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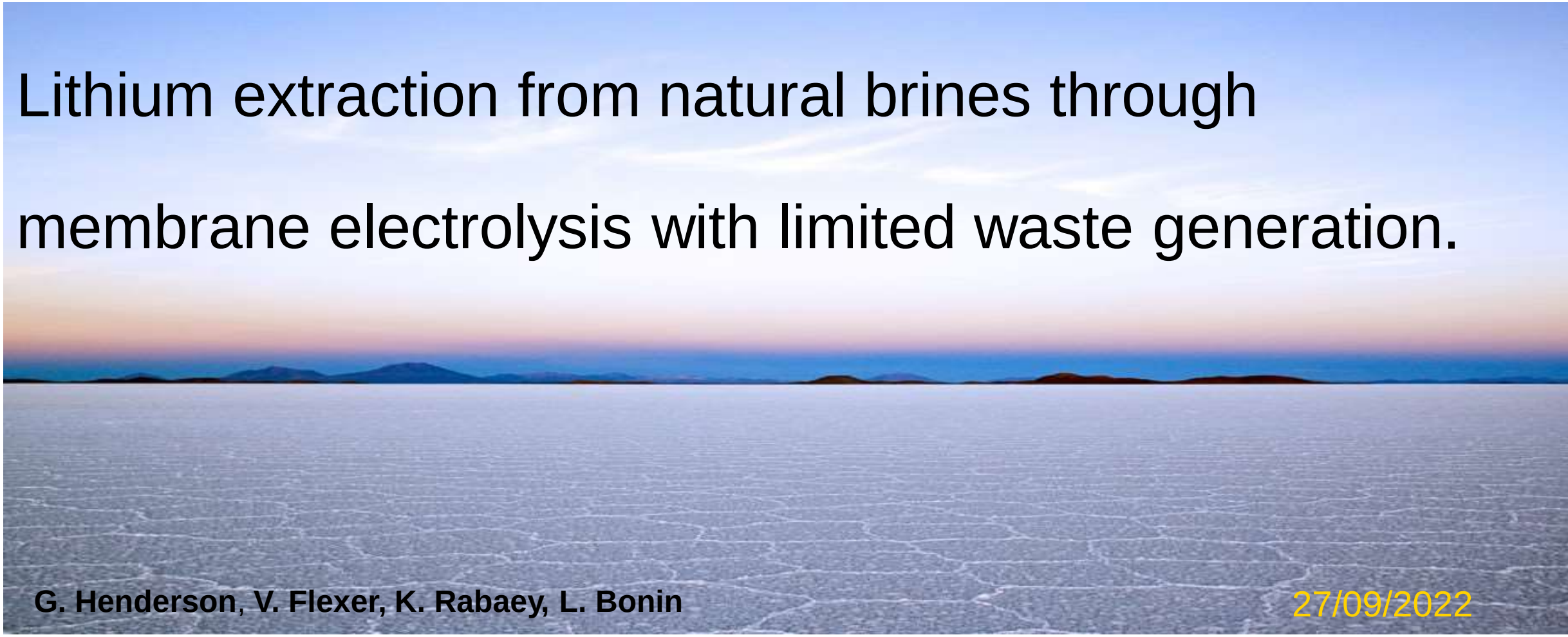
Lithium extraction from natural brines through membrane electrolysis with limited waste generation.



G. Henderson, V. Flexer, K. Rabaey, L. Bonin

27/09/2022

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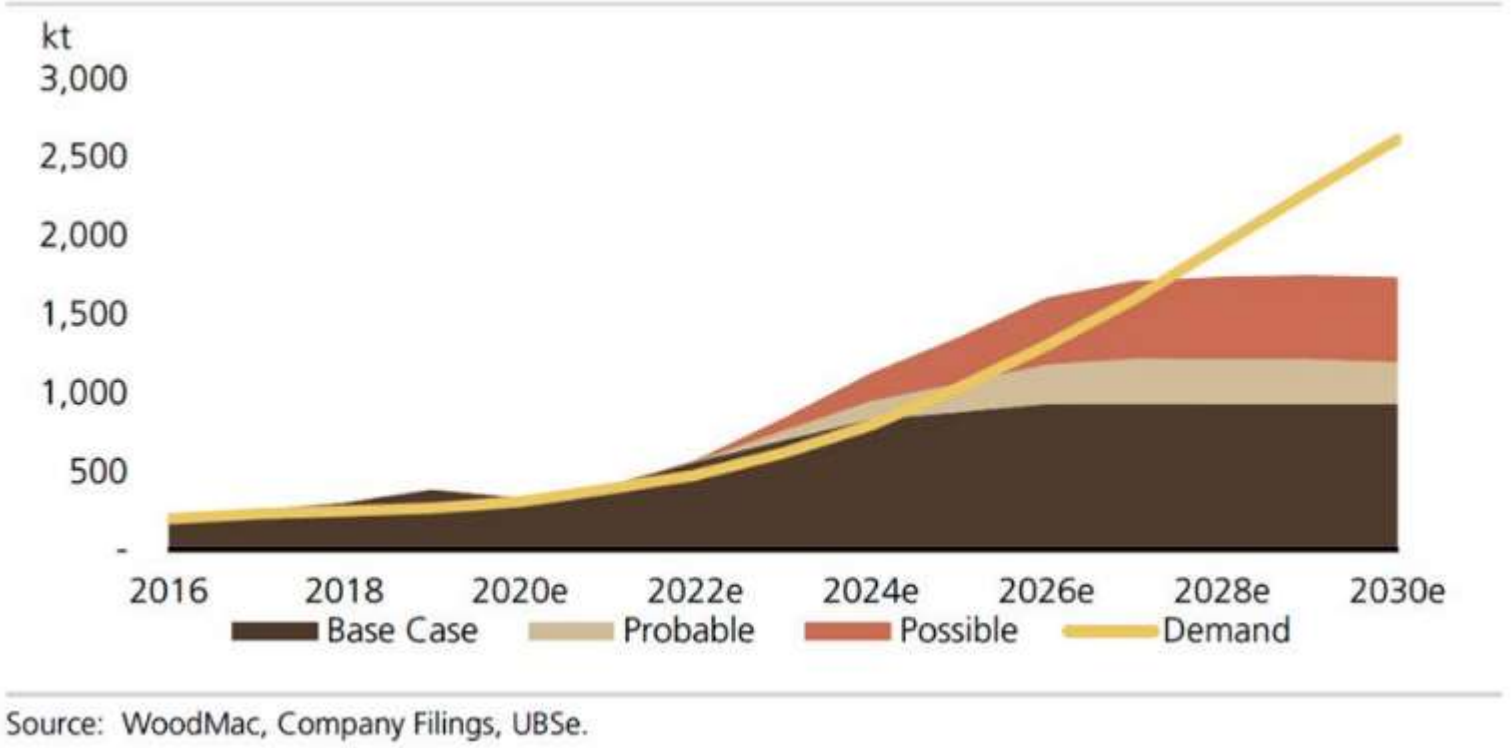
ERA-MIN 2
RESEARCH & INNOVATION PROGRAMME ON RAW MATERIALS TO FOSTER CIRCULAR ECONOMY

