

Realizing CO₂ Emissions Reduction in Lime and Soda Ash Manufacturing through Anion Exchange

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Supplementary Information

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1. Assumptions around Sodium Hydroxide

As one could expect, the use of sodium hydroxide is the main source of GHG emissions in the evaluation of the carbon footprint of the process. The main reason for that is the relatively high energy intensity of the NaOH production process. The chlor-alkali process uses a brine of NaCl, obtained from seawater, to produce NaOH, Cl₂ and H₂ through electrolysis. The consumption of electricity in the process depends on the type of cell design used. The main types in the chlor-alkali industry are membrane cell, diaphragm cell or mercury cell, being this last one obsolete and discarded for our calculations. As per many multiproduct systems in the industry, the impact derived from the electrolytic manufacturing is usually allocated among the main products: sodium hydroxide, chlorine, and hydrogen. An economic allocation,¹ i.e., allocation of impact per economic flows of the process, instead of mass allocation seems appropriate in this case due to the presence of the lightweight but valuable hydrogen by-product. Energy allocation is not possible either, since NaOH and Cl₂ are not energy products. Only membrane chlor-alkali processes were considered in the calculations, since it is the main technology used by the industry: up to 85% of the current chlor-alkali plants use membrane cells.² In any case, the process is extremely dependent on the impact associated to the electricity fed to the cell. Consequently, two main sources of NaOH were considered:

- *Commercial NaOH*, which is the alkali produced under current supply schemes. This would imply that the carbon intensity of electricity used in the electrolytic cell is the current European average emissions from the grid. For membrane cell-based manufacturing, the carbon footprint of sodium hydroxide is around 0.78 kg CO₂eq per kg, allocating 1.31 kWh of electricity at 0.386 kg CO₂eq per kWh for the European average. These emissions correspond to 65% of the total emissions associated to sodium hydroxide production (data from ecoinvent).³
- *Renewable NaOH*. This is the alkali produced under hypothetical future energy schemes, in which the source of electricity can be considered 100% renewable. This assumption is in line with future energy market prospects; in Europe, more than 50% of electricity would be produced from renewable sources by year 2030, and more than 90%-95% by year 2050.⁴

The chart in Figure S1 shows the evolution of the carbon footprint of sodium hydroxide over recent periods according to the evolution of the average GHG emissions associated to electricity generation in Europe. The use of 100% renewable energy (wind in this case) allows a further reduction down to 0.313 kgCO₂ per kg of sodium hydroxide.

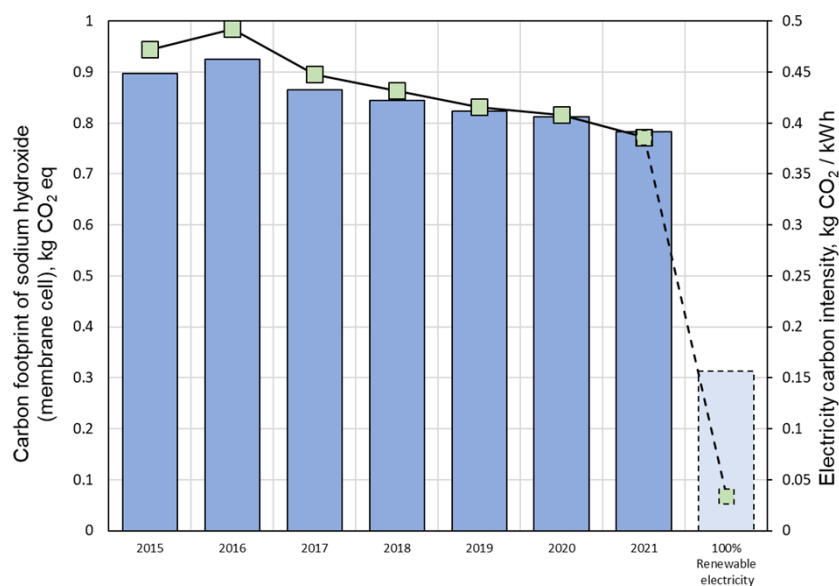


Figure S1: Evolution of the carbon footprint of sodium hydroxide produced in membrane electrolytic cells (bars, left y-axis) and carbon intensity of electricity generation electricity (green dots, right y-axis)

