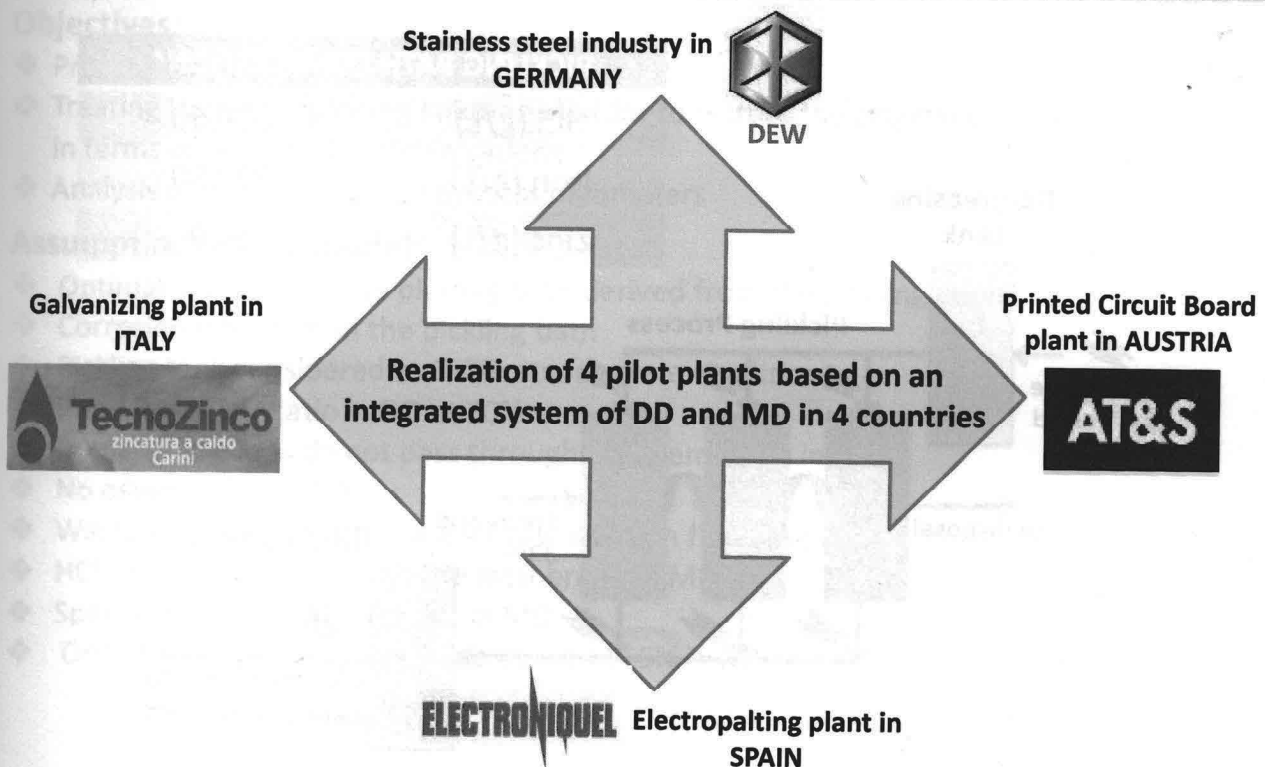
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**Fraunhofer ISE**
FRAUNHOFER INSTITUTE FOR SOLAR ENERGY SYSTEMS ISE
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**UNIVERSITÀ DEGLI STUDI DI PALERMO**
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ELECTRONIQUEL, SA



# The ReWaCEM project Consortium



# The ReWaCEM Project Achievements





# Hot-dip galvanizing under development

Tecnozinco srl



and

Università degli Studi di Palermo – UNIPA  
DIID



are involved for hot-dip galvanizing;

