Membrane electrolysis for selective lithium carbonate recovery from brines with concomitant freshwater production

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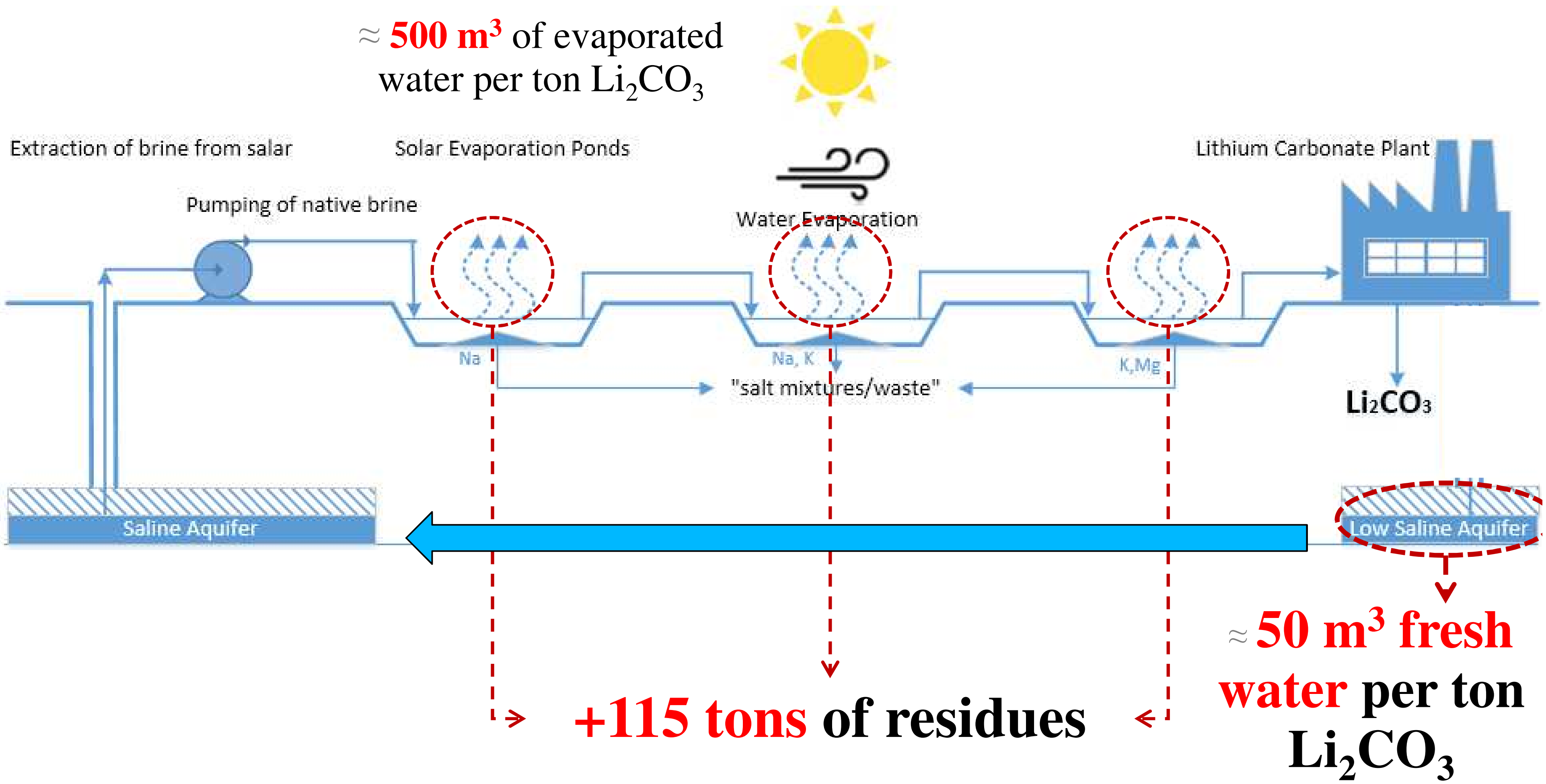
Green Batteries Conference 2021

Current methodology for lithium recovery: evaporitic technology

Potential environmental impact + slow and inefficient

+ maladapted to other lithium sources (e.g. European Brines)

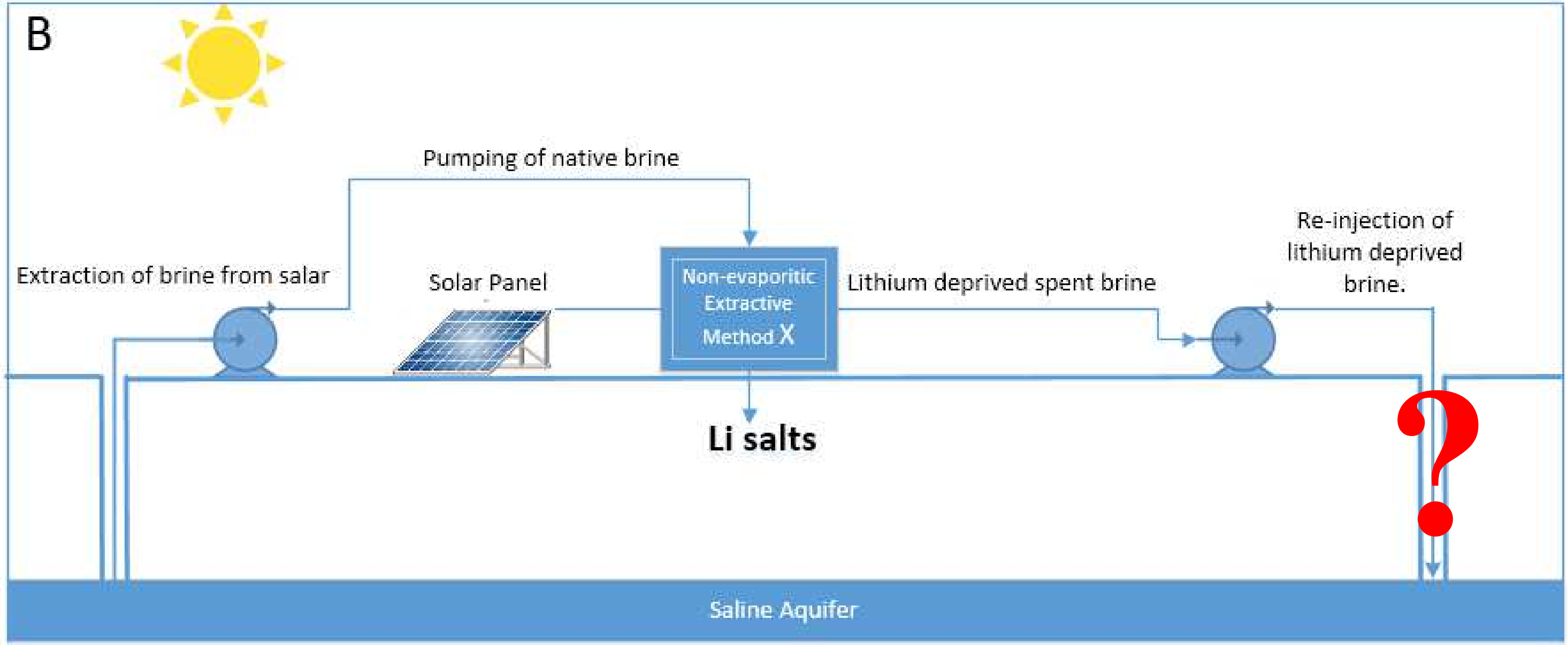


Flexer *et al.*, **Science of the Total Environment**, **2018**, 639, 1188

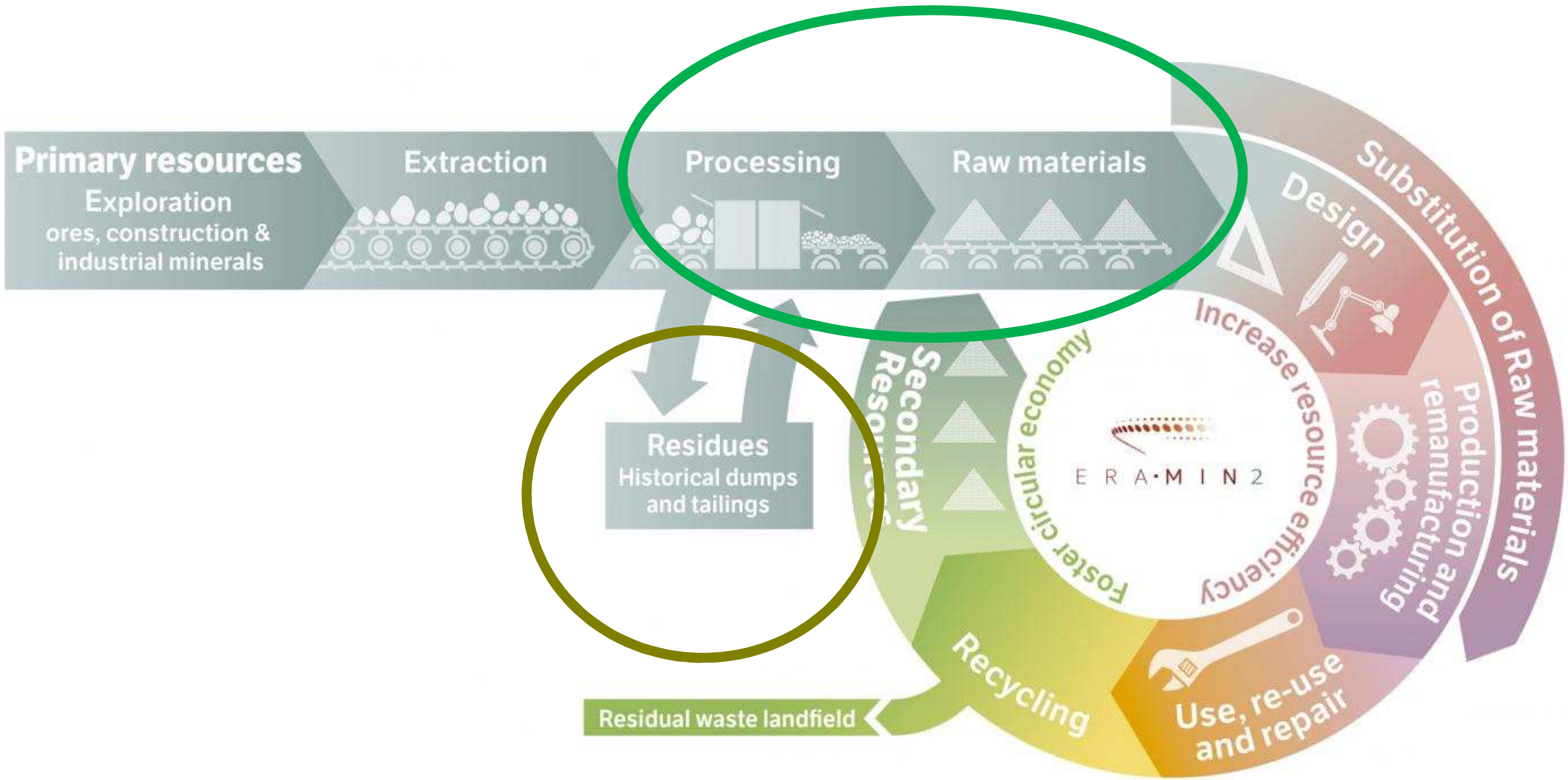
We all agree that we need a disruptive technology.

