ZERO BRINE

D2.1 Modelling a brine regeneration cycle using PHREEQC

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Deliverable 2.1	Simulation using PHREEQC
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[1] **R**=Document, report; **DEM**=Demonstrator, pilot, prototype; **DEC**=website, patent fillings, videos, etc.; **OTHER**=other

[2] **PU**=Public, **CO**=Confidential, only for members of the consortium (including the Commission Services), **CI**=Classified

Contents

List of abbreviations

DAF	Dissolved Air Flotation
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma – Mass Spectroscopy
IEX	Ion Exchange
M	Mol/L (unit of concentration)
MW	Molar Weight (in g/mol)
NF	NanoFiltration
NTUA	National Technical University of Athens
RO	Reversed Osmosis
SI	Saturation Index (see equation 1)
SPIRE	Sustainable Process Industry through Resource and Energy-efficiency
TDS	Total Dissolved Solids
TUD	Technical University Delft
UNIPA	Università degli Studi di Palermo (Palermo University)
USGS	United States Geological Service

1. Overview of the project

The ZERO BRINE project aims to facilitate the implementation of the Circular Economy package and the SPIRE roadmap in various process industries by developing necessary concepts, technological solutions and business models to redesign the value and supply chains of minerals and water while dealing with present organic compounds in a way that allows their subsequent recovery.
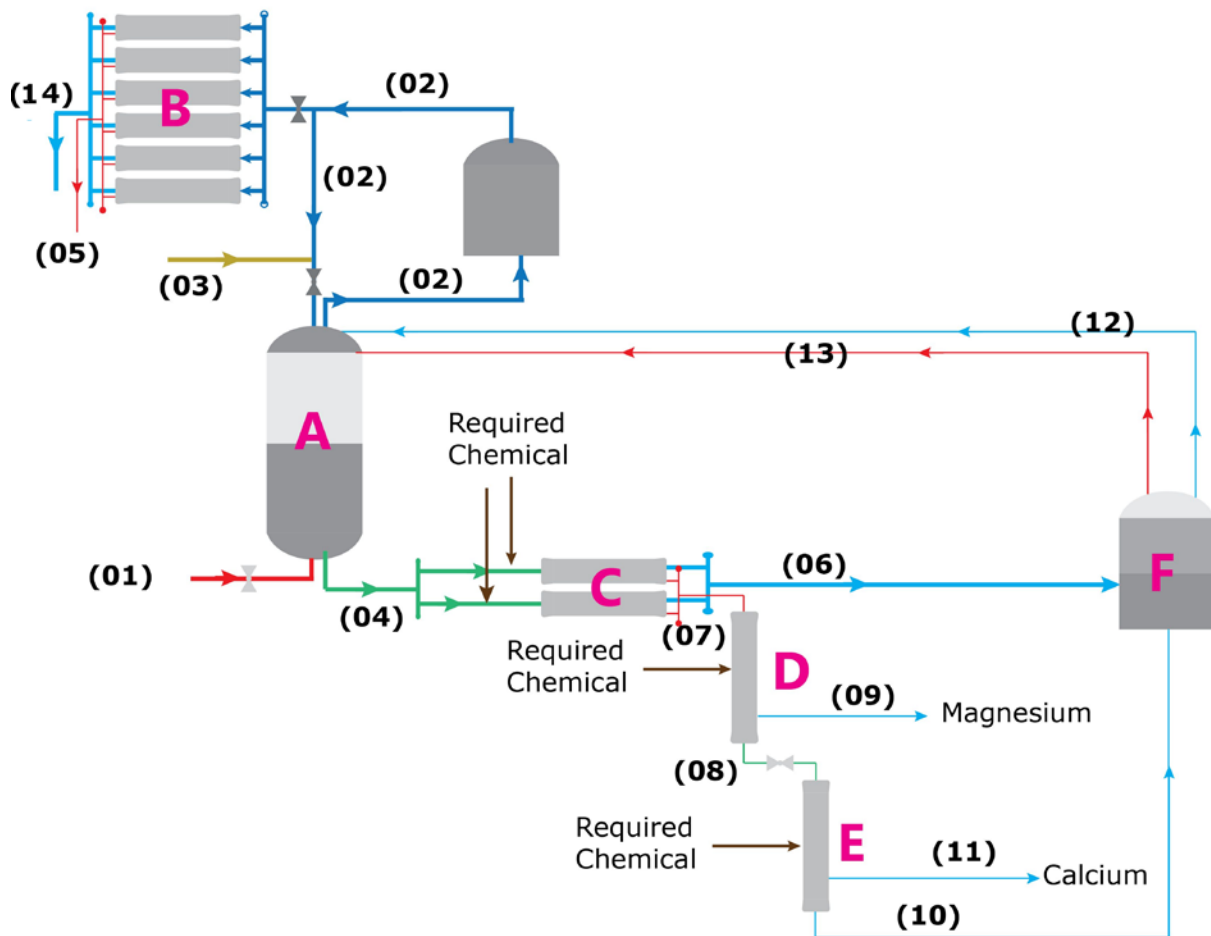
These resources will be recovered from saline impaired effluents (brines) generated by the process industry while eliminating wastewater discharges and minimizing the environmental impacts of industrial operations through brines (ZERO BRINE). ZERO BRINE brings together and integrates several existing and innovative technologies to recover products of high quality and sufficient purity to represent good market value. A large-scale demonstration plant will be tested in the Energy Port and Petrochemical cluster of Rotterdam Port by using the waste heat from one of the factories in the port. The quality of the recovered products will be aimed to meet local market specifications. Additionally, three large-scale pilot plants will be developed in other process industries in Poland, Spain, and Turkey, providing the potential for immediate replication and uptake of the project results after its successful completion.

2. Objectives

The ZERO BRINE project aims to recover minerals and water from the waste brine of industrial water and to minimize the impact of the waste brine on the environment. At the pilot located in the Botlek, The Netherlands, the objective is to recover Ca- and Mg-salts as well as demineralized water from the discharges of the water-softening unit. Objectives of this Deliverable (D2.1) are constructing a physicochemical model for simulating the chemical processes that will take place in the crystallization units that constitute the ZERO BRINE pilot plant at the Botlek. The aqueous chemical reactions inside these process units, but also in the nanofiltration pre-treatment unit and in the evaporator producing brine and distilled water, will be predicted using PHREEQC, a chemical model for simulation of reactions in water. The simulation results should indicate amounts and purity of recovered materials, and important process parameters, and will be used to adjust the process scheme and to fine-tune the proposed process flow diagram for the design of the pilot plant.