2. Sodium Carbonate

Sodium carbonate that is produced by the process after the reaction can be a substitute of commercially available sodium carbonate. This is a common approach in LCA, as the system would be expanded to include the “substituted” production process and an avoidance of emissions would then be allocated to the process, i.e. the avoided emissions are subtracted from the carbon footprint. The substituted source of sodium carbonate is commercial soda ash produced by the modified Solvay process, which would account for 0.306 kg CO₂eq per kg of Na₂CO₃·7H₂O (or 0.671 kg CO₂eq per kg of pure Na₂CO₃), produced as an avoided burden. In our case, the recommendation of ISO 14040³ was applied, i.e. the system was expanded applying substitution of co-products, as our main interest lies on the maximum potential of emissions reduction and not on product-specific footprint.

The LCA method is, in any case, attributional from the life cycle perspective. This means that the changes introduced in the process are marginal to the economic system and that the process would not significantly produce significant changes in the background system. So, all technosphere flows can be attributed to an impact on global warming measured as a carbon footprint. This approach was considered appropriate since the technology is still in a very early development stage.

3. Recycling sodium carbonate back into sodium hydroxide

Sodium carbonate recycling into sodium hydroxide can be driven thermally, through its direct customization, as in the direct air capture approach of Carbon Engineering,⁵ or through an electrolytic process,⁶ which was proposed in 1993 to decouple sodium hydroxide and chlorine markets. Due to the interest in driving a cleaner process, we opt to model the electrolytic approach, as it is easily integrated with renewable energy sources or, as for sodium hydroxide, the cleaner electricity market can drive lower emissions in future applications.

Process inventories for sodium hydroxide and the “substituted” commercial sodium carbonate were taken fromecoinvent, while the electrolytic regeneration of sodium hydroxide from sodium carbonate was modelled in a previous publication.⁷ The mass and energy balance per tonne of sodium carbonate fed to the electrolytic cell is shown in **Table S1**.

Table S1: Inputs and outputs for the electrolytic regeneration of solid NaOH from Na₂CO₃

Inputs	Outputs
Na ₂ CO ₃ : 1 kg	1.28 kg of 50% w/w NaOH solution
Water: 8.1 L	0.25 – 0.35 kg CO ₂ (150 bar, to storage)
Electricity: 0.59 kWh	4.5 L wastewater
Heat:	
8.7 MJ (solid NaOH)	
4.3 MJ (50% NaOH)	

Recent developments for direct air capture coupled to the electrolytic regeneration of sodium hydroxide from sodium carbonate shows an experimental potential energy consumption of 374 kJ/mol of captured CO₂ and a ~60% CO₂ capture efficiency,⁸ lower than the 85% CO₂ efficiency reported in other studies.⁷ This leads to different CO₂ removal potential (0.35 kg CO₂/kg of Na₂CO₃ for the highest efficiency, and 0.25 for the lower value). The heat consumption for evaporation of the water content, if solid NaOH is to be produced, can be halved as a concentration of 50% can be used in the anion exchange process.

Assuming a zero burden to CO₂ stored, or, in other words, assuming that all the impact is allocated to the regenerated sodium hydroxide, the impact of the regeneration process is 0.92 kg CO₂ per kg of regenerated sodium hydroxide, or 0.58 kg CO₂ if renewable electricity is assumed.

The cost of this process was calculated assuming \$10/t for transporting and storing CO₂ underground,⁹ and an electricity cost of 590 kWh/ton of Na₂CO₃ and 430 MJ/ton heating from natural gas.

4. Calculating Equipment Cost

The cost of the equipment was calculated using an exponential function as a function of the equipment size.

$$C_e = a + bS^n \quad (1)$$

Where C_e is the purchased equipment cost on a U.S. dollar basis of 2007 (CEPCI = 509.7), a and b are cost constants, S is the size parameter, and n is the exponent value. This correlation is valid only between a certain range of size of the equipment, S_{Lower} and S_{Higher} .

Table S2: Constants used in calculating equipment cost.