UNJu Universidad Nacional de Jujuy

IVL Swedish Environmental Research Institute

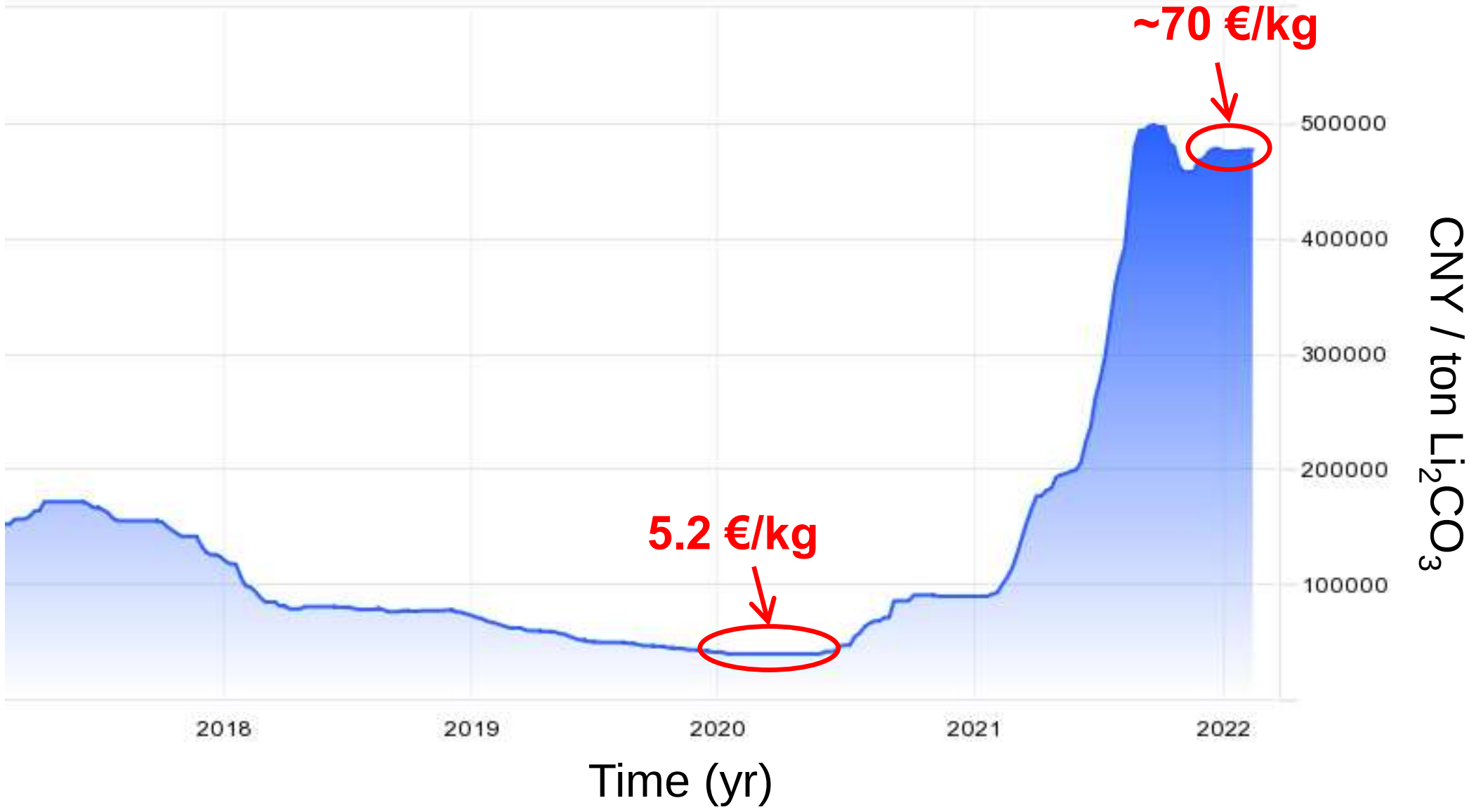
Lithium supply – Demand balance



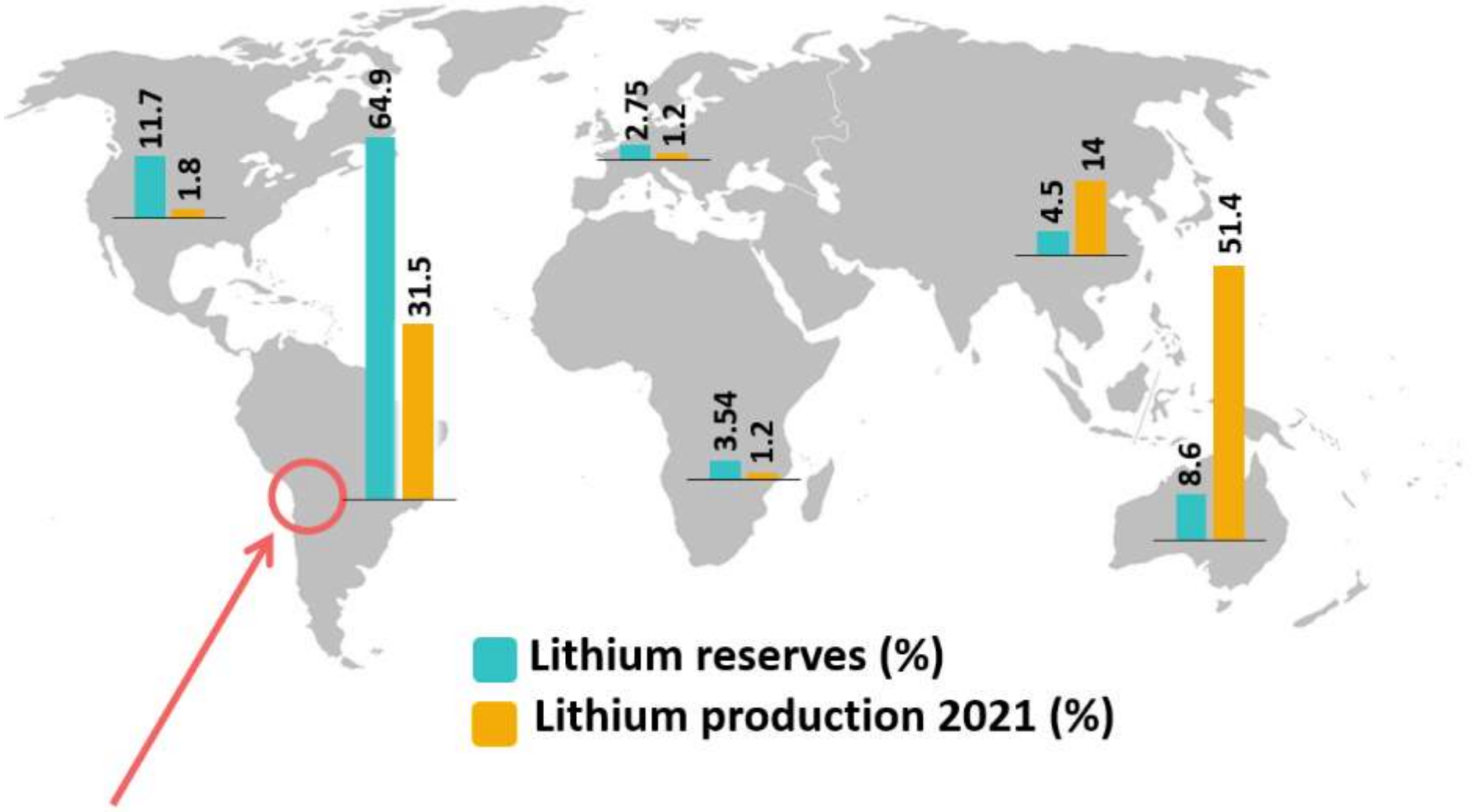
Source: WoodMac, Company Filings, UBSe.

Supply risk comes from **production capacity**

Price Li_2CO_3



Lithium distribution



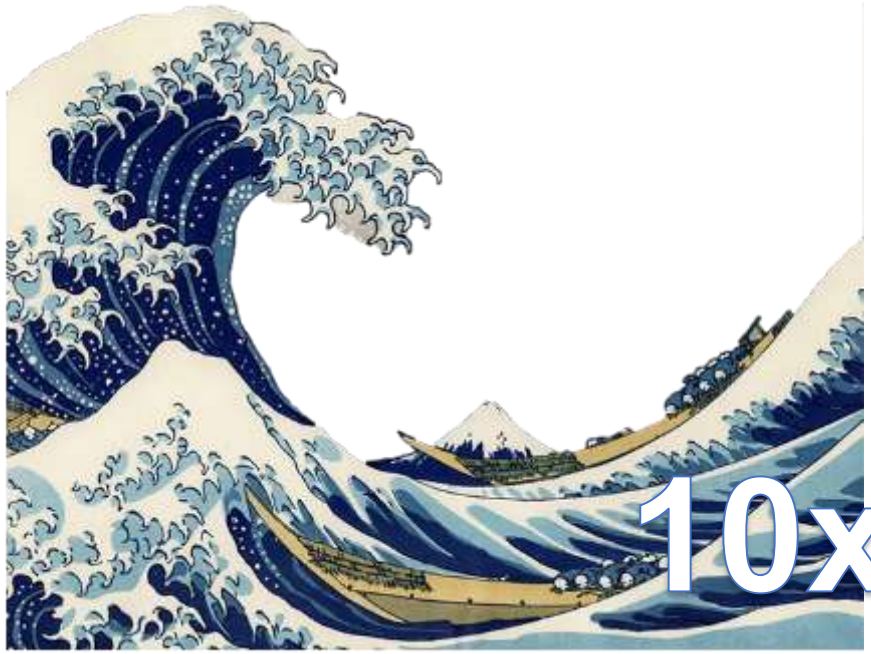
Lithium triangle

Lithium from brines

55-65% of the world's lithium resources.