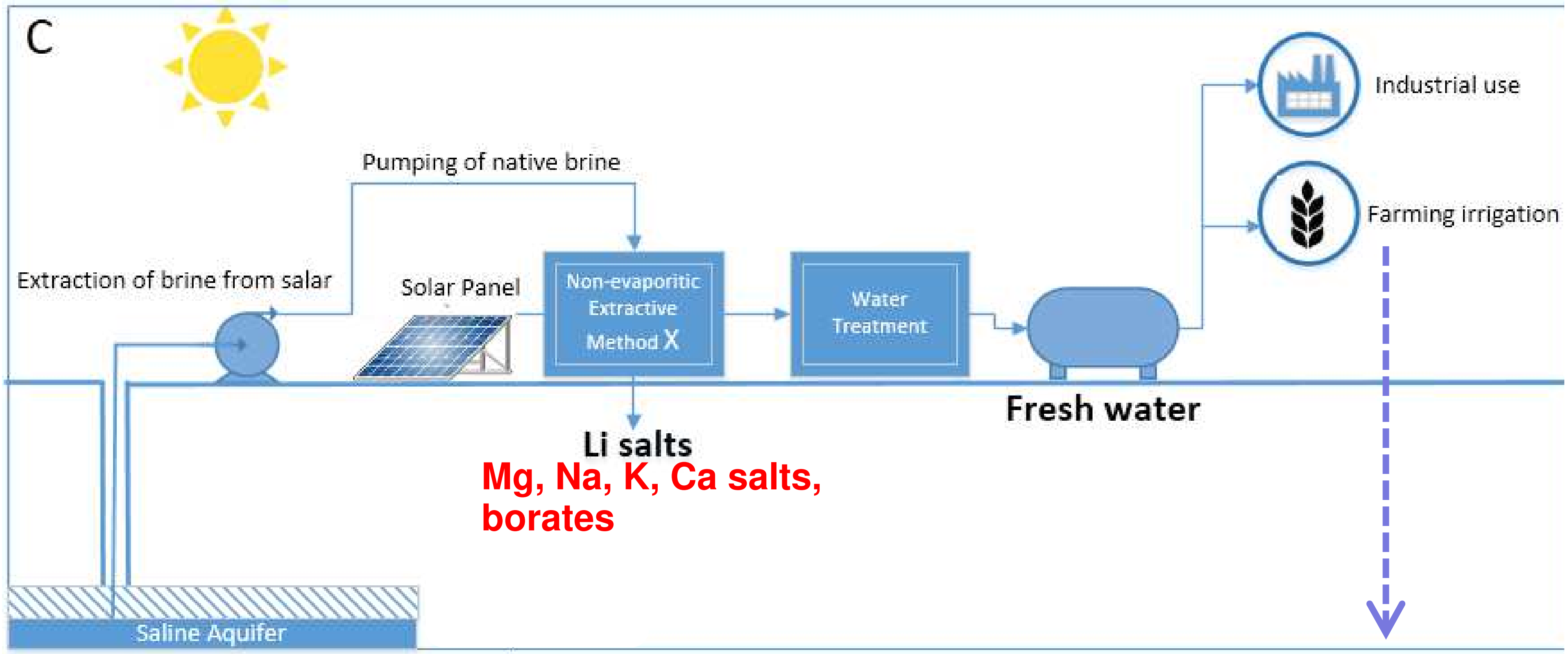
Which is the motivation behind our work in Jujuy, Argentina?

(Most) disruptive technologies



1- What happens with *spent brines* after successful lithium recovery?


Primary resources
Exploration
ores, construction &
industrial minerals
Extraction
Processing
Raw materials
Design
Substitution of Raw materials
Increase resource efficiency
Production and remanufacturing
Foster circular economy
ERA-MIN 2
Secondary Resources
Residues
Historical dumps
and tailings
Recycling
Use, re-use
and repair
Residual waste landfield



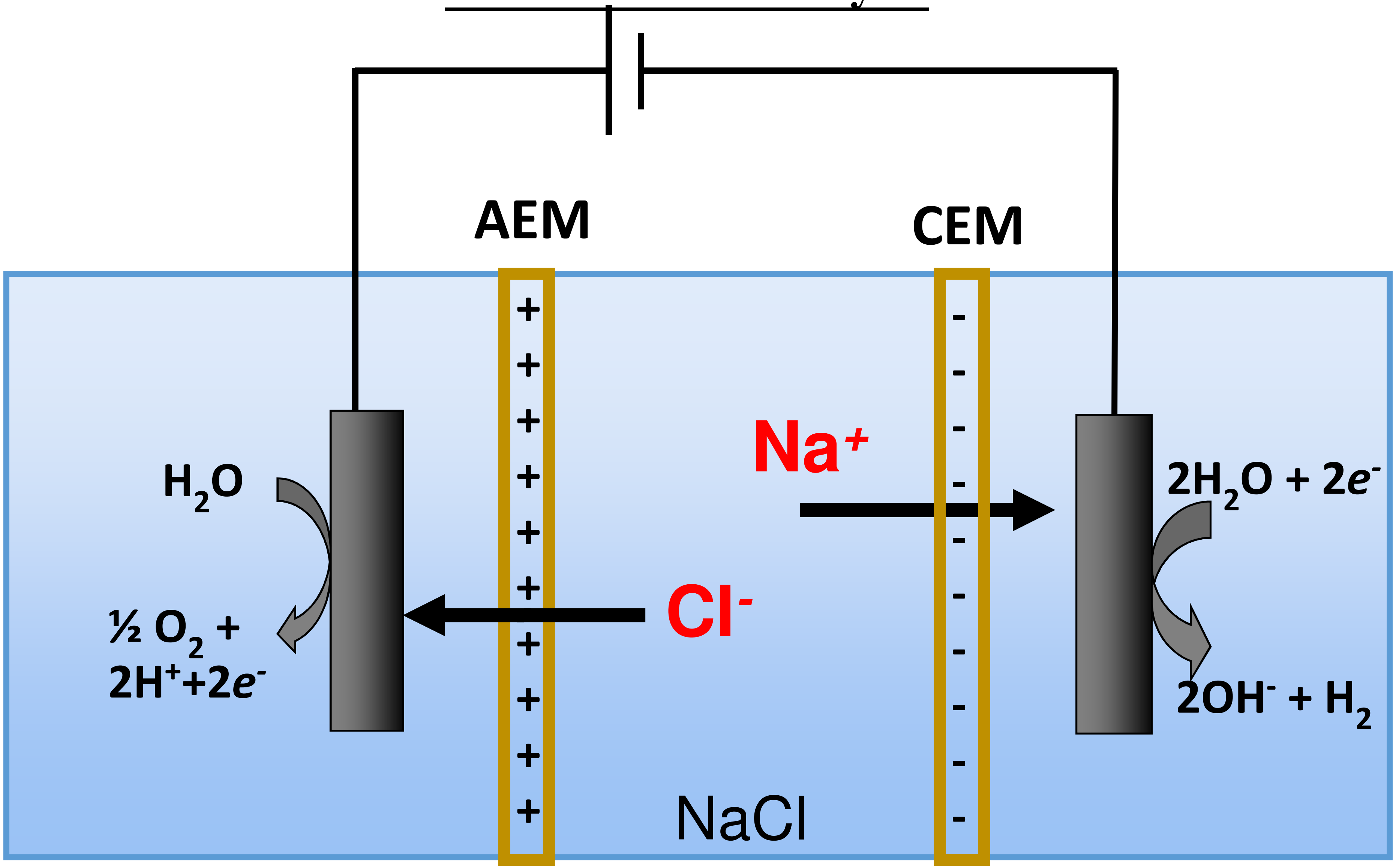
2- We look at the brine as a source of several by-products, and a potential source of *fresh water*

Non-evaporitic system

Lithium recovery by membrane electrolysis

3 membrane electrolysis reactors to recover Li_2CO_3
concomitantly with other industrial minerals and fresh water