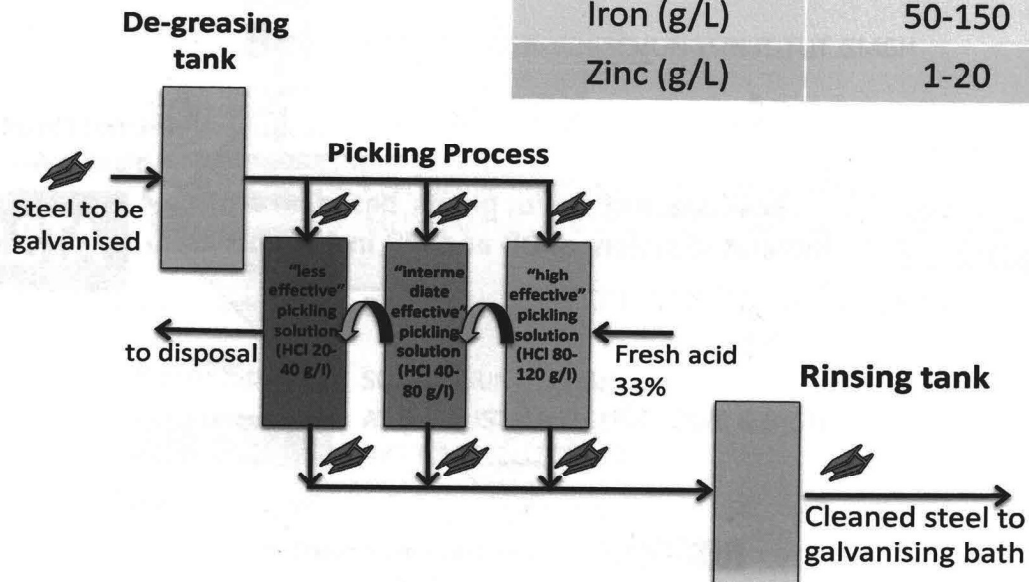
AIZ supports the adaptation of the technology to the sector as well as the data mining and will take care of the dissemination of the final results

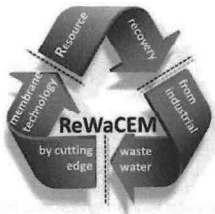


# Hot-dip galvanizing operational conditions

**PICKLING BATH COMPOSITION\***

HCl (g/L)	20-150
Iron (g/L)	50-150
Zinc (g/L)	1-20





# Hot-dip galvanizing

## driving force to recovery

Sector data*			
HCl acid	minimum	average	maximum
fresh acid 33% ( $\text{Kg}_{\text{HCl}}/\text{ton}_{\text{galv.steel}}$ )	10,53	20,52	28,66
spent liquor ( $\text{Kg}/\text{ton}_{\text{galv.steel}}$ )	13,53	28,78	43,75

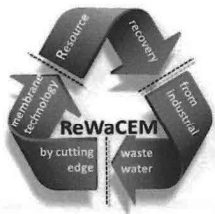
\*data from a benchmarking study among AIZ members (2008)

### data analysis:

acid consumption per plant depends on the steel items surface conditions

mix of steel carpentry with average oxidation			
HCl acid	range		up to*
fresh acid 33% ( $\text{Kg}_{\text{HCl}}/\text{ton}_{\text{galv.steel}}$ )	22	26	
spent liquor ( $\text{Kg}/\text{ton}_{\text{galv.steel}}$ )	25	35	≈45

\*realistic worst conditions



# UNIPA activity

## design of overall process

### Objectives:

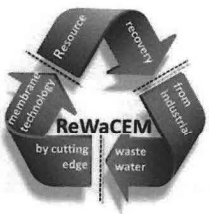
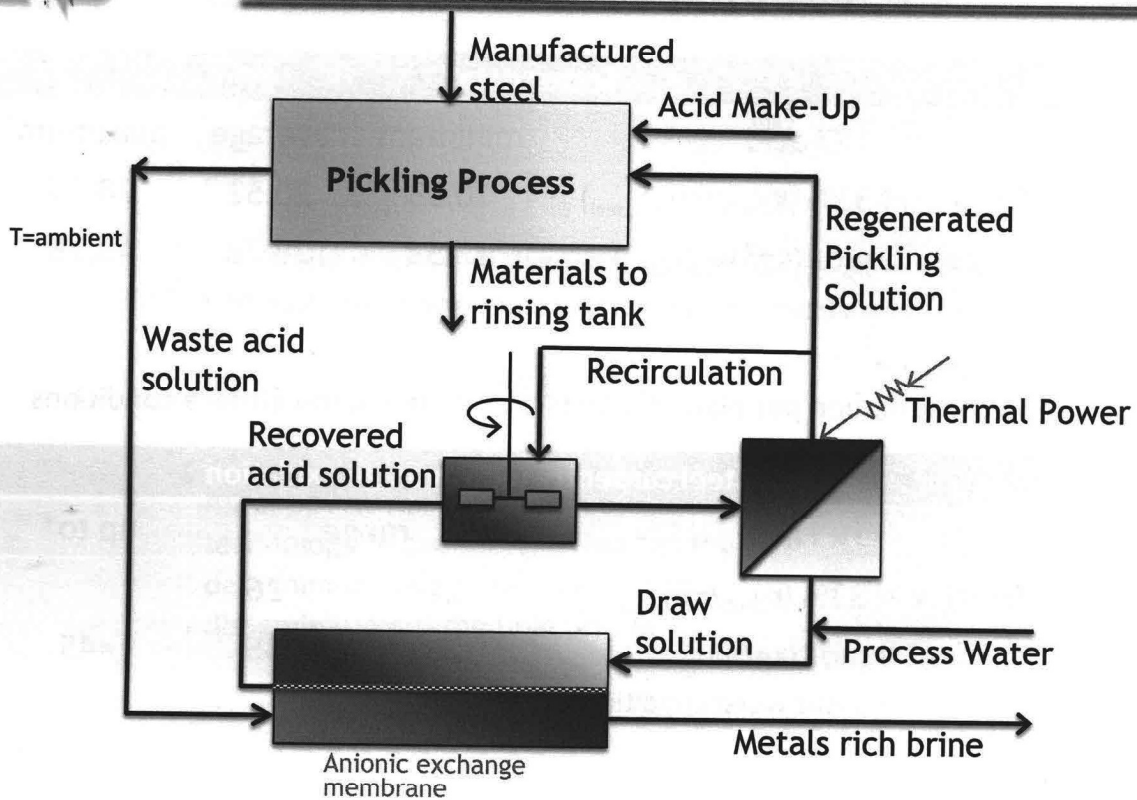
- ❖ Process modeling
- ❖ Treating the waste pickling solution in order to restore the original optimal conditions in terms of Fe and HCl concentrations
- ❖ Analysis of sensitivity of the process parameters