3. Introduction

The Botlek is an industrial district of the port of Rotterdam, with plants of companies like Huntsman (former ICI), Akzo Nobel, Cargill and Esso, as well as transhipping facilities of Vopak and Odfjell. Demineralized water is an essential commodity here because it is required for many production processes. Reverse osmosis (RO) has become one of the main processes for producing demineralized water, but reverse osmosis alone is not enough to produce water of the required purity from the available water (fresh surface water), and several pre- and post-treatment processes are used. At the Evides demiwater, one of the largest demineralised water production facilities in Europe, Reverse Osmosis is combined with ion-exchange softening, among others, as can be seen in Figure 1 below:

Figure 1: Process flow diagram of the ZERO BRINE project for the Evides site, with identification of process units and description of flows. Flow rates depending on selection of equipment to be installed..

process units		
A	IEX: ion exchanger (existing)	existing unit at Evides
B	RO: reverse osmosis unit (existing)	existing unit at Evides
C	NF: nanofiltration unit	provided by Lenntech for Zero Brine
D, E	crystallisation units for recovery of Mg and Ca	provided by UNIPA for Zero Brine
F	evaporator unit	provided by NTUA for Zero Brine
flows				
01	IEX influent: pretreated surface water	08	Mg crystallisation supernatant
02	IEX effluent (softened water), used as feed for RO and for regenerating IEX (current situation)	09	Mg salt suspension
03	NaCl brine for IEX regeneration	10	Ca crystallisation supernatant
04	spent regenerant (NaCl brine with exchanged cations)	11	Ca salt suspension
05	RO concentrate (existing); waste	12	evaporator condensate (distilled water)
06	NF permeate, intended to be evaporator feed	13	NaCl brine (concentrated), for IEX regeneration
07	NF concentrate, intended to be metal recovery feed	14	RO permeate

Demineralised water is produced from raw surface water by means of several processes, like softening and membrane filtration. The pretreated (coagulation/flocculation, DAF, filtration) surface water that enters the industry water plant (01) is withdrawn from the Brielse Meer. This pretreated water has the same ion strength as the water source, but may contain small residual amounts of Fe(III), as $FeCl_3$ is used as coagulant, added to the raw water to enhance its pretreatment. The ion exchange (IEX) softening unit (A) removes bivalent cations like Ca^{2+} and Mg^{2+}, amongst others, substituting them for Na^+ ions. The reverse osmosis (RO) unit (B) then separates the softened feed water into a permeate (14) and a concentrate stream (05). This concentrate

includes most of the ions of the feed water, albeit at higher concentrations (and with part of the cations substituted for sodium-ions), as well as small amounts of residual dissolved organic pollutants, and will be disposed in most cases. The permeate (14) is essentially almost pure water, but still contains a small amount of monovalent salts and is, therefore, not suitable to be distributed to the industrial district [1, 2]. Typically, polishing steps are used to remove the trace of salts in this permeate to make it suitable to be used as demineralized water.

As indicated, IEX softening is used as one of the pretreatment steps before RO to remove divalent ions and enhance the recovery of RO. Regeneration of the IEX resin is an essential procedure to maintain the required efficiency of this process, and is carried out daily. Regenerating IEX resin occurs typically by counter-current passing of a concentrated salt solution (NaCl brine), and the effluent from IEX regenerating contains valuable ions such as Magnesium (Mg^{2+}) and Calcium (Ca^{2+}), amongst others. Disposing of the IEX regeneration solution could be costly and harmful to the environment.

The main aim of the ZERO BRINE project at the Evides site 1 (Figure 1) is to treat the regeneration solution of the IEX unit (spent regenerant) and to recover valuable minerals and salts as well as water from this flow. This will be done by using several technologies. The spent regenerant (04) will first pass through a nanofiltration (NF) installation (C). The NF installation will produce a NaCl rich solution with a NaCl purity of around 96% as its permeate (06). The production of such permeate depends on parameters like permeate and reject flows, and reject percentages of different ions. The possibility of production of a permeate with such characteristics is under investigation at the moment by LENNTECH (one of the ZERO BRINE project partners in WP2). The NF concentrate (07) on the other hand contains water and salts of mainly multivalent ions. Recovery of these ions is possible as low solubility sulphates, carbonates, or hydroxides, as represented by thin dotted, solid, and thick dotted lines respectively in Figure 2. The least soluble compound is $CaMg(CO_3)_2$, dolomite, but precipitating this compound will not lead to separation of Mg and Ca and should thus be avoided, by keeping the (bi)carbonate concentration in the crystallisation reactor as low as possible. The second least soluble compound however is $Mg(OH)_2$, brucite, which's solubility (dark blue dotted line, closed markers) differs greatly from the solubility of $Ca(OH)_2$ (lighter blue dotted line, open markers), and thus permits sequential precipitation. Interference may result from the low solubilities of several carbonates (solid lines, marker depends on cation). The NF concentrate will thus pass through a two-stage crystallization process. In the first stage (D), magnesium, and in the second stage (E), calcium will be recovered as metal hydroxides, by means of slowly dosing stoichiometric amounts of NaOH. To avoid contamination of the produced brucite ($Mg(OH)_2$) and lime ($Ca(OH)_2$), the concentration of hydroxide ions but also of other anions will be shown to be of importance.
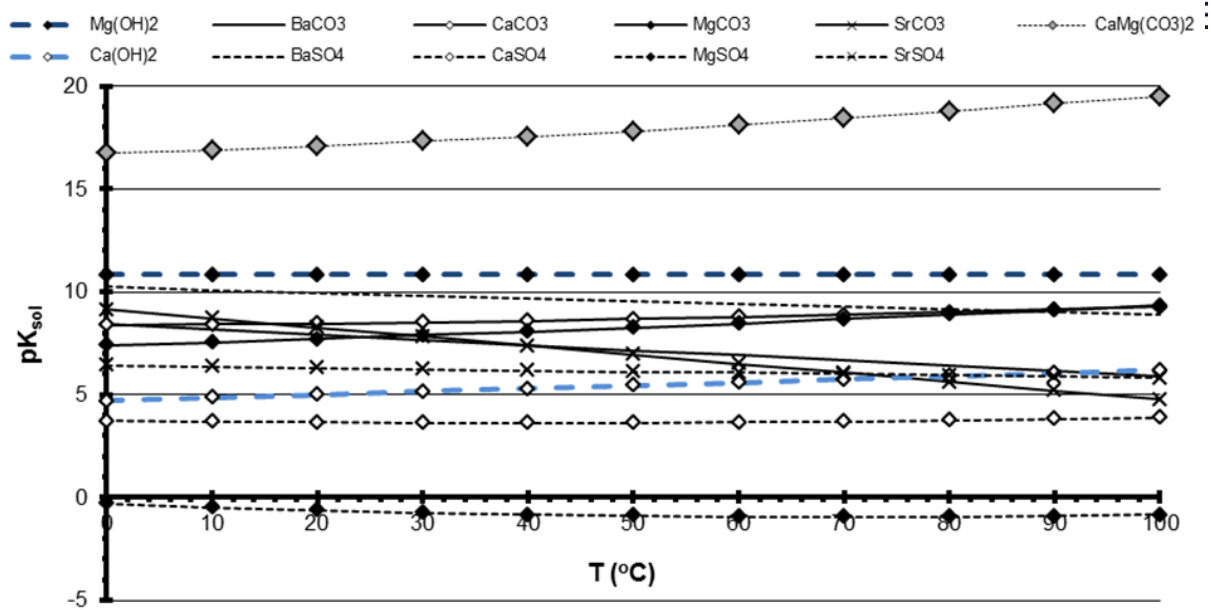
Figure 2: negative logarithms of solubility products (pK_{sol} = -log(K_{sp})) of a number of salts of bivalent cations and carbonate, sulphate, or hydroxide [3]. Least soluble is CaMg(CO_3)$_2$ (dolomite, essentially insoluble at 25 °C), most soluble is $MgSO_4$ (solubility approx. 351 g.L^{-1} at 25 °C). Mg(OH)$_2$ and Ca(OH)$_2$ identified with thicker dark and light blue dotted lines and closed and open markers, respectively (cations always use the same marker, anions the same line style). Relative solubilities depend on temperature, as the solubility of some minerals increases but of other minerals decreases with temperature.