Equipment	Unit of S	S_{Lower}	S_{Higher}	a	b	n
Reactor	Volume, m ³	0.5	25	11000	76000	0.4
Conveyor belt	Length, m	10	500	36000	640	1
Elevator	Height, m	10	30	15000	2300	1
Pump	Flow m ³ /h	0.2	126	6900	206	1
Pump Driver	Power, kW	1	2500	-950	1770	0.6
Dryer	Area, m ²	11	180	13000	9100	0.9
Evaporator	Area, m ²	11	640	280	30500	0.55
Filter press	Capacity, m ³	0.4	1.4	110000	77000	0.5
Propeller	Power, kW	5	75	15000	990	1
Tank	Volume, m ³	10	4000	5000	1400	0.7
Blower	Flow, m ³ /h	200	50000	3800	49	0.8
Compressor	Power, kW	93	16800	220000	2300	0.75

Table S3: Yearly Producer Price Indices for Europe and U.S., Chemical Engineering Plant Cost Index, and exchange rates USD/EUR

Year	PPI Cement (US)	PPI Industry (Europe)	USD/EUR	CEPCI
2011	188.5		1.39	586
2012	190.6	99.8	1.29	585
2013	199.3	100.6	1.33	567
2014	208.1	99.8	1.11	576
2015	223.4	100	1.11	557
2016	235.2	99.1	1.13	542
2017	246	99.4	1.18	567.5
2018	252.1	101.1	1.12	603.1
2019	258.1	105	1.14	607.5
2020	260.7	107.5	1.18	596.5
2021	271	110.9	1.11	701.4

Table S4: Experimental data from¹⁰ showing 71 different starting composition of H₂O, NaOH, and CaCO₃ along with the conversion efficiency.

ID	H ₂ O (g)	NaOH (g)	CaCO ₃ (g)	H ₂ O (wt.%)	NaOH (wt.%)	CaCO ₃ (wt.%)	Conversion (%)
1	67.53	46.05	10.03	54.6	37.3	8.1	96
2	63.02	56.04	10.02	48.8	43.4	7.8	95.6
3	223.32	100.02	10	67	30	3	93
4	135.03	92.17	10	56.9	38.9	4.2	90.6
5	15.04	12.01	9.98	40.6	32.4	27	86
6	10.03	10.03	10.06	33.3	33.3	33.4	83.7
7	45.04	36.08	10.06	49.4	39.6	11	81.1
8	20.06	12.06	10	47.6	28.6	23.7	78.7
9	20.08	19.98	9.89	40.2	40	19.8	78.5
10	30.04	24.03	9.97	46.9	37.5	15.6	78.1
11	60.03	30.07	10.08	59.9	30	10.1	78.1
12	12.07	12.07	10	35.4	35.4	29.3	77.7
13	15.04	10.05	9.98	42.9	28.7	28.5	73.8
14	30.01	20.04	10	50	33.4	16.7	70.6
15	40.04	25.04	10.06	53.3	33.3	13.4	70
16	87.53	27.51	10.02	70	22	8	69.3
17	25	15.06	10.03	49.9	30.1	20	69.2
18	20.06	14.98	10.08	44.5	33.2	22.3	69.1
19	8.02	8.06	10.02	30.7	30.9	38.4	69
20	15.05	15.01	9.99	37.6	37.5	24.9	67.8
21	40	20.01	9.97	57.2	28.6	14.2	67.4
22	13.5	11.99	10.03	38	33.8	28.2	66.3
23	12.09	9.99	9.97	37.7	31.2	31.1	62.8
24	7.03	8.03	10.02	28	32	40	61.4
25	14.06	12.98	9.99	38	35.1	27	59.6
26	10.02	8.05	10.03	35.7	28.6	35.7	58.5
27	10.05	12	10.02	31.3	37.4	31.2	57.6
28	30.02	15.04	10.01	54.5	27.3	18.2	55.2
29	8.06	10.07	10.07	28.6	35.7	35.7	53.3
30	15.03	8.01	9.98	45.5	24.3	30.2	52.5
31	20.02	13.02	10.04	46.5	30.2	23.3	52.2
32	15.09	11.06	10.04	41.7	30.6	27.7	51.9
33	12.02	8.08	10.03	39.9	26.8	33.3	51.9
34	9.98	11.44	10	31.8	36.4	31.8	51.1
35	15.02	20.06	10.01	33.3	44.5	22.2	48.5
36	25.01	13	10.05	52	27	20.9	47.4
37	25.01	11.99	12.03	51	24.5	24.5	46.1
38	15.04	13.09	10.02	39.4	34.3	26.3	45.9
39	50.03	64.99	10	40	52	8	45.4
40	30.06	11.99	10	57.8	23	19.2	41.7
41	20	11.04	10.05	48.7	26.9	24.5	40.8
42	40.16	15.05	10.04	61.5	23.1	15.4	39.4
43	26.05	13.02	10.02	53.1	26.5	20.4	38.2
44	7.02	10.07	10.02	25.9	37.1	37	31.9
45	20.01	8.05	10.02	52.5	21.1	26.3	31.9
46	5.02	12.06	10.02	18.5	44.5	37	31.8
47	12.05	15.05	10.09	32.4	40.5	27.1	30.1
48	40.05	12.08	10.07	64.4	19.4	16.2	29.4
49	50.02	15.03	10.07	66.6	20	13.4	28.7
50	10.03	15	10.01	28.6	42.8	28.6	28.5
51	21.35	35.33	10.03	32	53	15	27.7
52	10.04	15	12.09	27	40.4	32.6	26.7
53	6.06	14.98	10	19.5	48.3	32.2	26.3

