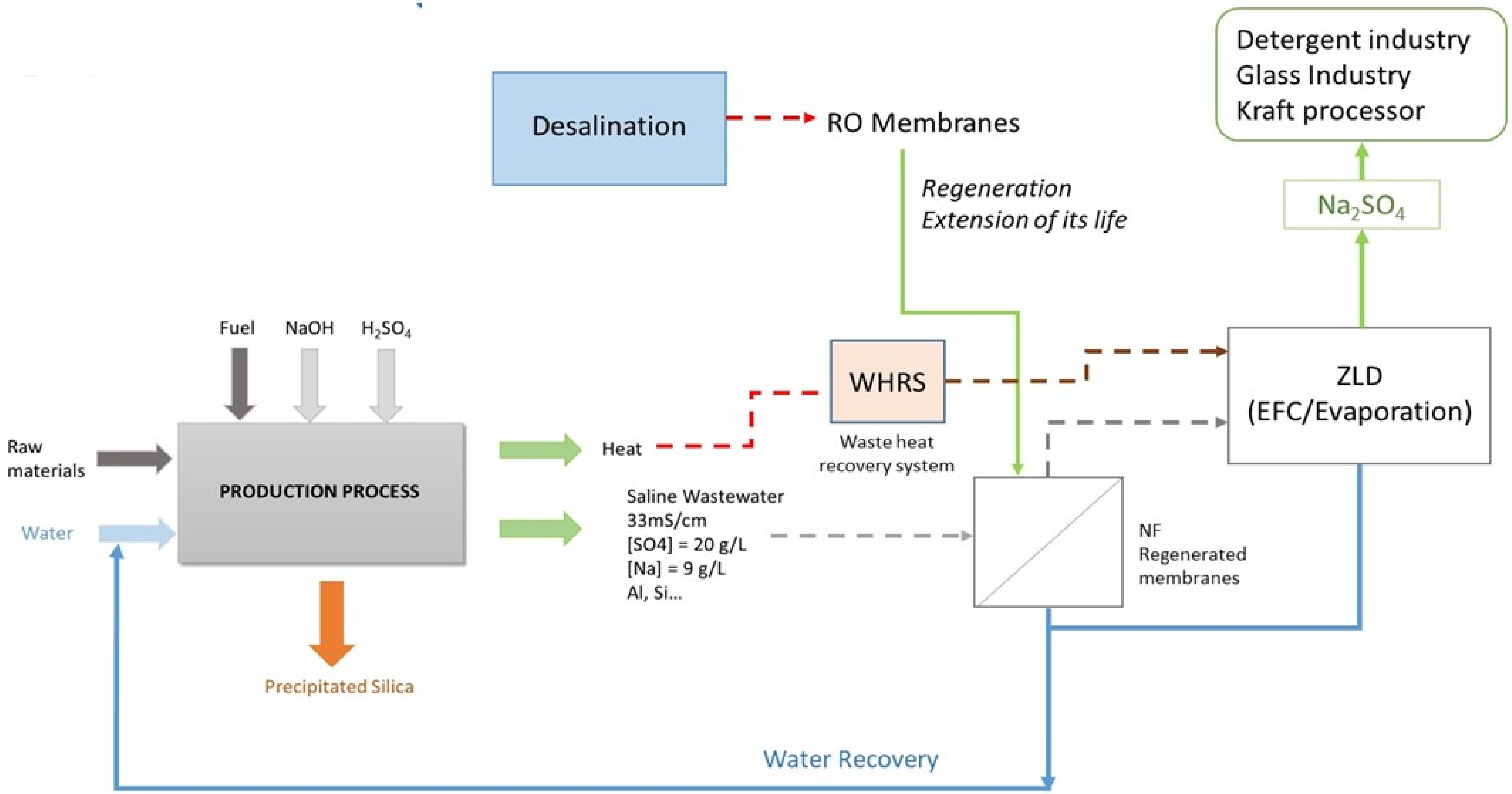
WP4

Promoting circular economy in the chemical sector: an innovative approach to recover resources from wastewater generated in the silica indutsry

The ZERO BRINE project (www.zerobrine.eu) has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 730390.