Li brines = Na, K, Mg, Ca, B, SO_4, Cl …

~1-2 g/L Li



Economist.com

HOW IS LITHIUM EXTRACTED FROM BRINES?

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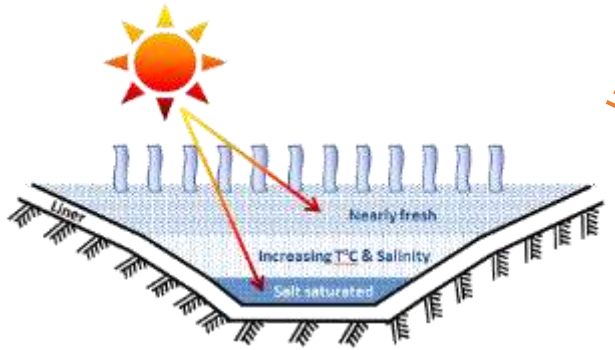
Salar de Olaroz

Solar evaporation

<u>Current process</u>:
evaporation/precipitation in open-air ponds

Conventional brine processing based on natural evaporation

Salar brines

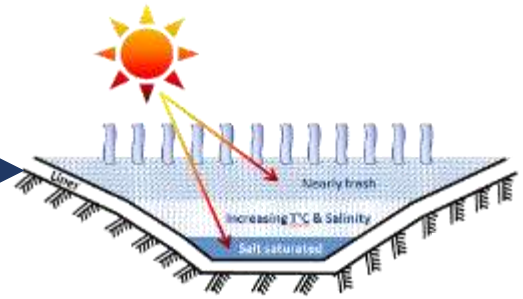


Evaporation ponds

~23 months

Base

SO_4^{-2} and Mg^{+2} removal



Evaporation ponds

Acids

Solvent

B removal

Base

Ca^{+2} and Mg^{+2} Precipitation

Polishing

Na_2CO_3

Li^{+2} Precipitation

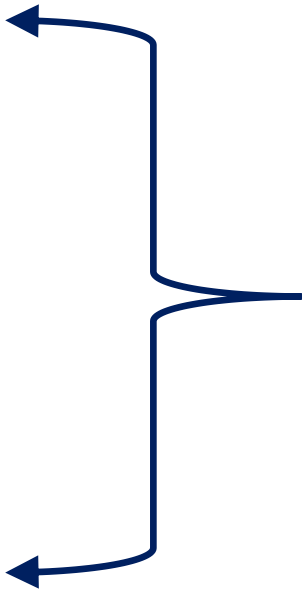
Filtration

Li_2CO_3

- **Water lost**
- **up to 50% Li lost**
- **115 ton waste per ton Li_2CO_3**

Conventional brine processing based on natural evaporation

- Brine concentration - water evaporation
- NaCl removal – water evaporation
- Mg and Ca removal – base addition
- B removal – acids + solvents addition
- Li_2CO_3 precipitation - Na_2CO_3 addition



- ✓ **Brine concentration**
- ✓ **Changes in pH**
- ✓ **CO_3^{-2} addition**

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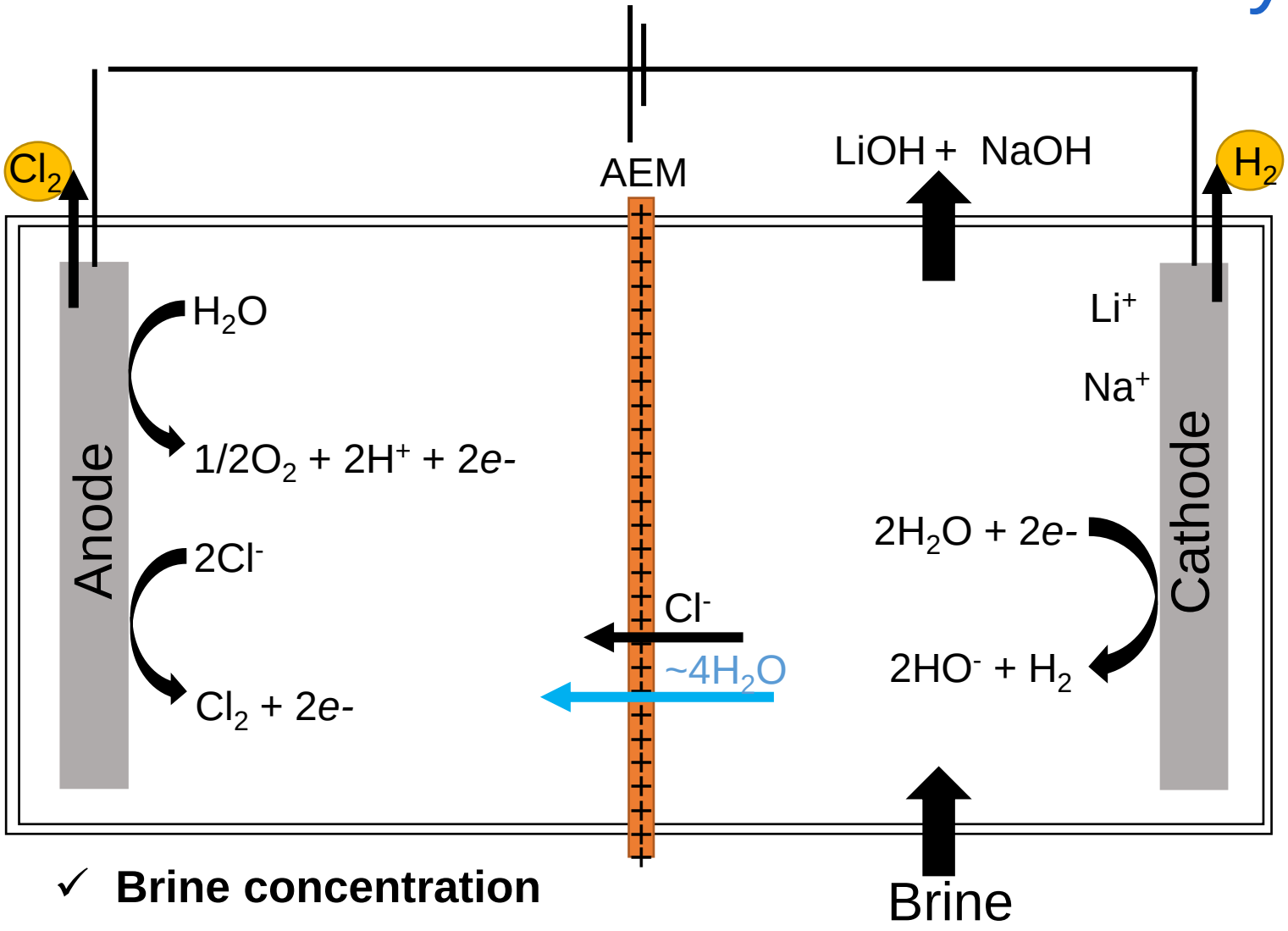
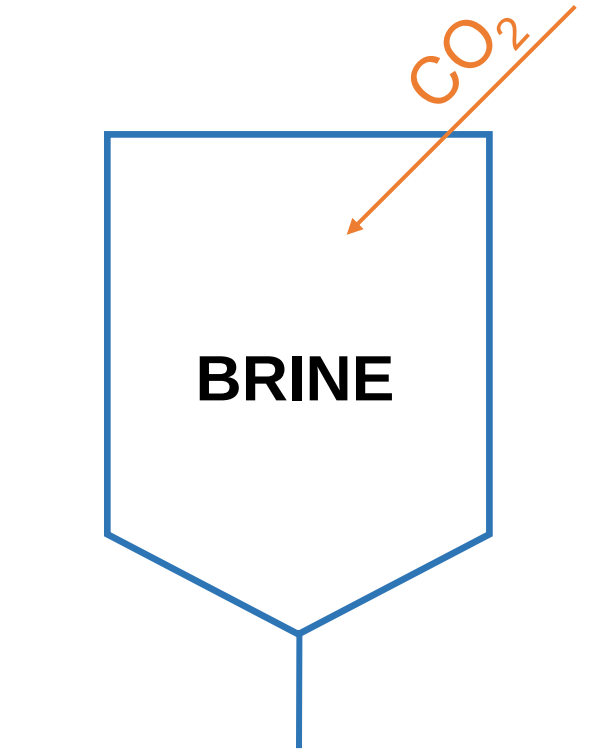
Li+WATER - Membrane electrolysis