The joined NF permeate (06, essentially a slightly polluted NaCl brine) and the effluent from the membrane crystallization (10) will then be treated with an evaporator. In the evaporator, the solution will be separated into condensate (12), and a solution with a high salinity (13). The condensate of the evaporator (11) is virtually free of any ions and can be used as demineralized water which is needed as well for the regeneration of the IEX columns. The high salinity brine will contain mostly NaCl, and can be used for regeneration of the IEX columns but, depending on conditions, unlimited recycling of the supernatant 10 may deem this brine too polluted with other cations. One of the objectives of this report is thus to analyse the consequences and (im)possibility of such recycling.

This report describes the chemical reactions that are expected to take place during passing of the spent regenerant through the different processes, using a solubility-constant based computer model (PHREEQC). The report also serves as a critical evaluation of initial design estimations and will be used for fine-tuning the process flow diagrams of Zero Brine at Evides site 1 and to give recommendations for a feasibility analysis of the full scale plant in WP7.

4. Material and Methods

Data Acquisition

The data used as a starting point for the modelling were determined from two sampling campaigns at the Evides Demineralised Water Plant. Samples were taken in December 2017, and in March 2018, after each ion-exchange column, to not only determine the average concentration levels of the individual ions, but to determine also the effect of operating time of the ion exchange resin on the presence of secondary pollutants (cations other than H^+, Na^+, Ca^{2+} and Mg^{2+}). The samples were stored at 4 °C and analysed at the TU Delft water laboratory by using ICP-MS for the cations and IC for the anions, using standard procedures, as described in

another report (Deliverable D2.2) on the Zero Brine project progress[3]. Bicarbonate was determined by titration of samples with 0.100 M HCl until a pH of 4.30 using a Metrohm 702SM Titrino automatic titrator. Temperature was determined on-site and pH was measured in the samples by means of a hand-held pH meter (WTW Multi 3410). Total Dissolved Solids (TDS) were determined gravimetrically. The results of these analyses are shown in the Results and discussions section.

Modelling

The calculations concerning the chemical reactions were performed using Excel for making initial estimations of flows and rejects, and using PHREEQC Interactive 3.4.0 for detailed calculations of chemical equilibria and solubility and precipitation/crystallisation. PHREEQC is a modelling program developed by the USGS [4, 5], and nowadays used for simulating a variety of reactions and processes in natural waters or in experiments. PHREEQC has several databases, including solubility products of different groups of minerals, which are used for determining speciation of elements involved in the system under different conditions. Given the species present in the brine and expected to be relevant, the Minteq v.4 database (that can be found among the databases provided with PHREEQC Interactive 3.4.0) was used rather than the smaller Pitzer or PHREEQC generic databases. Minteq was selected as database because it contained most measured elements.

The data obtained during the data-acquisition phase and presented in "Results and discussions section" are not exactly the input values used for the PHREEQC simulations. For practical reasons, a number of simplifications needed to be made:

1. to simplify simulation, elements with concentrations < 1 µg.L^{-1} were neglected in the simulation;
2. Cobalt (Co) and Molybdenum (Mo), which are not included in PHREEQC's Minteq database, were therefore excluded from the simulations;
3. Notably, for both samples, the amount of moles per litre of sulphur (S) as reported by ICP-MS is higher than the molar concentration of sulphate (SO_4^{2-}) as reported by Ion Chromatography. The same occurs for phosphorous (P) and phosphate (PO_4^{3-}). The PHREEQC simulations though were conducted assuming that all sulphur (S) is present as S^{6+} (i.e. as sulphate: SO_4^{2-}), and assuming that all phosphorus (P) is present as P^{5+} (i.e. as phosphate: PO_4^{3-}), using the concentrations obtained from ICP-MS.
4. As for the species that are already supersaturated in the feed (presented as phosphates, sulphates and carbonates), the arbitrary assumption was made that these compounds will already have precipitated somewhere, before entering the NF module. Consequently, concentrations of relevant elements (including Ca^{2+}, Mg^{2+}, and Ba^{2+}, and phosphate, sulphate and bicarbonate) were modified, by setting the saturation indices (SI) of those compounds to 0 and subtracting the amount of apparently precipitated ions from the NF feed flow (04). As a result, the feed solution used as input for PHREEQC simulations was in saturated but not in supersaturated state;

With the above 4 basic assumptions, a feed solution for the NF process, with an adjusted overall composition, was defined (see Annex A: NF feed solution as assumed for simulations).

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[3] Deliverable 2.2: Physiochemical composition of the water from Botlek area. This report was not completed at the time of writing of Deliverable 2.1: PHREEQC simulations.

For the flows 04, 06, 07, 08 and 10 (as indicated in Figure 1), the ion product (IP) of different minerals was calculated, as well as the SI (Saturation index), according to equation 1 below:

$$SI = \log(IP) + pKs \tag{eq. 01}$$

where pKs is the –log of the solubility product as provided by the PHREEQC database. When SI = 0 the solution is saturated. When SI < 0 saturation has not yet been reached, and when SI > 0, a supersaturated solution is observed, and salt is expected to precipitate until SI = 0 again. However, not always all minerals will immediately precipitate from a supersaturated solution, and very small (colloidal) particles may be present, without precipitation occurring. Thus, solutions with 0 < SI ≤ 0.1 are considered to be in a subsaturated state as well and not considered to produce precipitation.

The amount expected to precipitate and leave the system may be difficult to calculate as the possibility to separate solids depends on crystal size. Especially salts with a very low solubility may produce extremely small crystals (colloids) as nucleation speed depends stronger on the SI than the speed of crystal growth, favouring the formation of huge amounts of very small crystals already at a very small supersaturation. In order to obtain bigger and more handleable crystals often seeding is applied, in which small crystals are provided to the mother liquor.

In the simulations, variations of process operating conditions like reject and permeate flows, operating pH, and temperature were tested in order to optimise the process with regard to maximising Mg and Ca salt production and minimising secondary pollutant levels in the ion-exchange regenerant solution. Nanofiltration (NF) performance is an important parameter. In the first step, the spent IEX regenerant will be subject to nanofiltration, which tends to reject polyvalent ions and permit passage of monovalent ions. Thus the reject will be enriched in ions like Ca^{2+} and Mg^{2+}, whilst the permeate will be enriched in monovalent ions like Na^+ and K^+. To simulate the reject- and permeate flows of the NF unit, some assumptions were made:

1. The overall recovery of the NF process was assumed to be 70%, based on results from lab-scale experiments by Lenntech, the provider of the NF unit, and corresponding to the membrane foreseen to be used. This recovery corresponds to various salinity levels of the feed as well, regardless the impact of module configuration;
2. It was assumed that the NF membranes used are typical NF membranes meaning negatively charged in an aqueous environment. Therefore, and confirmed by ongoing laboratory tests with membranes likely to be used in the pilot setup, rejection of multivalent-anions was considered to be 80%, and rejection of multivalent cations slightly less, decreasing with feed concentration. The rejection of monovalent anions was then adjusted in order to maintain charge conservation and avoid a negatively charged permeate and a positively charged reject (seeTable 1).