Treatment scheme



Industrial Wastewater ◆ Resource Recovery ◆ Circular Economy

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OBJECTIVES

- To demonstrate the technical and economic feasibility of implementing a circulars economy scheme in the precipitated silica industry to recover water, sodium sulphate, waste heat, acids and alkalis.
- To demonstrate the technical feasibility of using recovered nanofiltration (NF) membranes for concentrating effluents with high salinity.
- To evaluate eutectic freeze crystallization (EFC) and forward-feed evaporation technologies to crystallize Na_2SO_4 from concentrated effluents.
- To demonstrate the technical and economic feasibility of the waste heat recovery system (WHRS) to reduce energy requirements of the circular economy scheme.
- To demonstrate the technical and economic feasibility of electrodyalisis with bipolar membranes (EDBP) to recover NaOH and H_2SO_4 from silica industry effluents

WP4 TASKS

Task 4.1:Bench-scale optimization of recovery processes (CTM)

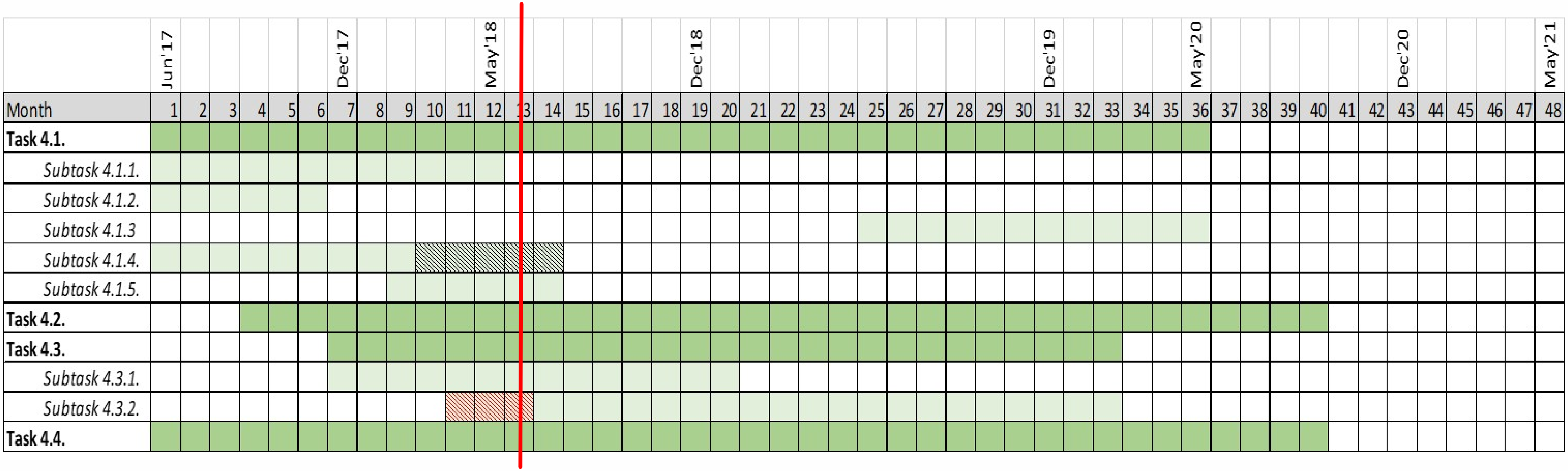
- Subtask 4.1.1. Wastewater characterization (**IQE**, CTM) ✓
- Subtask 4.1.2:Pre-treatment optimization (**CTM**, IQE, TYPSA) ✓
- Subtask 4.1.3:Evaluation of NaOH and H_2SO_4 recovery using bipolar membranes (**CTM**, IQE) *Not started*
- Subtask 4.1.4: Regeneration of reverse osmosis membranes from desalination plants (**TYPSA**, CTM, IQE) ✓
- Subtask 4.1.5:Design of the ZLD stage of the innovative sodium sulphate recovery process (**CTM**, TUDelft, SEALEAU) *Ongoing*