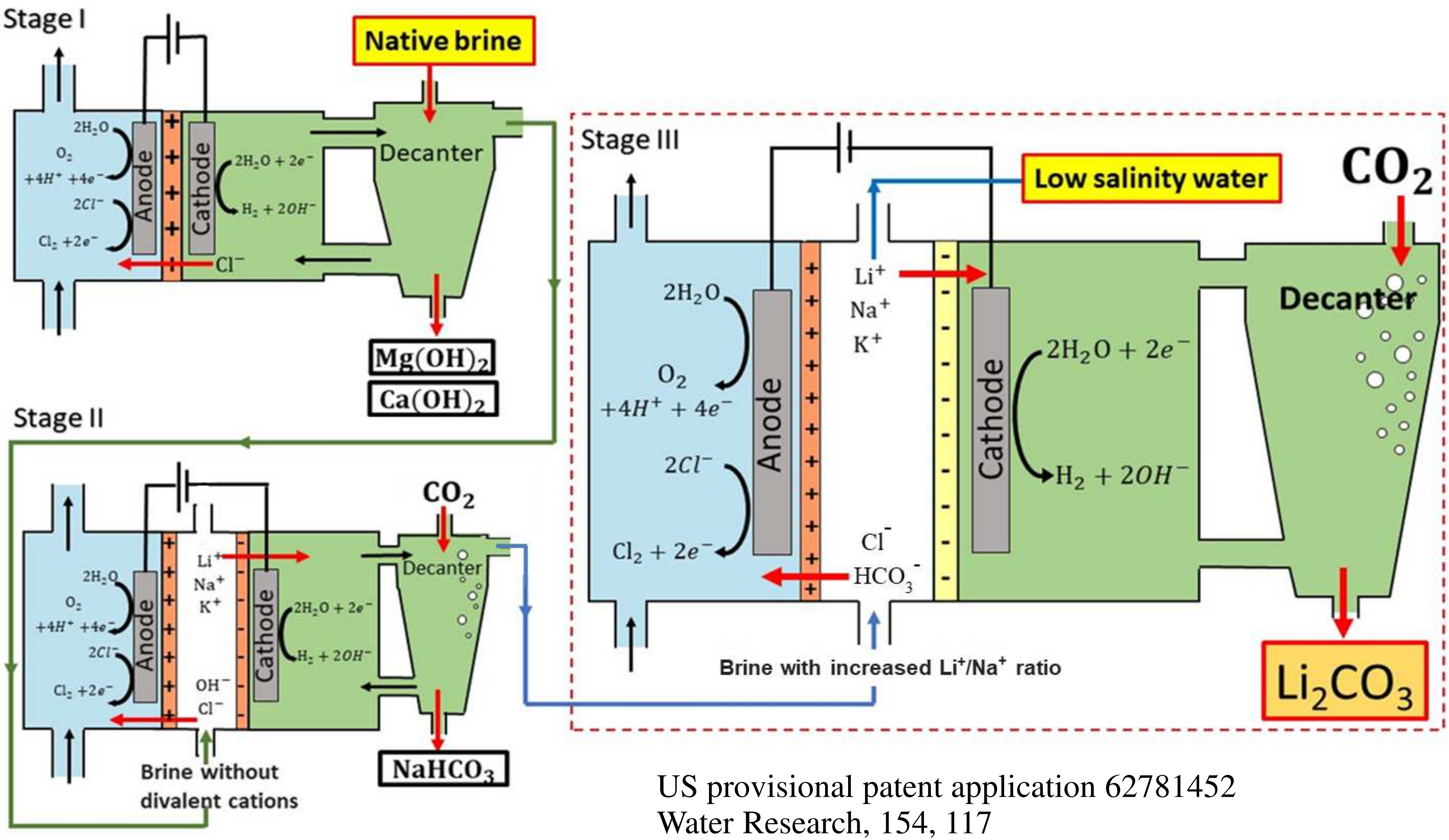
Membrane electrolysis



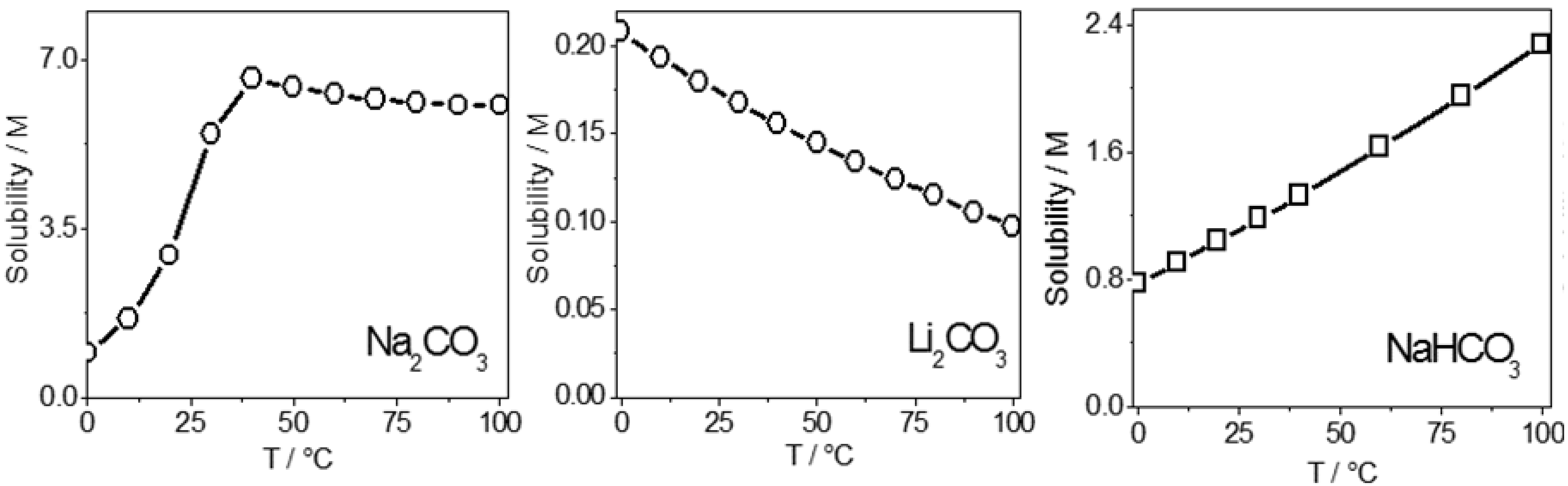
AEM: **anion** exchange membrane

CEM: **cation** exchange membrane

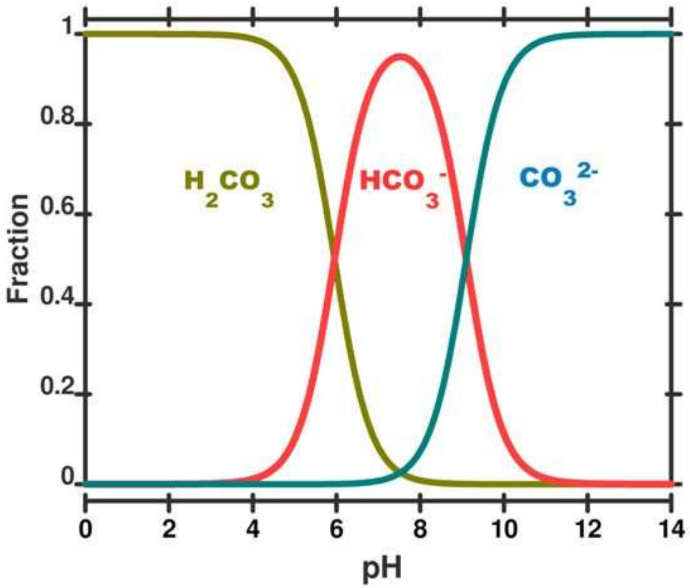
Our system



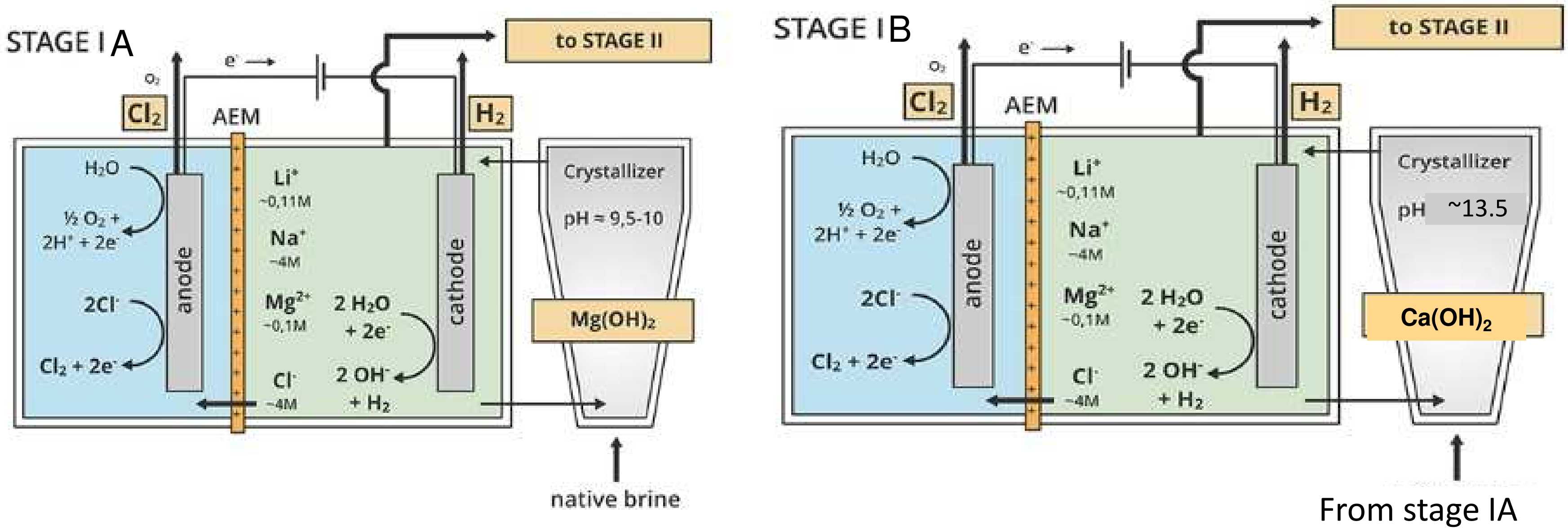
US provisional patent application 62781452
Water Research, 154, 117
Separation and Purification Technology, 252, 117410
Journal of Membrane Science, 615,118416
Work in collaboration with K. Rabaey (Ghent University), and T. Rydberg (IVL). ERA-MIN2 call, **Li+WATER** project



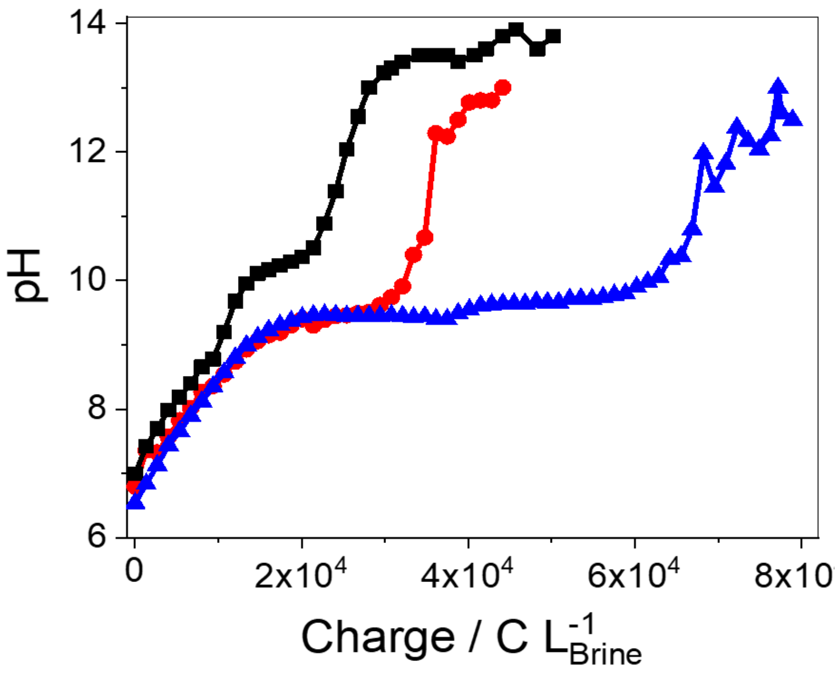
All experiments with different native brines

