

D3.10 – Lab-scale HRRO unit for integration with IX

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Table of Contents

1	Executive Summary	6
2	Introduction.....	6
3	Electrolyte recovery using standard RO system performed at THK.....	7
3.1	Objectives of the work	7
3.2	Comprehensive analytical investigation and potential challenges to overcome	7
3.3	HPRO Trials	10
3.4	Electroplating trials	14
3.5	Adsorption trials with powdered activated carbon (PAC)	16
4	Removal of anionic surfactants from rinsing bath solutions with granular activated carbon.....	19
4.1	Preliminary design of fixed bed columns for the removal of anionic surfactants.....	19
5	Low-pressure hybrid semibatch-batch HRRO system.....	21
5.1	Description of the system.....	21
5.2	Tests on hybrid semibatch-batch high recovery RO process using NaCl	23
5.2.1	Hydraulic SEC.....	23
5.2.2	Pump efficiency	25
5.2.3	Electrical SEC and rejection.....	27
5.2.4	Permeate conductivity	28
5.2.5	Batch conductivity and supply pressure over a cycle	29
5.2.6	Concentration factor and Recovery	29
5.2.7	Peak Pressure.....	30
5.3	Modelling of the system	31
5.3.1	Procedure.....	31
5.3.2	Results.....	32
6	Design of the high pressure HRRO system	35
6.1	Preliminary design of the system	35
6.1.1	Description of hardware	37
6.1.2	Safety aspects.....	40
7	Technical Risks.....	41
8	Conclusions.....	43
9	References.....	44
10	Appendices	44
10.1	Risk Assessment.....	44
10.2	Calculation summary of corrosion rate for 316L SS	46

List of Figures

Figure 1 - ATR-IR spectra for (A) Replenisher, (B) Buffer, (C) Wetting Agent and (D) Complexor	9
Figure 2 - (A) Photograph and (B) Piping & instrumentation diagram of the HPRO system used at TH Köln.....	12
Figure 3 - Measured osmotic pressure vs. concentration level during HPRO concentration.....	13



Figure 4 - Dependency of the permeate flux and the membrane permeability on the driving pressure (transmembrane pressure) difference during HPRO concentration.13

Figure 5 - Concentration of sulphate, boric acid and Cr(III) measured at different concentration levels.14

Figure 6 - (Left) - Surface tension measured in the permeate and the concentrate during HPRO concentration. (Right) – TOC content measured in permeates at different concentration levels.14

Figure 7 - Photograph of the Hull Cell used for the electroplating trials performed in this work.15

Figure 8 - Concentrations of Cr(III), boric acid and sulphate in CL16 (RO concentrate), restocked CL16 (RO concentrate restocked) and a Cr(III) electrolyte bath (Electrolyte TRILYTE Flash SF).16

Figure 9 - Photographs of the electroplated plates including thickness measurements for CL16 and CL16 restocked. The trials were performed in Hull Cell.16

Figure 10 - TOC content of Cr(III) rinse water with PAC contact time (Silcarbon).17

Figure 11 - TOC content of Cr(III) rinse waters in dependency of the volume fraction of rinse water before (black) and after (red) the treatment with powdered activated carbon (Silcarbon).17

Figure 12 - Chromium content in Cr(III) rinse water in dependency of the volume fraction of rinse water before (black) and after (red) the treatment with powdered activated carbon (PAC from Silcarbon).18

Figure 13 - Adsorbed TOC content on the four PACs with different TOC content of the rinse water.18

FIGURE 14 - PROCESS FLOW DIAGRAM OF FIXED BED SETUP FOR THE REMOVAL OF ANIONIC SURFACTANTS.20

Figure 15 - High-recovery batch RO prototype installed in the UoB laboratory (A and B) front view, (C) side view, (D) Back view.22

Figure 16 - Schematic diagram of high-recovery batch RO system (PT, CT and FT are pressure, conductivity and flow transmitters, respectively. W_1 , W_2 , and W_3 are weighing platforms for feed, permeate and brine tanks). From [2].23

Figure 17 - Model predictions (MOD) and experimental measurements (EXP) of hydraulic SEC of free-piston hybrid HRRO at various: (A) feed salinities, and (B) water fluxes.25

Figure 18 - Hydraulic and electrical SEC of the hybrid HRRO system over a cycle at various: (A) feed salinities, and (B) water fluxes.....27

Figure 19 - Permeate conductivity vs. time after start of the pressurization phase, at 1 g/L feed solution, and $J_w = 16.5$ LMH.28

Figure 20 - Batch conductivity and supply pressure changes vs. time after the start of the pressurization phase, at 1 g/L feed solution, and $J_w = 16.5$ LMH.29

Figure 21 - Experimental concentration factor and recovery vs water flux at 1 g/l feed concentration.30

Figure 22 - Peak pressure at end of pressurisation phase vs water flux. Model predictions and experimental values, at 1 g/l feed concentration.30

Figure 23 - SEC and peak pressure vs recirculation flow (ratio of recirculating flow/feed flow)33

Figure 24 - SEC, output and peak pressure vs water flux through membrane, with work exchanger volume of 0.04 m^334

Figure 25 - Process flow diagram of the high pressure HRRO system37

Figure 26 - General arrangement Diagram of the high pressure HRRO system38

Figure 27 - Flow paths and corresponding pressure drops for each pump and phase of operation. V_1 , V_2 and V_3 are the bypass, recirculation and purge valve respectively. Blue shading indicates open valves; black shading indicates closed valves. These flow paths and pressure drops justify the equations shown in Table 21.40

List of Tables

Table 1. Quality parameters for RO permeate recycling in rinsing baths.8

Table 2. Quality parameters for RO concentrate re-use in electroplating baths.9

Table 3. RO experiments parameters.10

Table 4. The electroplating conditions for Hull cell test.....15

Table 5. Removal of anionic surfactants from rinsing bath solutions after treatment with activated carbon.19



Table 6. Feed and recirculation pump efficiencies over a cycle for pressurization and purge-and-refill phases at various feed salinities, and $J_w=14.5$ LMH27

Table 7. The effect of varying flux on the important factors of hybrid HRRO system at 1.5 g/l feed salinity. System flux is the flux averaged over the whole cycle, considering the purge-and refill phase which is non-productive.28

Table 8. Input parameters to the model of the hybrid semi batch-batch HRRO system.31

Table 9. The effect of pump efficiency on SEC (kWh/m^3) (flux=17.2 LMH, Recirculation/feed flow =3).34

Table 10. The work packages and the produced documents of the preliminary design stage of high pressure HRRO rig. Please note that these work packages refer specifically to the subcontracted project of the HRRO rig development, and do not correspond therefore to the overarching work packages of IntelWATT.35

Table 11. Flow rate, pressure, and water displaced volume for each pump and phase of operation.....39

Table 12. Technical risks with likelihood and severity on a scale of 1 to 3. (L) is for an assessment of the likelihood of the hazard taking place, (S) for the severity of the risk. This table does not include all aspects of risk and hazard assessment relating to safety, which are covered instead in Appendix 10.1.42

Definitions and acronyms

Acronym	Extended definition
HPRO	High Pressure Reverse Osmosis
HRRO	High Recovery Reverse Osmosis
ICP	Inductively coupled plasma
IX	Ion Exchange
PLC	Programmable Logic Controller
RO	Reverse Osmosis
SEC	Specific Energy Consumption
WE	Work Exchanger
CL	Concentration Level
PFD	Process Flow Diagram
GA	General Arrangement
LMH	Litre per square meter per hour
TOC	Total Organic Carbon
HPRO	High Pressure Reverse Osmosis

1 Executive Summary

This document corresponds to the deliverable D3.10 “Lab scale HRRO unit for integration with IX”. Its main purpose is to demonstrate the lab scale high-pressure HRRO unit for concentration of rinse water. This deliverable includes the updated mathematical modelling, updated results of standard RO experiments, a description of the design of the proposed new high-pressure HRRO rig, and further experiments on the existing low-pressure HRRO rig. Results demonstrating concentration of chromium (III) from rinse water using standard RO are updated and expanded, showing an excellent chromium (III) rejection, and the electroplating trials are reported. Moreover, to reduce fouling of RO membrane, adsorption of TOC and anionic surfactants from rinse water using the powdered activated carbon and granular activated carbon, respectively, have been tested showing promising results.

The mathematical modelling of the hybrid semibatch-batch RO was modified and improved, resulting in an updated concept design including consideration of osmotic backflow adjustment, a more precise model of friction losses, and an improved model of longitudinal concentration gradient.

The low-pressure hybrid semibatch-batch high-recovery RO system has been demonstrated and tested for concentration of NaCl solution at pressure limit of 25 bar under several fluxes and salinities. Several parameters such as hydraulic and electrical SEC, permeate and batch conductivity, concentration factor, recovery, and peak pressure have been investigated to present the performance of the system. The results at this stage are promising in terms of rejection, system output, and SEC, supporting the feasibility of the operation of the final high-pressure HRRO system at 120 bar and with the chromium (III) rinse water as feed. At a flux of 14.5 LMH, a recovery of 0.96 and concentration factor of 20.6 have been achieved. The key design features of the high-pressure HRRO system, including process flow diagram, general arrangement, risk assessment, procedure and technical risks are presented; while the full design details of the system (including changes if required due to new findings) will be covered in an updated version of D3.10

2 Introduction

According to Case Study 3 of the intelWATT project, the high recovery reverse osmosis (HRRO) unit based on the hybrid semibatch/batch RO principle is to be used in the concentration of rinse water from electroplating processes. According to studies conducted by BIA, the treatment of the chromium bath is the most challenging task in this case study. For this reason, the intelWATT team decided to begin with this separation. The treatment of copper and nickel baths will be addressed by TH Köln in M16.

The proposed design is an evolution of an existing batch-RO system at University of Birmingham to meet the new requirements of high recovery and high pressure. In the deliverable D3.9, the concept design of HRRO was presented and the system was modelled using a mathematical model developed by University of Birmingham. A DuPont XUS180808 8-inch membrane element has been selected and work exchanger vessel size, flux through membrane and recirculation rate was designed and optimised. In D3.9, the preliminary tests of standard RO have shown successful concentration of the chromium rinse water in a RO system, to restore chromium ions to a concentration suitable of for the electrolyte bath.

This document was proposed to demonstrate the lab scale high pressure HRRO unit for concentration of rinse water. Due to the bottle necks in supplying of some of items required for HRRO rig, the final version of

this deliverable will be issued later, and this document is a provisional version. This version of document D3.10 includes the updated concept design, updated results of standard RO experiments, design details about the proposed new HRRO rig, further experiments on the existing HRRO rig (which is high recovery but not high pressure), model validation and projection for the new rig, and control software development.

Although this deliverable (D3.10) is titled “Lab Scale HRRO unit for integration with IX”, it was decided by the IntelWATT team to investigate alternative complementary processes to ion exchange (IX) for concentration and recovery of the electrolyte. According to this investigation, it is expected that the process can be accomplished by RO alone, with a possible secondary RO process to recover boric acid from the electrolyte mixture, rendering IX unnecessary. Nevertheless, the performance of ion exchangers for the recovery of electrolytes will be assessed in M16 and the corresponding results and conclusion will be part of the M18-review report.

3 Electrolyte recovery using standard RO system performed at THK

3.1 Objectives of the work

The main objectives of this investigation was:

- a. To develop an analytical strategy to identify organic and inorganic compounds of the Cr(III) electroplating electrolyte bath and the subsequent rinse waters.
- b. To quantify these compounds to evaluate the feasibility of a water treatment based on High Pressure Reverse Osmosis (HPRO).
- c. To perform HPRO trials to determine key operation parameters for RO system of UoB (operating pressure, permeate flux, treatment time) and provide data to support model development at UoB (rejection of heavy metals, boric acid, organic compounds).
- d. To assess the reusability of the RO concentrate for electroplating operations by performing Hull cell tests.

3.2 Comprehensive analytical investigation and potential challenges to overcome

Most inorganic compounds (Cr(III), boric acid and sulphate) were identified and quantified by means of Inductively Coupled Plasma - Optical Emission Spectrometry (ICP-OES) and the corresponding quality requirements for these compounds can be found Table 1 and 2. The composition of the organic compounds involved in the electroplating process was unclear at the beginning of the project. Manufacturers usually work with commercial formulations known as complexor, buffer, wetting agent and replenisher but their chemical composition is unknown. High Pressure Liquid Chromatography (HPLC) and Attenuated Total Reflection combined with InfraRed spectroscopy (ATR-IR) were used to identify organic key components as follows (for ATR-IR spectra see Figure 1):

Buffer: Potassium sulfate and boric acid (1:1 wt.)

Replenisher: Sodium saccharin

Complexor: DL-Malic acid

Wetting Agent: Sodium-1,4-bis(1,3-dimethyl-butyl)-sulfonato-succinate

According to this finding and the quality requirements for the RO concentrate, following potential challenges were identified that may interfere with the RO process:

- Sodium-1,4-bis(1,3-dimethyl-butyl)-sulfonato-succinate may block the RO membrane.
- High Total Organic Carbon concentration may cause membrane fouling.
- In electroplating operations, the temperature of the Cr(III) bath is set to 55-60°C. Boric acid solubility is high at such temperature but the RO system cannot work efficiently at temperatures above 30°C. The boric acid solubility decreases to 55 – 60 g/L for temperatures between 25 and 30°C. Consequently, boric acid crystallization may occur with the RO module and block the membrane.
- The pH value of the feed is lower than 5 leading to the full protonation of the boric acid. Complete rejection of protonated boric acid is difficult to achieve in commercial RO membranes and a residual amount of boric acid is expected in the permeate.

Table 1. Quality parameters for RO permeate recycling in rinsing baths.

Quality Parameter	Unit	Lower limit	Upper limit	Measurement Method
pH value	-	5	8	pH meter
Surface Tension	mN/m	60	72	Tensiometer
Chromium (III)	mg/L	0	10	ICP-OES
Nickel	mg/L	0	3	ICP-OES
Copper	mg/L	0	3	ICP-OES
Boric Acid	mg/L	0	100	ICP-OES
Sulfate	mg/L	0	150	ICP-OES / Titration
Malic Acid	mg/L	0	3	HPLC
Chloride	mg/L	0	50	Titration
Total Organic Carbon	mg/L	0	15	Difference method

Table 2. Quality parameters for RO concentrate re-use in electroplating baths.

Quality Parameter	Unit	Lower limit	Upper limit	Measurement Method
pH value	-	3.5	3.9	pH meter
Surface Tension	mN/m	30	50	Tensiometer
Chromium (III)	g/L	8	12	ICP-OES
Nickel	mg/L	0	15	ICP-OES
Copper	mg/L	0	3	ICP-OES
Boric Acid	g/L	80	110	ICP-OES
Sulfate	g/L	80	150	ICP-OES / Titration
Malic Acid	g/L	0.7	2.5	HPLC

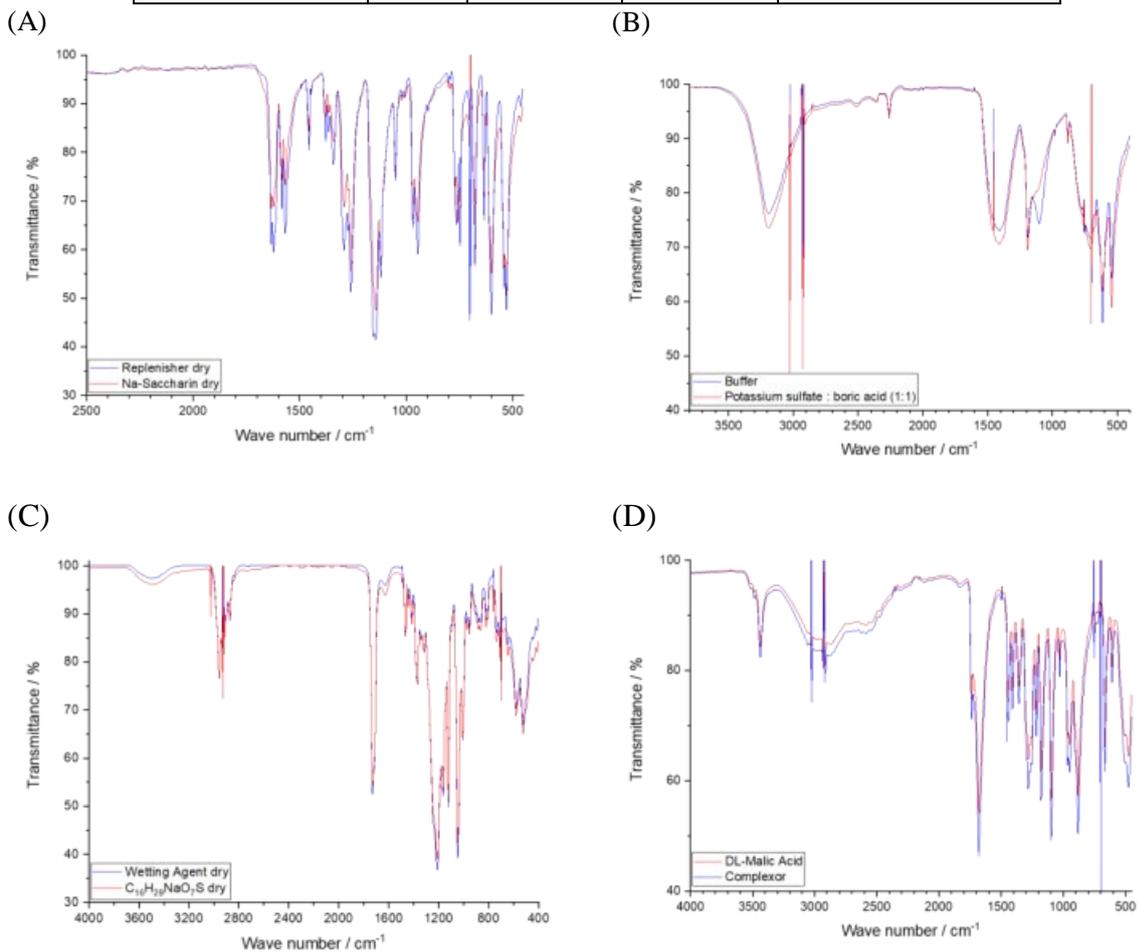


Figure 1 - ATR-IR spectra for (A) Replenisher, (B) Buffer, (C) Wetting Agent and (D) Complexor.