Task 4.2: Evaluation of heat waste recovery strategies (CTM)

Task 4.3: Validation of the sodium sulphate recovery process at pilot scale (IQE)

- Subtask 4.3.1: Site adaptation and pilot plant implementation (TYPSA, IQE, CTM, TUDelft) *Ongoing*
- Subtask 4.3.2: Operation and optimization of the sodium sulphate recovery process at pilot scale (IQE, CTM, TYPSA, TUDelft) *Not started*
- **Task 4.4: Data collection from the demonstration activity (CTM)** *Ongoing*

Gantt Chart


Jun'17
Dec'17
May'18
Dec'18
Dec'19
May'20
Dec'20
May'21
Month
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48
Task 4.1.
Subtask 4.1.1.
Subtask 4.1.2.
Subtask 4.1.3
Subtask 4.1.4.
Subtask 4.1.5.
Task 4.2.
Task 4.3.
Subtask 4.3.1.
Subtask 4.3.2.
Task 4.4.

DELIVERABLES

Deliverable number	Title	Type	Due date (months)	Status
D4.1	Characterization of wastewater production process of precipitated silica	Report	12	Submitted
D4.2	Regeneration and performance of reverse osmosis membranes from desalination plants	Report	12	Delayed to M14
D4.3	Innovative technologies for recovering compounds in the precipitated silica industry	Report	36	-
D4.4	Waste heat recovery opportunities in the precipitated silica industry	Report	40	-
D4.5	Innovative circular economy process in the precipitated silica industry: design and performance	Report	40	-
D4.6	Database of data collected during WP4 demonstration activity	Report	6	Submitted in M9

Tasks performed

- ✓ Wastewater characterization
- ✓ Pre-treatment definition
- ✓ Bench-scale evaluation of regenerated membranes
- ✓ Design and construction of regeneration membranes system
- ✓ Obtaining of regenerated membranes
- ✓ First bench-scale experiments of EFC. CTM training at TUDelft
- ✓ Site adaptation at IQE
- ✓ NF pilot plant refurbishment
- ✓ Analysis of waste heat recovery systems applied to EFC technology

Subtask 4.1.1. Wastewater characterization

- ✓ Data collection: process flowsheet, historical composition of the effluents
- ✓ Data evaluation: seasonal composition variability, definition of critical elements for membrane treatment, planning for sampling, definitions of characterization parameters
- ✓ Samples collection and characterization
- ✓ Deliverable 4.1. Submitted in May 2018

Product		Precipitated silica		Aluminium hydroxide	
Effluent		Filtration + Washing wastewater (n=6)		Filtration wastewater (n=3)	
Parameter	Units	Value	SD	Value	SD
pH	upH	4.8	1.3	7.9	0.1
EC	mS/cm	27.3	5.9	87.4	0.8
Turbidity	NTU	67.4	133	>800	n/a
Cl	mg/L	1,759	498	161	40.4
NO_3	mg/L	11.8	0.61	17.1	0.10
SO_4	mg/L	16,468	4,451	87,083	1,265
K	mg/L	434	11	25	4.0
Na	mg/L	7,325	2,061	43,078	2,486
Ca	mg/L	38.5	35.3	<2.0	n/a
Mg	mg/L	213	235	<5.0	n/a
TIC	mg/L	<5	n/a	502	16.4
Al	µg/L	2,272	2,876	2,450	70.7
Si total	mg/L	80.5	22.8	1.4	0.6
Si reactive	mg/L	77.1	23.0	<1.0	n/a
Mn	µg/L	278	182	9.6	3.4
Fe	µg/L	855	712	<20	n/a
Sr	µg/L	495	431	31.5	3.5
Ba	µg/L	49.2	16.4	11.5	4.9