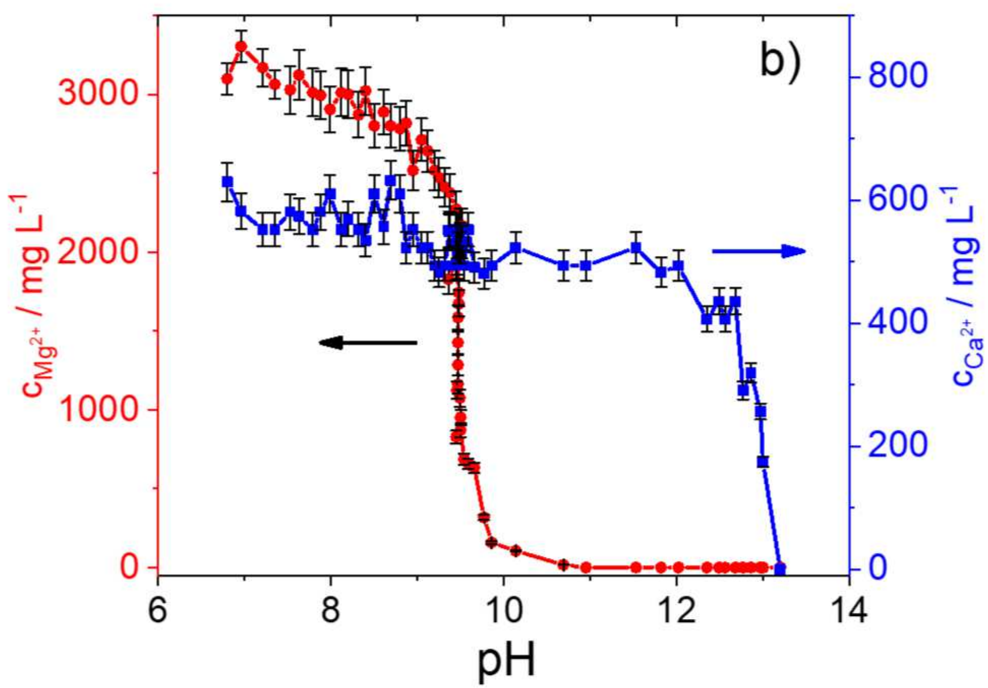


First stage: Mg^{2+} / Ca^{2+}



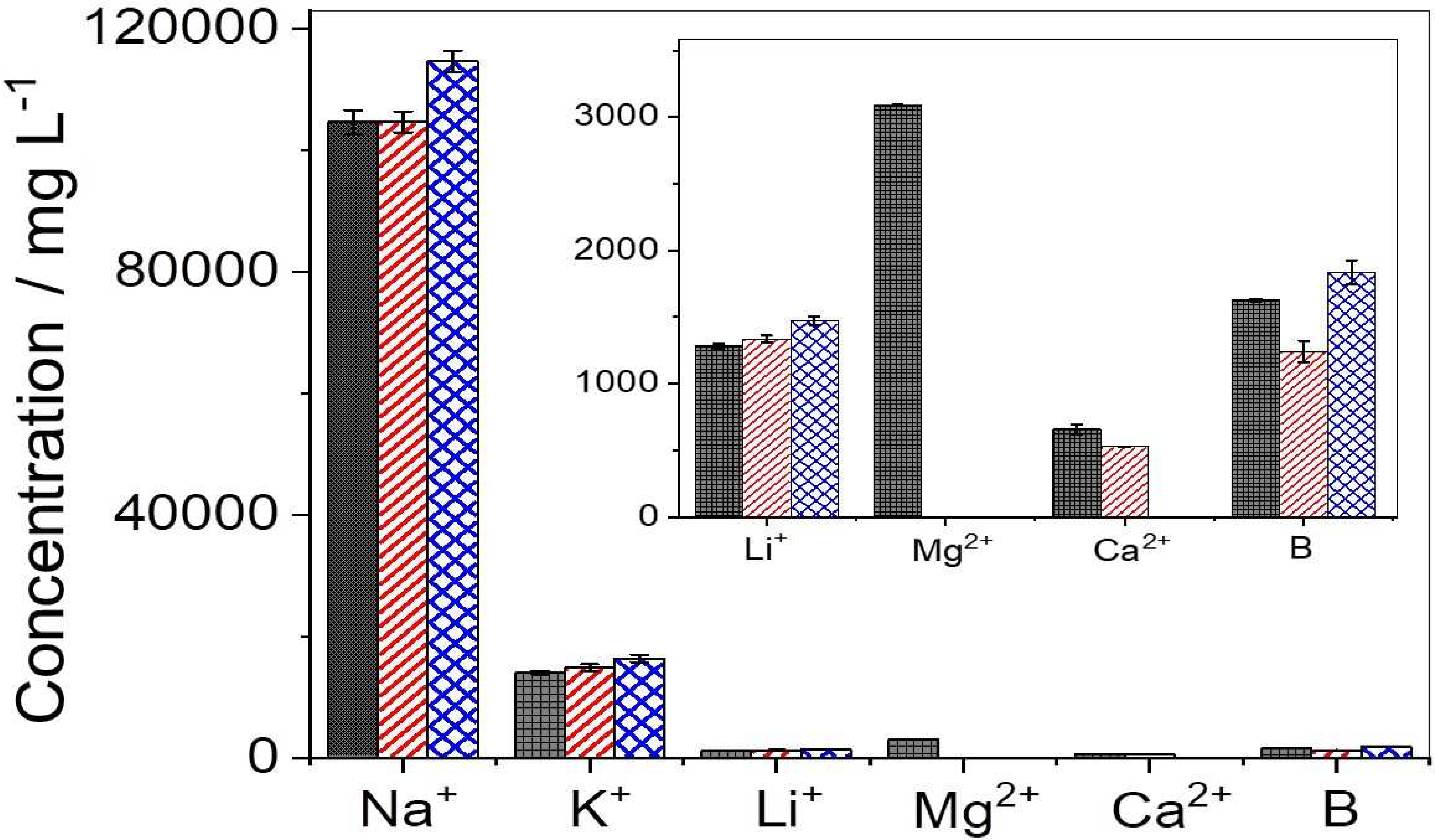
First stage: Mg^{2+} / Ca^{2+} Evolution of pH and concentrations





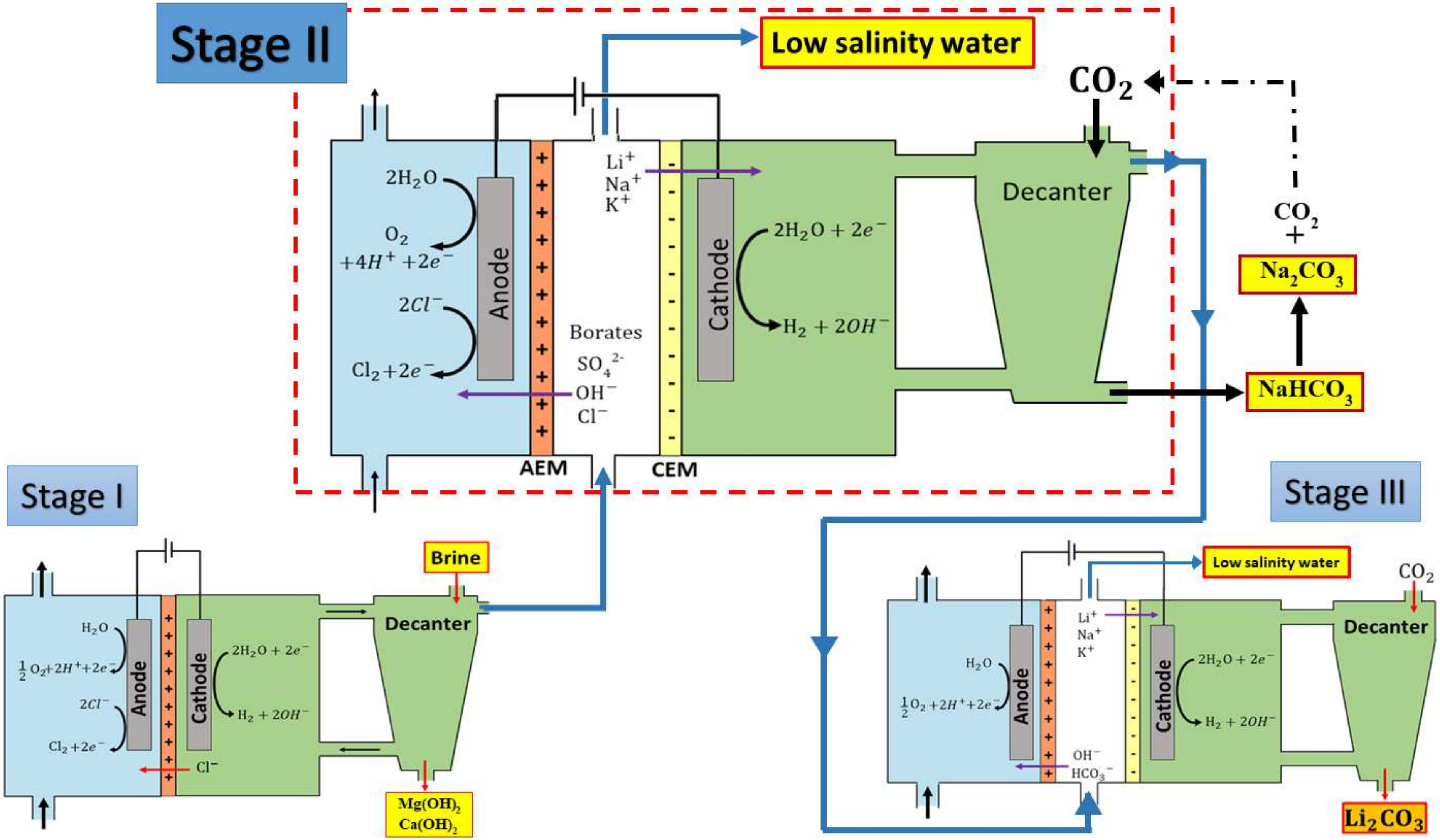
Brine	Li^+/ppm	Ca^{2+}/ppm	Mg^{2+}/ppm	B/ppm	Na^+/ppm	K^+/ppm	Cl^-/ppm	SO_4^{2-}/ppm
BI	1268	**685**	**3090**	1619	103239	14209	182850	11155
BII	589	**2109**	**2687**	518	63522	7973	116394	133
BIII	1268	**685**	**8748**	1619	103239	14209	199356	11155

