LIMENET - Calcium Bicarbonate Stability	*Document information* BIC. STAB. 001 - A	*Date* April 2023
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Draft technical report

CARBON STORAGE

BY

LIMENET

Abstract

This draft technical report discusses the LIMENET concept for sequestering CO_2 in seawater and, at the same, contrasting its acidification through the addition of calcium bicarbonates [$Ca(HCO_3)_2$]. It also presents measurements of the stability in seawater of calcium bicarbonate solutions discharged from a LIMENET prototype plant located in La Spezia (Italy), performed at the chemistry laboratories of the Politecnico di Milano. Under appropriate conditions (ratios of CO_2 and $Ca(OH)_2$, degree of dilution with seawater, etc.), the solutions are stable against calcium carbonate precipitation and degassing of CO_2, for a period of up to several weeks. The results agree with recent literature reports by Moras et al. (Biogeosciences Discuss. [preprint], December 2021, https://doi.org/10.5194/bg-2021-330) and by Hartmann et al. (Biogeosciences Discuss. [preprint], June 2022, https://doi.org/10.5194/bg-2022-126.).

Document Information

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Summary

CARBON STORAGE by LIMENET

1 Introduction

This preliminary document[1] illustrates the LIMENET approach to capture and store atmospheric or emitted CO_2 (e.g., from an industrial process). LIMENET is an evolution of the recently proposed Buffered Accelerated Weathering of Limestone (BAWL)[2]. The CO_2 storage process consists of introducing CO_2 into a reactor with seawater, followed by the injection of slaked lime [calcium hydroxide $Ca(OH)_2$] to buffer the acidity of the solution, bringing the pH close to that of the natural seawater value (ca. 8.2). The reaction between the slaked lime and carbon dioxide produces calcium bicarbonate, according to the equation:

$$CO_2(g) + Ca(OH)_2(aq) \text{ ® } Ca(HCO_3)_2(aq) + H_2O(l).$$

The addition of calcium bicarbonate into seawater increases its alkalinity and buffering power, counteracting the negative effects of ocean acidification, one of the first consequences of high concentration of CO_2 in the atmosphere. However, recent work by Moras et al.[3] and by Hartmann et al.[4] has demonstrated that, for such addition of alkalinity to be effective, it is crucial to avoid the precipitation of calcium carbonate, as this would lead to the release of CO_2 back into the atmosphere:

$$Ca(HCO_3)_2(aq) \text{ ® } CaCO_3(s) + CO_2(g) + H_2O(l).$$

The present document presents the results of a series of preliminary tests and measurements, performed both at the site of a LIMENT pilot plant installed in the harbour of La Spezia (Italy) and at the chemistry laboratories of the Politecnico di Milano. The principal aim of the experiments was precisely to assess the stability of calcium bicarbonate in seawater treated according to the LIMENT process.

1 The document has been written in few days by LIMENET S.R.L. BENEFIT for the Frontier proposal and lacks the necessary maturation and revision: it shows the raw results of the ongoing tests and trays to draw some preliminary conclusion. An article will be written by the professors and PhDs of the Politecnico di Milano at the end of the experiments.

[2] Caserini, S.; Cappello, G.; Righi, D.; Raos, G.; Campo, F.; De Marco, S.; Renforth, P.; Varliero, S.; Grosso, M. Buffered Accelerated Weathering of Limestone for Storing CO2: Chemical Background. *International Journal of Greenhouse Gas Control* **2021**, *112*, 103517. https://doi.org/10.1016/j.ijggc.2021.103517.

[3] Moras, C. A.; Bach, L. T.; Cyronak, T.; Joannes-boyau, R.; Schulz, K. G. Ocean Alkalinity Enhancement - Avoiding Runaway CaCO3 Precipitation during Quick and Hydrated Lime Dissolution. *Biosciences Discussions* **2021**, No. December. https://doi.org/10.5194/bg-2021-330

[4] Hartmann, J.; Suitner, N.; Lim, C.; Schneider, J.; Marín-samper, L. Stability of Alkalinity in Ocean Alkalinity Enhancement (OAE) Approaches - Consequences for Durability of CO2 Storage. **2022**, No. June, 1–29. https://doi.org/10.5194/bg-2022-126

1.1 Definitions

Alkalinity: a measure of the acid-neutralising capacity of water, usually determined by titration with a strong acid to the endpoint of the acid–base reaction[5].