Table 1: Assumptions regarding NF performance

	Sample 1		Sample 2	
Recovery	70%		70%	
anion rejection (monovalent / multivalent)	46%	80%	46%	80%
cation rejection (monovalent / multivalent)	30%	60%	30%	50%

Almost inevitably, the concentrate flow will contain combinations of ions that will exceed their solubility products. In practice, this may lead to scaling of the membrane, if the (unknown) residence time in the

membrane module is long enough. For the PHREEQC simulations, this problem was dealt with by considering precipitation of the species with the highest SI value (see Table 5). Location and effects of any eventual precipitation of salts in the NF unit however were disregarded as, within the scope of this project, these cannot be foreseen. The use of antiscalants to avoid precipitation and scaling was not considered as (i) the effect of these compounds on solubility products cannot be modelled adequately using PHREEQC, and (ii) the use of such compounds in a system with a closed loop water cycle will result in an undesirable accumulation of such compounds in the cycle; and should actually be avoided as much as possible.

Then the recovery of Magnesium and Calcium was calculated. These metals are expected to be recovered as their respective hydroxides. For this purpose:

1. In two separate process units (D and E in Figure 1 on page 5), sodium hydroxide is injected ("Required Chemical" in the scheme). As informed by UNIPA, the supplier of the crystallisation units, the amount of injected sodium hydroxide is calculated via a stoichiometric approach. That is, to precipitate 1 mol of Magnesium or Calcium, 2 moles of sodium hydroxide will be injected;
2. To quantify the amount of salts that can be recovered, a PHREEQC simulation is conducted in which the SI value of Brucite ($Mg(OH)_2$) or Portlandite (lime, $Ca(OH)_2$) is simply set to a value of 0.0.

As for the evaporator unit simulation, two scenarios were considered: first, only the NF permeate (stream 06) as the input to the evaporator unit; and second, a mix of NF permeate (stream 06) and crystallizer supernatant (stream 10) as the input. For both scenarios, the overall recovery of the evaporator unit was assumed to be 42%, i.e. 58% water remained as brine (stream 13). Based on this, ion concentrations can be recalculated and put into PHREEQC to estimate if there is a potential scaling problem. A preliminary estimation of these two types of feed will be conducted to check if some species were supersaturated. Otherwise, SI values of supersaturated species were set to 0.0 to ensure no specie exceed its solubility in the evaporator input.

A schematic illustration of the modelling approach can be seen in the flow chart on the next page (Figure 3):
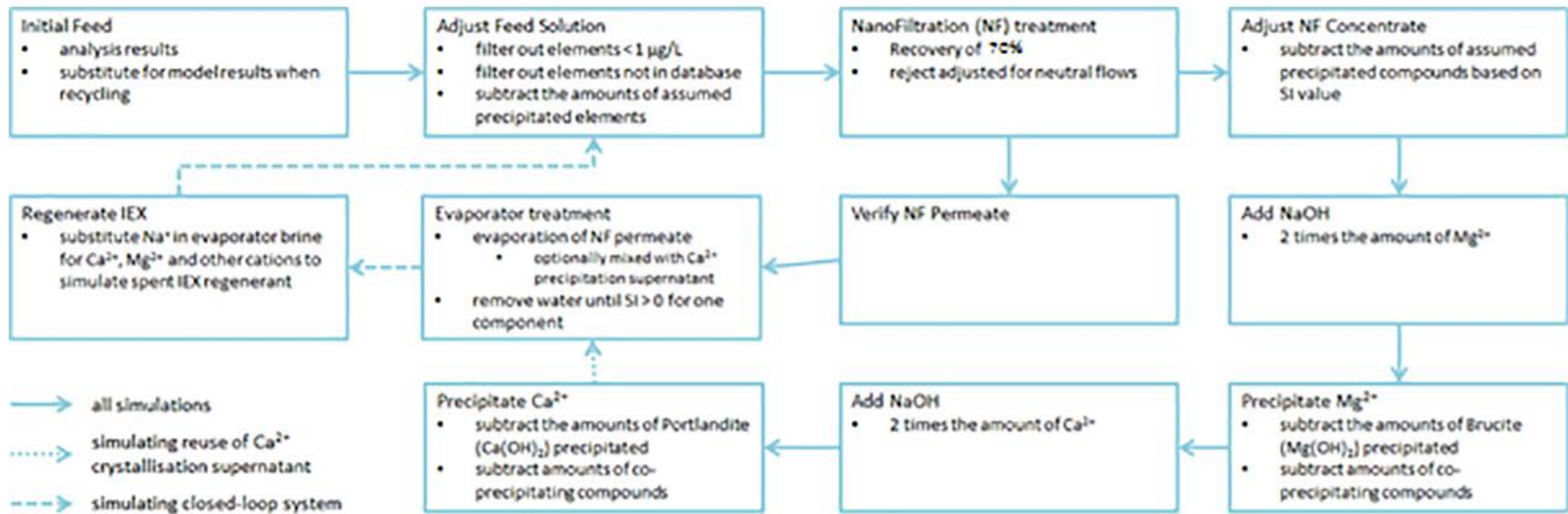
Figure 3: flowchart of the PHREEQC modelling approach

5. Results and discussions

Composition of analysed samples

Two series of measurements were obtained for spent IX regenerant (plant 1). The results are shown in Table 2. illustrates the main elements of the two samples. Sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}) ions are the major cations present in the samples of spent IX regenerant, with smaller amounts of potassium (K^+), and minor amounts (< 0.1%) of other metals, most notably, strontium (Sr^{2+}), iron (Fe^{3+}) and barium (Ba^{2+}) present as well.

Table 2: results of analysis of two samples of spent IEX regenerant. Concentrations in mM. To obtain concentrations in mg/L, multiply by molar weight (MW).

Cations		MW	Concentration[1,2] (mM)		Anions		MW	Concentration[1,2] (mM)	
		g/mol	sample 1	sample 2			g/mol	sample 1	sample 2
Calcium	Ca^{2+}	40.1	162.63	206.40	Chloride	Cl^-	35.5	528.99	808.78
Iron	Fe^{3+}	55.8	0.005 56	0.420	Fluoride	F^-	19.0	.< DL	.< DL
Magnesium	Mg^{2+}	24.3	51.28	55.15	Bromide	Br^-	79.9	.< DL	.< DL
Potassium	K^+	39.1	6.03	5.12	Nitrite	NO_2^-	46.0	.< DL	.< DL
Sodium	Na^+	23.0	99.96	349.49	Nitrate	NO_3^-	62.0	-.-	-.-
Aluminum	Al^{3+}	27.0	0.000 072	.< DL	Phosphate	PO_4^{3-}	95.0	0.02	0.30
Antimony	Sb^{5+}	121.8	0.000 004	0.000 081	Sulphate	SO_4^{2-}	96.1	1.55	34.10
Barium	Ba^{2+}	137.3	0.025 9	0.036 1	Silicate	SiO_4^{4-}	92.1	0.03	.< DL
Beryllium	Be^{2+}	9.0	.< DL	.< DL	Bicarbonate	HCO_3^-	61.0	2.34	2.29
Cadmium	Cd^{2+}	112.4	0.000 002	.< DL					
Cobalt	Co^{2+}	58.9	.< DL	0.000 469					
Copper	Cu^{2+}	63.5	0.000 53	.< DL					
Chromium	Cr^{3+}	52.0	0.000 27	0.001 59					
Lead	Pb^{2+}	207.2	.< DL	0.000 28					
Lithium	Li^+	6.9	0.017 1	0.020 2					
Manganese	Mn^{2+}	54.9	0.000 26	0.01					
Molybdenum	Mo^{4+}	95.9	0.000 015	0.000 14					
Nickel	Ni^{2+}	58.7	0.003 5	0.021 3					
Silver	Ag^+	107.9	.< DL	0.000 018					
Strontium	Sr^{2+}	87.6	0.342	0.478					
Titanium	Ti^{2+}	47.9	0.000 002	0.001 35					
Thallium	Tl^{3+}	208.4	.< DL	.< DL					
Vanadium	V^{5+}	50.9	0.001 7	0.016 7					
Zinc	Zn^{2+}	65.4	0.001 5	.< DL					
Total Dissolved Solids (TDS)[3]			**29 382**	**50 038**	mg/L		pH	7.26	7.10
			29 139	*46 176*	*mg/L*				