54	25.05	8.04	10.14	57.9	18.6	23.5	21.1
55	13.51	15.98	9.98	34.2	40.5	25.3	20.7
56	50	12.03	9.99	69.4	16.7	13.9	19.8
57	30.02	10.03	10.04	59.9	20	20	19.7
58	5.02	10.05	10.01	20	40.1	39.9	16.5
59	30.01	8.04	9.99	62.5	16.7	20.8	16.1
60	10.06	16.95	10.03	27.2	45.8	27.1	15.4
61	8.04	15.04	9.99	24.3	45.5	30.2	13.5
62	4.03	12.06	10.02	15.4	46.2	38.4	12.3
63	40.04	10.06	10.03	66.6	16.7	16.7	12.1
64	5.06	8.03	10.04	21.9	34.7	43.4	12
65	7.07	11.99	9.98	24.3	41.3	34.4	11.1
66	4.1	15.02	10.01	14.1	51.6	34.4	11.1
67	4.03	9.96	10.05	16.8	41.4	41.8	10
68	40	8	9.99	69	13.8	17.2	7.5
69	50.03	10.03	10.05	71.4	14.3	14.3	7.3
70	10.12	19	10.03	25.8	48.5	25.6	7.2
71	50	7.99	10	73.5	11.8	14.7	3.5