3.3 HPRO Trials

HPRO trials were performed at TH Köln in order to assess the feasibility of wastewater treatment based on HPRO and evaluate key operation parameters. The HPRO system used in this work is depicted on Figure 2. Simulated wastewater was prepared as a 12.5 fold dilution of a conventional Cr(III) electrolyte bath. This solution was subsequently filtrated through a 0.2 μm filter. The membrane used for this investigation was SW30 DuPont-Filmtec (membrane surface area was 160 cm^2), which consists of a Polyamide Thin-Film Composite and can be operated up to 80 bar. RO parameters as presented in Table 3 were set during the trials.

Table 3. RO experiments parameters.

$T / ^\circ\text{C}$	25
p_{max} / bar	80
$pH_{initial}$	4.7
$J_{max} / \text{L}/\text{m}^2\cdot\text{h}$	30
$v_{crossflow} / \text{m}/\text{s}$	0.25
$A_{M;total} / \text{cm}^2$	160
$A_{plant;inner} / \text{cm}^2$	≈ 4251



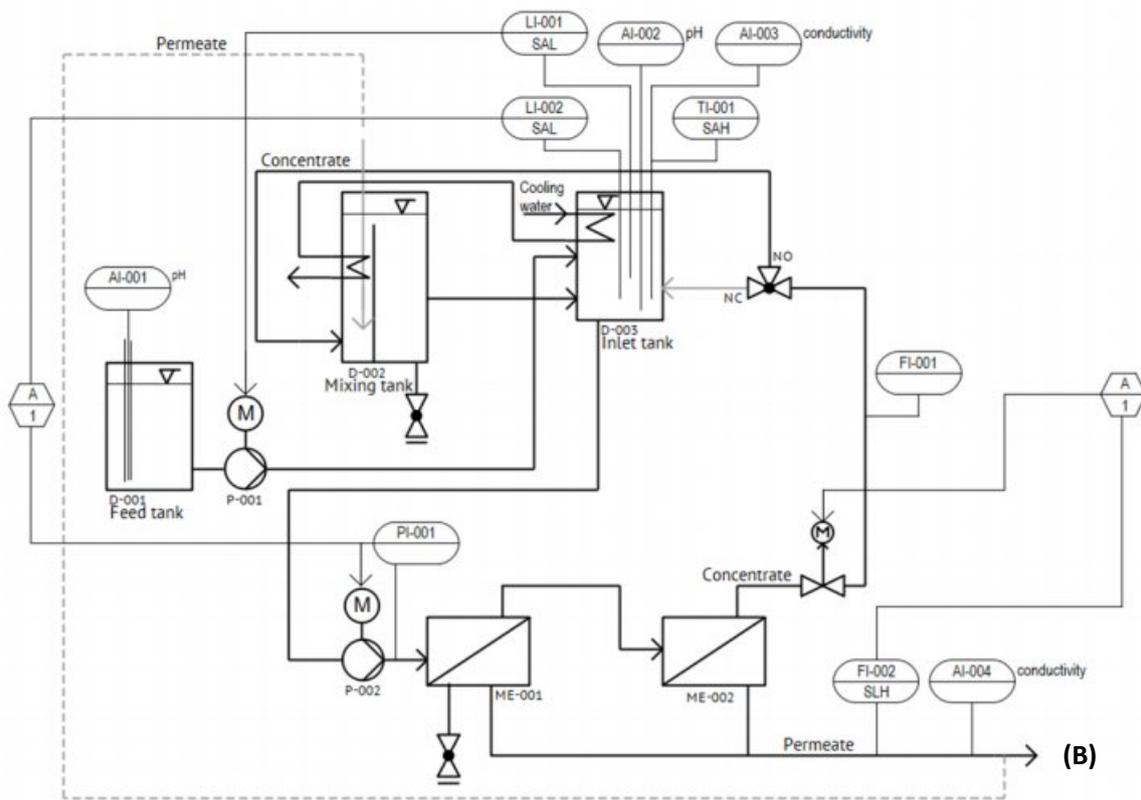


Figure 2 - (A) Photograph and (B) Piping & instrumentation diagram of the HPRO system used at TH Köln.

It is common practice to measure key operation parameters under steady state conditions. For this purpose, the RO trials were performed as a succession of steady state measurements, where permeate and concentrate were remixed after the filtration. In between, the feed concentration was increased by means of single pass trials leading to 16 Concentration Levels (CL) from 1 to 16. The Cr(III) concentration in CL16 is within the concentration range of Cr(III) electrolyte baths. Figure 3 shows the increasing osmotic pressure measured for the different CLs. As expected, the osmotic pressure grows during the concentration process to reach a maximal value of approx. 50 bar.

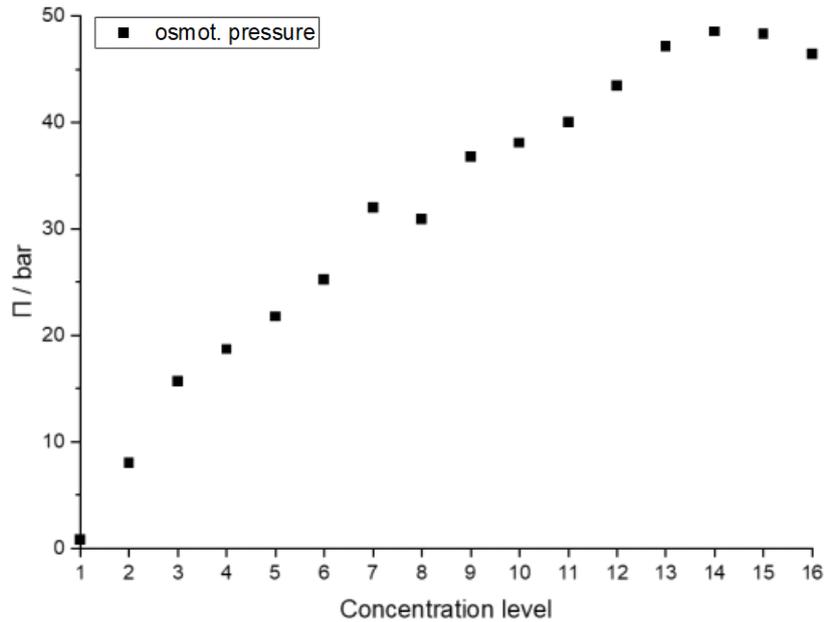


Figure 3 - Measured osmotic pressure vs. concentration level during HPRO concentration.

The dependency of the permeate flux and the membrane permeability on the driving pressure difference is depicted in Figure 4. The curve for CL16 corresponds to the final and maximal achievable concentration level for an operation pressure of 80 bar. As expected, the flow resistance of the membrane increases during the concentration probably due to membrane fouling, membrane compression and viscosity increase. This observation is confirmed by the measurement of the membrane permeability, which drops down from 2.5 to 0.25 L/m².h.bar at the end of the concentration process. Nevertheless, at highest CL, a permeate flux of approx. 7.5 L/m².h could be achieved at an operation pressure of 80 bar. UoB aims at performing HPRO trials with a permeate flux of 10 L/m².h, which should be easily reached by increasing the operation pressure to 120 bar.

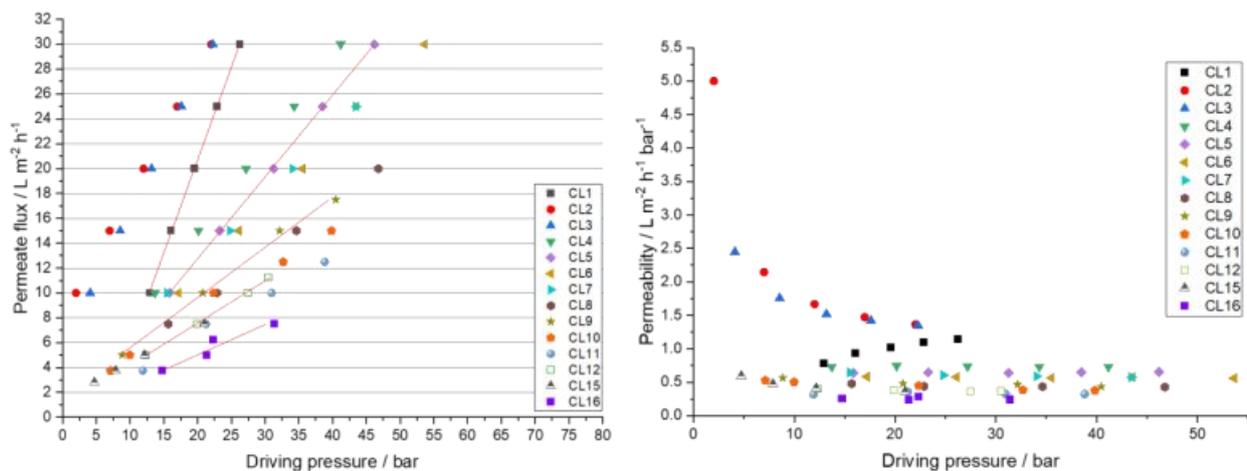
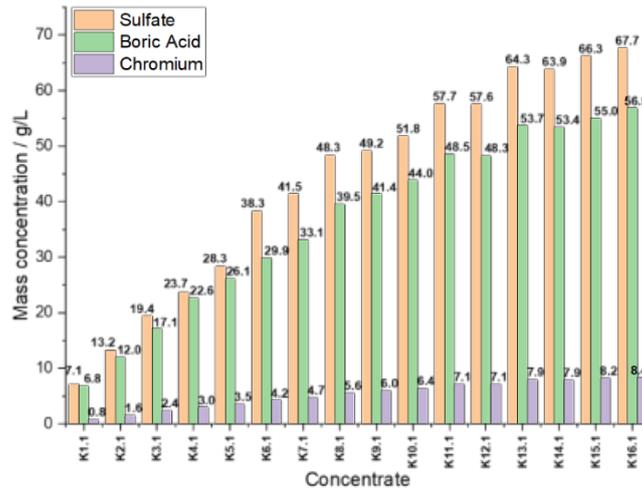


Figure 4 - Dependency of the permeate flux and the membrane permeability on the driving pressure (transmembrane pressure) difference during HPRO concentration.

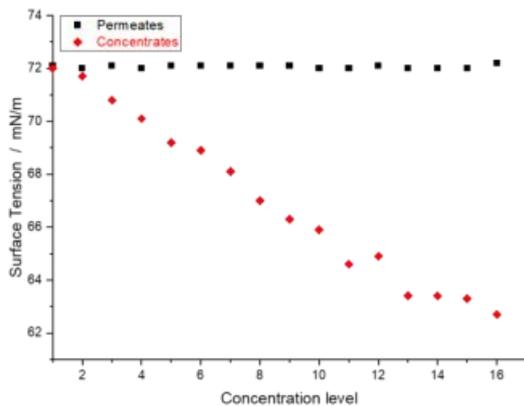
Figure 5 shows the concentration of sulphate, boric acid and Cr(III) measured at different concentration levels. Excellent Cr(III) rejection above 99.6% was achieved. The rejection of boric surprisingly steadily 958454 — intelWATT

increased from 65 to 90% during the concentration. This phenomenon might be related to observe membrane fouling during HPRO operation. The chemical composition of CL 16 is very close to the composition of the Cr(III) electrolyte bath. Most TOC was rejected by the membrane leading to an increase of the concentration of the wetting agent and a progressive decrease of the surface tension in the concentrate as depicted in Figure 6. A cumulated boric acid concentration of 2 g/L was determined in the permeate. This value is above the specification (100 mg/L) set in the corresponding list of quality requirements for the permeate (Table 1) and a post-treatment will be necessary.



	$\beta(Cr) / g/L$	$\beta(B(OH)_3) / g/L$	$\beta(SO_4^{2-}) / g/L$	$\gamma / mN/m$	pH
Cr(III) Electrolyte*	8-12	80-110	80-150	30-50	3.5-3.9
HPRO feed	0.75	3.55	7.12	72.0	4.7
Concentrate K16.1	8.39	56.89	67.72	63.7	3.85

Figure 5 - Concentration of sulphate, boric acid and Cr(III) measured at different concentration levels.



Total organic Carbon					
Concentrates		Permeates (J = 10 Lm ² h ⁻¹)		Permeates (J = 30 Lm ² h ⁻¹)	
K2.1	≤ 100 mg/L	P1.5	≤ 10 mg/L	P1.1	≤ 10 mg/L
K4.1	≤ 100 mg/L	P3.4	≤ 10 mg/L	P2.1	≤ 10 mg/L
K6.1	0.682 g/L	P5.4	≤ 10 mg/L	P3.1	≤ 10 mg/L
K8.2	1.13 g/L	P7.4	≤ 10 mg/L	P4.1	≤ 10 mg/L
K10.1	2.00 g/L	P9.3	≤ 10 mg/L	P5.1	≤ 10 mg/L
K12.1	2.31 g/L	P11.4	11.26 mg/L	P6.1	≤ 10 mg/L
K14.1	2.71 g/L	P13.4	12.55 mg/L		
		P15.4	10.56 mg/L		

Figure 6 - (Left) - Surface tension measured in the permeate and the concentrate during HPRO concentration. (Right) – TOC content measured in permeates at different concentration levels.

3.4 Electroplating trials

Electroplating trials were performed with CL16 and restocked CL16 in Hull Cell (see Figure 7). The composition of restocked CL16 is very close to the composition of a real Cr(III) electroplating bath (see

Figure 8). Photographs of the electroplated plates including thickness measurements are presented in Figure 9. According to BIA expertise, the electroplating results obtained with CL16 were acceptable and the results obtained with CL16 restocked were very satisfying. The electroplating conditions are summarized in the Table 4.

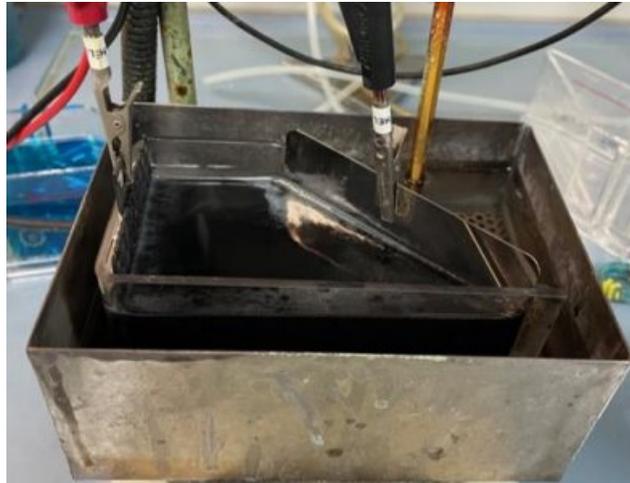


Figure 7 - Photograph of the Hull Cell used for the electroplating trials performed in this work.

Table 4. The electroplating conditions for Hull cell test

Parameter	
Current	5 A
Plating time	7 min
Temperature	55 °C
Anode	Ir/Ta oxide coated titanium
Substrate	Plated on nickel coated brass panel (7.5 cm x 10 cm)
Volume	250 mL RO concentrate as electrolyte

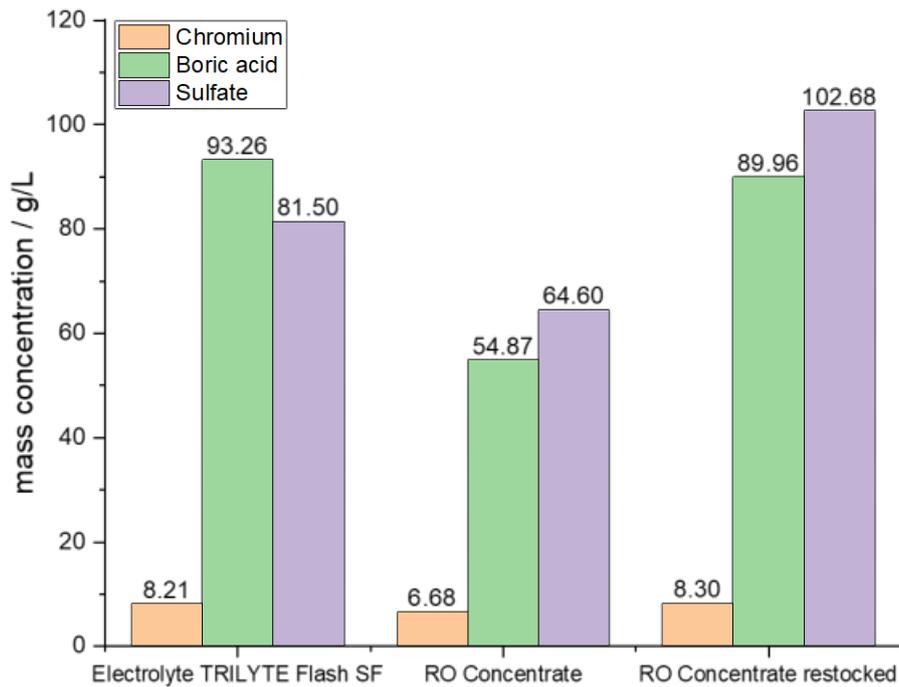


Figure 8 - Concentrations of Cr(III), boric acid and sulphate in CL16 (RO concentrate), restocked CL16 (RO concentrate restocked) and a Cr(III) electrolyte bath (Electrolyte TRILYTE Flash SF).