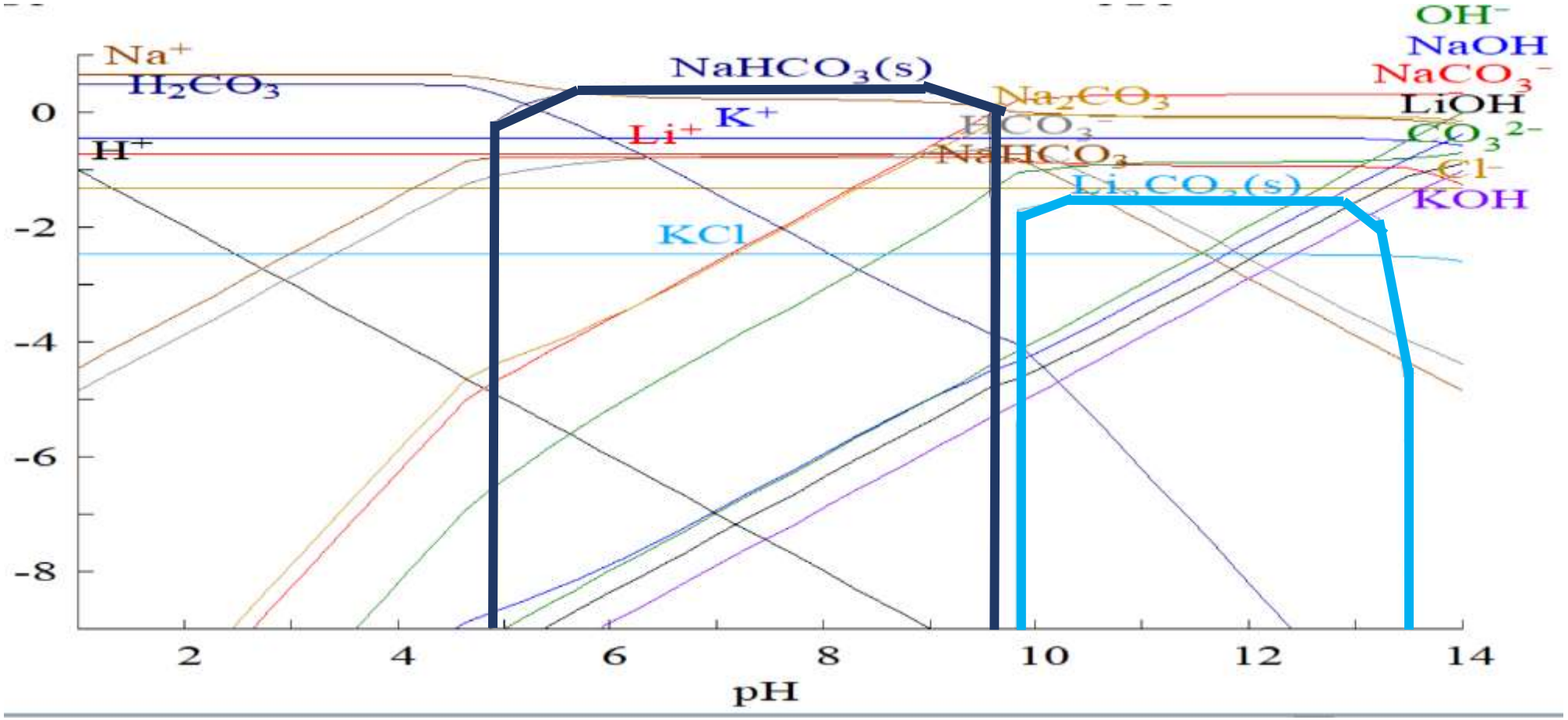


Na_2CO_3 or Li_2CO_3

- ✓ **Brine concentration**
- ✓ **Changes in pH**
- ✓ **CO_3^{-2} addition**

Experimental design

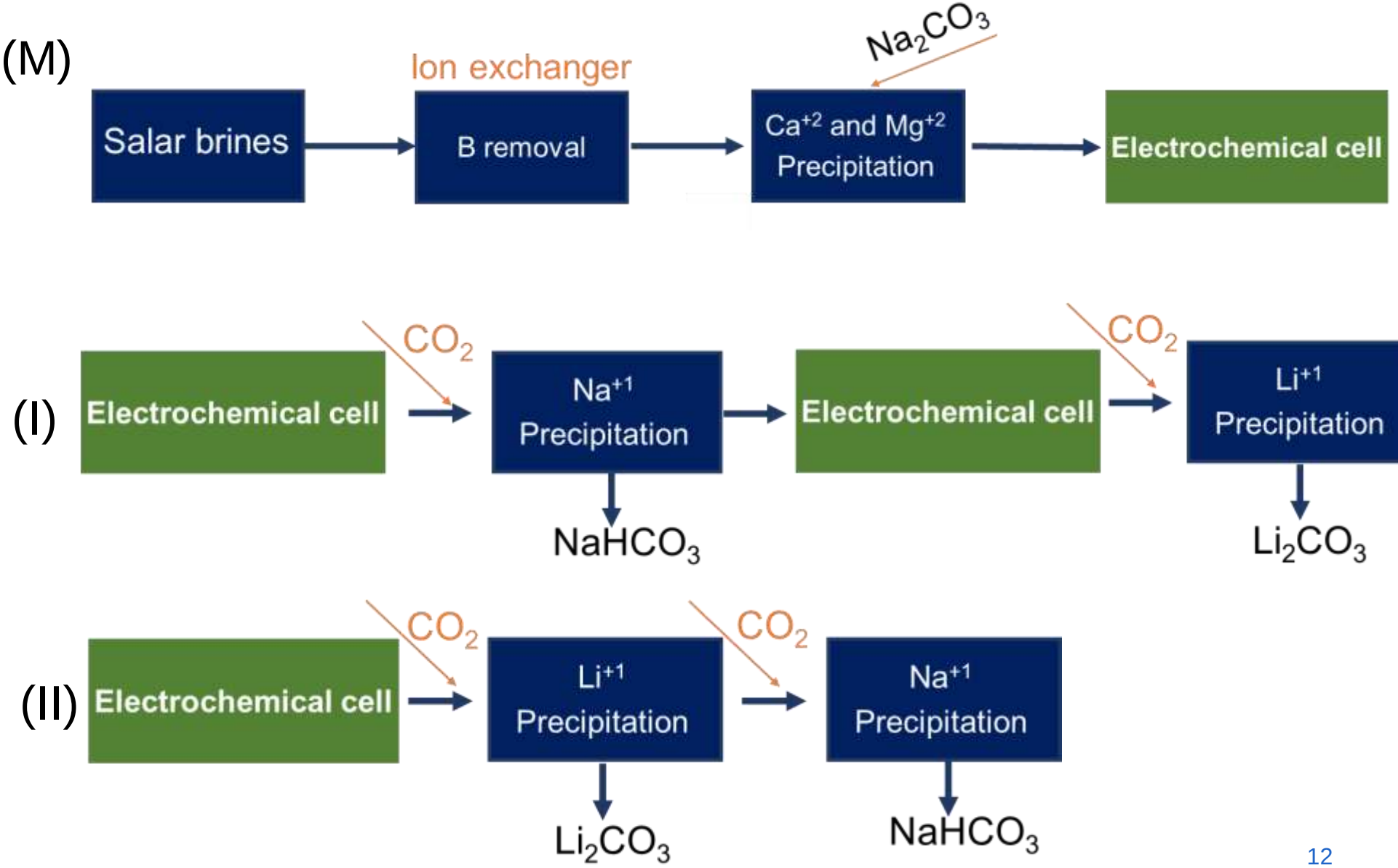
Na^+ (M)	Li^+ (M)	K^+ (M)	Cl^- (M)	SO_4^{2-} (M)
4.86	0.19	0.36	5.15	0.11