### Assumptions in the model:

- ❖ Optimal condition in the pickling bath derived from the pickling curve
- ❖ Corrosion inhibition in the pickling bath
- ❖ Pickling tank considered as CSTR: steady state condition
- ❖ Fixed Recovery Ratio in DD at 70%
- ❖ Iron and zinc ions do not pass through the membrane in DD
- ❖ No osmotic flux in DD
- ❖ Waste acid solution flow rate = Draw solution flow rate in DD
- ❖ HCl does not pass through the membrane in MD
- ❖ Specific Energy = 400 kWh/m<sup>3</sup> in MD
- ❖ Once through Conversion Ratio assumed: 5% in MD



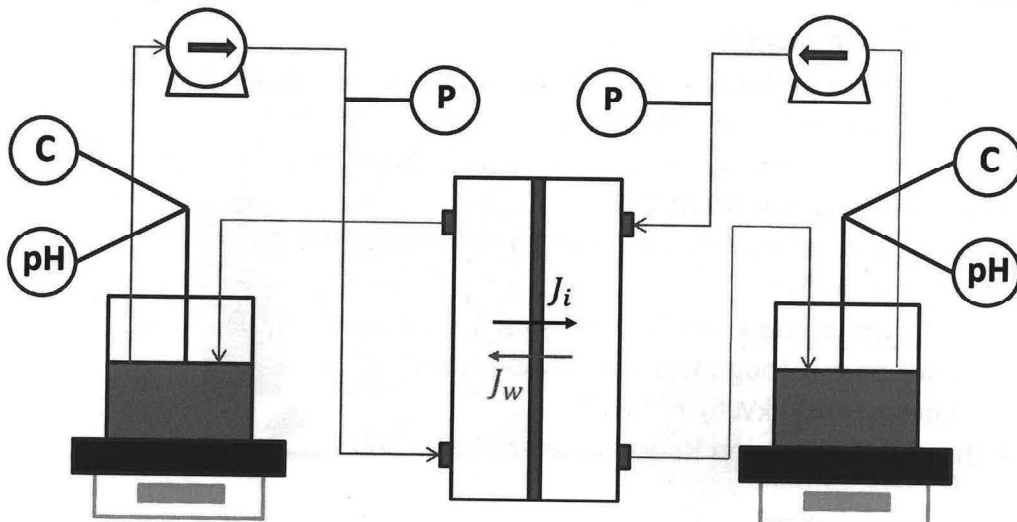
# Design of overall process



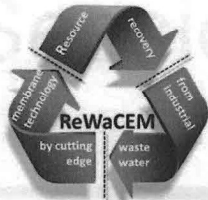
# Diffusion Dialysis Design

UNIPA activity objectives:

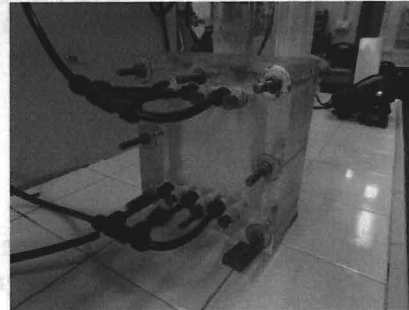
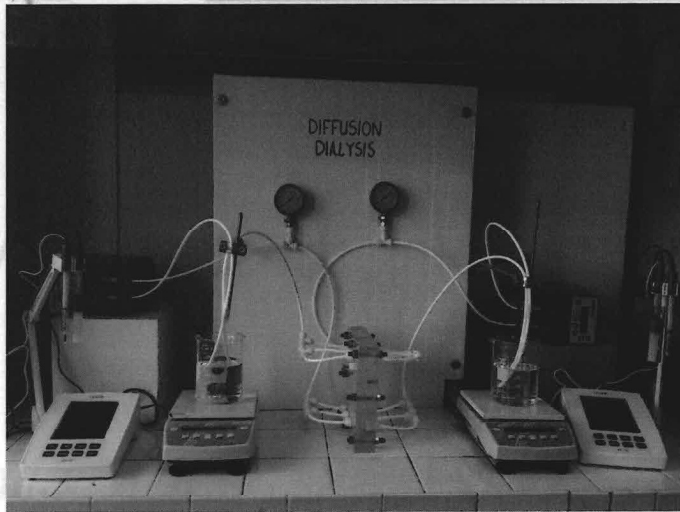
- ❖ Developing a model for a design of the DD system
- ❖ Testing and experimental investigations aiming at the validation of the model



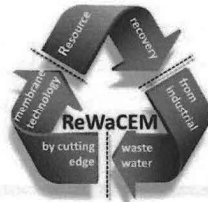




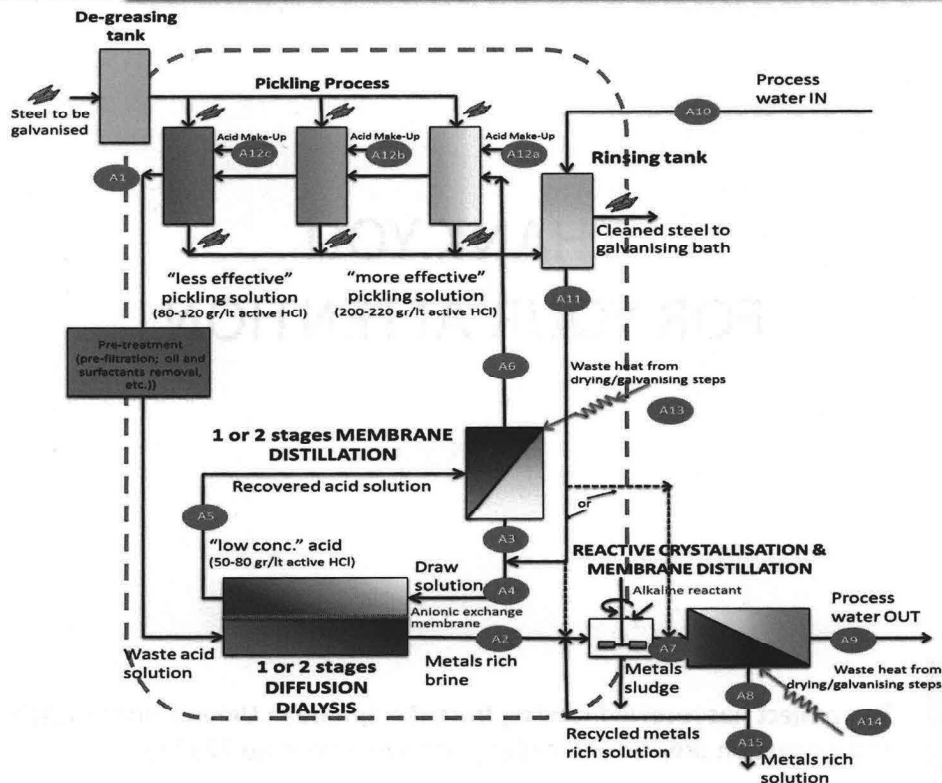
# Diffusion Dialysis Design



- ❖ Plate and Frame configuration
- ❖ Stack geometry
- ❖ Feed channels and output channels
- ❖ Peristaltic pumps
- ❖ Dimensioning membrane area



# Demo at Tecnozinco design of overall process





## Further information

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<http://www.rewacem.eu>

For any questions concerning the ReWaCEM Project, please contact [info@rewacem.eu](mailto:info@rewacem.eu)



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## ReWaCEM

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THANK YOU  
FOR YOUR ATTENTION



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