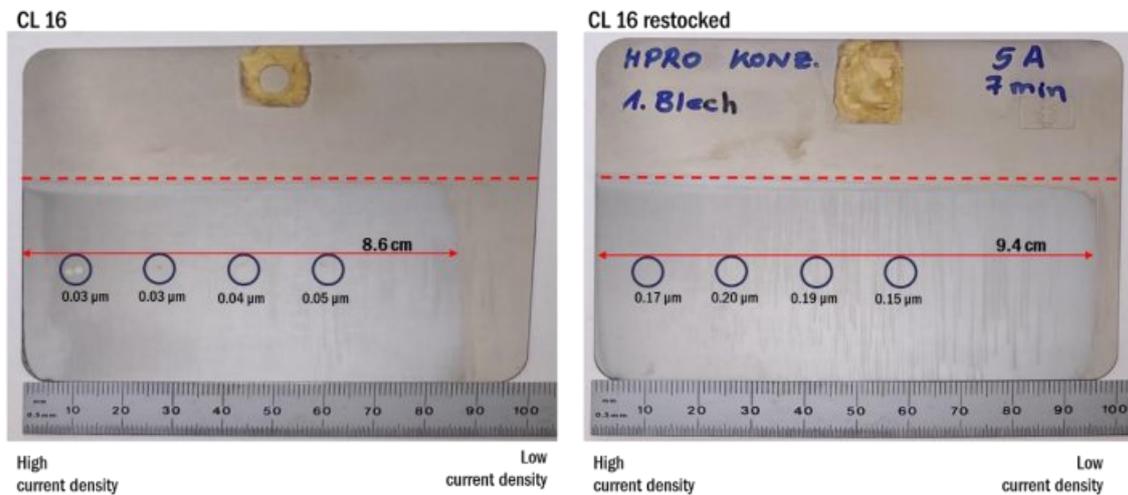


Figure 9 - Photographs of the electroplated plates including thickness measurements for CL16 and CL16 restocked. The trials were performed in Hull Cell.

3.5 Adsorption trials with powdered activated carbon (PAC)

To reduce membrane fouling and improve membrane permeability, the ability to treat the emerging rinse water with powdered activated carbon was investigated. The reduction of the total organic carbon contents (TOC) and unchanged chromium values were favourable.

The activated carbon in powdered form (PAC) from four different manufacturers (Silcarbon, Erbslöh, Jacobi and Donau Carbon) were investigated. Kinetically investigations (see Figure 10) showed, that adsorption

equilibrium was obtained after 1-2 hours contact time. The majority of TOC was adsorbed in the first 30 minutes of treatment time, which is crucial for the economically rinse water treatment.

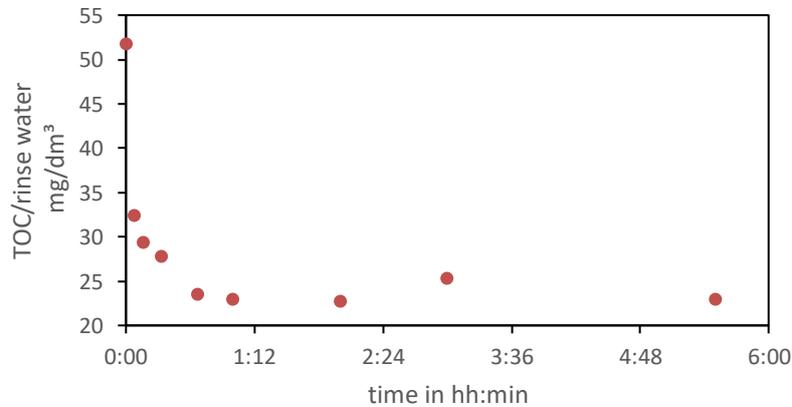


Figure 10 - TOC content of Cr(III) rinse water with PAC contact time (Silcarbon).

To investigate adsorption capacities under different rinse water concentrations, the real water samples were thinned down to different degrees. Resulting in volume concentration from 10 % to 100 % rinse water concentration. As Figure 11 shows, the TOC content of a wide variety of concentrations were reduced with a PAC treatment (Silcarbon, 24h contact time). The PACs of the other manufacturers showed similar results.

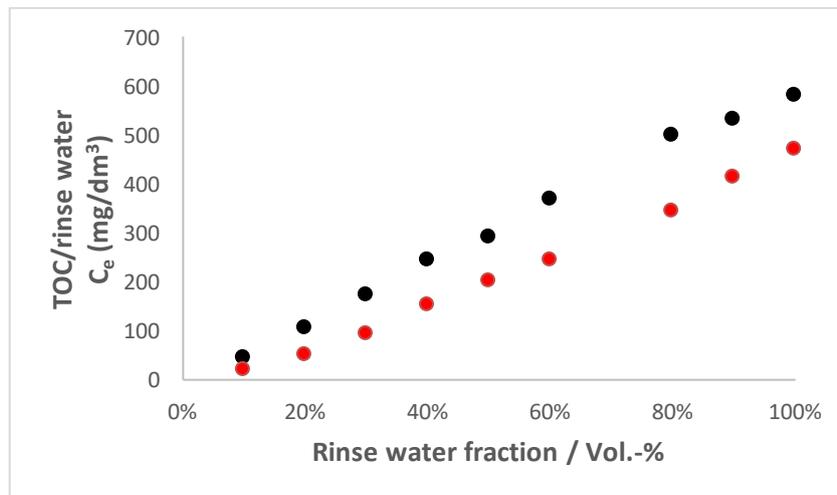


Figure 11 - TOC content of Cr(III) rinse waters in dependency of the volume fraction of rinse water before (black) and after (red) the treatment with powdered activated carbon (Silcarbon).

Figure 12 shows that the chromium content of the rinse water remained almost unchanged during the PAC treatment. This and the reduction of TOC proves the suitability of the PAC treatment for the rinse water. The other PACs showed similar results, although this behaviour was best with the PAC by Silcarbon.

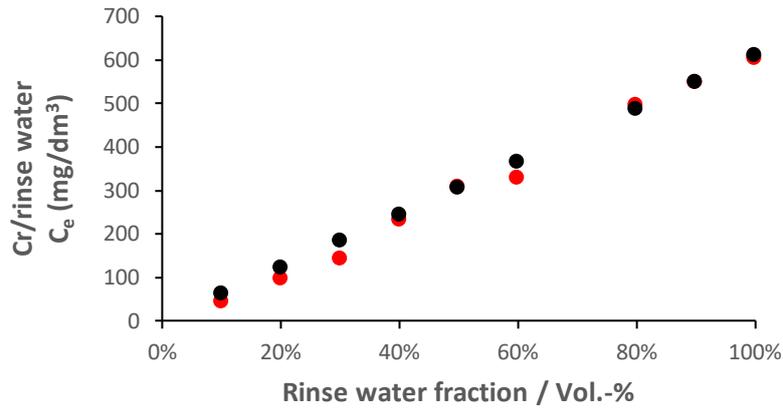


Figure 12 - Chromium content in Cr(III) rinse water in dependency of the volume fraction of rinse water before (black) and after (red) the treatment with powdered activated carbon (PAC from Silcarbon).

Maximum adsorption capacities were around 150 mg TOC per gram PAC for Silcarbon and Jacobi (Figure 13). For the TOC concentration range from 100-500 mg/dm³ the adsorption capacities of Silcarbon, Jacobi and Donau Carbon showed high values from at least 70 mg/g (TOC/PAC), proving the applicability of the products for this purpose.

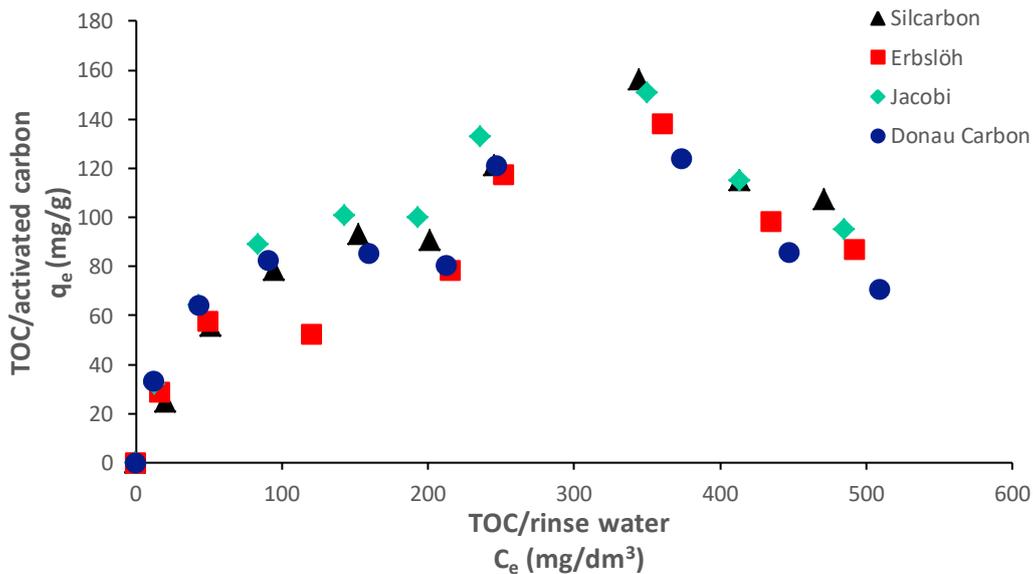


Figure 13 - Adsorbed TOC content on the four PACs with different TOC content of the rinse water.

The fit of the experimental data with common adsorption isotherm equations showed mixed results with a Langmuir like behaviour for low TOC values and a Redlich-Peterson like behaviour, due to the decreasing adsorption capacity in the field of high TOC contents.

4 Removal of anionic surfactants from rinsing bath solutions with granular activated carbon

Activated carbon (10 g/L) was added in 100 mL samples of copper, nickel and chromium rinsing baths, in 250 mL bottles and stirred for 21 h in a linear shaker (350 rpm). Surfactant content is presented in Table 5, with copper, nickel and chromium concentrations not affected by activated carbon treatment while surfactant levels drastically reduced (>90%) in all experiments.

Table 5. Removal of anionic surfactants from rinsing bath solutions after treatment with activated carbon.

Surfactant	Copper rinsing bath		Nickel rinsing bath		Chromium rinsing bath*	
	Initial concentration	Removal	Initial concentration	Removal	Initial concentration	Removal
mg/L SDSA ¹	21	92.4 %	10	91.0 %	12	91.7 %
mg/L SDBS ²	27	92.6 %	13	91.5 %	15	92.0 %
mg/L SDS ³	22	92.3 %	11	91.8 %	12	91.7 %
mg/L SDOSSA ⁴	34	92.4 %	17	91.2 %	19	92.1 %

Notes:

- 1) Calculated as sodium 1-dodecanesulfonate.
- 2) Calculated as sodium dodecylbenzenesulfonate.
- 3) Calculated as sodium dodecyl sulfate.
- 4) Calculated as sodium dioctyl sulfosuccinate.

*The chromium rinse solution was prepared by diluting the electrolyte bath solution 10-fold (following the procedure of the technical data sheet).

4.1 Preliminary design of fixed bed columns for the removal of anionic surfactants

A preliminary design of the process flow diagram of the setup for the removal of anionic surfactants from rinsing bath solutions with the use of fixed bed upflow columns filled with granular activated carbon Silcarbon K814 (Silcarbon Aktivkohle GmbH, Kirchhundem, Germany) is presented in Figure 14.

The setup is composed of two fixed bed columns filled with granular activated carbon and four tanks. The rinsing bath solution to be processed will be pumped from the feed tank into one of the columns, while the other column will (or can) be backwashed for the regeneration of activated carbon. A mesh pre-filter placed before the pump will retain any large solids. The purified feed water will be led to the effluent tank. A temperature probe (T_1) will provide input to make sure that the temperature of feed to the column is not above a threshold limit. Also, two pressure gauges will give input of $\Delta P_1 = P_{1,in} - P_{1,out}$ in order to prevent high pressure build up and to activate backwashing when head loss reaches a threshold limit. The temperature and pressure limits are to be defined. A specialty sensor on the outlet will provide information on the effluent water quality, while the flow (F_1) will be recorded. When backwashing is needed the flow of feed water is directed by the valves into the other column, and the content of the first column is drained back to

the feed tank with the use of three- way valves. The backwashing feed temperature is monitored by probe T_2 , the pressure gauges provide $\Delta P_2 = P_{2,in} - P_{2,out}$, and flow meter F_2 monitor the flow.

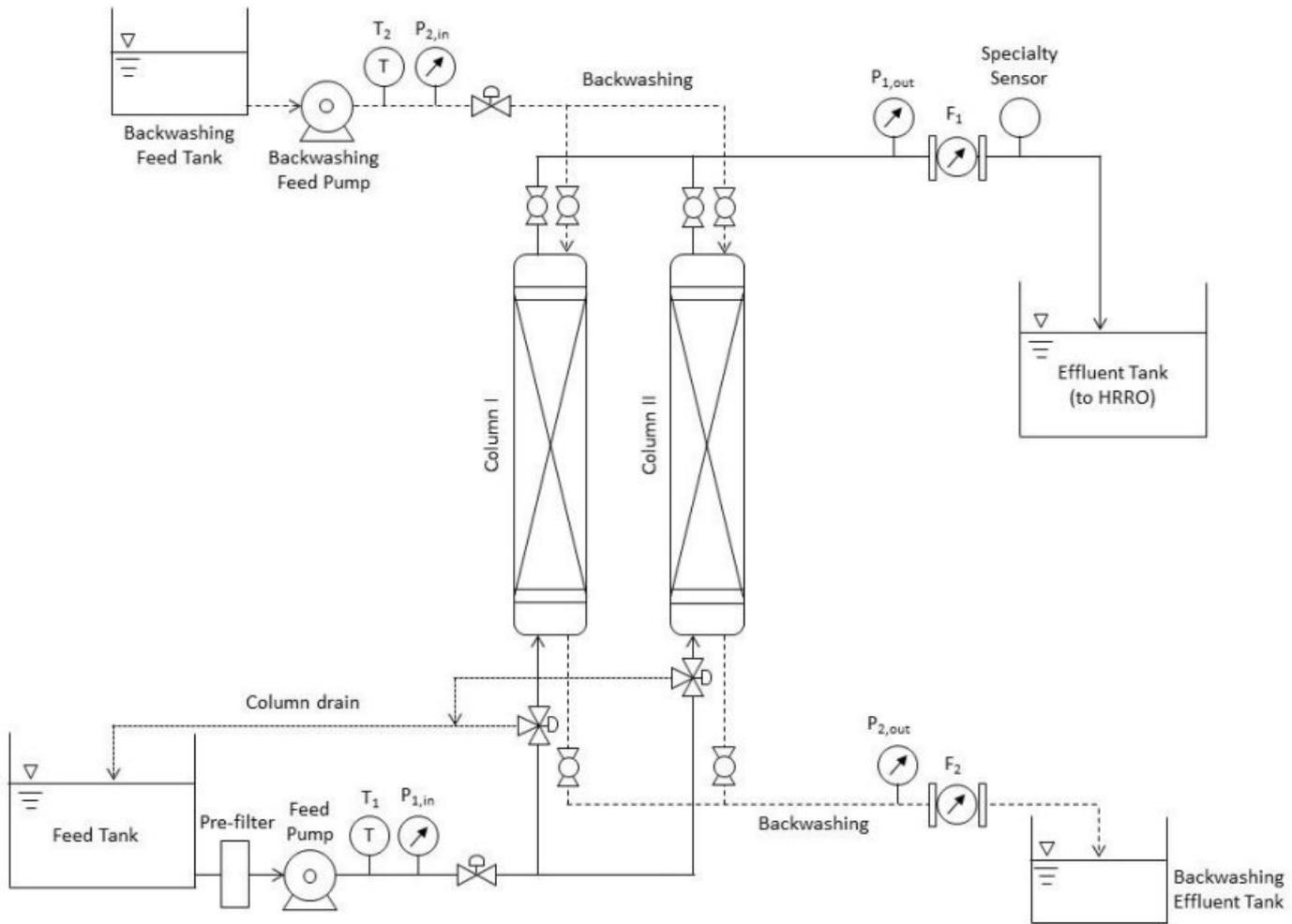


FIGURE 14 - PROCESS FLOW DIAGRAM OF FIXED BED SETUP FOR THE REMOVAL OF ANIONIC SURFACTANTS.

In this preliminary design, the following calculations – assumptions were made:

- The feed of rinsing bath solution into the feed tank is $2.5 \text{ m}^3/\text{h}$. For 8 h of operation, the total volume to be processed every day is 20 m^3 .
- The main feed and effluent tanks will be designed for a volume of 20 m^3 plus the safety limits, to accommodate for the whole batch.
- Copper, Nickel, Chromium rinses were measured to contain anionic surfactants of 22, 11, 12 mg/L SDS (calculated as sodium dodecyl sulfate, SDS), respectively. Therefore, the design concentration will be 25 mg/L SDS and the total amount of anionic surfactants to be removed is 500 g SDS.
- Preliminary experiments showed at least 90% removal of surfactants by 1 g of activated carbon (based on apparent density of 500 g/L, as provided by the producer, it corresponds to 2 mL of apparent volume) per 100 mL solution (under shaking for 21 h). So, the amount of activated carbon needed for the removal of 90% of anionic surfactants in 20 m^3 rinse solution is 200 kg, which has an apparent volume of 0.4 m^3 . This is under the assumption of complete regeneration of activated carbon after every cycle.
- Backwashing will start based on head loss and on the quality of the effluent as measured by a specialty probe before the effluent tank. Since an online method for the measurement of

surfactants is difficult, the probe will measure the concentration of a dye or some other indicator that still needs to be defined. The replacement of activated carbon will have to take place in batch mode when backwashing is not effective.