Atmospheric carbon dioxide: Carbon dioxide in the atmosphere at respective concentrations (concentration can vary across daytime, month and year. For indicative purposes, the global monthly mean in August 2020 was 409.50 ppm according to NOAA (2020))

Bicarbonate: a salt characterized by the presence of the HCO_3^- anion. Bicarbonates include calcium bicarbonate ($Ca(HCO_3)_2$) and magnesium bicarbonate $Mg(HCO_3)_2$.

Calibration: a set of operations that established, under specified conditions, the relations between values indicated by a measuring instrument or measuring system, or values represented by a material measure, or a reference material and the corresponding values of a quantity realized by a reference standard.

Carbon Dioxide Removal (CDR): anthropogenic activities that seek to remove CO_2 from the atmosphere and durably store it in geological, terrestrial or ocean reservoirs, or in products. CO_2 is removed from the atmosphere by enhancing biological or geochemical carbon sinks or by direct capture of CO_2 from air and storage (DAC+S).

Carbonate Minerals: minerals characterized by the presence of the carbonate ion (CO_3^{2-}) in their structure. Carbonate minerals include calcite ($CaCO_3$), aragonite ($CaCO_3$), magnesite ($MgCO_3$), siderite ($FeCO_3$), ankerite ($Ca(Fe,Mg,Mn)(CO_3)_2$), and dolomite ($CaMg(CO_3)_2$).

CO2 Storage: the storage of CO_2 in the sea, mainly in the form of bicarbonates at the natural seawater pH value of 8.2.

Monitoring Period: The time interval dedicated to verify that there is bicarbonate stability.

Ω: the saturation state of seawater with respect to aragonite can be defined as the product of the concentrations of dissolved calcium and carbonate ions in seawater divided by their product at equilibrium: $([Ca^{2+}] \times [CO_3^{2-}]) / [CaCO_3] = \Omega$; where dissolved calcium $[Ca^{2+}]$ is the seawater concentration of dissolved calcium ions, $[CO_3^{2-}]$ is the seawater concentration of carbonate ions, $[CaCO_3]$ is the solubility of aragonite in seawater, and Ω is the calculated saturation state[6].

pH: pH is a measure of the hydrogen ion concentration in solution and is also referred to as the degree of acidity or alkalinity[7].

[5] https://www.sciencedirect.com/science/article/pii/B9780444531599000036
[6] http://www.soest.hawaii.edu/mguidry/Unnamed_Site_2/Chapter%205/Figures/Box3SeawaterSaturationState.pdf
[7] https://www.sciencedirect.com/science/article/pii/B9780444531599000036

TIC: total inorganic carbon (IC), carbonate, bicarbonate, and dissolved carbon dioxide (CO_2).

Uncertainty: parameter, associated with the result of the determination of a quantity, that characterises the dispersion of the values that could reasonably be attributed to the particular quantity, including the effects of systematic as well as of random factors, expressed in per cent, and describes a confidence interval around the mean value comprising 95 % of inferred values taking into account any asymmetry of the distribution of values.

1.2 Scope of work

The research aims to demonstrate the chemical CO_2 storage stability over a long period. Indeed, even if the concept of ocean DIC (Dissolved Inorganic Carbon) lifetime is a well-established theory and is accepted within the community to lie somewhere between 10,000 and 100,000 years[8] we have decided to measure it and so reduce to zero the uncertainties for abiotic and secondary precipitation of $CaCO_3$.[9]

The bicarbonate stability study consists in a weekly continuous monitoring of the TIC concentration in the LIMENET discharged high alkalinity treated solution for at least three months. Namely, we store the treated solution in several open-air glass containers, diluted with fresh seawater to reproduce the LIMENET plume's dilution after the discharge (See Appendix 1).