5. Supplementary Figures

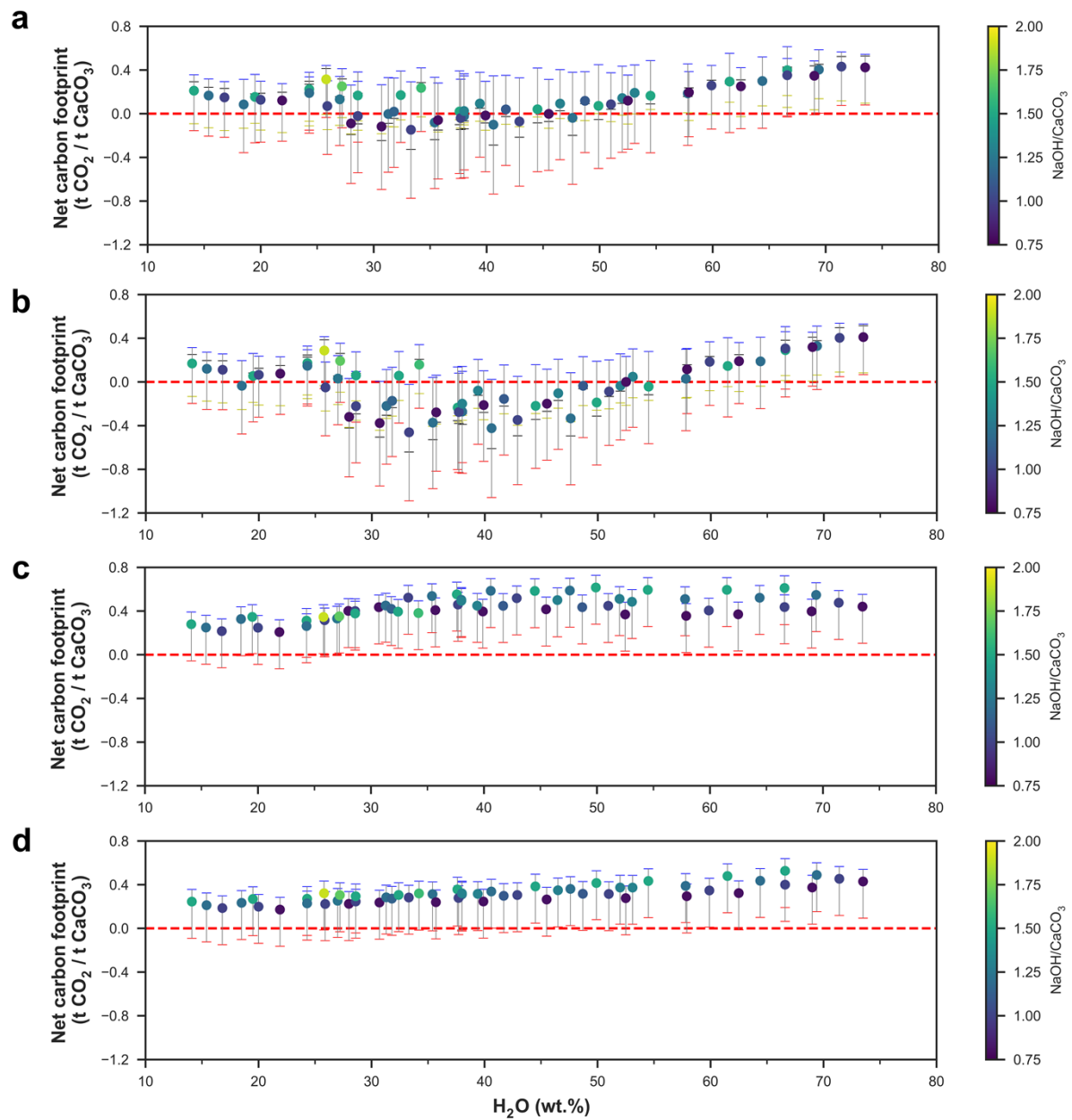


Figure S2: Net carbon footprint of process A expressed in $t\ CO_2$ per $t\ CaCO_3$ processed compared to current CaO and Na_2CO_3 production scenarios. The four materials cases are plotted in (a) commercial $NaOH$ and commercialised Na_2CO_3 , (b) renewable $NaOH$ and commercialised Na_2CO_3 , (c) commercial $NaOH$ and recycled Na_2CO_3 , and (d) renewable $NaOH$ and recycled Na_2CO_3 . The solid circles show representative net carbon footprint. The coloured dashes on the error bar represent the following types of carbon footprint used while calculating the net carbon footprint: both $NaOH$ and Na_2CO_3 minimum carbon footprint – blue, both $NaOH$ and Na_2CO_3 maximum carbon footprint – red, $NaOH$ minimum and Na_2CO_3 maximum carbon footprint – black, and finally, $NaOH$ maximum and Na_2CO_3 minimum carbon footprint – yellow. The colour of the points in all the figures represents the $NaOH$ and $CaCO_3$ ratio in the mix design, as shown in the colour bar.