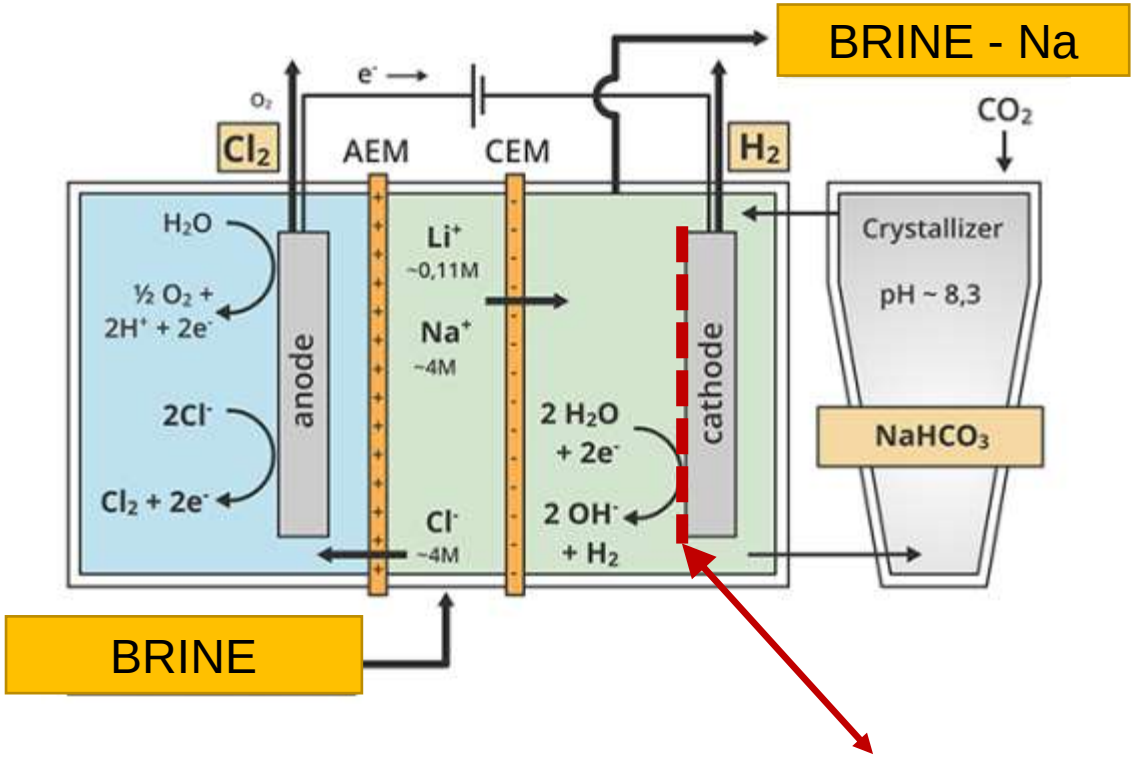
Li+WATER process - Experimental design

Brine composition (M)

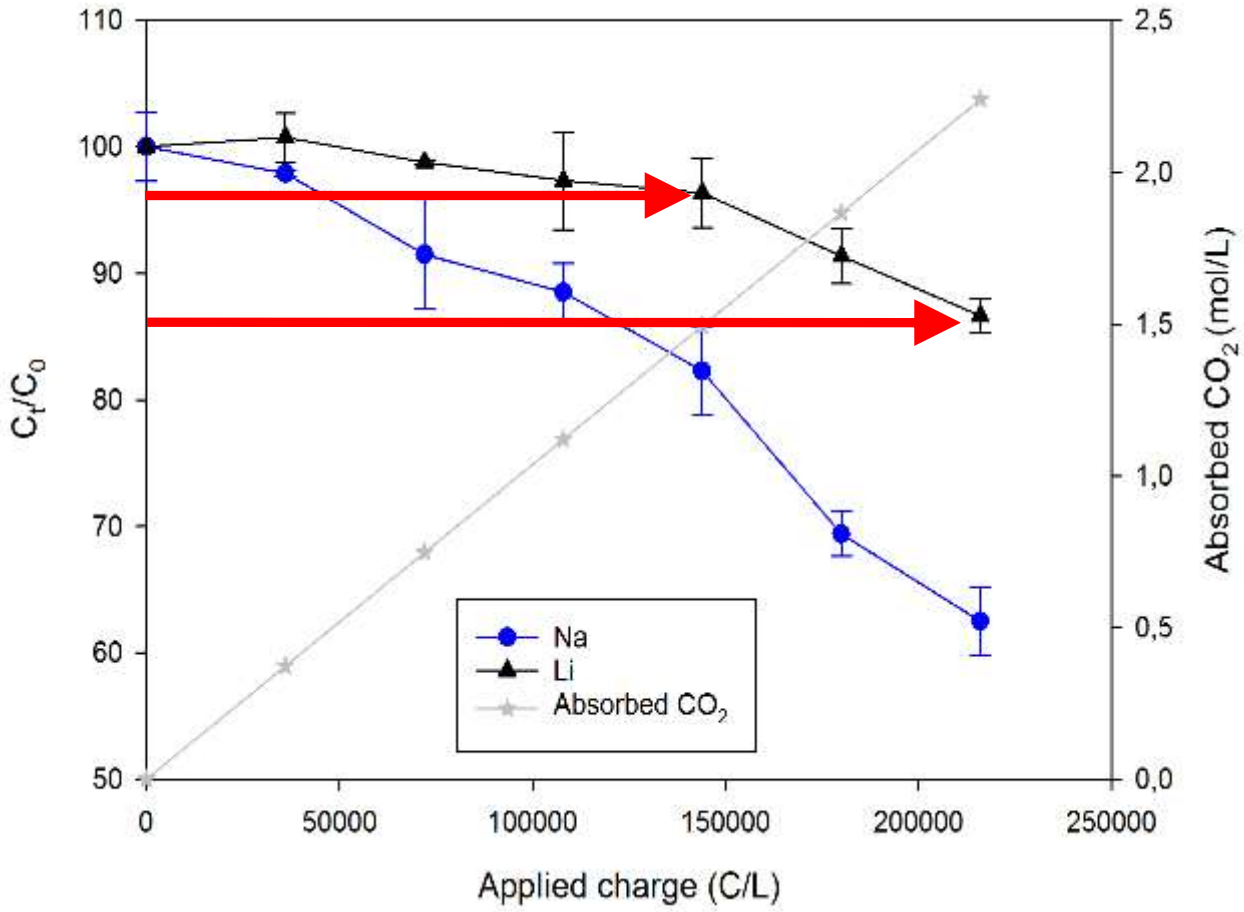
Li^+	0.18
Ca^{2+}	0.02
Mg^{2+}	0.12
B	0.14
Na^+	4.49
K^+	0.36
Cl^-	5.15
SO_4^{2-}	0.11