1: for simulations, all elements assumed to be present in the form of the ion most abundant in aerated surface water, as listed; 2: .< DL: below detection limit (generally < 1 µg/L), 3:TDS as **sum of all ions** (calculated) and *as measured*.

The concentration of Ca^{2+} is around 3.5 times the concentration of Mg^{2+}, with the ratio between Na^+ and the bivalent cations depending on the stage of the regeneration process. Chloride (Cl^-) is the most abundant anion (>96%), next to minor amounts of bicarbonate (HCO_3^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}). Trace amounts of elements like Arsenic (As^{5+}), boron (B^{3+}), manganese (Mn^{4+}), copper (Cu^{2+}), zinc (Zn^{2+}) and cadmium (Cd^{2+}) are

present in sample 1 while not in sample 2. Meanwhile, sample 2 contains around 100 times more iron (Fe^{3+}) and manganese (Mn^{2+}) then sample 1. As elements were measured using ICP-MS, their oxidation state in the samples is not confirmed. Given the origin of the raw water and the treatment processes involved, elements are assumed to be present in the oxidation state predominant in aerobic aqueous environments, as indicated.
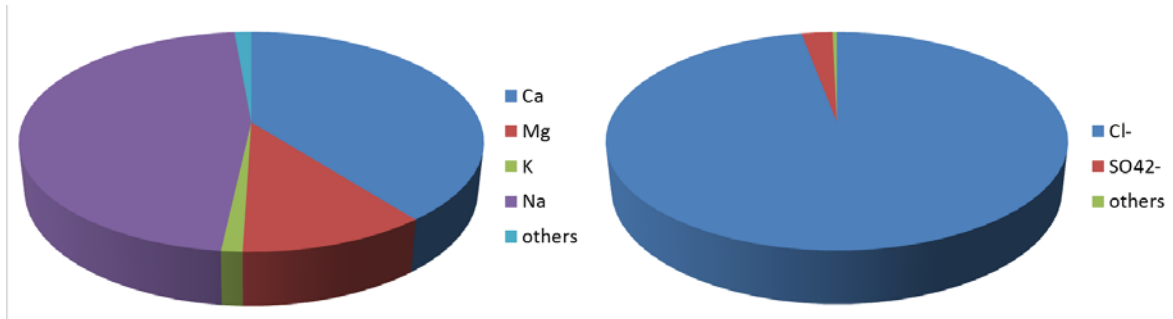

Figure 4: composition of spent IEX regenerant in terms of cations (left) and anions (right). Bivalent cations Ca^{2+} and Mg^{2+} are major constituents and may be recovered.

As discussed above, samples 1 and 2 differed significantly. However, without additional data, it is arbitrary to attribute the variations in concentrations of each element to seasonal effects, as operational conditions, for example the time of use of the ion-exchange resin and the amount of water used during the regeneration process may also lead to different compositions of spent regenerants. The fact that for both samples the calculated TDS concentration (sum of weights of identified anions and cations) is slightly higher than the measured (gravimetry) TDS concentration confirms that no or very little additional (organic) reagents (coagulants, flocculants, anti-scaling agents etc.) were present in the samples, as these would increase the measured TDS but not the calculated TDS.

After obtaining these results a problem was detected, as several combinations of ions (most notably involving Ca^{2+}, Ba^{2+}, CO_3^{2-} and SO_4^{2-}) result in solubility products being exceeded. Preliminary PHREEQC simulations showed that species that might precipitate in the NF module (SI > 0.1) are different between sample 1 and sample 2. Not all predicted precipitations however are relevant. In sample 2 for instance, magnetite (Fe_3O_4) exhibits the highest scaling potential (SI = 23.75) but at a concentration level < 1 $\mu g.L^{-1}$. When considering only species with precipitation potentials above 1 $\mu g.L^{-1}$ levels, 8 species remain, of which the SI values are generally below 2.00 (Table 3). In sample 1, in total 24 species are supersaturated, amongst which 5 species with SI values > 10. In this case again, Fe is the most sensitive element, due to its low solubility in the water matrix. In practice, only eight species are capable of precipitating more than 1 $\mu g.L^{-1}$, and only three species will actually precipitate from both samples More detailed information can be found in Table 3. As can be seen, only very small amounts of minerals (in general: sulphates or carbonates) are precipitated:

Table 3: Saturation Indexes (SI) of mineral species relevant for samples 1 and 2 (selection of SI > 0.1), and amounts precipitated (subtracted) to obtain a non-supersaturated NF feed solution.

No.	Mineral specie	Formula	Sample 1*		Sample 2*	
			SI	precipitated (mg/L)	SI	precipitated (mg/L)
1	Anhydrite	$CaSO_4$			0.61	0.026 6
2	Aragonite	$CaCO_3$	0.91		0.94	
3	Barite	$BaSO_4$	0.61	0.000 019 8	1.95	0.000 036 4
4	Calcite	$CaCO_3$	1.05	0.000 36	1.07	
5	Dolomite	$CaMg(CO_3)_2$	1.71		1.7	
6	Gypsum	$CaSO_4 \cdot 2H_2O$			0.56	
7	Hydroxyapatite	$Ca_5(PO_4)_3OH$	12.02	0.000 018 9	15.96	0.000 324
8	Magnesite	$MgCO_3$	0.16		0.13	

PHREEQC modelling results

i. NF concentrate composition

For each sample, based on the assumptions made regarding recovery and anion and cation reject, as well as the mass balance, the concentration of each element can be calculated for each stream (concentrate and permeate). A summary of concentrate quality of the two samples is shown in Table 4. Feed, permeate and concentrate composition for NF considering 70% recovery are presented in Annexes B.