First stage: Mg^{2+} / Ca^{2+} Evolution of concentrations

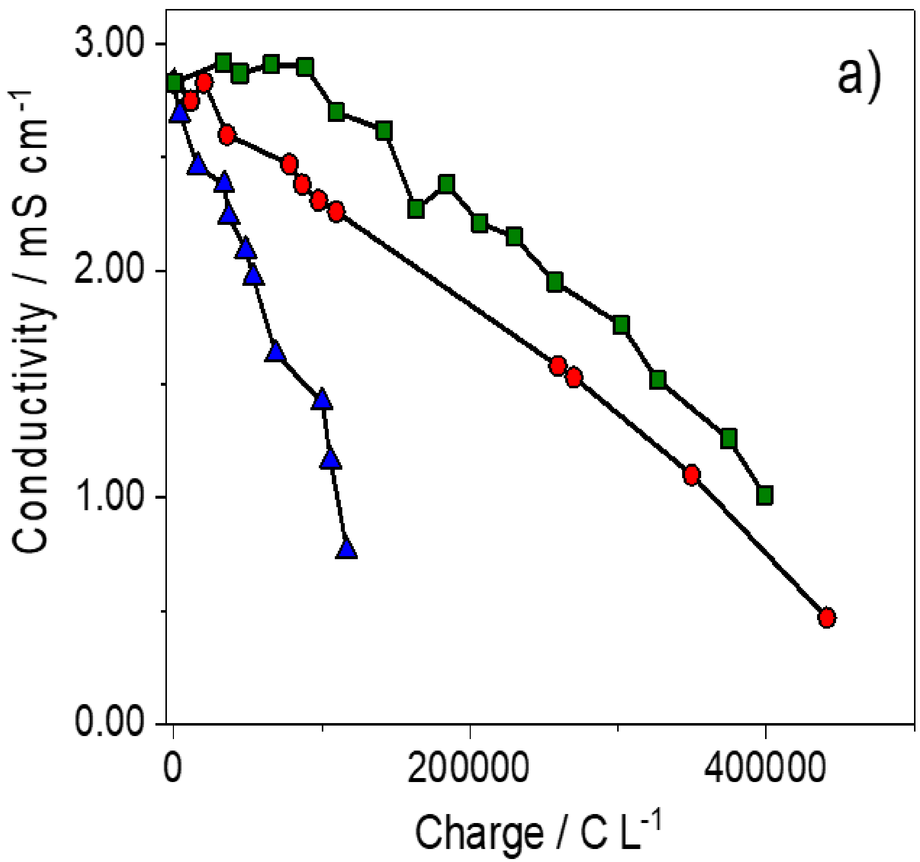


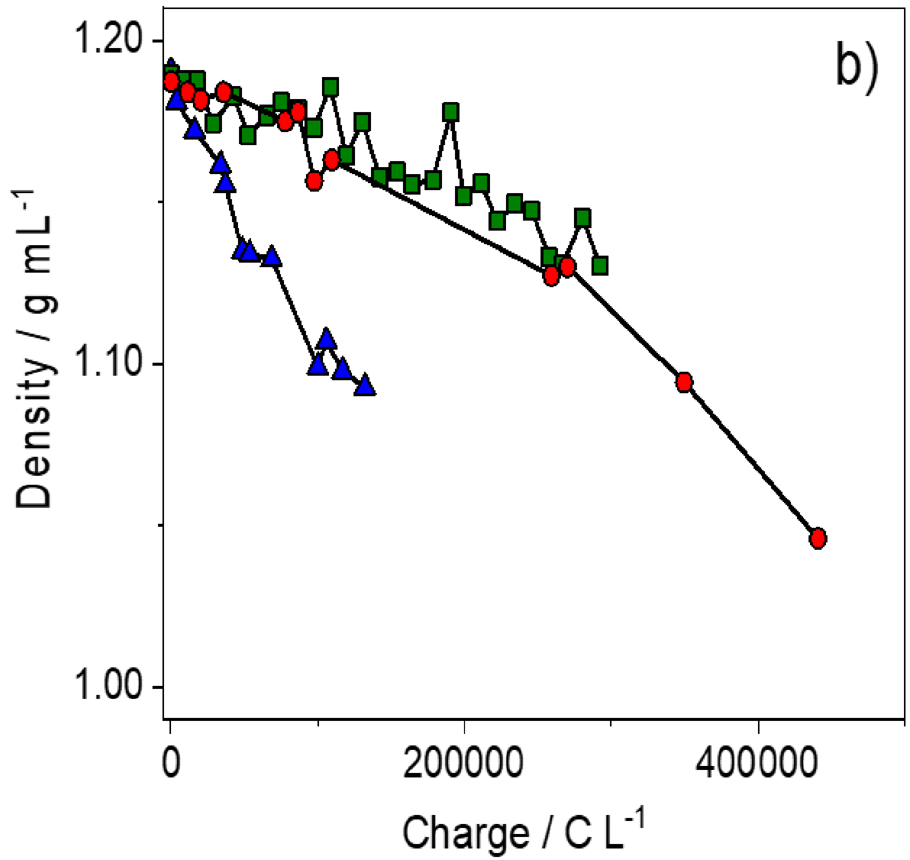
BLACK: native brine
RED: pH = 10.5
BLUE: pH =13.1

Second stage: Na^+



Second stage: Na^+ removal/recovery
Evolution of density and conductivity in the brine





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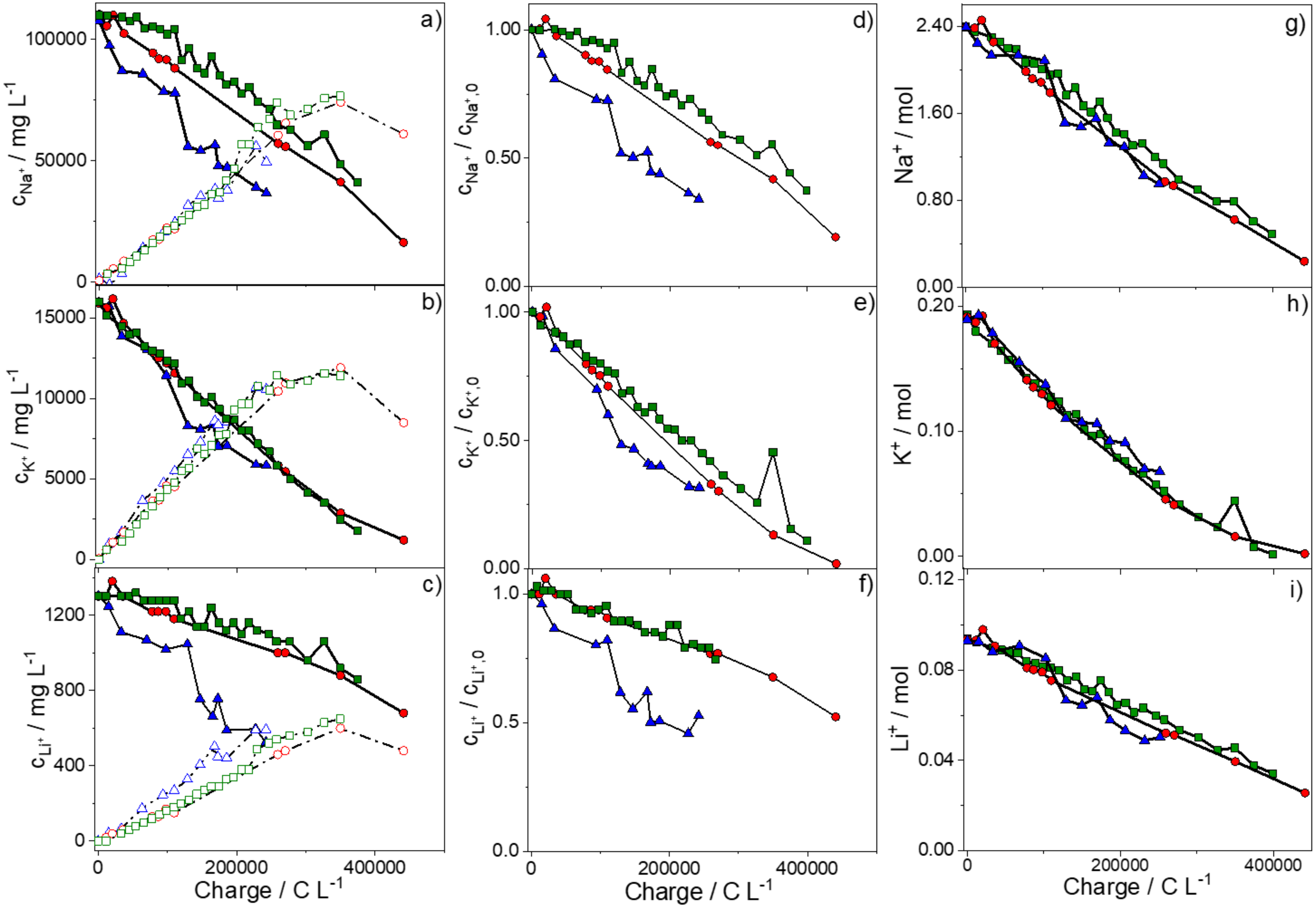
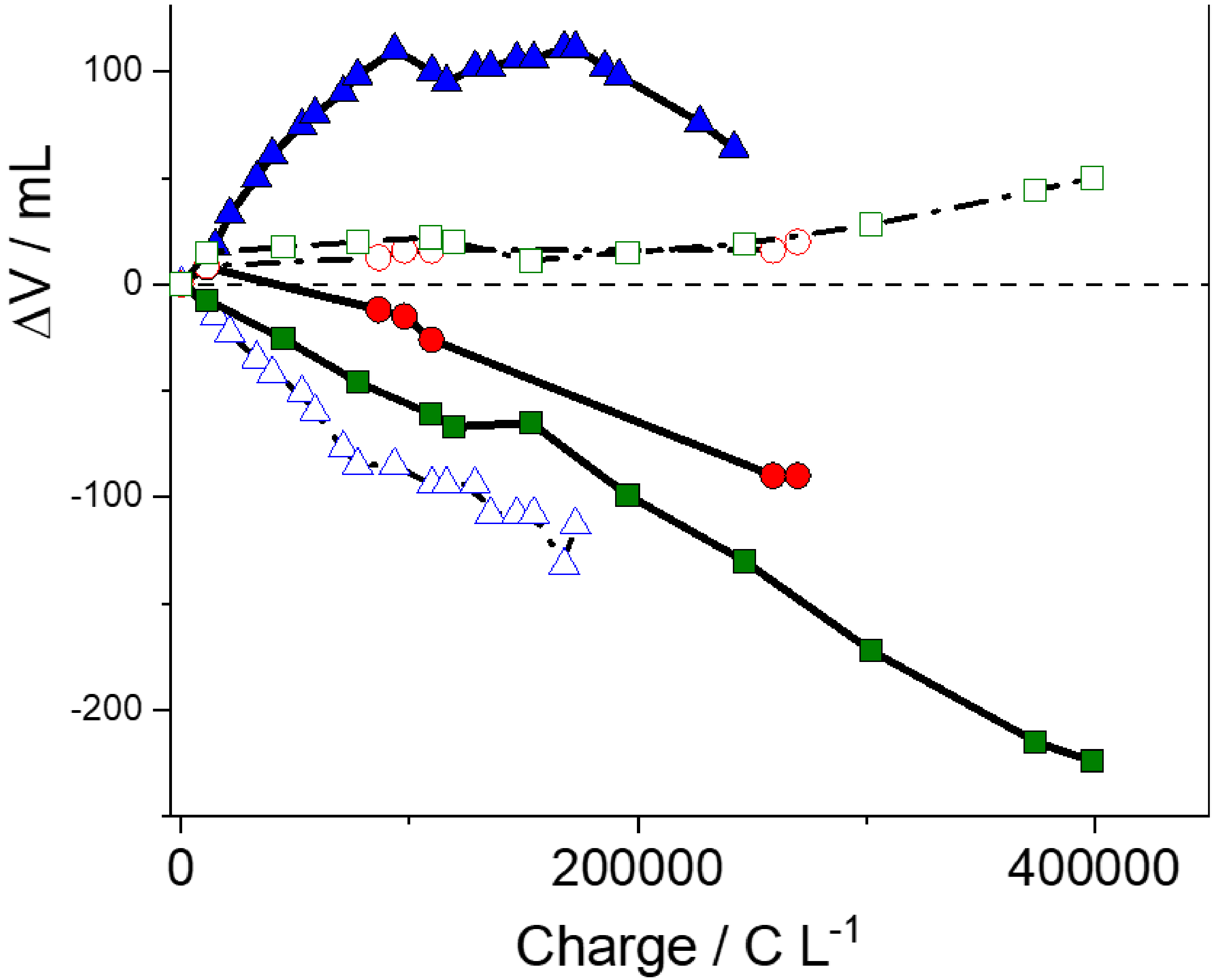
Current density = **10**, **50**, **300** A m^{-2}

Second stage: Na^+ removal/recovery
Evolution of density and conductivity in the brine



Full symbols: middle compartment. Empty symbols: cathodic compartment. Current density = 10, 50, 300 A m^{-2}

Second stage: Na^+ removal/recovery
Volume changes in middle and cathodic compartments