The research is divided into two phases:

1) First phase:
   Identify the optimal ratio between CO_2 and H_2O (seawater) flowing in the LIMENET storage section, evaluate the storage efficiency, the properties of the discharged water, and precipitation of the carbonates through different dilution ratios.
   The glass containers used for the experiments were small borosilicate containers filled with 0.5 litre of the alkaline seawater taken at the discharge point, mixed with fresh seawater in different proportions to simulate the dilution behaviour inside the plume.
2) Second phase:
   Evaluate the storage efficiency and precipitation of carbonates on a more realistic simulation. In this case the containers that will be used to store the alkaline seawater discharged by the LIMENET plant with different dilution ratios are 9 m^3 plastic swimming pools settled at La Spezia CSSN port.

[8] Caldeira and Rau, (2000) - Accelerating carbonate dissolution to sequester carbon dioxide in the ocean: Geochemical implications - https://doi.org/10.1029/1999GL002364
[9] https://carbonplan.org/research/cdr-verification/ocean-alkalinity-enhancement-mineral

2 Methods

The LIMENET pilot plant is located in La Spezia at CSSN (Liguria, Italy); the measurements reported in this document refer to experiments carried out from August to October 2022.

LIMENET process injects CO_2 into a seawater stream and adds $Ca(OH)_2$ to buffer the CO_2 until the discharged solution reaches the same pH of the untreated seawater.

Different ratios $H_2O:CO_2$ were tested injecting different flows of CO_2 inside a fix stream of seawater at 0.3 Mpa. A slurry of Ca(OH)2 was injected into the acidic stream of seawater and CO2 to reach the same pH of the fresh seawater (i.e. approx. pH 8) . The buffered alkaline solution were thus discharged into the sea. Different ratios $H_2O:CO_2$ were tested, namely 2000:1, 3000:1 and 4000:1 by weight. For each of these ratios the buffered alkaline solution discharged by the plant was diluted in different proportion with fresh seawater and put into glass containers along with a fresh seawater sample as blank reference. The dilution ratios, alkaline solution: fresh seawater used for each of the above mentioned cases were 1:1; 1:10; 1:20 and 1:100. The prepared samples were closed and transported by car from La Spezia to Politecnico laboratory in Milano without any thermostatic storage device.

2.1 LIMENET plant and Politecnico di Milano chemistry laboratory

2.1.1 La Spezia LIMENET plant

LIMENET prototype plant is located at La Spezia port (CSSN - 44.095863, 9.862471). Here it is studied the LIMENET concept for sequestering CO2 in seawater.

The process parameters of the treated water measured during the experiments are:

- pH[10]
- Temperature[11]
- Turbidity[12]
- CO_2 injection mass-flow[13]
- $Ca(OH)_2$ injection volumetric-flow[14]
- Water volumetric flow[15]
- Alkalinity[16]

[10] PI instruments
[11] PI instruments
[12] PI instruments
[13] Bronkhorst
[14] https://www.wmfts.com/it-it/marchi/pompe-watson-marlow/
[15] SMC
[16] Hanna instrument

The environmental weather conditions are measured by local weather station[17].

2.1.2 *Politecnico di Milano*

Politecnico di Milano chemistry department is located at Via L. Mancinelli 7, 20131 Milano, Italy (45.490111609405524, 9.227240290588668). Here is studied bicarbonate stability through time of LIMENET La Spezia plant.

The process parameters of the samples measured through time are:

- pH[18]
- Alkalinity[19]
- TIC[20]

Laboratory environment conditions are measured by an environmental condition sensor[21].