Table 4: Composition of NF concentrates at 70% recovery

NF concentrate compositions (in mol/L)							
cations and anions present		Sample 1			Sample 2		
		mg/L	M	precipit. (M)	mg/L	M	precipit. (M)
Barium	Ba^{2+}	2.18	1.49E-05	1.02E-05	0.58	3.79E-06	
Calcium	Ca^{2+}	15 487	3.62E-01	3.20E-04	20 257	4.54E-01	2.38E-02
Cromium	Cr^{3+}	0.03	6.02E-07		0.23	4.03E-06	
Copper	Cu^{2+}	0.08	1.19E-06				
Iron	Fe^{3+}	0.74	1.24E-05		65.9	1.06E-03	
Potassium	K^+	442	1.06E-02		399	9.16E-03	
Lithium	Li^+	0.22	3.01E-05		0.28	3.60E-05	
Magnesium	Mg^{2+}	2 958	1.14E-01		3 761	1.39E-01	
Manganese	Mn^{2+}				1.54	2.52E-05	
Sodium	Na^+	4 295	1.75E-01		16 022	6.26E-01	
Nickel	Ni^{2+}	0.49	7.80E-06		3.52	5.38E-05	
Lead	Pb^{2+}				0.16	6.96E-07	
Strontium	Sr^{2+}	71.4	7.63E-04		118	1.21E-03	
Tellurium	Tl^{2+}				0.81	3.48E-06	
Vanadium	V^{5+}	0.21	3.81E-06		2.39	4.22E-05	
Zinc	Zn^{2+}	0.24	3.42E-06				
Bicarbonate	HCO_3^-	215	3.30E-03	3.23E-04	340	5.00E-03	
Chloride	Cl^-	43 580	1.15E+00		69 559	1.76E+00	
Sulphate	SO_4^{2-}	464	4.53E-03	1.02E-05	2 832	2.65E-02	2.38E-02
Phosphate	PO_4^{3-}	0.04	3.76E-07	1.44E-07	0.71	6.74E-06	6.69E-06

As a result of concentrating the ions present in the concentrate flow, for some species the solubility product might be exceeded, resulting in a supersaturated solution, subject to precipitation. It can be seen that some 5%

of calcium would precipitate as a result of the presence of sulphate in sample 2. A consequence might be scaling of process equipment. The value of the saturation index (SI, eq. 1) indicates if this might be the case. However, the effect is only relevant if not only the SI exceeds a minimum value, but also the amount of material available for precipitation is significant. Some ions are present in such low concentrations that the amount that might precipitate would be only in the order of micrograms per litre. Species that both have a saturation index SI > 0.1 and a concentration level of $mg.L^{-1}$ (rather than µg.L-1) are listed in Table 5.

As can be seen, when fed with sample 1, four species will become supersaturated in the NF concentrate stream, with hydroxyapatite being the most saturated (SI = 2.94). For sample 2, the number of supersaturated species is 5, with again hydroxyapatite being the most supersaturated compound, with SI = 10.53. As the amount of hydroxyapatite precipitating is small though, the most serious scaling might actually occur by precipitation of aragonite in sample 1 or anhydrite in sample 2, the latter as a result of the higher sulphate concentration in that sample. This means the NF process may experience more severe calcium scaling when fed with sample 2. Given the fact that most of the potentially supersaturated species contain calcium (Ca^{2+}) and magnesium (Mg^{2+}), this also means a potential loss of target mass, and lower recovery of the target compounds in the subsequent crystallization processes.

Table 5: Scaling potential of NF concentrate, considering operating conditions as defined in Table 1. Main risk of scaling, depending on anion concentrations in the sample.

Species		Sample 1		Sample 2	
name	formula	SI	Precip. (M)	SI	Precip. (M)
Anhydrite	$CaSO_4$			0.72	2.38E-02
Aragonite	$CaCO_3$	0.51	3.20E-04		
Barite	$BaSO_4$	1.05	1.02E-05	0.45	
Calcite	$CaCO_3$	0.65			
Dolomite	$CaMg(CO_3)_2$	0.94			
Gypsum	$CaSO_4 \cdot 2H_2O$			0.65	
Hydroxyapatite	$Ca_5(PO_4)_3OH$	10.53	1.44E-07	2.94	6.69E-06
Magnesite	$MgCO_3$				

ii. Salt recovery

Table 6 presents the amounts of brucite and portlandite that are supposed to be recovered and their respective purities. The overall recovery of calcium and magnesium for each litre of spent IEX regenerant fed to the NF is listed in Table 7. Results for both samples are consistent, both suggest that more than 50% of the amount of target salts can be recovered, and with high quality, especially for calcium with more than 97% purity for both samples. Some low-solubility species (listed in Table 8) may be co-precipitated, especially in the first crystallizer (D), intended for magnesium recovery, resulting in a slightly lower purity of magnesium. This is possible when the solubility index of such a compound has a value of SI > 0. Still Mg^{2+} will be of 96.4% purity even in the worst case (sample 2), with $Ca(OH)_2$ and $CaCO_3$ the major pollutants (1.8% each of the precipitate in moles). In the second crystalliser, the situation is inverted: now $Ca(OH)_2$ is the predominant material, and $Mg(OH)_2$ is the main impurity, but in this case the best quality product is obtained from sample 2 (99.1% purity) and a lesser quality

product obtained from sample 1 (97.4% purity, with $Mg(OH)_2$ being the main pollutant). More detailed information can be found in Table 7.

Table 6: Amount of recovered salts (g/L) of NF feed in crystallisers D (Mg-crystalliser) and E (Ca-crystalliser)

		Mg-crystalliser (D)		Ca-crystalliser (E)	
	Species	Sample 1	Sample 2	Sample 1	Sample 2
Barite	$BaSO_4$	0.000 20			
Brucite	$Mg(OH)_2$	6.52	8.75	0.54	0.23
Calcite	$CaCO_3$	0.32	0.56		
Hydroxyapatite	$Ca_5(PO_4)_3OH$	0.000 04	0.000 14		
Portlandite	$Ca(OH)_2$			25.80	32.91
Purity (mass fraction)		95%	94%	98%	99%

Table 7: Recovery of Mg and Ca as their hydroxides and as other salts

	Sample 1		Sample 2	
Recovered ions	Mg-crystalliser	Ca-crystalliser	Mg-crystalliser	Ca-crystalliser
Mg^{2+} as $Mg(OH)_2$	60.0%	4.98%	70.2%	1.82%
Mg^{2+}, as other minerals				
Ca^{2+} as $Ca(OH)_2$		58.6%		63.4%
Ca^{2+}, as other minerals	0.54%		0.79%	

Table 8: Saturation Indices (SI) of minerals during salt recovery steps (omitted when SI < 0)

		Saturation Index (SI) values			
	Species	Mg Recovery		Ca Recovery	
		Sample 1	Sample 2	Sample 1	Sample 2
Aragonite	$CaCO_3$	2.75	3.03		
Artinite	$MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$	6.88	7.21	2.3	1.31
Barite	$BaSO_4$	0.11			
Brucite	$Mg(OH)_2$	6.1	6.21	6.11	5.79
Calcite	$CaCO_3$	2.89	3.17		
Dolomite	$CaMg(CO_3)_2$	4.99	5.54		
Huntite	$CaMg_3(CO_3)_4$	5.12	6.18		
Hydromagnesite	$Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$	5.97	7.07		
Hydroxyapatite	$Ca_5(PO_4)_3OH$	14.58	16.37	2.62	2.25
Magnesite	$MgCO_3$	1.61	1.87		
Periclase	MgO	1.45	1.58	1.47	1.16
Portlandite	$Ca(OH)_2$	1.1	1.24	2.6	2.77