Osmosis vs electro-osmosis

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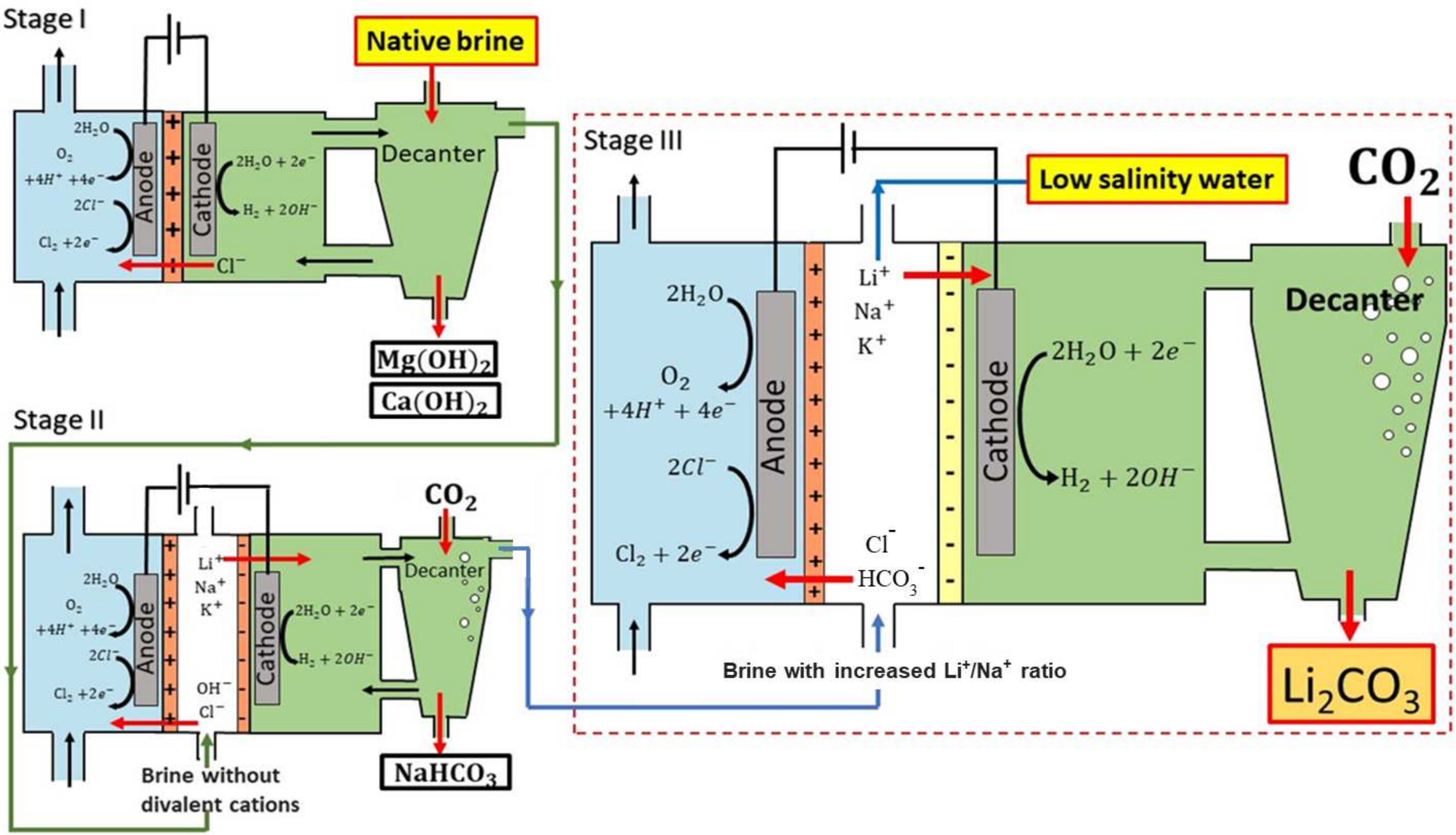
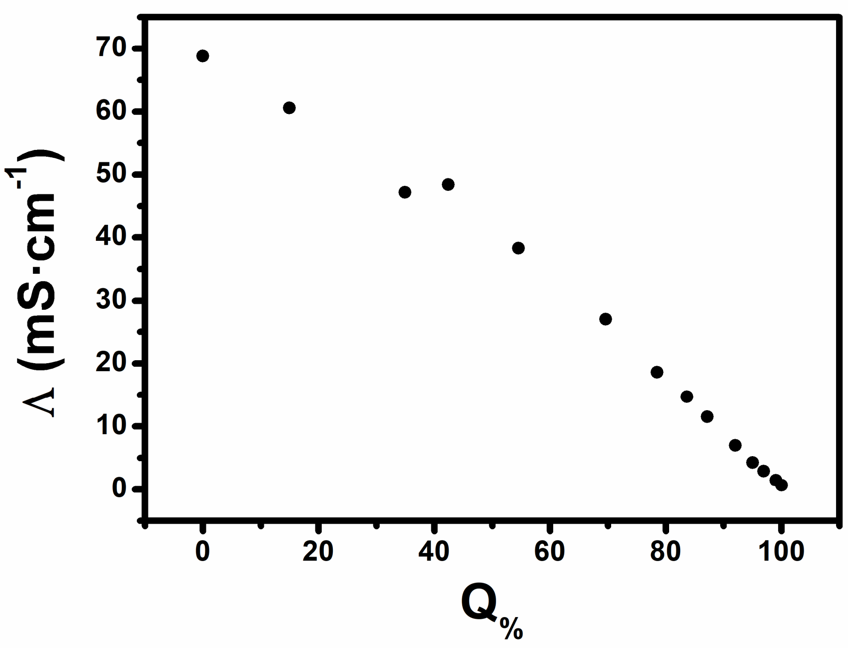
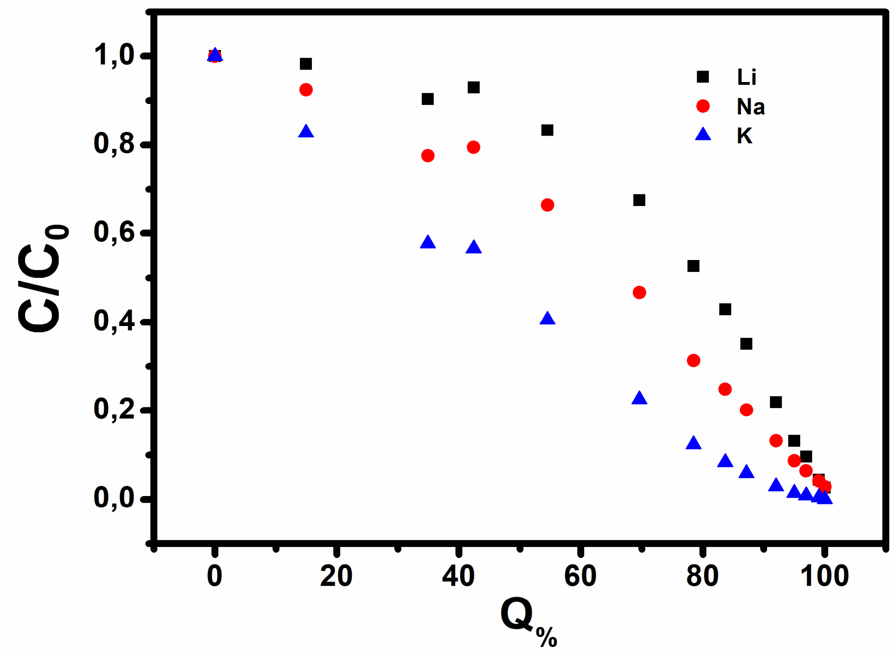
Full symbols: middle compartment. Empty symbols: cathodic compartment. Current density = **10**, **50**, **300** A m^{-2}