- The detailed design parameters will be calculated based on analysis of the maximum adsorption capacity of surfactants on granular activated carbon, on the kinetics and after research about the best regeneration method.

5 Low-pressure hybrid semibatch-batch HRRO system

5.1 Description of the system

In this deliverable, we have demonstrated high recovery operation in the low-pressure HRRO system shown in Figure 15 (A-D). Major components of this system include a work exchanger vessel housing the piston, an 8-inch spiral-wound RO module, a high-pressure plunger pump, a recirculation centrifugal pump, and three motorized ball valves. The maximum allowable operating pressure of the system is 25 bar and the system automatically shuts down if this pressure is exceeded. Brackish water is supplied to the RO system using the high-pressure feed pump. A 5-micron cartridge pre-filter is used after pump to remove particles and inhibit membrane fouling. The recirculation pump is used to recirculate the batch during the pressurization phases and to restore the piston to its initial position during the refill phase. Nine sensors have been used to measure pressure, conductivity and flow rates of streams as shown in Figure 16. The operation and safety of the system is controlled by a Programmable Logic Controller (PLC). The PLC program has been updated to operate automatically in three phases: semi-batch, batch, and purge-and-refill phases, as described below. These phases are executed in a continuous cycle.

Semi batch phase

The semi-batch phase is used to concentrate the supplied feed by reverse osmosis up to a certain pressure. Initially the piston in the pressure exchanger is at the start position. In the semi-batch phase, the feed pump is running, the bypass valve is open, the brine valve is closed, the recirculation pump is running, and the recirculation valve is open. The certain point for ending the semi batch phase is a predetermined amount of feed pumped into the system, or a pre-set system pressure.

Batch Phase

When the semi-batch phase ends, the bypass valve closes, and the supplied feed pushes the piston along the pressure exchanger vessel. The recirculation pump works, and the recirculation valve is open. By moving the piston, the concentration of the water in the batch increases and the treated water permeates the membrane. The pressure required to move the piston increased as the concentration rises. The end of batch phase occurs when the piston reaches its end position and then the purge-and-refill step starts.

Purge and refill phase

During the purge-and-refill phase, the concentrated brine from the system is removed and replaced fills the system with a new batch of feed solution being pumped into the system. The bypass valve and the brine valve open and the recirculation valve closes simultaneously. The brine valve is closed when the concentration of this brine drops to a pre-set level. At the same time, the piston moves from the end (right) position to the start (left) position under the pressure generated by the recirculation pump, and the purge-and-refill phase ends.

(A)



(B)



(C)



(D)



Figure 15 - High-recovery batch RO prototype installed in the UoB laboratory (A and B) front view, (C) side view, (D) Back view.

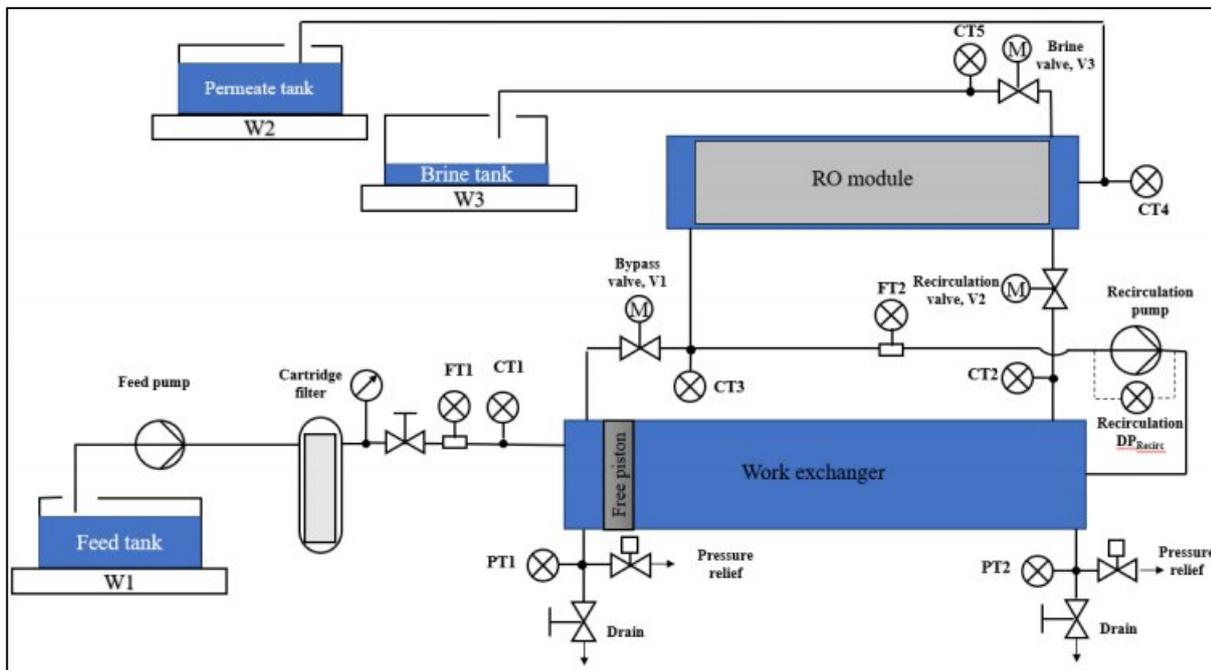


Figure 16 - Schematic diagram of high-recovery batch RO system (PT, CT and FT are pressure, conductivity and flow transmitters, respectively. W_1 , W_2 , and W_3 are weighing platforms for feed, permeate and brine tanks). From [2].

5.2 Tests on hybrid semibatch-batch high recovery RO process using NaCl

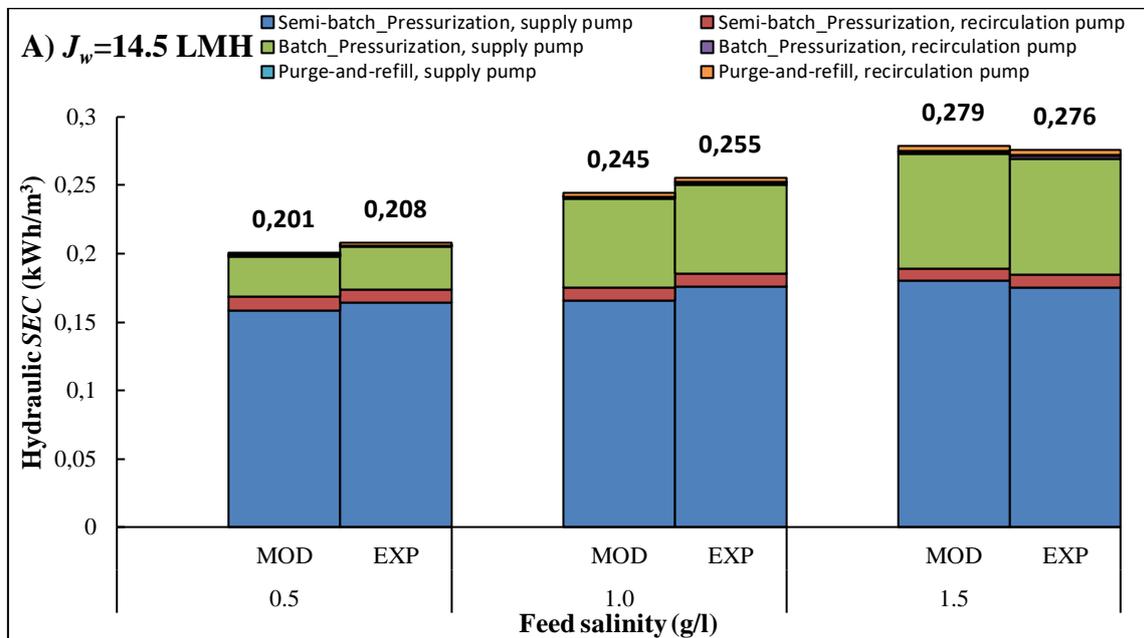
In order to evaluate performance of the HRRO system in hybrid mode of operation (semi-batch/batch mode), a series of experiments were carried out at various feed salinities and water permeate fluxes. The system has been built for the treatment of brackish water in the batch mode and has a pressure limit up to 25 bar. Therefore, feed concentrations of 0.5, 1.0, and 1.5 g/l and water fluxes of 10-24 LMH were selected. Simulated feed solution was prepared using tap water and analytical grade sodium chloride (purity >99.5%). In addition, 3 g of sodium metabisulfite was added to 1 m³ of prepared feed solution to counteract free chlorine in the tap water and prevent membrane oxidation. All parameters, including time, weight of the tanks, conductivities, differential pressure of recirculation pump, power consumption of pumps, pressures, and flow rates are logged at a frequency of at least once per second, resulting in at least 3,000-8,000 sets of readings per cycle. These data were used to calculate the major parameters affecting performance of RO systems. The comparison between experimental and modelling results of hydraulic SEC and peak pressure is presented in this section (5.2) and will be used for validation of model in section 5.3. In the following sections (5.2.1- 5.2.7) different feed concentrations and salinities were used to investigate the HRRO performance in terms of hydraulic and electrical SEC, permeate and batch -conductivity, supply pressure, concentration factor and recovery, pump efficiency and peak pressure.

5.2.1 Hydraulic SEC

In this report, the experimental hydraulic work of the hybrid semibatch-batch HRRO system was calculated by integrating the differential pressure of each pump by the amount of water displaced by that pump at each measuring point. We also compared the experimental measurements against the model predictions to evaluate the accuracy of the model.

Figure 17 (A) and (B) compares hydraulic SEC measured experimentally and predicted by our model at different feed salinities (Figure 17 A), and water fluxes (Figure 17 B). At $J_w=14.5$ LMH, and feed salinities of 0.5, 1.0, and 1.5 g/l, the total experimental hydraulic SEC were 0.21, 0.25, and 0.28 kWh/m³ respectively, giving a maximum error of 4% against model predictions. Main contribution to the SEC is supply pump at pressurization phases for both semi-batch and batch modes of operation. Hydraulic work of the recirculation pump is small and unimportant in all phases of operation, comprising less than 6% of the total SEC. When feed salinity increased from 0.5 to 1.5 g/l, only the supply pump hydraulic work in pressurization phases of semi-batch and batch modes increased because of the increased osmotic pressure of the feed solution and no effect was seen on other SECs.

We also investigated the effect of water fluxes on the hydraulic SEC of the hybrid HRRO system. As it can be seen in Figure 17 B, by increasing water fluxes from 11.8 to 23.6 LMH, the experimental hydraulic SEC increased by 37%. However, this can improve the water rejection and total output of the system. Model accuracy was also investigated and the biggest error was about 4%, showing a good agreement between the experimental measurements and model predictions.



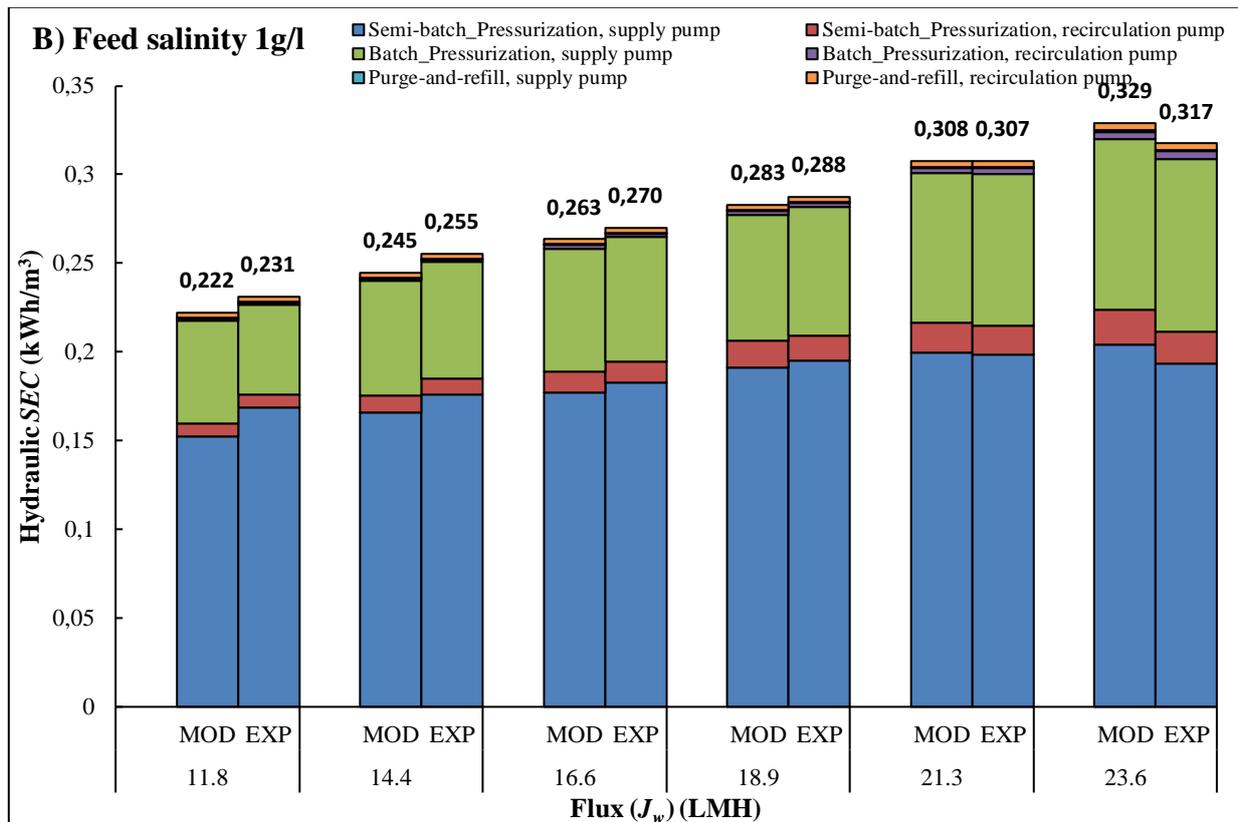
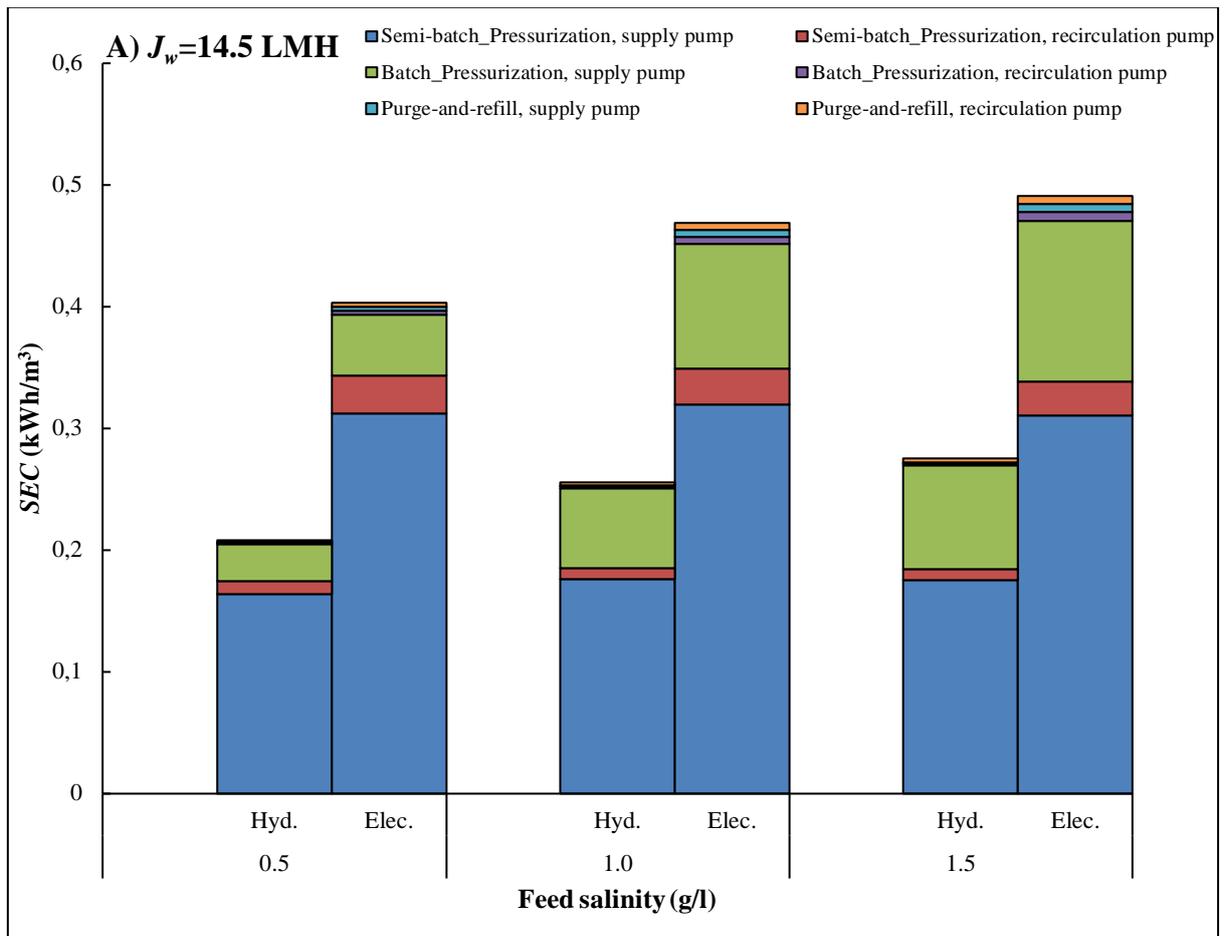


Figure 17 - Model predictions (MOD) and experimental measurements (EXP) of hydraulic SEC of free-piston hybrid HRRO at various: (A) feed salinities, and (B) water fluxes.