The effect of running the process under conditions of different temperature and pH were not calculated as not deemed very relevant. As can be seen in Figure 1, solubilities of key precipitates brucite and portlandite hardly vary in a range of temperatures of 10-35 °C (and lower temperatures negatively affect membrane filtration, where higher temperatures incur costs of heating large volumes of dilute solutions), making it likely that the process will be run at available water temperature. The effect of altering the pH was not studied as adding any additional amount of base will increase precipitation of species increasing impurities in the product, whereas dosing less hydroxide, or adding acid to decrease the amount of hydroxide ions will reduce the amount of

minerals precipitated. Hydroxide dosing in the crystallisation reactors will need to be done stoichiometrically considering the amounts of cations to be precipitated rather than aiming at a specific pH.

iii.   Evaporator

To close the water cycle, an evaporation step is foreseen, which produces distilled (pure) water and a brine (containing predominantly sodium chloride, NaCl). This evaporation step, as mentioned before, can be fed in two ways: besides receiving only the NF permeate, a mix of NF permeate and the crystallizer effluent can also be defined as the input to the evaporator. A summary of the composition of the two mixed feeds is listed in Table 9:

Table 9: Composition of mixed solution as feed to evaporator

		NF Perm. + Crys. Eff		NF Perm.	
		Sample 1	Sample 2	Sample 1	Sample 2
pH		12.15	12.16	6.37	
Cations [mol/L]					
Barium	Ba^{2+}	4.42E-06	3.15E-06	3.50E-06	6.49E-07
Calcium	Ca^{2+}	5.04E-02	4.52E-02	8.79E-02	7.76E-02
Chromium	Cr^{3+}	4.93E-07	3.35E-06	1.45E-07	6.90E-07
Copper	Cu^{2+}	9.76E-07		2.89E-07	1.82E-04
Iron	Fe^{3+}	1.02E-05	8.80E-04	3.01E-06	3.87E-03
Potassium	K^+	9.29E-03	8.30E-03	4.57E-03	1.52E-05
Lithium	Li^+	2.64E-05	3.26E-05	1.30E-05	2.38E-02
Magnesium	Mg^{2+}	8.30E-03	7.15E-03	2.77E-02	4.31E-06
Sodium	Na^+	8.50E-01	1.45E+00	7.57E-02	2.65E-01
Nickel	Ni^{2+}	6.40E-06	4.47E-05	1.89E-06	9.20E-06
Strontium	Sr^{2+}	6.26E-04	1.00E-03	1.85E-04	1.19E-07
Vanadium	V^{5+}	3.12E-06	3.51E-05	9.24E-07	2.06E-04
Zinc	Zn^{2+}	2.80E-06		8.29E-07	5.96E-07
Manganese	Mn^{2+}		2.09E-05		4.20E-06
Lead	Pb^{2+}		5.78E-07		1.16E-07
Tellurium	Tl^{2+}		2.89E-06		5.80E-07
Anions [mol/L]					
Bicarbonate	HCO_3^-	2.68E-04	4.03E-04	8.84E-04	1.34E-03
Chloride	Cl^-	9.54E-01	1.51E+00	3.15E-01	4.72E-01
Sulphate	SO_4^{2-}	3.48E-03	4.54E-03	3.32E-04	1.90E-03
Phosphate	PO_4^{3-}	8.20E-09	1.45E-07	2.73E-08	4.83E-07

Since 42% of the water will be evaporated, a concentrated solution will be obtained. Table 10 presents an estimation of the composition of this concentrated solution, for both situations: feeding the evaporator only with the NF permeate, or feeding the evaporator with a mix of NF permeate and crystallization supernatant. For both samples, sodium and chloride are the dominant cation and anion respectively. Ca is the second most abundant cation in the product, with 3% (sample 2) or 6% (sample 1) of the total cation concentration. When using only the NF permeate as feed, these percentages become even higher. Thus, alternatives for reusing this brine for IEX regeneration have to be studied. When it comes to the foreseeable scaling in the evaporator, if NF permeate was the only influent no scaling will be detected for either sample. However, when using the mixed feed, the situation is different. Some species will become supersaturated in the evaporator (see Table 11), and scaling might occur. Moreover, calcium contributes to a large extent to the possible scaling problem in the evaporator unit.

Table 10: Solution composition after evaporation

		NF Perm. + Crys. Eff		NF Perm.	
		Sample 1	Sample 2	Sample 1	Sample 2
pH		12.07	12.12		
Cations [mol/L]					
Sodium	Na	1.47E+00	2.50E+00	4.57E-01	1.31E-01
Calcium	Ca	8.64E-02	7.72E-02	1.34E-01	1.52E-01
Potassium	K	1.60E-02	1.43E-02	6.68E-03	7.88E-03
Strontium	Sr	1.08E-03	1.73E-03	3.56E-04	3.19E-04
Iron	Fe	1.75E-05	1.52E-03	3.13E-04	5.19E-06
Nickle	Ni	1.10E-05	7.71E-05	1.59E-05	3.26E-06
Vanadium	V	5.39E-06	6.05E-05	1.25E-05	1.59E-06
Lithium	Li	4.55E-05	5.63E-05	2.62E-05	2.25E-05
Manganese	Mn		3.61E-05	7.44E-06	
Chromium	Cr	8.51E-07	5.77E-06	1.19E-06	2.51E-07
Barium	Ba	4.82E-06	5.43E-06	1.12E-06	6.03E-06
Tellurium	Tl		4.99E-06	1.03E-06	
Lead	Pb		9.97E-07	2.05E-07	
Magnesium	Mg	8.73E-07	6.70E-07	4.11E-02	4.77E-02
Copper	Cu	1.68E-06			4.98E-07
Zinc	Zn	4.84E-06			1.43E-06
Anions [mol/L]					
Bicarbonate	HCO_3^-	1.65E+00	2.61E+00	4.77E-02	1.52E-03
Sulphate	SO_4^{2-}	5.99E-03	7.85E-03	3.28E-03	5.72E-04
Chloride	Cl^-	1.61E-05	2.24E-05	8.15E-01	5.44E-01
Phosphate	PO_4^{3-}	2.63E-11	2.67E-11	8.32E-07	4.70E-08

Table 11: Amount of species possibly precipitating during evaporation (mol/L)

	Species	NF Perm. + Crys. Eff		NF Perm.	
		Sample 1	Sample 2	Sample 1	Sample 2
Barite	$BaSO_4$	8.65E-07	1.05E-06	-	-
Brucite	$Mg(OH)_2$	2.58E-07	3.39E-07	-	-
Calcite	$CaCO_3$	6.53E-06	4.51E-06	-	-
Hydroxyapatite	$Ca_5(PO_4)_3OH$	3.46E-12	3.27E-12	-	-

6. Conclusions

Magnesium and calcium may be separated with great efficiency from spent IEX regenerant, however complete (> 99%) recovery of these materials is not possible. Especially in the case of calcium, a small part of the material might end up as scaling before reaching the crystallisation step.

Even though selective precipitation of $Mg(OH)_2$ and $Ca(OH)_2$ is possible theoretically, under the actual conditions, it is almost impossible to produce the hydroxides in pure form. That is because together with the hydroxides, also carbonates, sulphates and other minerals may co-precipitate, depending on the anions present. The presence of these impurities varies as different concentration of anions were found in the different samples. Still, the salts contain Mg and Ca with at least 97% purity in all cases studied.