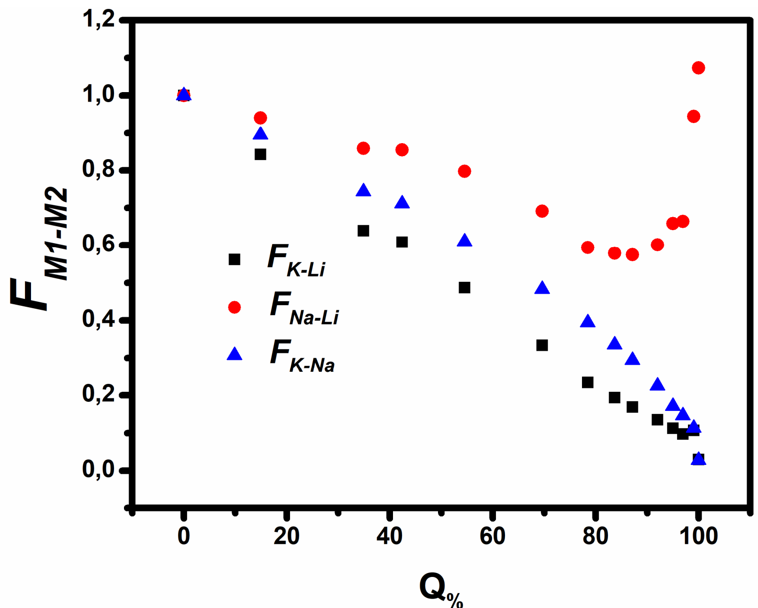
Third stage: Li_2CO_3 recovery

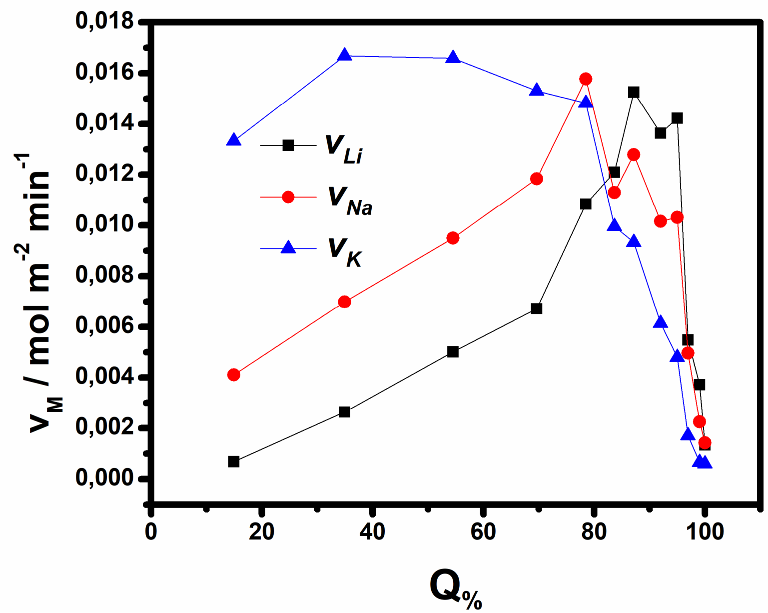


Third stage: Li_2CO_3 recovery







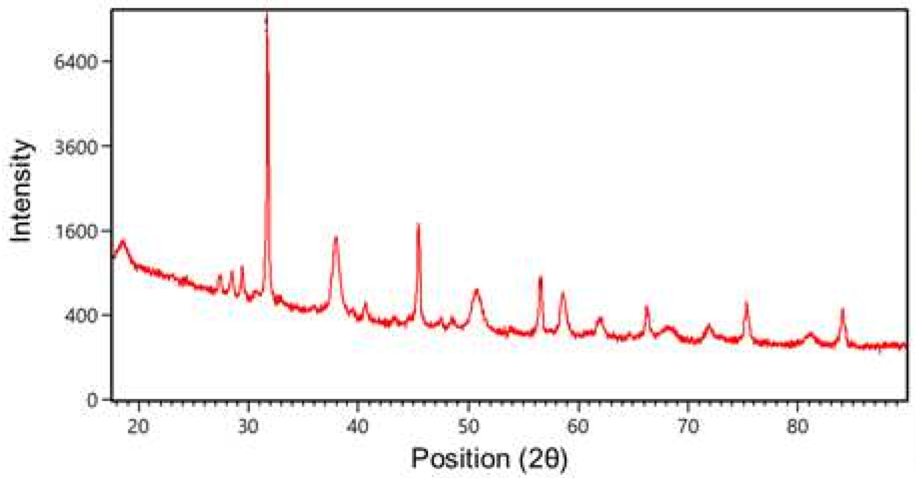


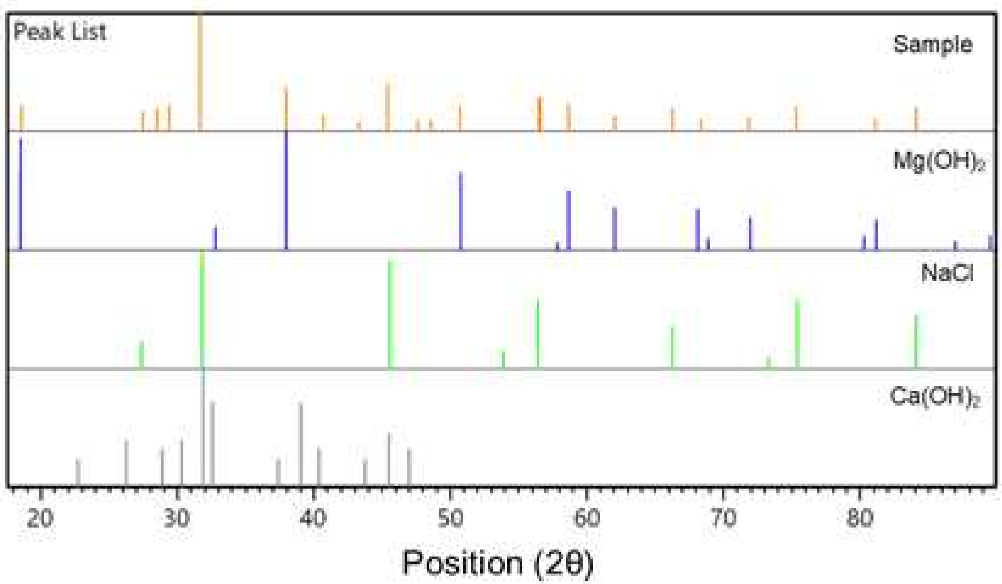
Analysis of solids recovered
Stage I

% w/w of selected elements in solids harvested at different pH values (ICP-OES analysis after re-dissolution)

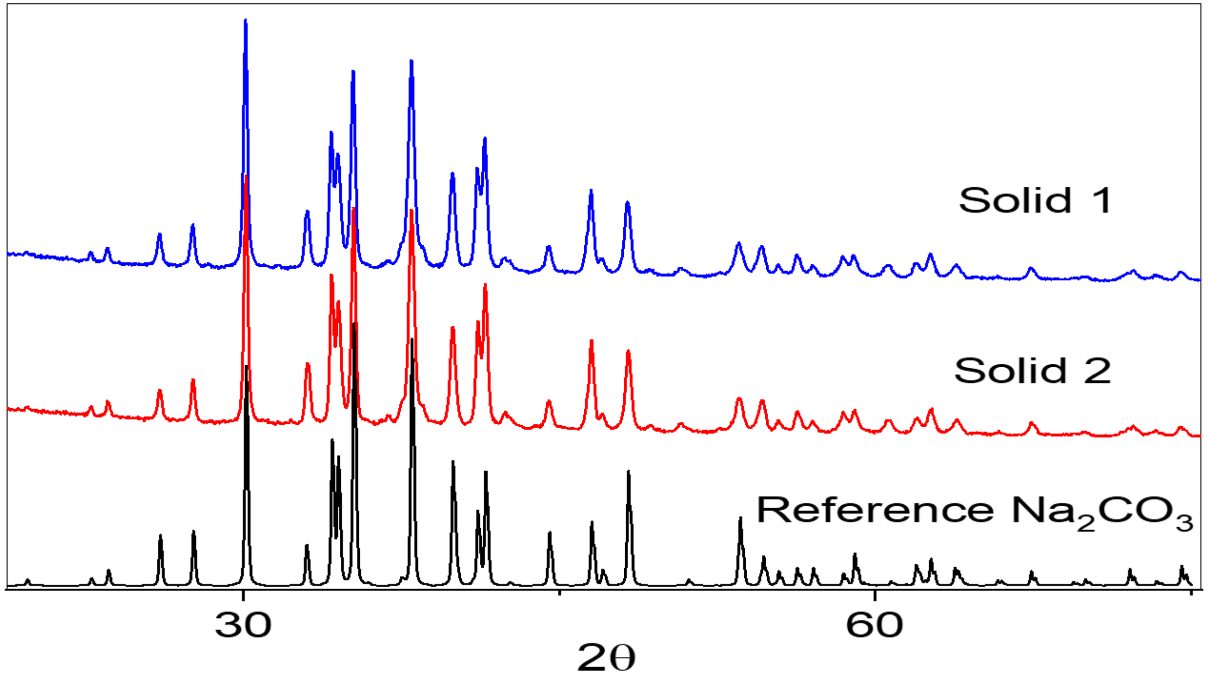
	Li	Ca	Mg	B	Na	K
Solid at **pH =10.5**	0.255	0.177	3.604	0.804	19.879	1.898
Solid at **pH =13.1**	ND	2.586	17.395	0.423	11.519	CDL

ND: not detected
CDL: close to detection limit



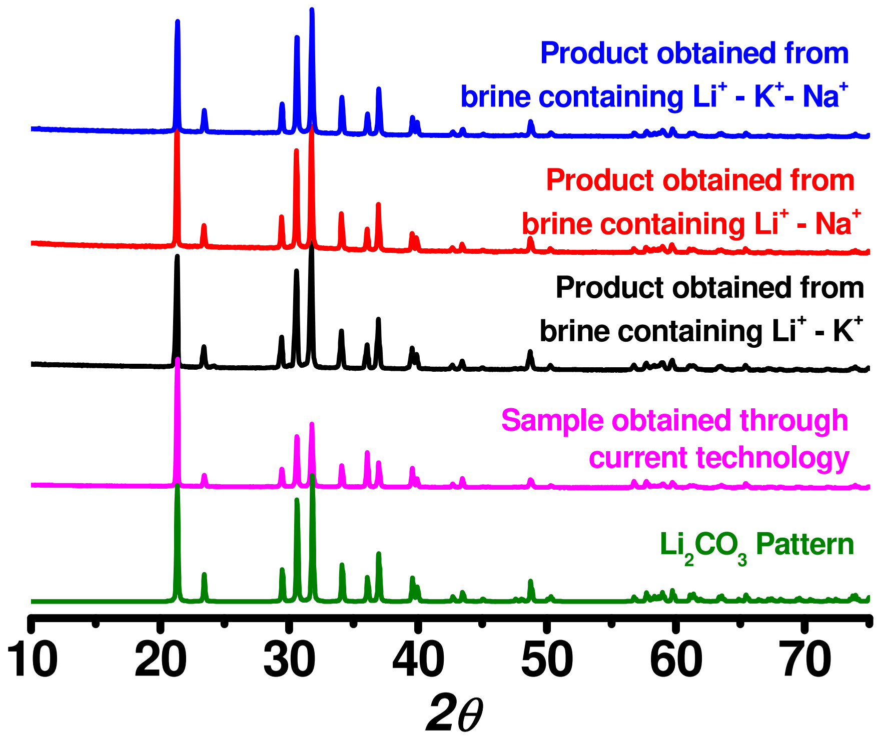


Analysis of solids recovered. Stage II



	Solid 1	Solid 2
Na^+	99.45 %	99.58 %
CO_3^{2-}	99.7 %	99.5 %
K^+	0.50 %	0.38 %
Li^+	0.05 %	0.04 %
HCO_3^-	N/D	N/D
Cl^-	0.001 %	0.001%
SO_4^{2-}	0.002%	0.004
B	N/D	N/D

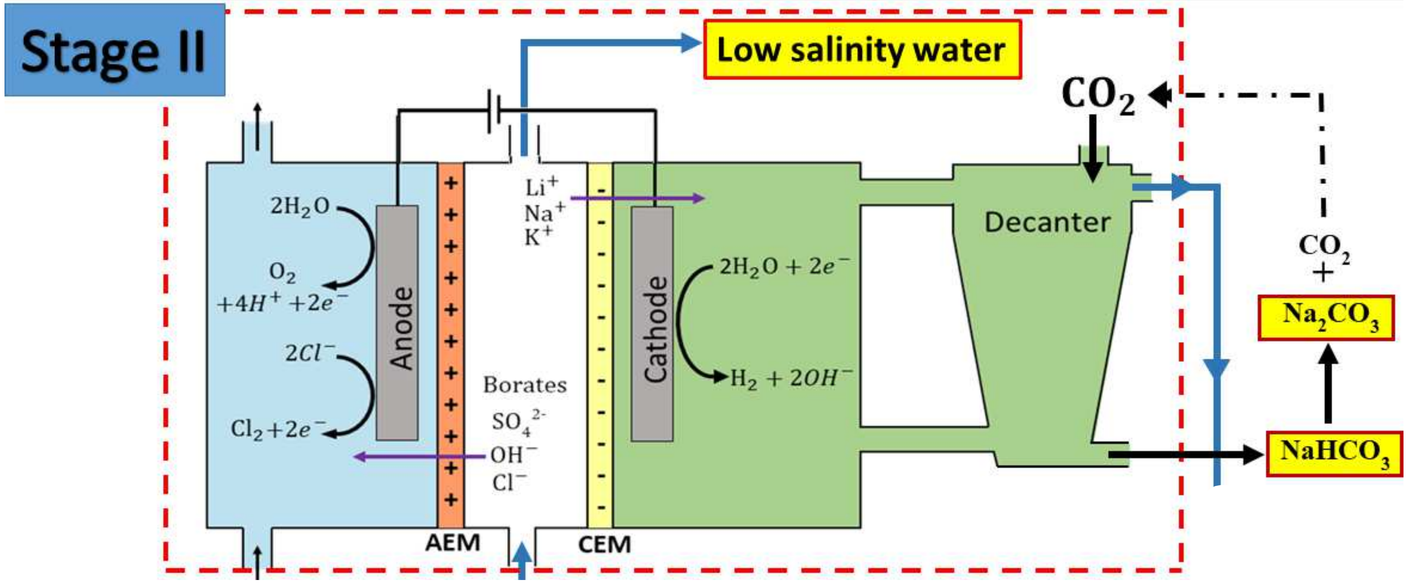
Analysis of solids recovered. Stage II



Experimental Moles g_{solid}^{-1}			Expected Value Moles g_{solid}^{-1}
Potassium	Sodium	**Lithium**	**Lithium**
(3.9 ± 0.3) x 10^{-5}	(1.0 ± 0.2) x 10^{-5}	**(2.64 ± 0.26) x 10^{-2}**	**2.707 x 10^{-2}**