5.2.2 Pump efficiency

Electrical SEC was calculated by integrating measured power over time for each pump, and dividing by water output volume. Figure 18 compares the experimental hydraulic and electrical SEC breakdown of the hybrid semibatch-batch HRRO system at different salinities, and water fluxes. At $J_w=14.5$ LMH, the total measured electrical SEC for 0.5, 1.0, and 1.5 g/l feed solutions were 0.4, 0.47, and 0.49 kWh/m³ respectively. The difference between electrical and hydraulic SEC is because of the pump inefficiencies, and it becomes smaller at higher feed salinities showing an increase of the supply pump efficiency with pressure (Table 6). For example, the electrical SEC was 1.95 and 1.78 times higher than the hydraulic SEC at 0.5 and 1.5 g/l respectively, since the supply pump efficiency at 1.5 g/l was higher for both semi-batch and batch pressurization phases (main contributions to the SEC).

Measurement of electrical and hydraulic SEC at 1 g/l and different water fluxes (Figure 18 B) showed that, by increasing water flux from 11.8 to 23.6 LMH, both SECs increased, giving a 37% and 20% rise in hydraulic and electrical SEC, respectively. However, we should consider that the system's output is in direct proportion to the water flux. Therefore, there is a trade-off between output and SEC. For example, when flux was doubled at 1 g/l feed solution, electrical SEC increased by 20% while system output increased by 91%.



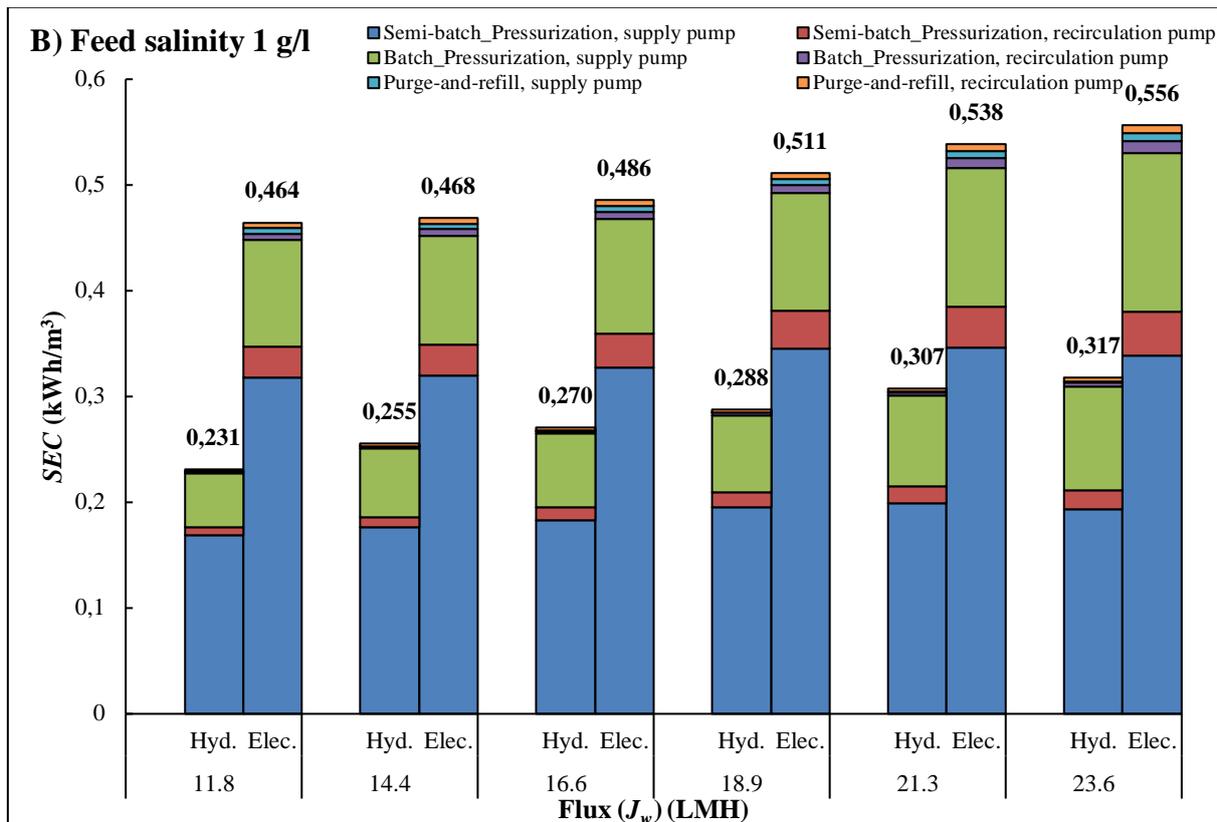


Figure 18 - Hydraulic and electrical SEC of the hybrid HRRO system over a cycle at various: (A) feed salinities, and (B) water fluxes.

Table 6. Feed and recirculation pump efficiencies over a cycle for pressurization and purge-and-refill phases at various feed salinities, and $J_w=14.5$ LMH

Feed salinity (g/l)	Pump efficiency (%)					
	Supply pump			Recirculation pump		
	Semi-batch pressurization	Batch pressurization	Purge-and-refill	Semi-batch pressurization	Batch pressurization	Purge-and-refill
0.5	52.5	61.7	12.3	32.3	24.7	48.0
1.0	55.0	63.5	12.6	32.3	24.5	47.6
1.5	56.5	64.5	14.1	32.1	24.4	47.3

5.2.3 Electrical SEC and rejection

Permeate water flux also has an important effect on the hybrid semibatch-batch HRRO system's performance and its effect should be considered to select the most optimized water flux based on our requirements and limitations. We measured the effect of permeate water flux on the main factors of the system including electrical SEC, output and rejection (see Table 7). Electrical SEC increased with flux as expected. However, at higher fluxes, the system output was higher and this trade-off between SEC and output must be taken into account. At $J_w=12.0$ LMH, system's output and electrical SEC were $11.4 \text{ m}^3/\text{day}$ and 0.484 kWh/m^3 , while at $J_w=23.4$ LMH, these amounts were $21.04 \text{ m}^3/\text{day}$ and 0.587 kWh/m^3 , meaning 84% increase in output compared to just 21.3% increase in electrical SEC. Additionally, at lower fluxes, permeate quality worsened, and by increasing the system flux, rejection of batch RO system slightly

improved. System flux is lower than the permeate flux, because of the reset time in the purge-and-refill phase when permeate output is paused.

Table 7. The effect of varying flux on the important factors of hybrid HRRO system at 1.5 g/l feed salinity. System flux is the flux averaged over the whole cycle, considering the purge-and refill phase which is non-productive.

Flux during Press. (LMH)	System Flux (LMH)	Semi-batch duration (Sec)	Batch duration (Sec)	Purge-and-refill duration (Sec)	Transition pressure semi-batch to batch (bar)	Rejection Rs	Output (m3/day)	Peak Pressure \hat{P} (bar)	Electrical SEC (kWh/m3)
12.0	11.6	1737	515	77	9.4	0.89	11.41	24.5	0.484
14.3	13.7	1500	430	77	9.8	0.91	13.533	24.97	0.491
16.5	15.7	1194	372	76	10.1	0.922	15.456	24.85	0.51
18.8	17.7	922	324	77	10.5	0.944	17.443	24.65	0.534
21.2	19.8	793	288	77	10.8	0.938	19.475	25	0.559
23.4	21.4	527	259	75	10.8	0.944	21.036	23.65	0.587

5.2.4 Permeate conductivity

Figure 19 illustrates permeate conductivity as a function of time for 1 g/l feed solution at $J_w=16.5$ LMH. Permeate quality was poor at the start of every cycle but it improved drastically after the low quality permeate left the system, then conductivity increased slowly with time. The average permeate quality over the cycle was around 0.08 g/l. The initial low quality permeate is mainly ascribed to the salt diffusion when system is depressurized (purge-and-refill phase). This was because, during purge-and-refill phase, salt passed through the membrane and reached the permeate spacer, even with no permeate flux. Then, at the start of the pressurization phase, this accumulated salt was washed out as the permeate flow resumed.

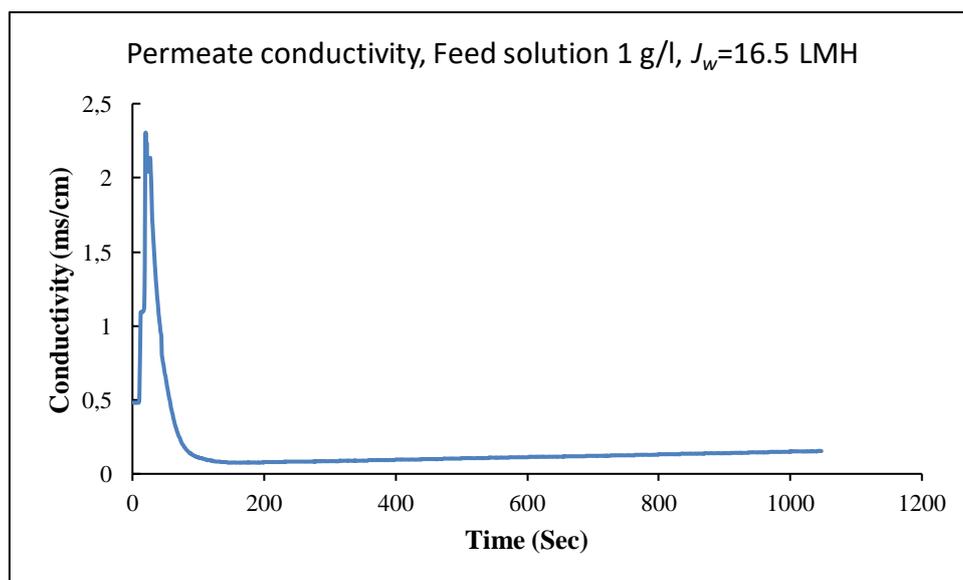


Figure 19 - Permeate conductivity vs. time after start of the pressurization phase, at 1 g/L feed solution, and $J_w = 16.5$ LMH.

5.2.5 Batch conductivity and supply pressure over a cycle

Batch conductivity, which is the feed conductivity entering the RO module, and supply pressure variations over time of one cycle of hybrid HRRO system are shown in Figure 20. Every cycle starts with semi-batch pressurization, experiencing a small peak of pressure due to retained salt inside the system. The applied supply pressure increased slowly during the semi-batch process since the increment in batch conductivity rate was small and thus the osmotic pressure increased slightly. After the initial peak, the applied supply pressure increased from around 6 to 9.8 bar while feed conductivity increased from about 4.5 to 9.6 mS/cm, when the semi-batch phase ended and batch phase started (after about 1620 seconds). Unlike the semi-batch phase, during which the incoming feed mixes with the brine exiting the RO module (recirculation loop solution), there is no incoming feed during the batch phase. Therefore, by proceeding the process and production of permeate the batch conductivity increased sharply and to compensate the increased osmotic pressure the same pattern occurred to applied supply pressure. Supply pressure increased from 9.8 to 24 bar while batch conductivity increased from 9.6 to 34.8 mS/cm.

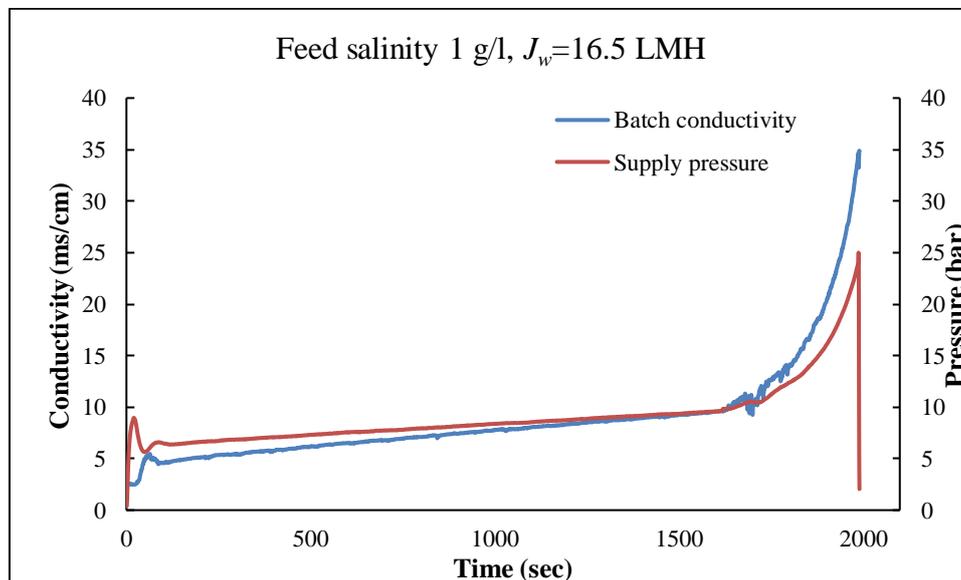


Figure 20 - Batch conductivity and supply pressure changes vs. time after the start of the pressurization phase, at 1 g/l feed solution, and $J_w = 16.5$ LMH.

5.2.6 Concentration factor and recovery

Concentration factor was measured to investigate hybrid HRRO system's performance regarding its ability to concentrate the feed solution at high rates. This factor is the ratio of feed concentration per brine concentration (average concentration of the stream leaving the RO system at purge phase). Figure 21 presents concentration factor and recovery at different water fluxes and 1 g/l feed solution. Experimental measurement showed that hybrid HRRO system is capable of concentrating the feed up to 21 times, confirming its suitability for the electrolyte recovery operation. In addition, recovery of the system was between 0.94 to 0.96 over this set of tests. For example, at $J_w = 14.5$ LMH, concentration factor and recovery were 20.6 and 0.96 respectively.

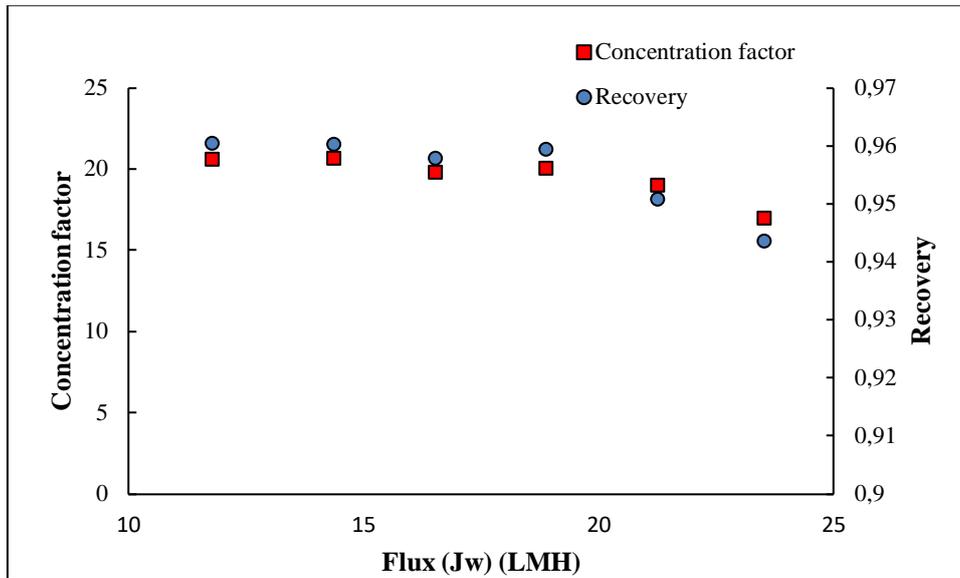


Figure 21 - Experimental concentration factor and recovery vs water flux at 1 g/l feed concentration.

5.2.7 Peak Pressure

Maximum peak pressure is reached at the end of the pressurization phase. This value is of major importance, since materials and components used in the fabrication of the system must be selected to withstand it. Figure 22 compares experimental final peak pressure against the value predicted by model, at different water fluxes for 1 g/l feed concentration. At all water fluxes, experimental measurements were lower than model predictions. This may be because of the salt entering the permeate – resulting in less salt in the feed solution and lower osmotic pressure. Nonetheless, the discrepancy between model predictions and experimental values was less than 7%.

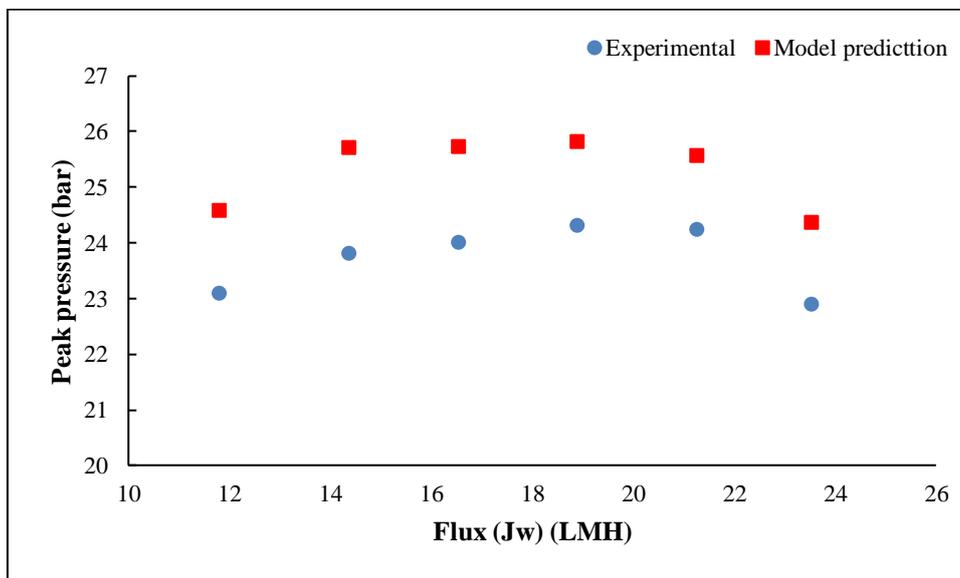


Figure 22 - Peak pressure at end of pressurisation phase vs water flux. Model predictions and experimental values, at 1 g/l feed concentration.