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[17] https://www.meteoapuane.it/50LASPEZIA/
[18] https://www.mt.com/it/it/home/products/Laboratory_Analytics_Browse/pH-meter/pH-meters/benchtop-pH-meter/sevenexcellence.html
[19] https://hanna.it/hi84531-minititolatore-per-analisi-di-alcalinita-titolabile-nellacqua
[20] https://fkv.it/prodotti/analisi-chimiche/analisi-toc-tox-eox-pox/multi-n-c-2100s-duo
[21] https://www.itsensor.it/sonda-di-qualita-aria-ambiente-voc-e-co2-con-uscita-modbus-cod-rlq-co2-modbus.html?gclid=EAIaIQobChMI8cHl0uvI-gIVTI1oCR3rIgzCEAYYASABEgINiPD_BwE

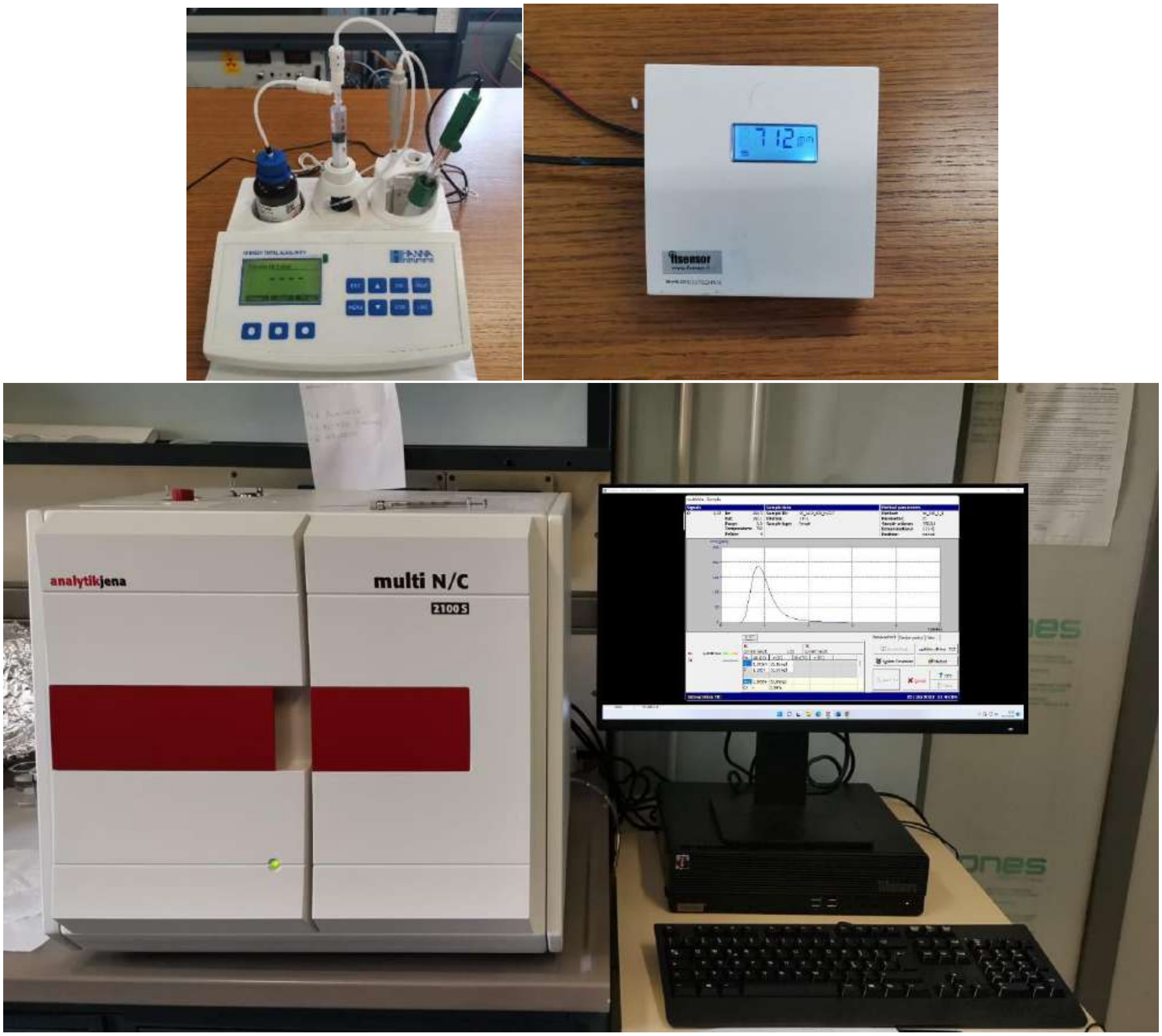


Figure 1 Politecnico di Milano, chemistry department instruments. Alkalinity (up-left), CO_2 ppm (up-right), TIC meter (down).

2.1.3 Calibration procedure

Instruments are calibrated according to procedure reported in appendix 1. For each instrument, calibration is repeated before starting the measurements of the weakly delivered samples.