(I) - Sodium bicarbonate precipitation



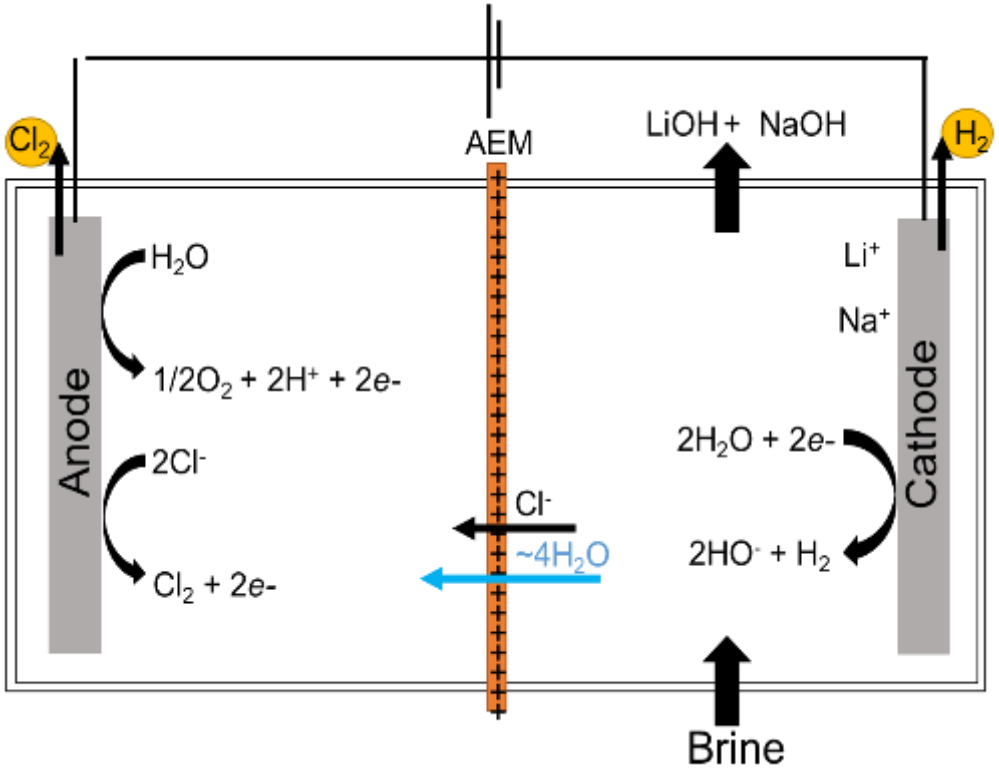
Higher pH in the cathode interface

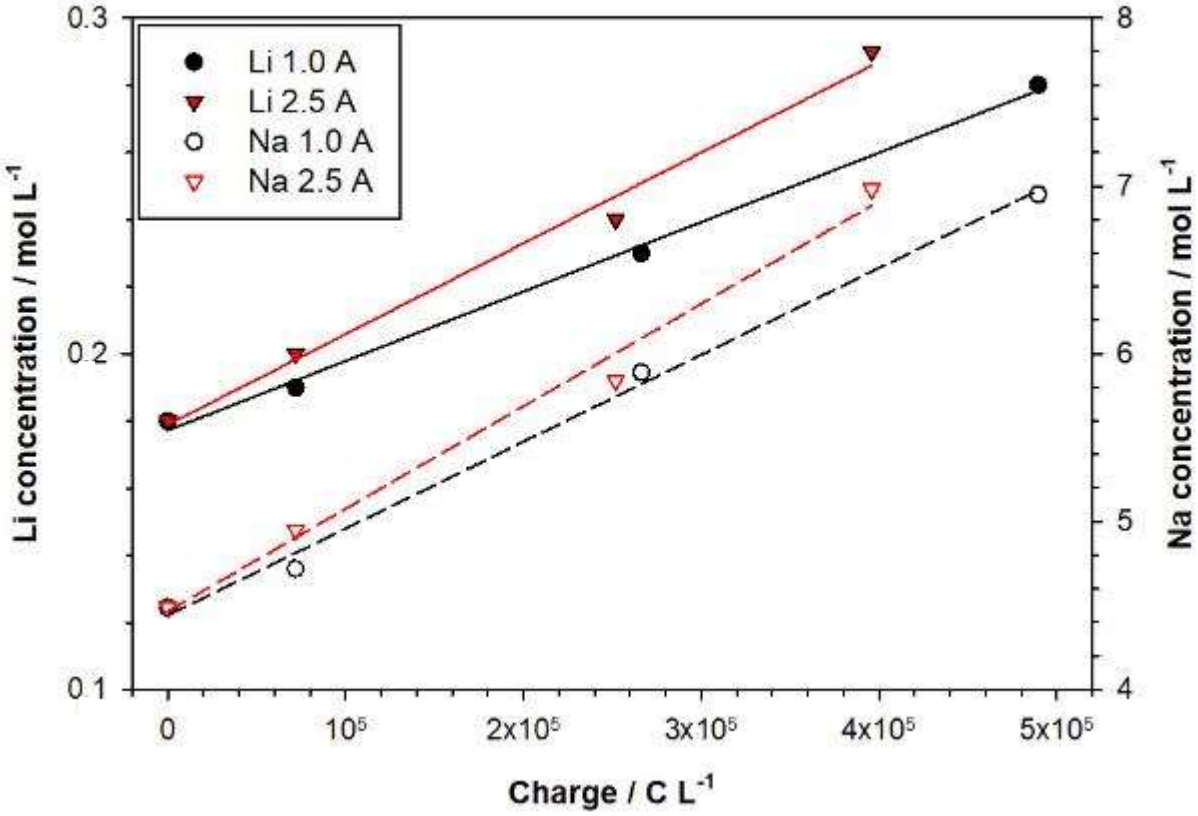


- Lithium lost during Na extraction
- It is possible to extract Li first?

(II) – Lithium carbonate precipitation

OH^- Generation





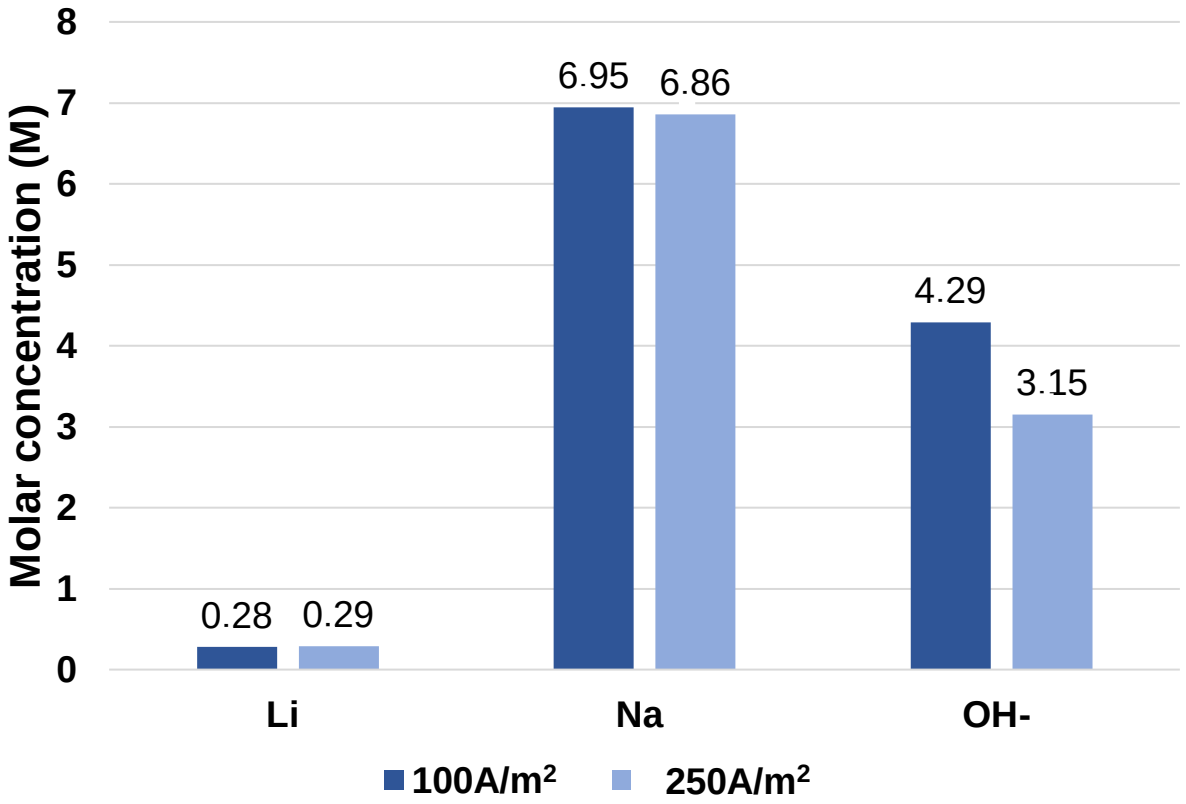
Li and Na concentration increase in the cathode