5.3 Modelling of the system

5.3.1 Procedure

The experiments presented in section 5.2 enabled our model of the hybrid semi batch-batch HRRO system to be validated and used to check and optimise the design. The model has been described previously in D3.9 as well as in two recent publications [1-2]. Compared to the modelling presented in D3.9, the main improvements are:

- Incorporate osmotic backflow adjustment (at 4 litres per cycle) to allow for backflow at the end of the pressurization cycle when the rig depressurizes
- A more precise model of friction losses in pipes and valves, adjusted through the validation experiments above.
- The model of longitudinal concentration gradient has been improved, with separate correction factors included for each phase of the cycle (i.e.. Semi-batch and batch)

At this stage, full characterisation of the electrolyte rinsing solution with regard to how it will behave in the hybrid HRRO system is lacking. Therefore, we have modelled the system based on using a NaCl solution of equivalent osmotic pressure, which is also the approach taken in the validation experiments described above (see section 5.2). The validation of the model was confirmed by a good agreement between model and experimental results obtained from several experiments as above mentioned in Figure 17 (A) and (B) and Figure 22. Input parameters to the model are summarised in Table 8.

Table 8. Input parameters to the model of the hybrid semi batch-batch HRRO system.

Parameter	Unit	Value	Explanation
Feed NaCl concentration	g/l	5.06	Osmotic pressure 4 bar, similar to electrolyte rinse bath
Final NaCl concentration	g/l	101.2	20 times concentrated, giving final concentration of 80 bar
Membrane area	m ²	30.6	For DuPont XUS180808 8-inch membrane element, based on data sheet
Spacer thickness	mm	0.0864	0.034 inch (from data sheet)
Length	m	1.02	From data sheet
Membrane permeability (A)	L/m ² /h/bar	1.393	Inferred from data sheet
Membrane salt transport diffusion (B)	m/s	1 x 10 ⁻⁸	Inferred from data sheet
Batch vessel swept volume	L	40	According to design presented in next section
Connecting pipe diameter	mm	21.2	Corresponding to 1-inch Stainless Steel pipe
Valve diameter	mm	19	Corresponding to 1-inch valves

Supply pump efficiency	%	50	
Recirculation pump efficiency	%	50	
Recovery	%	95	This recovery provides a nominal concentration factor of 20. The real concentration factor achieved may be less because of solute passage through the membrane

5.3.2 Results

The modelling is incorporated in a spreadsheet and used to generate the following results that help to optimise and predict performance.

The model has been used to explore and optimise sensitivity to various parameters as follows:

(i) Recirculation flow rate, at the exit of the RO module, as a ratio to the feed flow. This affects SEC and peak pressure as shown in the Figure 23. The recirculation flow has a weak effect on SEC such that any value in the range 2-5 is expected to be suitable. The high-pressure HRRO rig has been designed to allow this to be explored further (Flux = 17.2 LMH). The rig has been designed for a peak pressure of 120 bar, and the result suggest that the operating pressure will be in this range. However, compaction of the membrane or fouling could result in decreased membrane permeability and thus higher pressures than predicted.

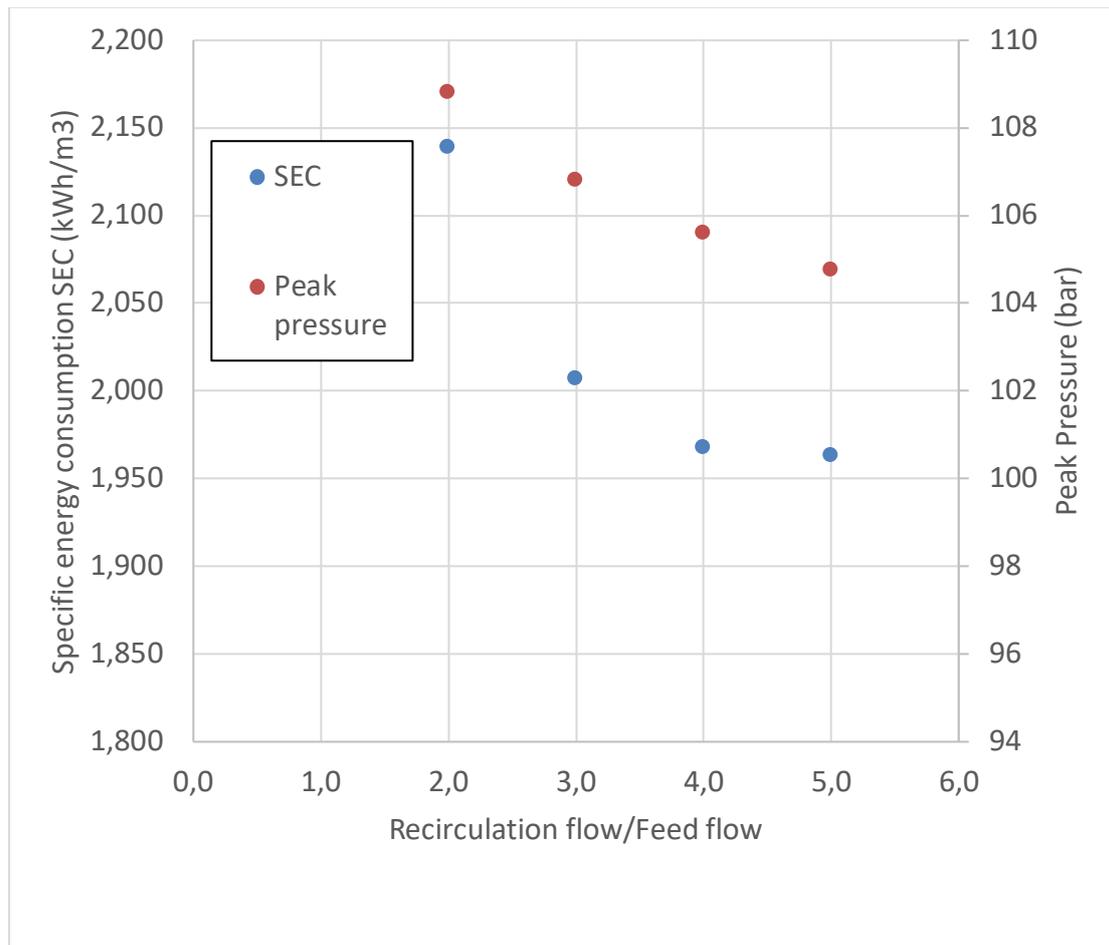


Figure 23 - SEC and peak pressure vs recirculation flow (ratio of recirculating flow/feed flow)

(ii) Effect of flux. Increasing the flux will increase the output, but also increase the SEC and peak pressure as presented in Figure 24. The high pressure HRRO rig has also been designed to explore the effect of flux. (Recirculation flow/feed flow=3). The target SEC for this project is $<2.5 \text{ kWh/m}^3$ and the target output is $0.5 \text{ m}^3/\text{hr}$. The output of pure water as one of the key performance indicators (KPI) at the 6-month consortium meeting was proposed to be $0.6 \text{ m}^3/\text{hr}$, however, the realistic target is $0.5 \text{ m}^3/\text{hr}$ to achieve $\text{SEC} < 2.5 \text{ kWh/m}^3$.

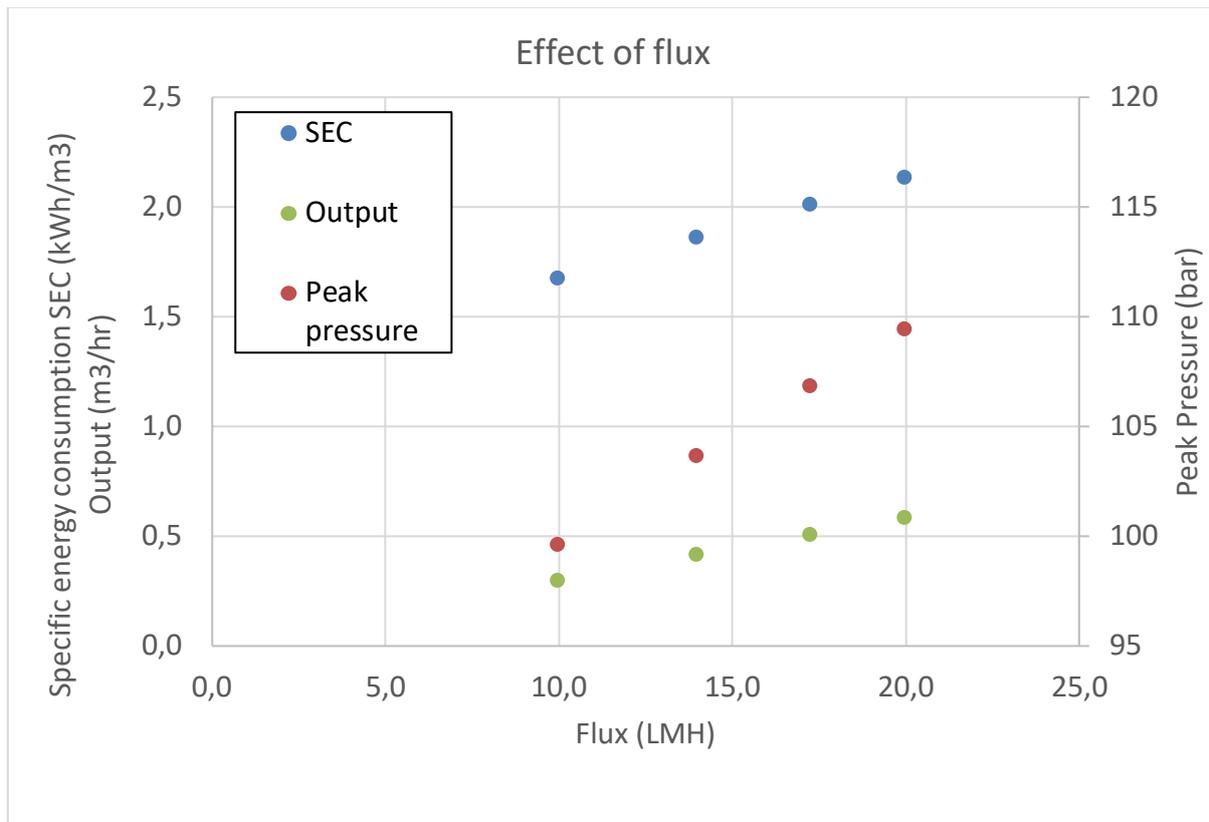


Figure 24 - SEC, output and peak pressure vs water flux through membrane, with work exchanger volume of 0.04 m³.

(iii) Effect of pump efficiency. The pump efficiency is an important factor in determining SEC. If pump efficiency is halved, SEC will double. The above results assume pump efficiencies of 50% (supply and recirculation pump). However, in recent experiments, recirculation pump efficiencies were typically 20-30% while supply pump efficiency was around 60%. The pumps to be used in the new high-pressure HRRO rig are of different type to these, so the efficiencies are likely to differ. Table 9 shows the effect of pump efficiency on SEC (flux=17.2 LMH, Recirculation/feed flow =3). It can be seen that the supply pump has the larger effect on efficiency.

Table 9. The effect of pump efficiency on SEC (kWh/m³) (flux=17.2 LMH, Recirculation/feed flow =3).

Recirculation pump efficiency	Supply pump efficiency		
	40%	50%	60%
20%	2.54	2.04	1.71
35%	2.51	2.02	1.69
50%	2.50	2.01	1.68

6 Design of the high-pressure HRRO system

High-pressure high-recovery reverse osmosis HRRO system is an evolution of the existing high recovery reverse osmosis rig at the University of Birmingham. The high HRRO system is a prototype system for the concentration and purification of rinse water from electroplating processes. Feed of this treatment system is wastewater from electroplating industry which is a complex mixture containing boric acid, sulphates, chromium (III) ions, wetting agent, and complexing agent. This technology will purify the water as the permeate stream to be re-used in the rinse baths and the brine stream will potentially re-used in the plating baths.

The system uses a hybrid semibatch-batch reverse osmosis process to maximise recovery of metal and water and minimise energy consumption. The design of the system is quite similar to the existing RO system at University of Birmingham as explained in section 4.1. The main difference is that the new system will operate at 120 bar whereas the existing system has the pressure limit of 25 bar. Another difference is that the electroplating wastewater feed of new system will be more acidic and corrosive than NaCl solution and a higher corrosion resistant material with higher percent of alloy content was used for piping, instrumentations, and membrane module. Compared with the existing RO system, the new system has been also equipped with more sensors to indicate and transmit pressure, conductivity, flowrate of streams as well as the position of piston in WE. Moreover, in the new system, a manually operated sampling point is incorporated to allow a small sample of high-pressure batch liquid to be depressurized and removed from the system at any time for further characterisations.

The engineering design process of the high pressure HRRO system includes the following stages: 1. Concept design, 2. preliminary design, 3. detailed design, 4. manufacture, installation and commissioning.

The concept design has been provided and presented in D3.9. The preliminary design stage of the High Pressure RO system has been completed and is presented in section 6.1. The outline plan for stages 3 and 4 has been approved by the University of Birmingham and the details of the implementation will be given in the final version of the present deliverable (D3.10). The detailed design (stage 3) will take the initial design work and develop it into a package ready for manufacture. Further details will come out of the preliminary design stage including detailed GAD, detailed system schematic, set of manufacturing drawings, full parts list, documentation for both technical and user information, manufacturing schedule, control system schematic drawings, completion of PLC programming. The manufacture, installation and commissioning stage (stage 4) will cover the building and testing of the equipment at *ETS Design* and the installation and commissioning at University of Birmingham.

6.1 Preliminary design of the system

The main aim of the preliminary design stage is to specify the equipment and identify the major components. Table 10 shows the work packages and the produced documents at each work package related to the preliminary design stage.

Table 10. The work packages and the produced documents of the preliminary design stage of high pressure HRRO rig. Please note that these work packages refer specifically to the subcontracted project of the HRRO rig development, and do not correspond therefore to the overarching work packages of IntelWATT.

WPs No.	WPs title	Related documents
WP1	Specification of the equipment	Specification document, Compliance matrix, Description of the equipment

WP2	Outline design of the system	System schematic, Description of the control system, Description of the operating procedures
WP3	Identification of the major components	Initial parts list
WP4	Outline design of the physical rig	General arrangement drawing
WP5	Assessment for safety and UKCA marking	List of relevant directives and standards, Preliminary risk assessment
WP6	Costing for the subsequent stages	-

WP1. Specification of the equipment

At this stage of the design, the specification was expanded to include more detail on the equipment performance, ergonomics, environment and safety. The compliance matrix outlines how the equipment will meet the specification. The limits of the equipment was established at this stage and was used in the assessment of the safety requirements (see appendix 10.1). The material selection of pipings was done based on the corrosion calculations (see appendix 10.2).

WP2. Outline design of the system

The aim of this work was to complete the system design to meet the needs of the specification based on the concept design document provided earlier. A process flow diagram schematic was generated as a graphical way for describing the process and indication the general flow of process and equipment. Operating procedure and control system were described separately.

WP3. Identification of the major components

The major components essential to the performance of the system were specified at this stage. A parts list based on the system schematic and specification and supplier datasheet directory was produced.

WP4. Outline design of the physical rig

The General Arrangement Drawing (GAD) was produced at this work package to provide information on the dimensions of the equipment, ergonomic considerations and the functional layout of the system components based on the developed specification.

WP5. Assessment for safety and UKCA marking

The high pressure HRRO rig was assessed against relevant directives and standards a route to conformance was established as part of the conformance procedure for UKCA marking. An initial Risk Assessment (RA) based on the outline design of the system was completed at this stage. The RA identified the hazards which may arise from the equipment and established the methods for lowering the risks arising from these hazards (see appendix 10.1).

WP6. Costing for the subsequent stages

This work package included a costing and proposal for the subsequent stages (Detail design and the Manufacture, installation and commissioning).

6.1.1 Description of hardware

Figure 25 and Figure 26 shows the process flow diagram (PFD) and the general arrangement diagram (GAD) of the system. The main components of the system as shown are as follows:

- RO module and RO vessel
- Work exchanger vessel
- Supply and recirculation pump
- Supply pump support framework including anti vibration mounting
- Bypass, Recirculation and Brine valves
- Pressure, conductivity, proximity sensors and flowmeters
- Sampling point
- Main Tank
- Support frame for main tank
- Control System

A DuPont XUS180808 8-inch membrane element has been selected as the only commercially available candidate to be able to operate at 120 bar. The supply pump is a plunger pump with a variable frequency drive and the recirculation pump is a bespoke centrifugal pump. All of piping and instrumentation’s material are calculated to be SS 316L (see appendix 10.2). The actuator for bypass valve is pneumatic one and for the brine and recirculation valve are motorized. The system is equipped with a non-return RO check valve on permeate stream to prevent the backflow of the permeate stream. A Swagelok sampling valve was considered to allow a small sample of batch liquid to be depressurized and removed from the system for further characterization which was not possible to be done at high pressure of batch loop.