Subtask 4.1.2. Pre-tretament optimization

- ✓ Modelling: prediction of scaling problems during NF treatment
  - Scaling due to Al, Fe, Ba and Si

- ✓ Identification of strategies to remove critical elements and evaluation at laboratory scale
- ✓ Definition of the pre-treatment step

Antiscalant agent

pH 7 → UF → pH 9

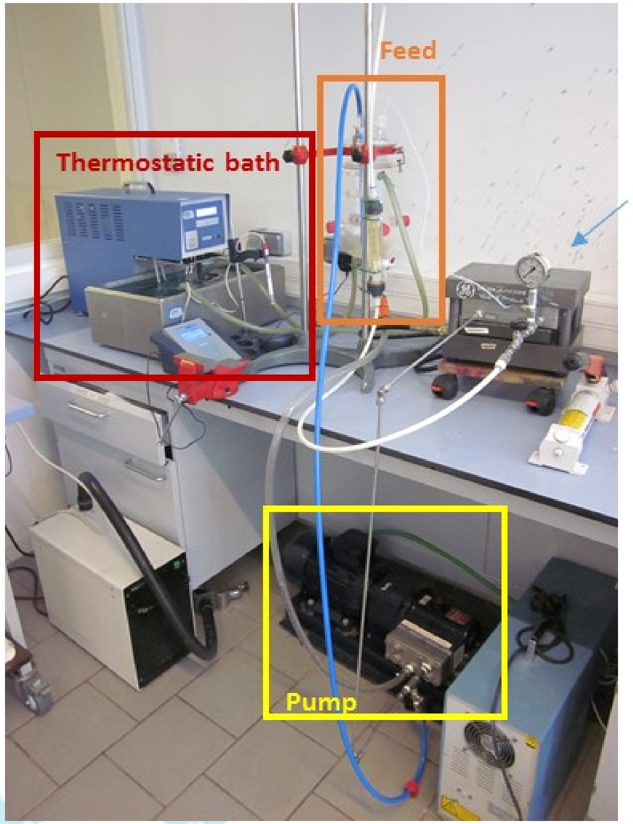
pH increase to precipitate Al and Fe

pH increase to increase Si solubility

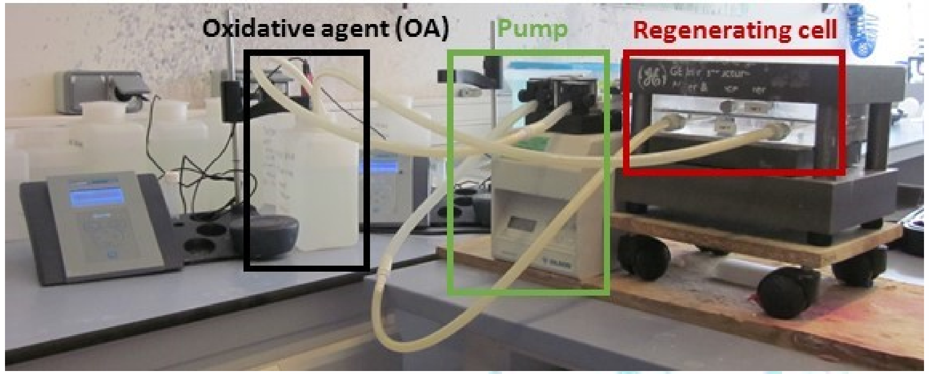
Subtask 4.1.4. Membranes regeneration

Bench-scale experiments

- Membrane characterization using standard test
- Regeneration process using different conditions
- Selection of the optimal conditions according permeate quality requirements