(II) – Lithium carbonate precipitation

- Catholyte volume 650 mL
- Charge applied

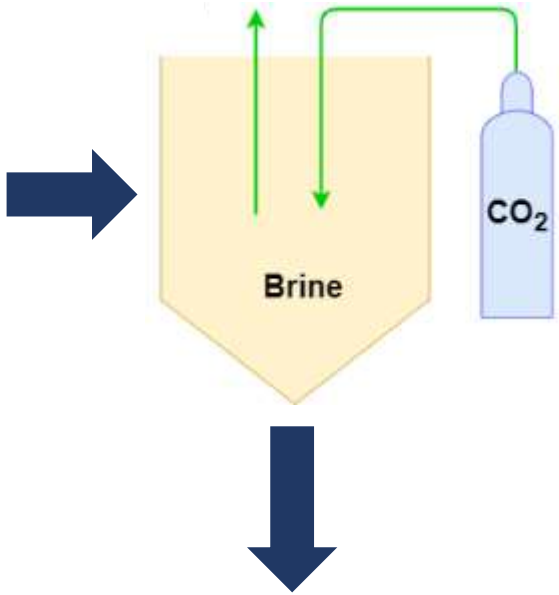
100A/m^2 = 489 kC

250A/m^2 = 396 kC



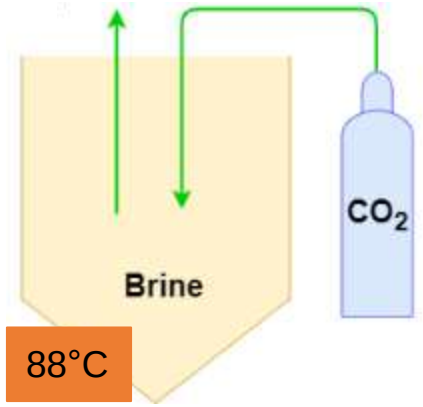
Li_2CO_3 crystallization

➢ CO_2 fluxing until pH 11- 88°C

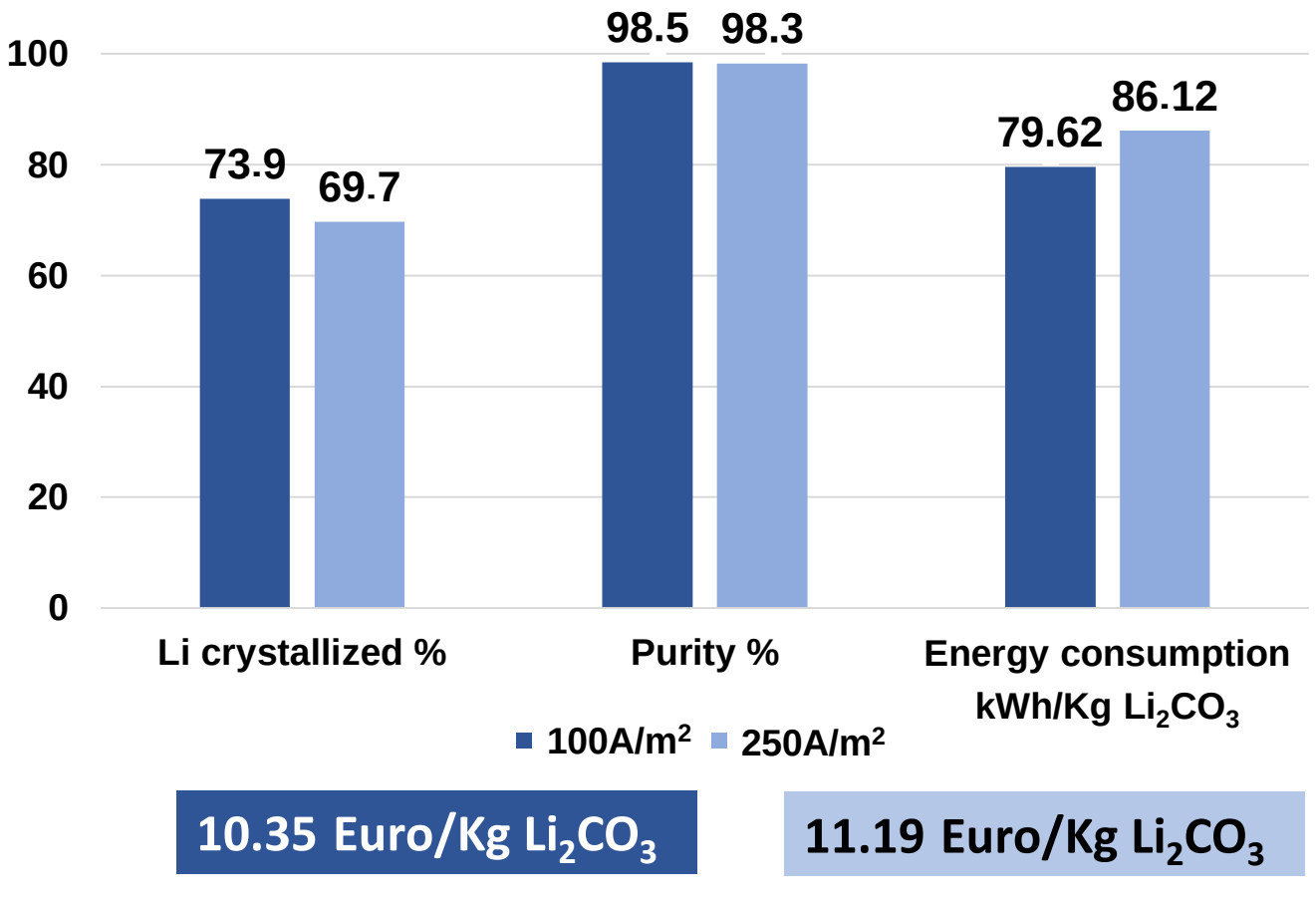


Li_2CO_3

(II) – Lithium carbonate precipitation



Li_2CO_3



10.35 Euro/Kg Li_2CO_3

11.19 Euro/Kg Li_2CO_3

100A/m²

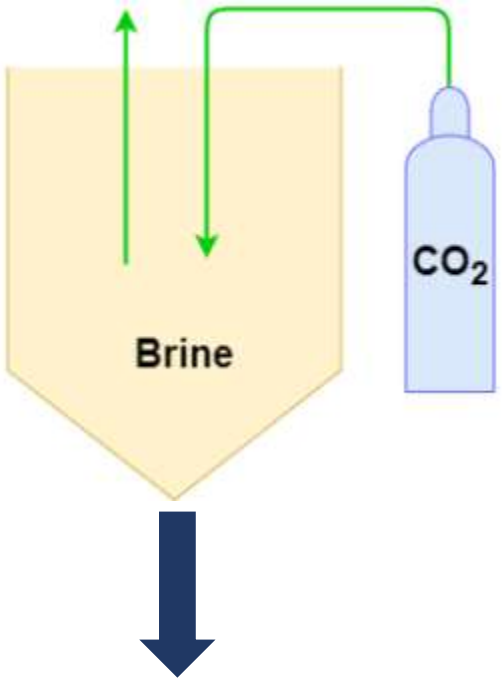
	mol/L
Li^+	0.07
Na^+	7.02

250A/m²

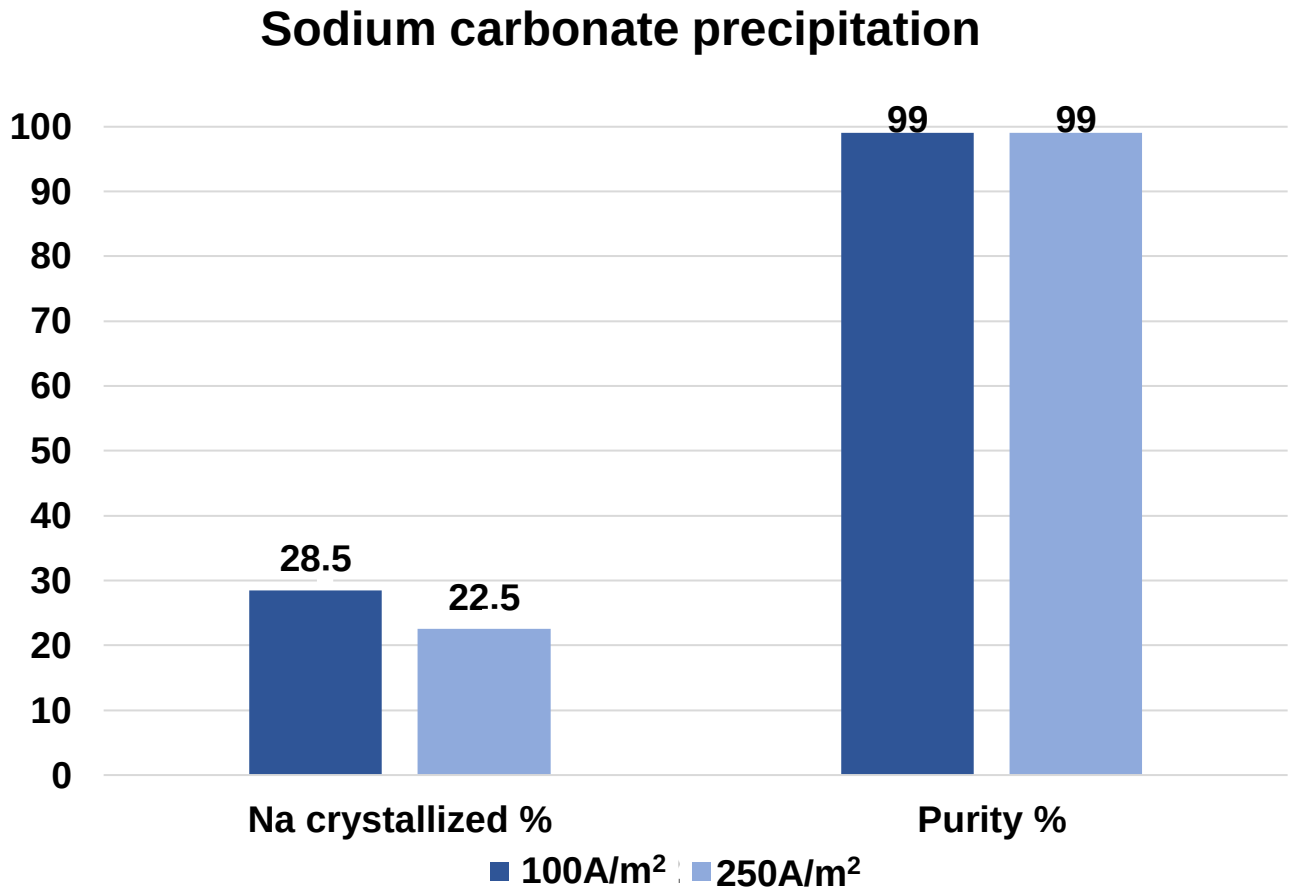
	mol/L
Li^+	0.08