Once the piston has reached the end of its travel, the brine valve and bypass valves are opened and the recirculation valve is closed. This allows incoming feed water to purge the highly concentrated brine from the RO module and at the same time the pressure generated by the recirculation pump causes the piston in the work exchanger vessel to return to its starting position.

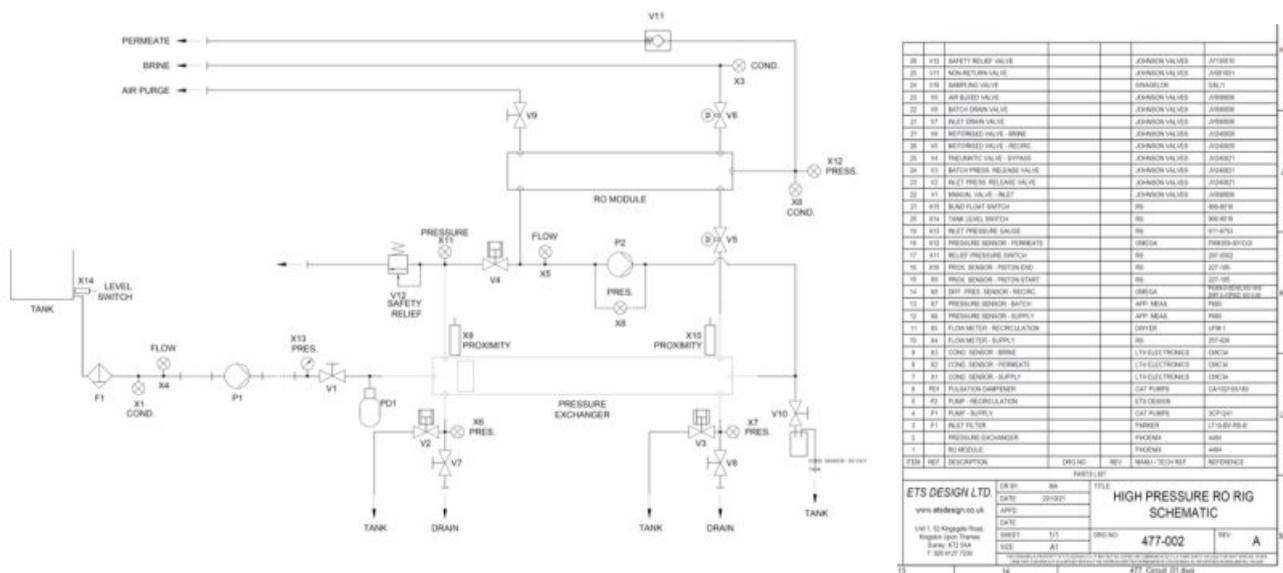


Figure 25 - Process flow diagram of the high pressure HRRO system



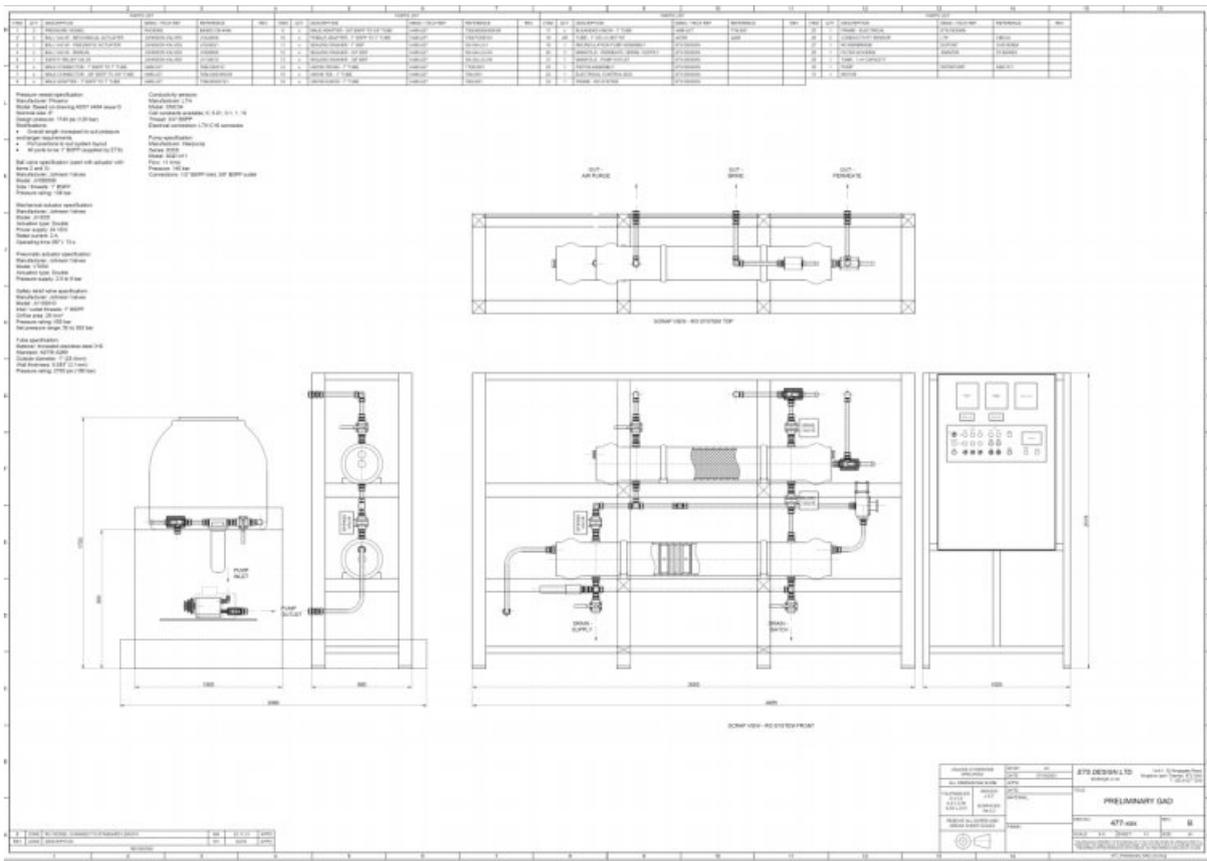


Figure 26 - General arrangement Diagram of the high pressure HRRO system

The system works as a three-phase process including (a) Semi batch phase, (b) Batch pressurisation phase, (c) Purge and refill phase.

During the Semi Batch Phase, the system works as a continuous RO system, but with the feed liquid being continuously recirculated with the liquid in the work exchange vessel in order to prevent high concentrations at the membrane. During the Batch Pressurisation the bypass valve is closed and the feed from the supply pump is used to drive the piston along the work exchanger vessel. The recirculation pump is used to minimise the variation of concentration at the membrane. The explanations of the flow paths of each phase and corresponding serial pressure drops are shown in Table 11 and Figure 27.

Table 11. Flow rate, pressure, and water displaced volume for each pump and phase of operation.

		Pressurisation 1 (semibatch) phase	Pressurisation 2 (batch) phase	Purge-and-refill phase
Flow rate Q [m ³ /s]	Supply pump	Q _f	Q _f	Q _f
	Recirc pump	Q _f + Q _r	Q _r	Q _r
	RO module permeate (Q _{perm})	Q _f	Q _f (J _w =Q _f /A _m)	zero
	RO module cross flow (Q _m)	Q _r + ½ Q _f	Q _r + ½ Q _f (1)	Q _f
	Bypass valve (V1)	Q _f	zero	Q _r + Q _f
	Recirc valve (V2)	Q _r + Q _f	Q _r + Q _f	zero
	Purge valve (V3)	zero	zero	Q _f
Pressure P [kPa]	Supply Pump	$\bar{P} = S_p S_L S_R \pi_{feed} \left[1 + \frac{v_{p1}}{2(V_{b0} + V_{pg} + V_{pipe,R})} \right] + \frac{J_w}{A} - \frac{1}{2} \Delta P_m + \Delta P_{V1}$	$\bar{P} = S_p S_L \pi_2 \frac{1}{r_p} \ln \frac{1}{1-r_p} + \frac{J_w}{A} + \frac{1}{2} \Delta P_m + \Delta P_{V2} + \Delta P_s$ $\pi_2 = \pi_{feed} \left[1 + \frac{v_{p1}}{(V_{b0} + V_{pg} + V_{pipe,R})} \right]$	$P = \Delta P_{V1} + \Delta P_m + \Delta P_{V3} + \Delta P_{Venturi}$ (2)
	Recirculation Pump	ΔP _m + ΔP _{V2}	ΔP _m + ΔP _{V2}	ΔP _s + ΔP _{V1}
Displaced volume ΔV [m ³]	Supply pump	V _{p1}	V _{b0}	V _{pg} - V _{backflow}
	Recirc pump	V _{p1} (α+1)	αV _{b0} (3)	V _{b0}

Notes: (1) the average of the input and output flows of the RO module; (2) the last term is an additional pressure drop introduced by a Venturi suction effect at the tee-junction downstream of the bypass valve;; (3) α is the ratio Q_r/Q_f. See reference [2] for further explanation of symbols and modelling approach.

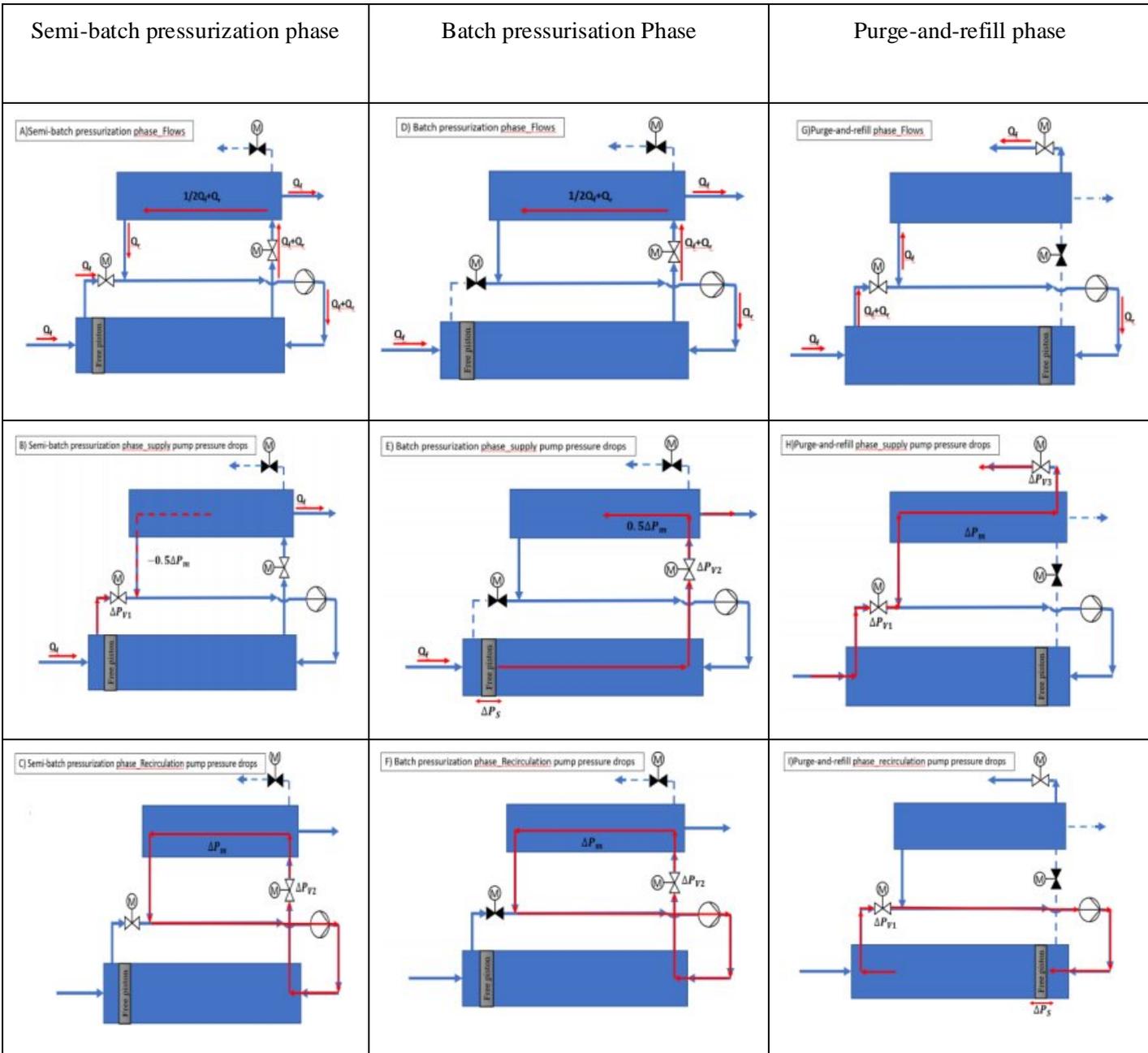


Figure 27 - Flow paths and corresponding pressure drops for each pump and phase of operation. V_1 , V_2 and V_3 are the bypass, recirculation and purge valve respectively. Blue shading indicates open valves; black shading indicates closed valves. These flow paths and pressure drops justify the equations shown in Table 11.

6.1.2 Safety aspects

The control system uses two Siemens Programmable Logic Controllers (PLCs). One PLC controls and monitors the safety of the system and the second PLC controls the process itself. This allows changes to be made to the program controlling the process without the risk of inadvertently compromising the safety functions.

The following safety considerations have been incorporated in the safety PLC:

- The system will have a hard-wired safety circuit incorporating a safety relay and a dedicated safety PLC.
- In the event of a power failure, or when the system is switched off, all pressure will automatically be released from the system.
- The system will have an emergency-stop button.
- The system will have a safety pressure relief valve. If the system pressure causes the excess pressure switch to be activated, the control system will detect this and safely shut the system down and release any pressure.
- The system will have a bund below the rig and tanks.
- The system will be fitted with polycarbonate safety screens with safety switches.
- The system will be fitted with a tank level switch
- The system will be fitted with a bund level switch

The control system is designed to ensure the safety of the operators and the integrity of the process, while at the same time allowing process parameters to be altered. At any time, if a safety event is triggered, or if the mode switch is switched to the off position, then both pumps will stop, the three main valves will open and the two pressure release valves will open. This ensures that there will be no pressure remaining in the system. The system cannot be restarted until the valve switches are set to the open position and the reset button is pressed. The safety events that would trigger this are an excess pressure, the bund switch being triggered, the 'tank low' switch being triggered or the emergency stop switch being pressed. The control hardware will be housed in a cabinet connected to the RO system but located outside the bund in order to reduce the risk of liquid coming into contact with electrical components.

Moreover, Safety regulations have been considered at this stage of design and the rig shall conform to the following UK Directives:

- Supply of Machinery (Safety) Regulations 2008/1597
- The Electrical Equipment (Safety) Regulations 2016/1101
- Electromagnetic Compatibility Regulations 2016/1091
- Pressure Equipment (Safety) Regulations 2016/1105

The above directives are generally equivalent to the previously applicable EU directives for Machinery, LVD, EMC and PED

7 Technical Risks

The conceptual design exercise has identified the following technical risks that need to be acted as the design progresses (see Table 12 below).

Table 12. Technical risks with likelihood and severity on a scale of 1 to 3. (L) is for an assessment of the likelihood of the hazard taking place, (S) for the severity of the risk. This table does not include all aspects of risk and hazard assessment relating to safety, which are covered instead in Appendix 10.1.

Technical Risks	L	S	L x S	Mitigations
The output target cannot be met because of excess pressures and/or reduced membrane permeability because of fouling, membrane compaction, or change in membrane properties at the high concentration of electrolyte.	3	2	6	Reduce flux to lower pressure and increase membrane area accordingly. Variable speed pump and gearing specified in HRRO rig to allow this. Use additional unit processes to accomplish whole process.
Semibatch/batch process does not work according to model	1	2	2	Experiments have been conducted with the existing rig, to show that the model is accurate.
Feedpump is not efficient over range of pressures and flows needed	2	1	2	Liaise with pump manufacturer to request performance to prediction. Consider options of DC or AC motor to drive pump and alternative speed control approaches. The hydraulic work will be measured independently of electrical work, to separate the assessment of pump efficiency from desalination process efficiency.
Pressure spike at end of batch pressurisation phase	2	2	4	A proximity sensor will be used to detect the piston position before it reaches the end of travel. Pneumatically actuated bypass valve for fast opening (<1s), in preference to motorised valve. Use pulsation damper to absorb pressure spike Include safety release valve
Air trapped in system prevents recirculation pump from priming	2	1	2	Provide vent points at high points in system
The membrane specified is only available from one supplier	2	1	2	The membrane has been ordered in advance of completing the design. Alternative suppliers are being identified.
The concentration of the feed solution may differ from the standard one assumed in the calculations	2	1	2	The control system can cope with different feed concentrations by switching from semibatch to batch phase once a threshold pressure is reached, thus giving variable recovery and concentration factor.

Rapid depressurisation may cause the membrane to delaminate at the start of the purge phase	3	2	6	A speed control on the purge valve allows more gradual depressurisation. Spare membranes are being ordered, in case the membrane gets damaged.
Compaction of the membrane or fouling could result in pressures higher than 120 bar	2	2	4	The pressure relief valve was used to release the system pressure in case of pressure exceed.
Inefficient pumps lower than 50% over range of pressures and flows needed	2	2	4	Liaise with pump manufacturer to request performance to prediction. Consider options of DC or AC motor to drive pump and alternative speed control approaches.