Flat-sheet membrane module



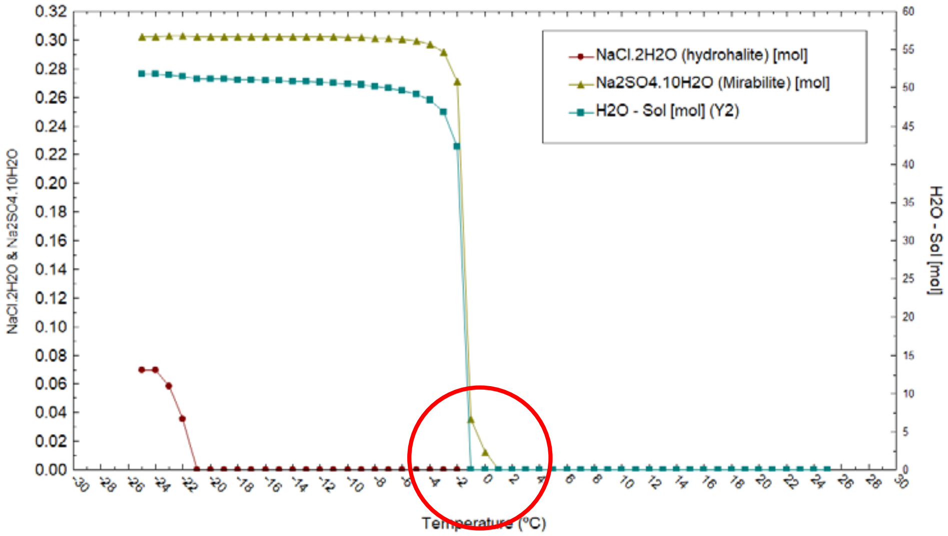
Subtask 4.1.4. Membranes regeneration

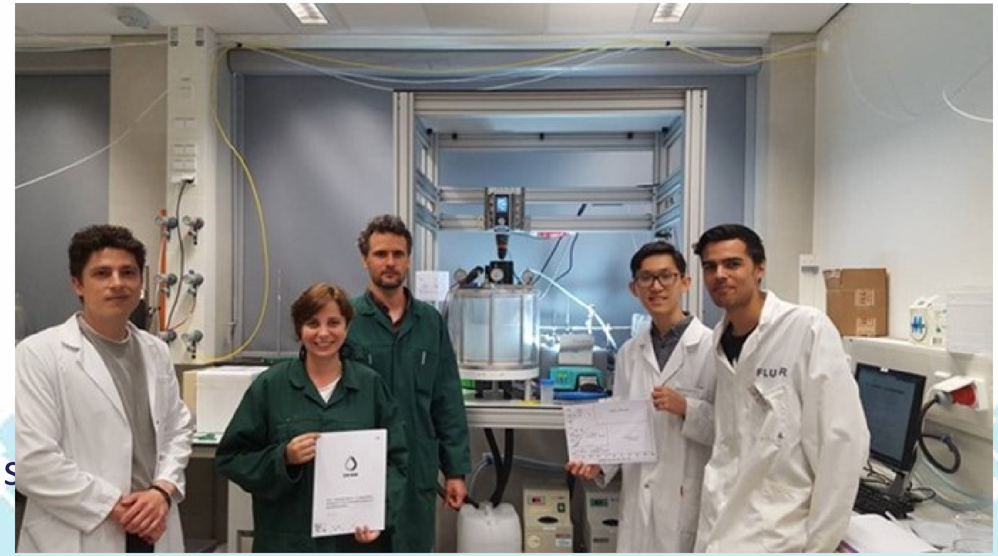
Regeneration Pilot plant

- Production of regeneration membranes at selected conditions
- 2 different membranes obtained

Subtask 4.1.5. Design and optimization of Na_2SO_4 crystallization

- Comparison of EFC and Forward Feed evaporation
- Bench scale evaporation not available. Comparison will be made at pilot scale.
- Thermodynamic simulations
- CTM visit at TUDelft: training about EFC
- Bench-scale experimental system construction at CTM with the support of TUDelft
- Evaluation of the technology during the following months





$Na_2SO_4 \cdot 10H_2O$ crystallization a 1ºC.
Eutectic point at -1.5ºC.