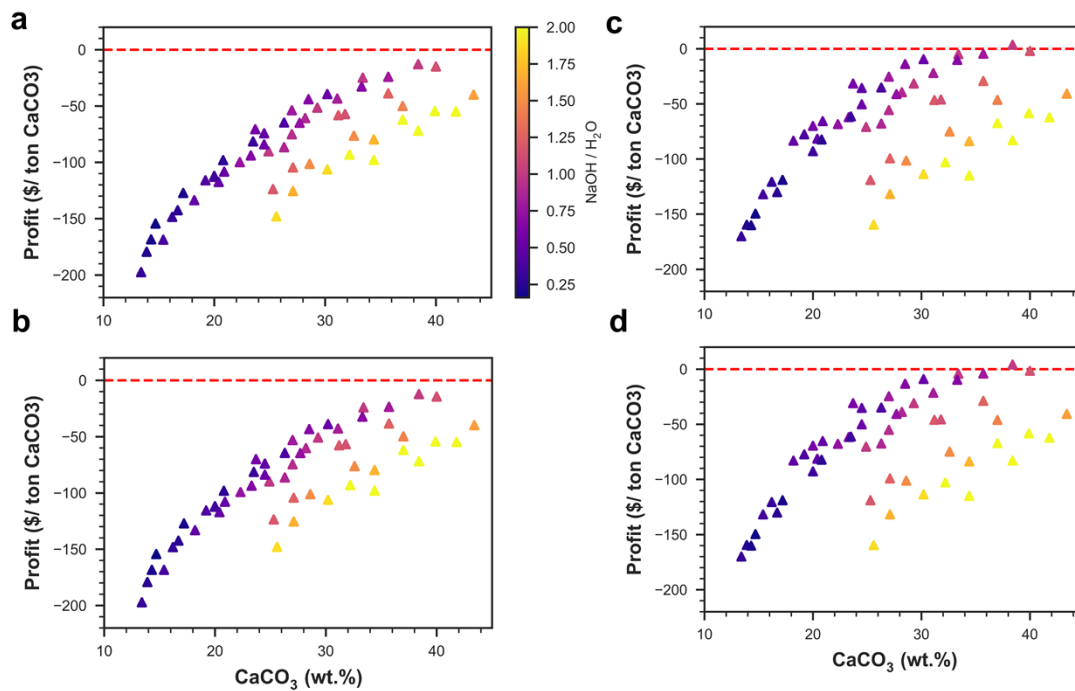


Figure S3: Profitability of the anion exchange process for different mix designs. Process A was not profitable for both cases (a) commercial NaOH and commercialised Na₂CO₃, (b) renewable NaOH and commercialised Na₂CO₃. Process B turned a small profit for both cases (c) commercial NaOH and commercialised Na₂CO₃, (d) renewable NaOH and commercialised Na₂CO₃.

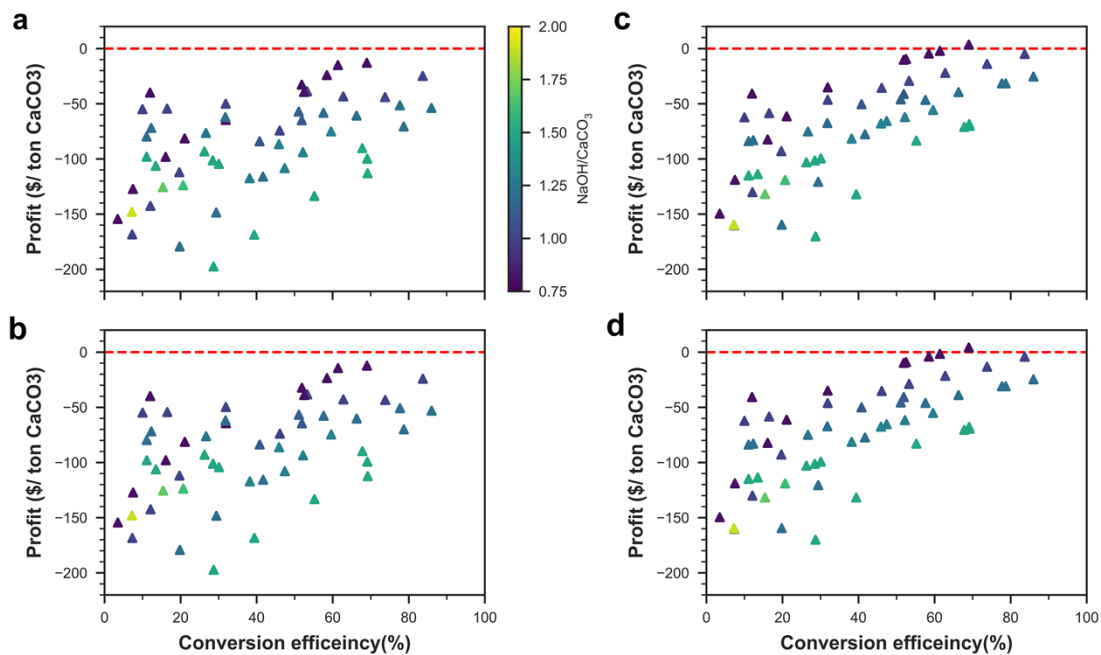


Figure S4: Profitability of the anion exchange process vs. conversion efficiency. Process A was not profitable for both cases (a) commercial NaOH and commercialised Na₂CO₃, (b) renewable NaOH and commercialised Na₂CO₃. Process B turned a small profit for both cases (c) commercial NaOH and commercialised Na₂CO₃, (d) renewable NaOH and commercialised Na₂CO₃.