The amount of hydroxides recovered is directly dependent of the amount of hydroxide dosed, as metal hydroxides are the main minerals precipitated, and the amount of material precipitated is limited by the amount of hydroxide ion present. Thus, dosing of hydroxide should be well controlled as, especially in the first crystallization reactor, excess NaOH dosed might cause $Ca(OH)_2$ to precipitate prematurely. Control of hydroxide dosing for Mg^{2+} and Ca^{2+} precipitation can probably be based on supernatant pH, as in the case of correct stoichiometric dosing, this pH will be around 9.7 and around 12.5 after Mg^{2+} and Ca^{2+} precipitation, respectively, for both samples, practically independent on initial metal ion concentration.

No scaling problem will occur at the evaporator unit if only NF permeate is fed, and the quality with respect to the abundance of sodium and chlorine ions is higher than compared to the situation that a mixture of the NF permeate and the crystallizer effluent is fed to the evaporator. However, one drawback of feeding a mixture is a possible calcium scaling at the evaporator unit. Another drawback of feeding the mixture is that the salts produced by the evaporator cannot be used for regeneration of IEX columns anymore because the impurities present will cause a faster exhausting of the IEX column. This will result in a more frequent regeneration of the IEX column, more frequent replacement of resin and consequently higher operational costs. In the authors' view and based on the calculations done in this document, it is essential to study the effluent of the crystallizer carefully and consider other possible options before deciding on mixing it with NF permeate as the feed for evaporator.

In spite of the great detail of the modelling results, the exact effect of closing the water cycle in the process can't yet be calculated. In the first place because a large variation between samples (process cycle input) was observed, and in the second place because the exact process conditions and process regulation is not yet defined. However, even with the actual, limited results, it can be foreseen that adjustments may be necessary, as in the scheme as suggested no bleed is present. This means that all ions present in the feed but not removed as product, like for instance Ni^{2+}, Zn^{2+}, Sr^{2+} and nitrate, to name a few, will over time accumulate in the regeneration cycle, causing deterioration of the process and product specifications in the long run. Bleeding however may be as simple as releasing part of the mother liquor of Ca-precipitation; or releasing part of the NF permeate. This can be calculated once process conditions are better defined, and once additional measurements of the process feed give a better indication of what will enter the process cycle.

7. Bibliography

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Annexes

Annex A: NF feed solution as assumed for simulations

As explained in the Composition of analysed samples part of the Results and discussions section, the composition of the feed solution for the NF process as used for modelling the process differed slightly from the average composition of the spent IEX regenerant as obtained from sample analyses. Below the NF feed solution as used for modelling purposes:

cations and anions present		Adjusted Feed brine	
		sample 1	sample 2
		[mmol.L^{-1}]	[mmol.L^{-1}]
Barium	Ba^{2+}	1.58E-03	6.86E-03
Calcium	Ca^{2+}	1.89E+02	1.67E+02
Chromium	Cr^{3+}	1.68E-03	2.78E-04
Copper	Cu^{2+}	0	5.51E-04
Iron	Fe^{3+}	4.42E-01	5.74E-03
Potassium	K^+	5.39E+00	6.22E+00
Lithium	Li^+	2.12E-02	1.77E-02
Magnesium	Mg^{2+}	5.80E+01	5.28E+01
Manganese	Mn^{2+}	1.05E-02	0
Sodium	$Na+$	3.68E+02	1.03E+02
Nickel	Ni^{2+}	2.24E-02	3.60E-03
Lead	Pb^{2+}	2.90E-04	0
Strontium	Sr^{2+}	5.03E-01	3.52E-01
Tellurium	Tl^{2+}	1.45E-03	0
Vanadium	V^{5+}	1.76E-02	1.76E-03
Zinc	Zn^{2+}	0	1.58E-03
Alkalinity	HCO_3^-	2.41E+00	1.59E+00
Chloride	Cl^-	8.51E+02	5.57E+02
Sulphate	SO_4^{2-}	9.26E+00	1.58E+00
Phosphate	PO_4^{3-}	2.35E-03	1.31E-04
pH		5.71	6.38

Annex B: NF feed, permeate and reject for 70% recovery

cations and anions present		Flow compositions (in mol/L)					
		Sample 1			Sample 2		
		feed	reject	permeate	feed	reject	permeate
Barium	Ba^{2+}	1.58E-06	3.79E-06	6.32E-07	6.86E-06	1.49E-05	3.43E-06
Calcium	Ca^{2+}	1.89E-01	4.54E-01	7.56E-02	1.67E-01	3.62E-01	8.35E-02
Chromium	Cr^{3+}	1.68E-06	4.03E-06	6.72E-07	2.78E-07	6.02E-07	1.39E-07
Copper	Cu^{2+}				5.51E-07	1.19E-06	2.76E-07
Iron	Fe^{3+}	4.42E-04	1.06E-03	1.77E-04	5.74E-06	1.24E-05	2.87E-06
Potassium	K^{+}	5.39E-03	9.16E-03	3.77E-03	6.22E-03	1.06E-02	4.35E-03
Lithium	Li^{+}	2.12E-05	3.60E-05	1.48E-05	1.77E-05	3.01E-05	1.24E-05
Magnesium	Mg^{2+}	5.80E-02	1.39E-01	2.32E-02	5.28E-02	1.14E-01	2.64E-02
Manganese	Mn^{2+}	1.05E-05	2.52E-05	4.20E-06			
Sodium	Na^{+}	3.68E-01	6.26E-01	2.58E-01	1.03E-01	1.75E-01	7.21E-02
Nickel	Ni^{2+}	2.24E-05	5.38E-05	8.96E-06	3.60E-06	7.80E-06	1.80E-06
Lead	Pb^{2+}	2.90E-07	6.96E-07	1.16E-07			
Strontium	Sr^{2+}	5.03E-04	1.21E-03	2.01E-04	3.52E-04	7.63E-04	1.76E-04
Tellurium	Tl^{2+}	1.45E-06	3.48E-06	5.80E-07			
Vanadium	V^{5+}	1.76E-05	4.22E-05	7.04E-06	1.76E-06	3.81E-06	8.80E-07
Zinc	Zn^{2+}				1.58E-06	3.42E-06	7.90E-07
Bicarbonate	HCO_3^{-}	2.41E-03	5.00E-03	1.30E-03	1.59E-03	3.30E-03	8.59E-04
Chloride	Cl^{-}	8.51E-01	1.76E+00	4.60E-01	5.57E-01	1.15E+00	3.01E-01
Sulphate	SO_4^{2-}	9.26E-03	2.65E-02	1.85E-03	1.58E-03	4.53E-03	3.16E-04
Phosphate	PO_4^{3-}	2.35E-06	6.74E-06	4.70E-07	1.31E-07	3.76E-07	2.62E-08
pH		5.71	5.71		6.38	6.37	

X = number of the brine: Brine 1: Sim 1.1, Sim 1.2, etc.
Brine 2: Sim 1.2, Sim 1.3, etc.

Composition of NF Permeate and NF Concentrate is based on Excel calculations, including recovery, ion rejection, charge and mass balances