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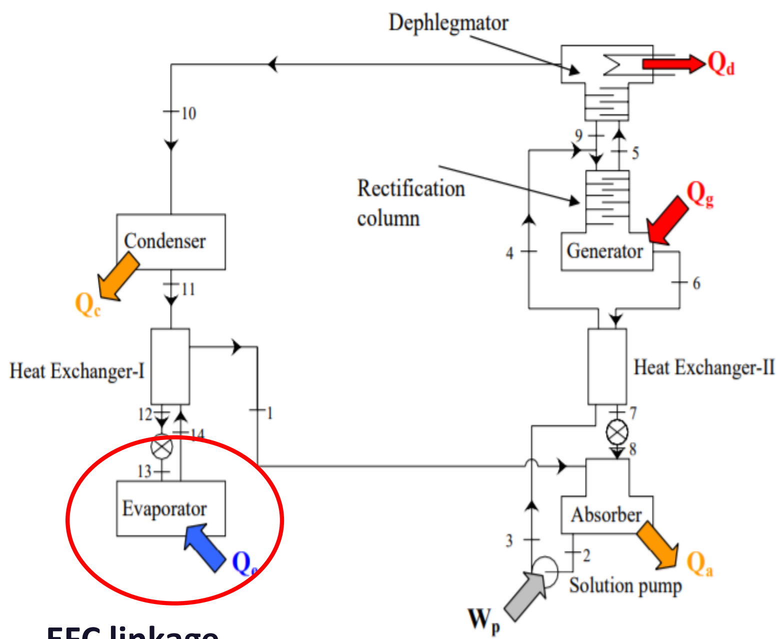
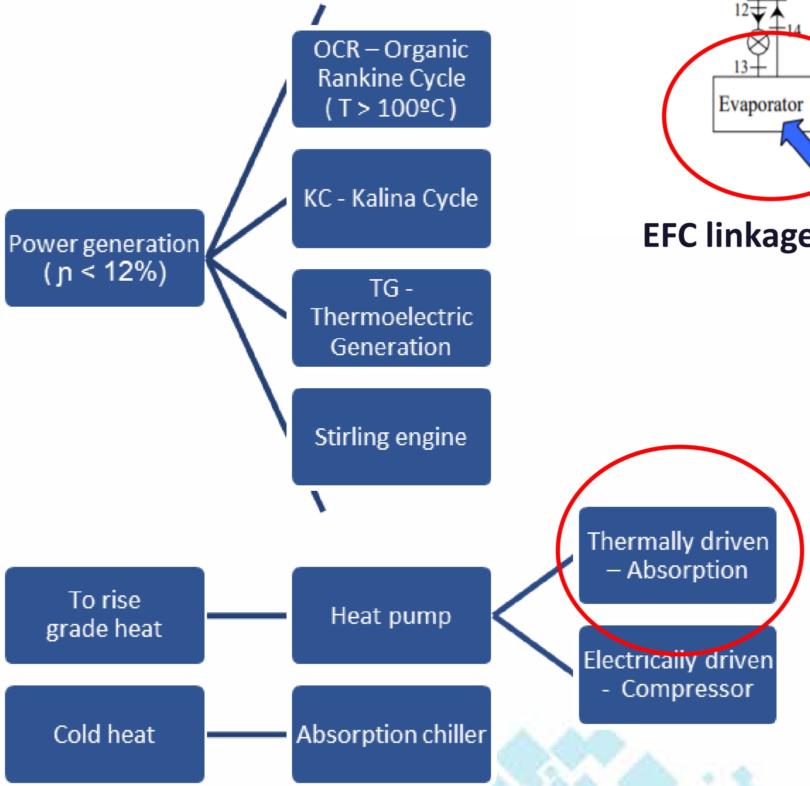
Task 4.2 Evaluation of heat recovery systems

Tasks carried:

1. **Extended State of the Art of Waste Heat Recovery Systems: Which options are feasible to be integrated?**
    1. **Electro-mechanical options**: ORC (Organic rankine cycle) and Kalina. (Expensive!)
    2. **Thermally driven**: absorption, adsorption.
        1. Dynamic numerical modelisation of a single-stage LiBr-Water absorption cycle (not implemented because of eutectic temperature points)
        2. Steady-state numerical modelisation of **a single-stage NH3-Water absorption cycle** (**not implemented but feasible option**)
2. **Link of the energy harvesting system and EFC / ED.**



EFC linkage



Subtask 4.3.1. Site adaptation and plant implementation

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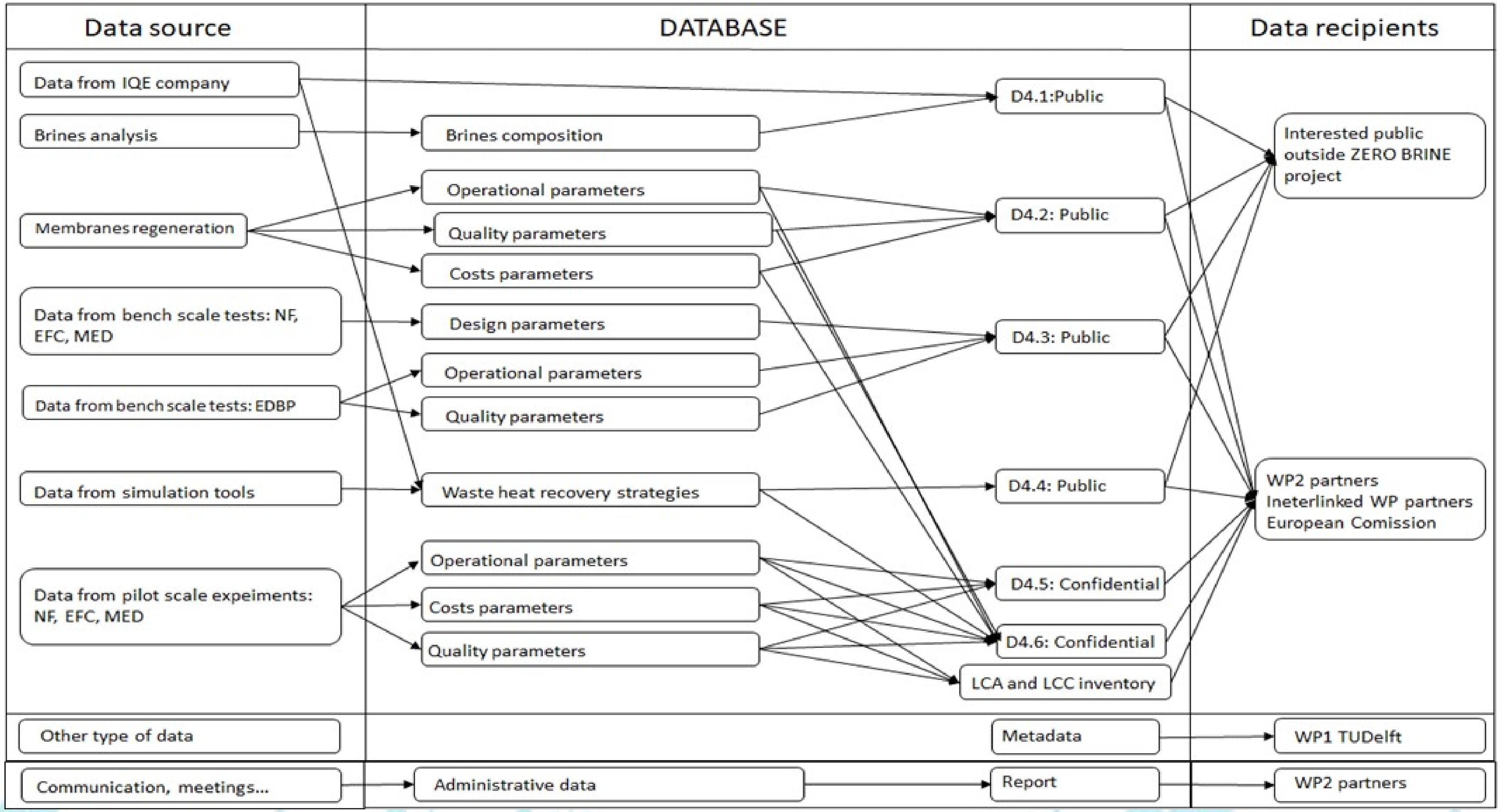
Subtask 4.3.1. Site adaptation and plant implementation