Na^+	7.02

(II) – Sodium bicarbonate precipitation

- 20°C
- CO_2 fluxing until pH 8.5



$NaHCO_3$



1.9 kg Na_2CO_3 / kg Li_2CO_3

CONCLUSIONS

- ✓ **Membrane electrolysis** based process
- ✓ Controllable and **weather independant**
- ✓ No **water lost**
- ✓ No chemicals except CO_2
- ✓ Extration of **by-products / limited waste** generation
- ✓ **Energy cost still high**

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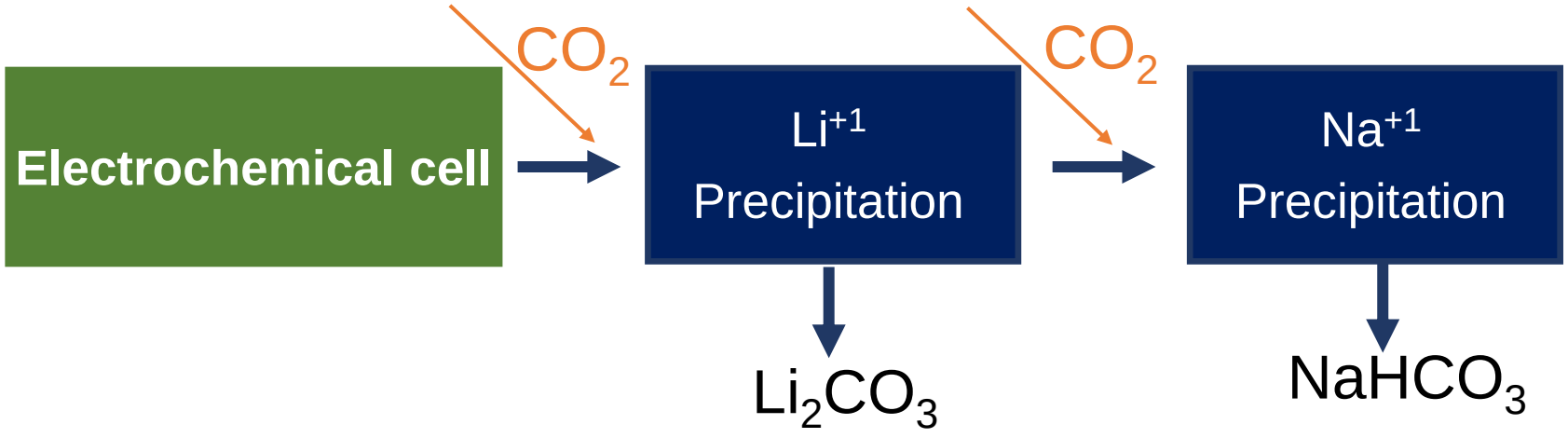

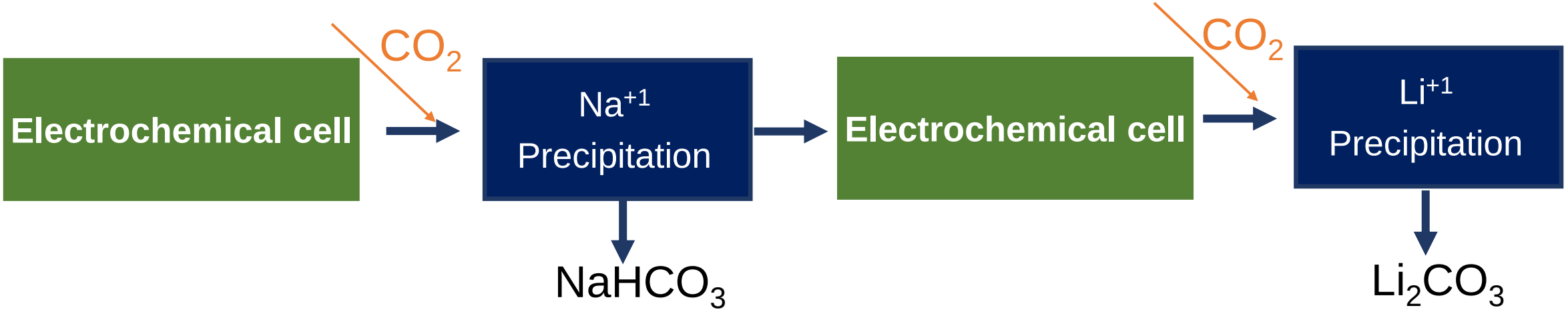

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