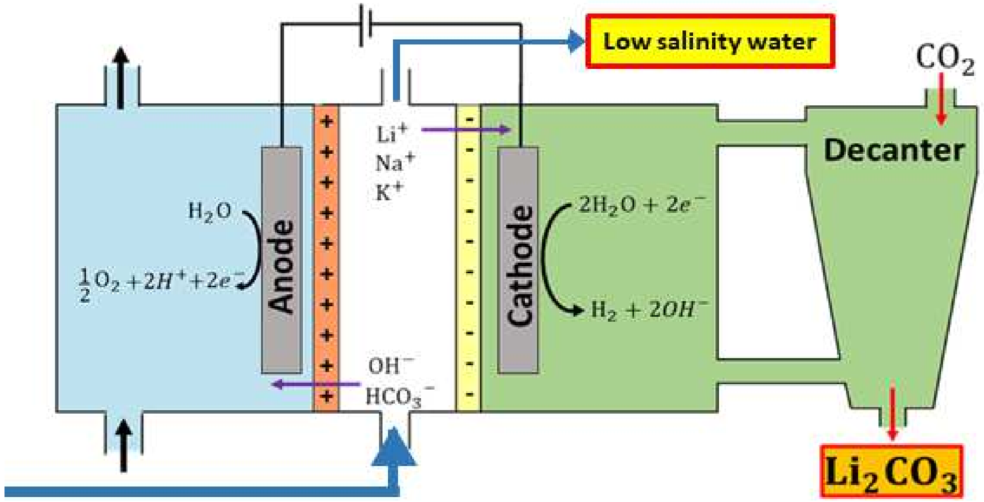
Experimental CO_3^{2-} / Moles g_{solid}^{-1}	**Expected CO_3^{2-} Moles g_{solid}^{-1}**	**Experimental HCO_3^{-} Moles g_{solid}^{-1}**	**Li_2CO_3 Purity**
(1.339 ± 0.005) x 10^{-2}	1.353 x 10^{-2}	(1.12 ± 0.06) x 10^{-4}	**97.5 %**

Fresh water recovery



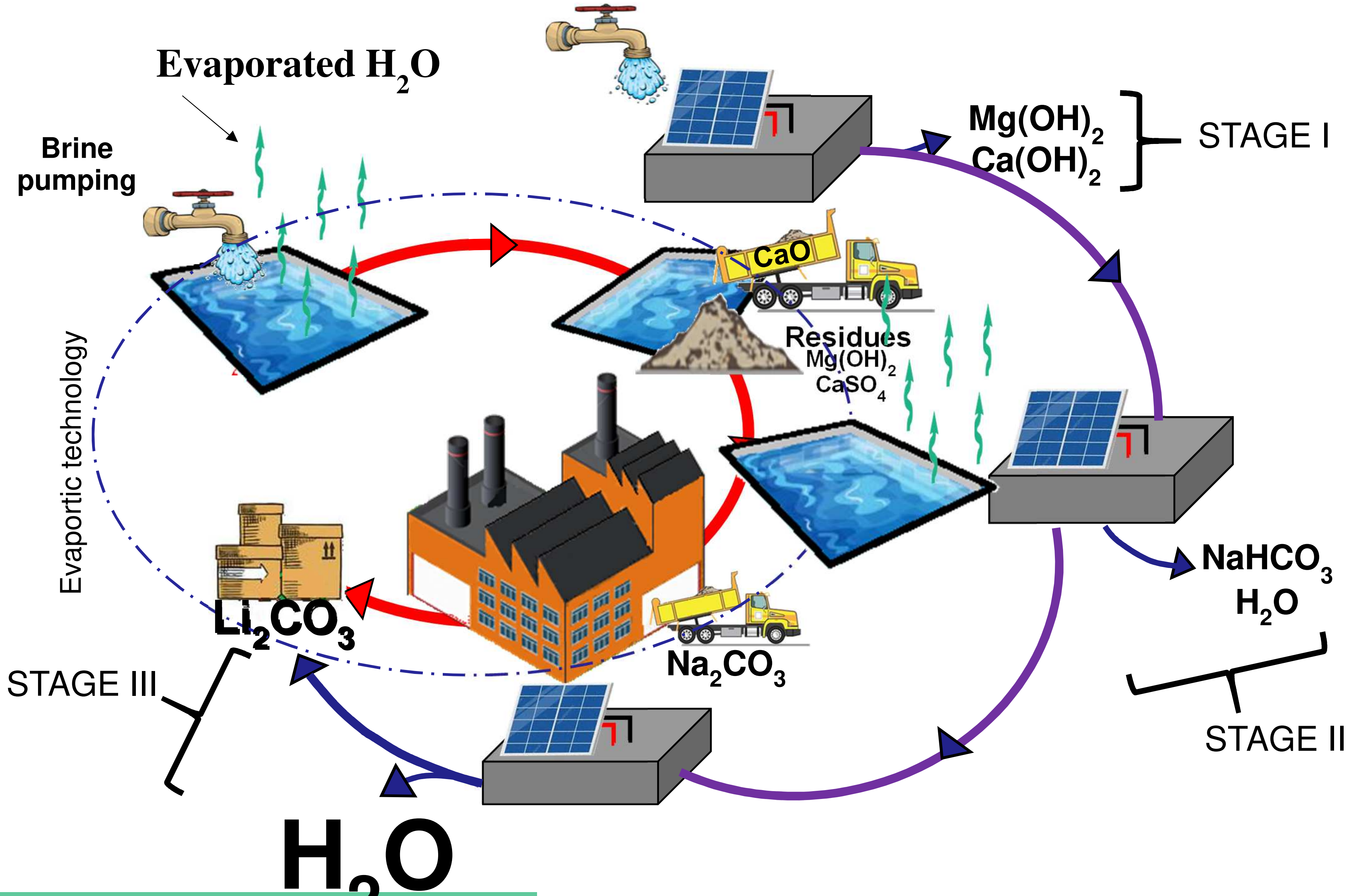
Circulated Charge / C L^{-1}	Na^+ / mg L^{-1}	K^+ / mg L^{-1}	Li^+ / mg L^{-1}	Conductivity / mS cm^{-1}	Density / g mL^{-1}	TDS/ g L^{-1}
0	114660	16376	1300	249.7	1.1763	310
458640	19860	1160	700	76.7	1.0695	53
481500	5560	180	300	23.9	1.0342	12.8
495180	120	40	0	0.032	1.0082	0.41
522720	12	0	0	0.0025	1.0060	0.0016

Fresh water recovery

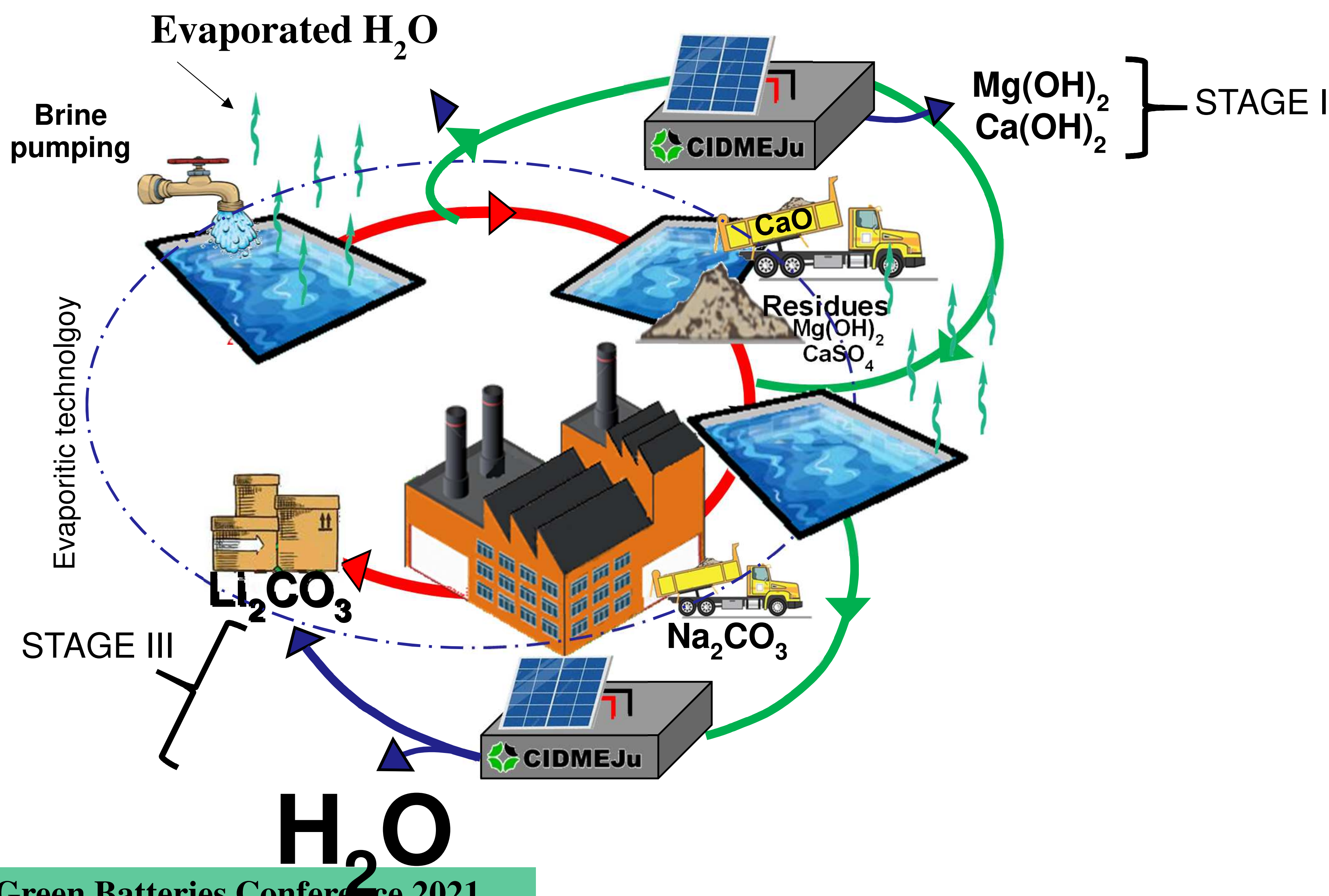


Solutions IN/OUT of the middle compartment							
$[Li^+]_{IN}$ g L^{-1}	**$[Li^+]_{OUT}$ ppm**	$[Na^+]_{IN}$ g L^{-1}	**$[Na^+]_{OUT}$ ppm**	$[K^+]_{IN}$ g L^{-1}	**$[K^+]_{OUT}$ ppm**	TDS_{IN} g L^{-1}	**TDS_{OUT} g L^{-1}**
1.394	**30 ± 1**	5.540	**150 ± 4**	14.030	**10 ± 1**	49.14 ± 0.04	**0.584 ± 0.008**

Final product from middle compartment				
Density / g L^{-1}	**pH**	**Conductivity / mS cm^{-1}**	**Cl$^-$ / g L^{-1}**	**Final E_{cell} V**
0.9940 ± 0.0001	8.62± 0.02	0.660 ± 0.010	0.019 ± 0.003	30



Evaporated H_2O
Brine pumping
Evaporitic technology
$Mg(OH)_2$
$Ca(OH)_2$
STAGE I
CaO
Residues
$Mg(OH)_2$
$CaSO_4$
$NaHCO_3$
H_2O
STAGE II
Li_2CO_3
Na_2CO_3
STAGE III
H_2O


Evaporated H_2O
Brine pumping
Mg(OH)$_2$
Ca(OH)$_2$
STAGE I
CIDMEJu
CaO
Residues
Mg(OH)$_2$
CaSO$_4$
Evaporitic technolgoy
Li_2CO_3
Na_2CO_3
STAGE III
CIDMEJu
H_2O