8 Conclusions

This provisional version of D3.10 reports several steps that progress task 3.3 of the intelWATT project. It covers experimental and modelling results about high-recovery reverse osmosis (HRRO) for the concentration of rinse water from metal plating wastewater. The final version of this deliverable (D3.10) will be produced later. To summarise the main results so far:

- The results from the electrolyte recovery using the standard RO system were updated. Sufficient Cr(III) rejection above 99.6% was achieved while the rejection of boric acid increased from 65 to 90% during the concentration. Electroplating trials using the concentrated rinse water were performed and the obtained results were acceptable.
- The total organic carbon (TOC) content of rinse water was reduced using adsorption with powdered activated carbon (PAC) while the chromium content of the rinse water remained almost unchanged.
- Adsorption with granular activated carbon was used for the removal of anionic surfactants and at least 90% removal of surfactants was observed.
- A comprehensive series of experiments at various feed salinities and water permeate fluxes were performed to evaluate and demonstrate the performance of hybrid semi-batch/batch high recovery reverse osmosis system with pressure limit of 25 bar. The results showed that at system flux of 17.7 LMH, the rejection was 94.4 % with electrical SEC of 0.53 kWh/m³. The recovery of 95% with the concentration factor of >20 was achievable using the hybrid semibatch/batch RO operation, using low concentration solutions as constrained by pressure limitations of the existing equipment.
- The mathematical modelling described previously in D3.9 was modified in this document with some detailed improvements. The experimental results were in good agreement with modelling results with biggest error of about 4% confirming the model is validated. This model is used to support the design of the high-pressure system.
- The concept design stage of the high-pressure RO system has been completed. The detailed design, manufacture and installation stages are being commissioned by the University of Birmingham, for execution by the subcontractor. The details of the implementation will be given in the final version of the present deliverable (D3.10).

- Technical risks have been identified relating to the performance of the high-pressure RO system and mitigating measures put in place. These include deterioration in the permeability of the membrane at high pressure (mitigated by variable pump speed to control pressure) and delamination of the membrane during rapid depressurisation (mitigated by variable valve opening speed to control depressurisation rate).

-The next step of the present task will be the implementation of stages 3 and 4 of the design of high-pressure HRRO system including detailed design and the manufacture, installation and commissioning. Details of that will be given in the final version of the present deliverable (D3.10).

Simulated feed, like the metal plating rinse water, will be synthesized and the concentration of chromium (III) using the high pressure HRRO system will be performed. The water recovery, rejection of the various solutes, SEC, peak pressure, and system output will be reported. Extended tests will be carried to ensure reliability of the process and resistance to membrane fouling and flux decline. Sensitivity of the performance to flux, feed concentration and pH will be studied. The model will be validated and used to scale up the design by a factor of about 5, as required for the pilot-scale process to be implemented at BIA. Moreover, a journal paper will be written based on the findings of section 5.2 of the present version of D3.10, and submitted to a well-recognised journal such as Desalination or Water Research.

In summary, the experience so far is very promising in relation to the feasibility of the proposed system and its scale up from lab-scale to pilot scale at the BIA plant, under the scope of the intelWATT project.

9 References

- 1 Park, K., & Davies, P. A. (2021). A compact hybrid batch/semi-batch reverse osmosis (HBSRO) system for high-recovery, low-energy desalination. *Desalination*, 504, 114976.
- 2 Hosseinipour, E., Park, K., Burlace, L., Naughton, T., and Davies, P. A. (2022). A free-piston batch reverse osmosis (RO) system for brackish water desalination: experimental study and model validation. *Desalination* (in press).

10 Appendices

10.1 Risk Assessment

Key

11 Severity of harm	
Death, loss of an eye or arm	4
Broken limb, loss of finger(s)	3
Reversible: Medical treatment required	2
Reversible: First aid required	1

Probability of occurrence	
Probable	A
Possible	B
Improbable	C

Phase	Function	Hazard zone	Task / operation	Accident scenario				Description of measures / solutions (before)	Severity of harm (before)	Probability of occurrence (before)	Risk (before)	Description of measures / solutions (after)	Severity of harm (after)	Probability of occurrence (after)	Risk (after)								
				Hazard origin	Hazard consequence	Hazardous situation	Hazardous event																
Operation	Manual control	Pipework and pressure vessel assembly	Pressurising the system (manually operated pump controls)	High pressure fluid (brine in the system)	Piercing	Running system to full pressure	Projection of high pressure fluids	System components rated above max. working pressure	Death, loss of an eye or arm	Improbable	4C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C								
			Splashing		Projection of fluids		Reversible: First aid required		1C														
			Relieving the system pressure	High pressure fluid (brine in the system)	Piercing	Opening a 'back to tank' valve	Projection of high pressure fluids	None	Death, loss of an eye or arm	Possible	4B	Possible	1B	Commissioning to include connection to tanks	Reversible: Medical treatment required	Improbable	2C						
			Splashing		Projection of fluids		Reversible: First aid required																
			Unexpected start-up	High pressure fluid (brine in the system)	Piercing	Restart after stopping	Projection of high pressure fluids	Safety relay reset circuit only operates with pumps switched off	Death, loss of an eye or arm	Improbable	4C	Improbable	1C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C						
			Unexpected start-up		Splashing		Projection of fluids		Reversible: First aid required														
	Control box	Manual control	Live parts (switches and buttons on the control panel)	Electrocution	Operating controls	Contact with electrical charge	Control switches and buttons rated to IP67 24V control system	Reversible: Medical treatment required	Improbable	2C													
		Manual control	Location of control devices and indicators (control panel layout)	Discomfort	Operating controls	Painful and tiring postures	Controls designed for use in standing position	Reversible: Medical treatment required	Improbable	2C													
	PLC control	Unexpected start-up	High pressure fluid (brine in the system)	Piercing	Switching to PLC mode	Projection of high pressure fluids	Safety relay cannot be reset with PLC outputs high	Death, loss of an eye or arm	Improbable	4C	Improbable	1C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C							
				Splashing		Projection of fluids		Reversible: First aid required															
		Pressurising the system (Programmed controls)	High pressure fluid (brine in the system)	Piercing	Running system to full pressure	Projection of high pressure fluids	System components rated above max. working pressure Pre-set safety relief valve and solenoid valves fully relieve the system pressure if triggered	Death, loss of an eye or arm	Improbable	4C	Improbable	1C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C							
				Splashing		Projection of fluids		Reversible: First aid required															
	Start-up / Shut-down	Starting the system	High pressure fluid (brine in the system) left in the system	Piercing	Starting the system	Projection of high pressure fluids	Pressure released when machine is off or loses power	Death, loss of an eye or arm	Improbable	4C	Improbable	1C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C							
				Splashing		Projection of fluids		Reversible: First aid required															
		Stopping the system	High pressure fluid (brine in the system) left in the system	Piercing	Stopping the system	Projection of high pressure fluids		Death, loss of an eye or arm	Improbable	4C	Improbable	1C	Polycarbonate Screens Fitted to Rig	Reversible: Medical treatment required	Improbable	2C							
				Splashing		Projection of fluids		Reversible: First aid required															
	Any	Any	Fluid in System	Spillage	Leakage from components	Liquid on floor	None	Reversible: First aid required	Possible	1B	Band Fitted to system	Reversible: First aid required	Improbable	1C									
															Supply Pump Motor	Pump Running	Rotating Parts	Trapping	Motor Running	Trapping of fingers	Warning Signs next to pump	Broken limb, loss of finger(s)	Possible
Maintenance	Purging air from the system	Pipework and pressure vessel assembly	Purging the air from the system	High pressure fluid (brine in the system)	Piercing	Releasing pressure from the situation	None	None	Death, loss of an eye or arm	Possible	4B	Commissioning to include connection to tanks	Reversible: Medical treatment required	Improbable	2C								
					Splashing		Projection of high pressure fluids		None							Reversible: First aid required	Possible	1B					
					Spillage		Projection of fluids		None							Broken limb, loss of finger(s)	Possible	3B	Commissioning to include connection to tanks Note in manual to clean up spillages	Reversible: First aid required	Improbable	1C	
	Changing of components	Pipework and pressure vessel assembly	Changing the RO Module	High pressure fluid (brine in the system)	Projection	Removing the RO module	Release of stored energy	None	Broken limb, loss of finger(s)	Improbable	3C	Warning signs next to RO Module about dangers when changing module Wearing of safety glasses and gloves Specialist equipment used for removal	Reversible: First aid required	Improbable	1C								
																Low Pressure Fluid	Splashing	Projection of fluid	None	Reversible: First aid required	Possible	1B	Warning signs next to RO Module about dangers when changing module Wearing of safety glasses and PPE Specialist equipment used for removal
Changing the piston	High pressure fluid (brine in the system)	Projection	Removing the piston	Release of stored energy	None	Broken limb, loss of finger(s)	Improbable	3C	Warning signs next to the Pressure Vessel about dangers when changing the piston Wearing of safety glasses and PPE Specialist equipment used for removal	Reversible: First aid required	Improbable	1C											

				Low-Pressure Fluid	Splashing		Projection of fluid	None	Reversible: First aid required	Possible	1B	Warning signs next to the Pressure Vessel about dangers when changing the piston Wearing of safety glasses and PPE Specialist equipment used for removal			
				Location of components (RO module)	Discomfort		Painful and tiring postures	None	Reversible: Medical treatment required	Improbable	2C				
	Changing drive ratio	Supply Pump Motor	Changing drive pulleys	Rotating Parts	Trapping	Motor Running	Trapping of fingers	Warning Signs next to pump	Broken limb, loss of finger(s)	Possible	3B	Training given to operators. Warning sign to isolate electrical supply before removing cover	Reversible: Medical treatment required	Improbable	2C
Transport	Lifting and loading	Machine and surroundings	Lifting the machine	Instability when lifting	Crushing, cutting or severing	Moving the machine	Loss of stability	Space for multiple pallet trucks or fork lifts under machine	Broken limb, loss of finger(s)	Improbable	3C	Lifting points to be marked on machine Manual lifting assessment to be carried out beforehand	Reversible: Medical treatment required	Improbable	2C
				Position of lifting points	Discomfort		Painful and tiring postures	None	Reversible: Medical treatment required	Improbable	2C				

10.2 Calculation summary of corrosion rate for 316L SS

Automatic Chemistry Model

Aqueous (H⁺ ion) Databanks:

Corrosion

Public

Redox selected

Chromium

Iron

Isothermal Calculation

Temperature 30 °C
Pressure 130 atm

Stream Inflows

Water	55.5087	mol
Boric acid	0.07279	mol
Chromium(III) sulfate	5.70E-03	mol
Sulfuric(VI) acid	0.111879	mol
Potassium hydroxide	0.23	mol
Iron	0	mol

Calculated Rates

Corrosion Rate	6.28E-04	mm/yr
Corrosion Potential	-0.3197	V (SHE)
Repassivation Potential	>2.0	V(SHE)
Current Density	0.058128	μA/sq-cm
Pit Current Density	4.02E-09	μA/sq-cm

Stream Parameters

Row Filter Applied: Only Non Zero Values

Mixture Properties

Stream Amt - Total Inflow	55.929	mol
Temperature	30	°C
Pressure	130	atm

Aqueous Properties

pH	4.05869	pH
Ionic Strength	5.44E-03	mol/mol
ORP	0.4298	V (SHE)
Osmotic Pressure	6.4705	atm
Elec Cond, specific	0.025941	1/(ohm-cm)
Elec Cond, molar	62.3976	cm ² /ohm-mol
Viscosity, absolute	0.821983	cP
Viscosity, relative	1.02996	cP/cP H ₂ O

	Unit	Total	Aqueous	Vapor	Solid	2nd Liquid
Density	g/ml		1.01909	0	5.224	0
Enthalpy	cal	-3.86E+06	-3.86E+06	0	-299.42	0
Heat Capacity	cal/(g K)	0	0	0	0	0

Total and Phase Flows (Amounts)

	Total	Aqueous	Vapor	Solid	2nd Liquid
Mole (True)	56.1417	56.1406	0	1.10E-03	0
Mole (App)	56.1308	56.1297	0	1.10E-03	0
Mass	g	g	g	g	g
	1030.62	1030.45	0	0.167146	0
Volume	L	L	L	L	L
	1.01119	1.01116	0	3.20E-05	0

Scaling Tendencies



Row Filter Applied: Only Non Zero Values

Solids	Tendency	Temperature Range	
		data valid	
Chromium(III) oxide	1	through range	inside range
Boric acid	0.067549	0.0 - 160.000 °C	inside range
Potassium sulfate(VI)	0.025467	9.70000 - 292.000 °C	inside range
Chromium(III) Oxide Hydroxide	0.014189	data valid	inside range
Chromium (III) hydroxide (amorphous)	1.17E-05	through range	inside range
Potassium bisulfate(VI)	4.93E-06	data valid	inside range
Chromium(IV) oxide	3.41E-07	through range	inside range
Potassium metaborate	4.40E-14	data valid	inside range
Potassium hydroxide dihydrate	1.48E-14	0.0 - 33.0000 °C	inside range
Dipotassium tetraboron heptaoxide	4.29E-19	data valid	inside range
Potassium hydroxide	6.91E-22	through range	inside range
Dipotassium hexaboron decaoxide	6.33E-23	data valid	inside range
Dipotassium octaboron tridecaoxide	1.23E-24	through range	inside range
Potassium chromate(VI)	1.08E-28	0.0 - 300.000 °C	inside range
Chromium(VI) trioxide	2.62E-31	data valid	inside range
Chromium	1.00E-35	through range	inside range
Potassium dichromate(VI)	1.00E-35	0.0 - 150.000 °C	inside range

Species Output (True Species)

Row Filter Applied: Only Non Zero Values

	Total mol	Aqueous mol	Vapor mol	Solid mol	2nd Liquid n/a
Water	55.7354	55.7354	0	0	0
Boric acid	0.072787	0.072787	0	0	0
Sulfuric(VI) acid	4.96E-19	4.96E-19	0	0	0
Sulfur trioxide	6.19E-23	6.19E-23	0	0	0
Chromium (III) hydroxide (amorphous)	2.02E-12	2.02E-12	0	0	0
Oxygen	1.61E-40	1.61E-40	0	0	0
Chromium(III) oxide	1.10E-03	0	0	1.10E-03	0

Hydrogen	3.34E-26	3.34E-26	0	0	0
Potassium bisulfate(VI)	4.37E-07	4.37E-07	0	0	0
Hydrogen ion(+1)	1.35E-04	1.35E-04	0	0	0
Triboron trioxide tetrahydroxide ion(-1)	6.17E-07	6.17E-07	0	0	0
Diboron oxide pentahydroxide ion(-1)	8.98E-08	8.98E-08	0	0	0
Boron tetrahydroxide ion(-1)	1.02E-06	1.02E-06	0	0	0
Hydroxide ion(-1)	2.68E-10	2.68E-10	0	0	0
Tetraboron pentaoxide tetrahydroxide ion(-2)	1.09E-11	1.09E-11	0	0	0
Chromium(III) tetrahydroxide ion(-1)	6.85E-20	6.85E-20	0	0	0
Chromium(III) dihydroxide ion(+1)	4.45E-10	4.45E-10	0	0	0
Chromium(III) sulfate ion(+1)	9.20E-03	9.20E-03	0	0	0
Chromium ion(+3)	2.96E-07	2.96E-07	0	0	0
Chromium(III) monohydroxide ion(+2)	2.45E-07	2.45E-07	0	0	0
Bisulfate(VI) ion (-1)	2.23E-04	2.23E-04	0	0	0
Sulfate ion(-2)	0.092874	0.092874	0	0	0
Dichromate(VI) ion(-2)	2.05E-46	2.05E-46	0	0	0
Chromium ion(+2)	5.95E-24	5.95E-24	0	0	0
Bichromate(VI) ion(-1)	1.98E-24	1.98E-24	0	0	0
Chromate(VI) ion(-2)	2.74E-26	2.74E-26	0	0	0
Potassium sulfate(VI) ion(-1)	0.026682	0.026682	0	0	0
Potassium ion(+1)	0.203318	0.203318	0	0	0
Total (by phase)	56.1417	56.1406	0	1.10E-03	0

Molecular Output (Apparent Species)

Row Filter Applied: Only Non Zero Values

	Total mol	Aqueous mol	Vapor mol	Solid mol	2nd Liquid n/a
Water	55.8447	55.8447	0	0	0
Diboron trioxide	0.036395	0.036395	0	0	0
Sulfur trioxide	0.128979	0.128979	0	0	0
Chromium(III) oxide	5.70E-03	4.60E-03	0	1.10E-03	0
Dipotassium oxide	0.115	0.115	0	0	0
Total (by phase)	56.1308	56.1297	0	1.10E-03	0

Element Balance

958454 — intelWATT

D3.10 – Lab-scale HRRO unit for integration with IX

49/50



	Total mol	Aqueous mol	Vapor mol	Solid mol	2nd Liquid n/a
H(+1)	111.689	111.689	0	0	0
K(+1)	0.23	0.23	0	0	0
FE(+2)	0	0	0	0	0
FE(+3)	0	0	0	0	0
O(-2)	56.473	56.4697	0	3.30E-03	0
S(+6)	0.128979	0.128979	0	0	0
CR(+6)	2.00E-24	2.00E-24	0	0	0
H	6.68E-26	6.68E-26	0	0	0
O	3.22E-40	3.22E-40	0	0	0
B(+3)	0.07279	0.07279	0	0	0
FE(0)	0	0	0	0	0
Cr(+2)	5.95E-24	5.95E-24	0	0	0
CR(+3)	0.0114	9.20E-03	0	2.20E-03	0
FE(+6)	0	0	0	0	0
Cr(0)	0	0	0	0	0
Cr(+4)	0	0	0	0	0