2.2 First phase

In the preliminary phase, samples are prepared as it follows:

- Sea water is treated and diluted with the corresponding dilution parameters.
  500 ml samples in borosilicate glass containers (See Figure 2) are delivered to Politecnico di Milano chemical laboratory. The solutions are filtered and then analysed.

The initial analysis is carried out at least within 24 hours since the collection. When possible, the first measurement occurs within 5 hours and is repeated within 24 hours since the sampling, for sake of homogeneity. The analyses are repeated for one month on a weekly basis to assess any variations in the analysed parameters.

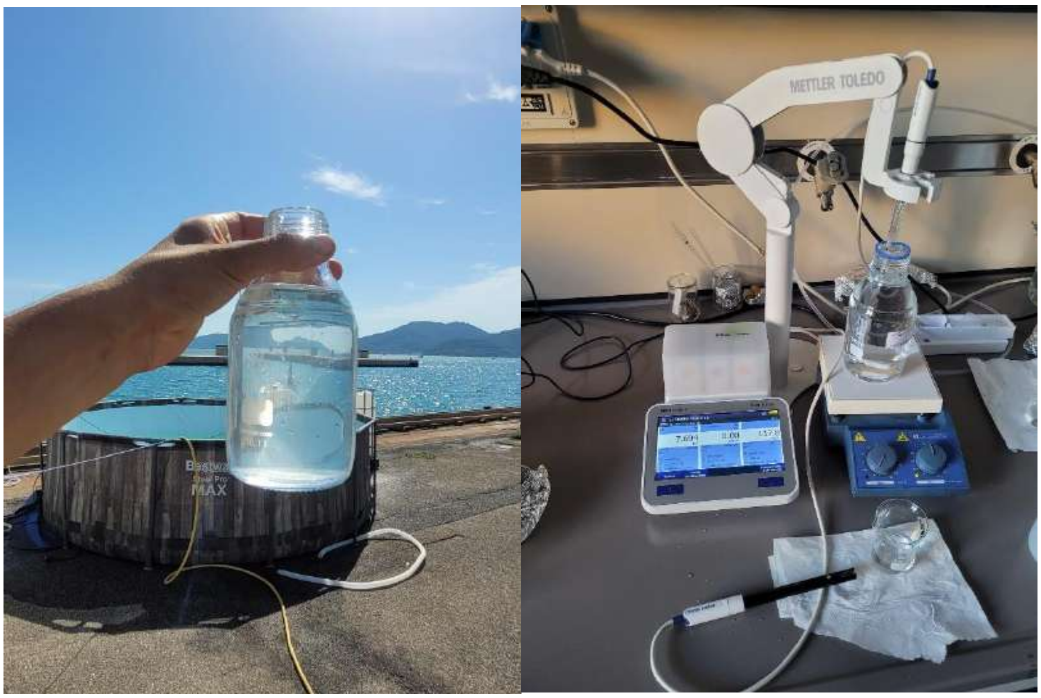


Figure 2 Sample of preliminary phase at La Spezia port (left), at Politecnico di Milano laboratory (right).