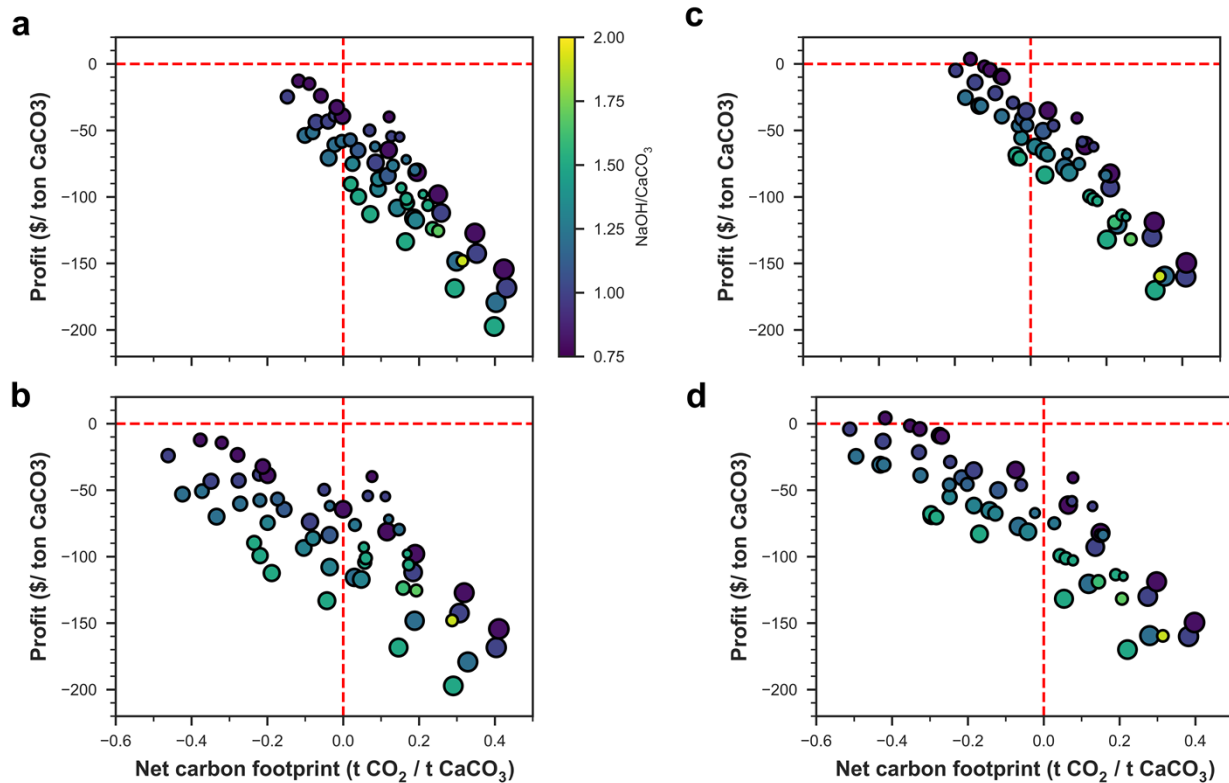


Figure S5: Profitability vs net carbon footprint of the anion exchange process. Process A - (a) commercial NaOH and commercialised Na_2CO_3 , (b) renewable NaOH and commercialised Na_2CO_3 . Process B - (c) commercial NaOH and commercialised Na_2CO_3 , and (d) renewable NaOH and commercialised Na_2CO_3 . The colour of the scatter plot depends on the NaOH to CaCO_3 ratio in the mix design, whereas the sizes of the scatter points are proportional to the water content in the mix design.

6. References

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