- ✓ Start-up on July 2018
- ✓ EFC pilot plant delayed

Subtask 4.3.2. Operation and optimization of the sodium sulphate recovery process at pilot scale

- Start-up on July 2018
- RO/NF stage optimization: September – December 2018
- RO/NF stage operation until end of 2019
- Crystallization stage: treatment of concentrate from RO/NF and wastewater from Aluminum hydroxide wastewater
- Tentative schedule
    - EFC pilot plant available first half 2019?
    - Evaporation pilot plant second half 2019?

Task 4.4 Database



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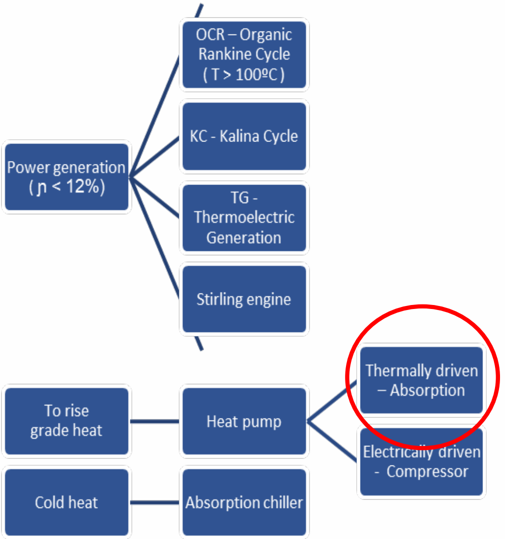

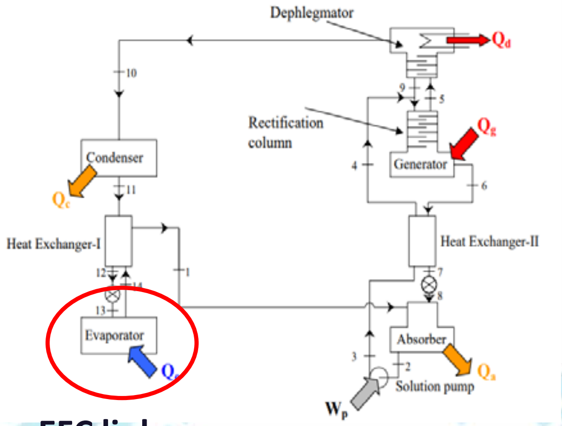

EFC linkage

Task	Responsible	Deadline
Definition of the study methodology	CTM	October 2017
Gather information regarding the IQE process and identification of potential waste heat sources.	CTM	December 2017
Waste heat sources characterization	CTM	March 2018
Gather information regarding the EU silica industry	CTM	March 2018
Case studies identification based on the IQE process and the EU silica industry identification: characterization of the EU silica industry regarding production process and production capacity.	CTM	August 2018
Identification and modelling of the most potential heat recovery, heat transformation and heat upgrade technologies (Heat Exchangers, ORC, Kalina Cycle, Thermoelectric Generation, Absortion Chillers)	CTM	January 2019
Definition of the energy monitoring system for the EFC/Evaporator technologies operation at the pilot scale.	CTM	January 2019

Fig. NH3-Water single-effect absorption cycle