The analysis methodology involves the measurement of pH and conductivity, to verify their compatibility against the preliminary measurements carried out on the field. Each sample is filtrated with sieves of 2-3 µm porosity, to remove large particles that could affect the subsequent analyses. Moreover, the filtration allows for identifying the precipitates' nature and composition with X-ray diffraction analysis (XRD).

After the filtration, we measure the pH and the conductivity using electrode sensors, the alkalinity by titration with a 0.56%, solution of sulfuric acid and the total amount of inorganic carbon (TIC) obtained by conversion of inorganic carbon into CO_2 and stripping of the same, under nitrogen flow. After the filtration, the measurements are repeated the day after the arrival of the samples and then on a weekly basis for the entire duration of the experiment. The samples are kept open in the laboratory to allow them reaching the equilibrium of CO_2 exchange at the laboratory conditions (See Figure 3).

Figure 3 The samples kept open in the laboratory

As shown in the following table, twelve samples were analysed in this the preliminary phase of the project.

Table 1 Sample process parameters.

	Sample	*Water_CO_2 ratio*		
		2000	**3000**	**4000**
Dilution ratio	1:1	*Sample* 1	*Sample* 5	*Sample* 9
	1:10	*Sample 2*	*Sample 6*	*Sample 10*
	1:20	*Sample 3*	*Sample 7*	*Sample 11*
	1:100	*Sample 4*	*Sample 8*	*Sample 12*

2.2.1 Ω calculation

The estimation of Ω is performed using the software PHREEQC. The calculation of aragonite's Ω starts from a composition of natural seawater taken from the literature[22]. Then, we added to this composition the moles of carbon corresponding to carbon dioxide dissolved in the seawater (1 ton in 2000, 3000, and 4000 cubic meters diluted with the different ratios). We have also increased the amount of calcium corresponding to the amount of calcium hydroxide added (4% higher than the stoichiometric amount). Considering that the dosage of calcium hydroxide allows us to obtain

[22] https://images.peabody.yale.edu/publications/jmr/jmr03-02-04.pdf

a pH of treated water like that of the untreated seawater, the software automatically speciates the solution and calculates the saturation index of all the possible carbonate species.

Table 2 Mediterranean Sea water composition.

Mediterranean Sea water composition		
Br	0,000808511	
C(4)	0,002278689	
Ca	0,009982535	
Cl	0,535399154	
F	6,84211E-05	
K	0,00971867	
Mg	0,052324146	
Na	0,459160505	
S(6)	0,027572351	
Sr	0,000151792	
B	0,000420644	
Si Ar	0,41	
Ω Ar	2,57	
Si Calc	0,55	
Ω Calc	3,55	
Total CO2	2,28E-03	mg/kg
TIC	27,35	mg/kg
Alk	2,44E-03	eq/kg
Alk	122,06	mg/kg

Table 3 Ω value with different pH. See how Ω changes.

Ω - pH 8		*Water_CO_2 ratio*		
		2000	**3000**	**4000**
Dilution ratio	**1:1**	11,2	7,9	6,5
	01:10	3,9	3,5	3,2
	01:20	3,2	3,0	2,9
	01:100	2,7	2,6	2,6

Ω - pH 8.10		*Water_CO_2 ratio*		
		2000	**3000**	**4000**
Dilution ratio	**01:1**	14,1	10,0	8,1
	01:10	4,8	4,3	4,0
	01:20	4,0	3,7	3,5
	01:100	3,3	3,3	3,2

In Table 3, the Ω variation is reported as a function of pH.

2.2.2 *Remarks:*

1) At the collection site in La Spezia, the seawater has a pH oscillating between 8.0 and 8.1.
2) The LIMENET procedure aims at obtaining the same pH of the input water in the output.

3) The pH of the output water slightly oscillates around 8.1.
4) Due to this small oscillation, it is difficult to precisely confirm which is the final pH and so the calculated Ω of the discharging solution (See Figure 4 and Figure 5)

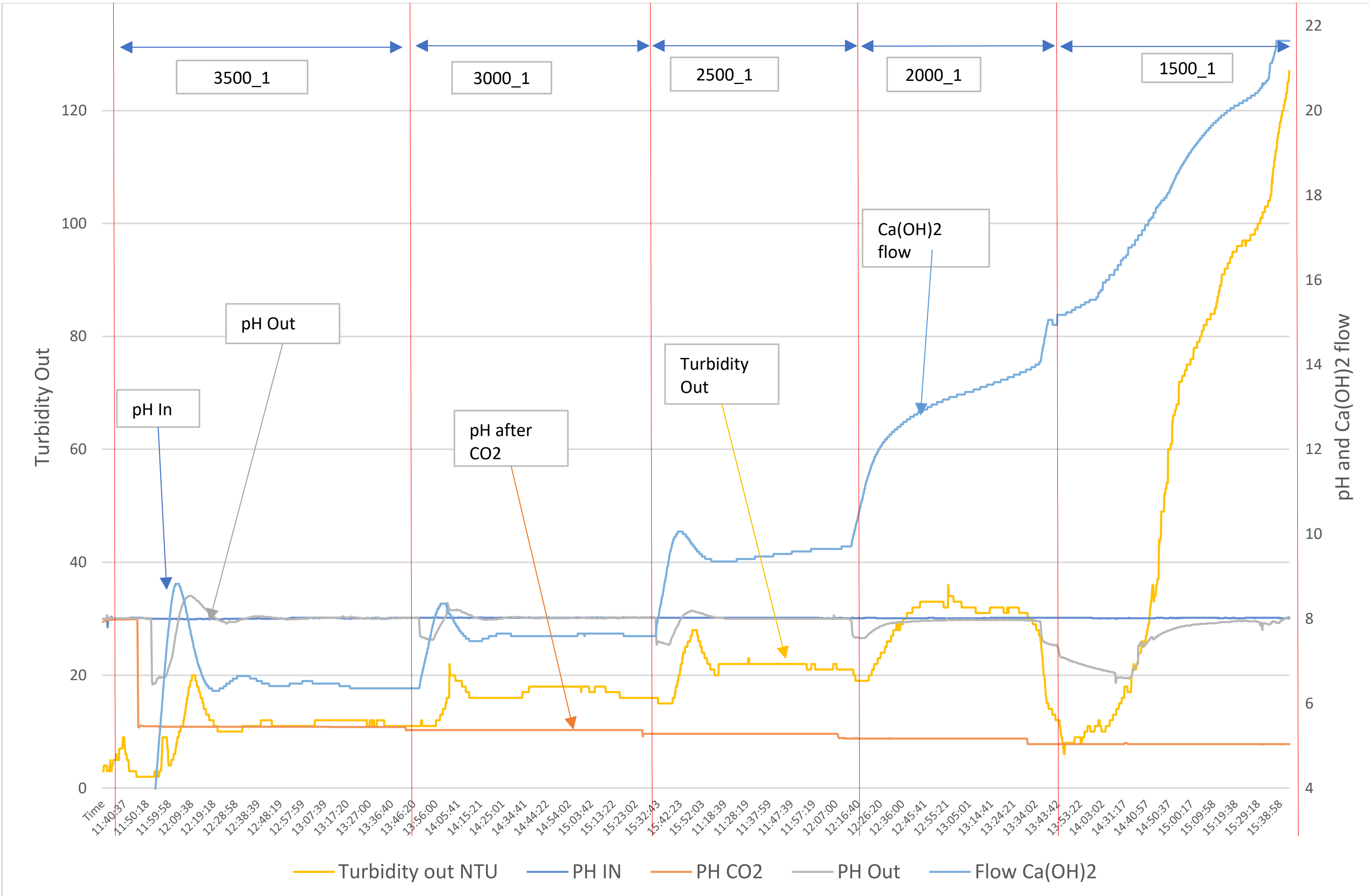


Figure 4 LIMENET industrial plant sample realizations (21-22/09/2022).

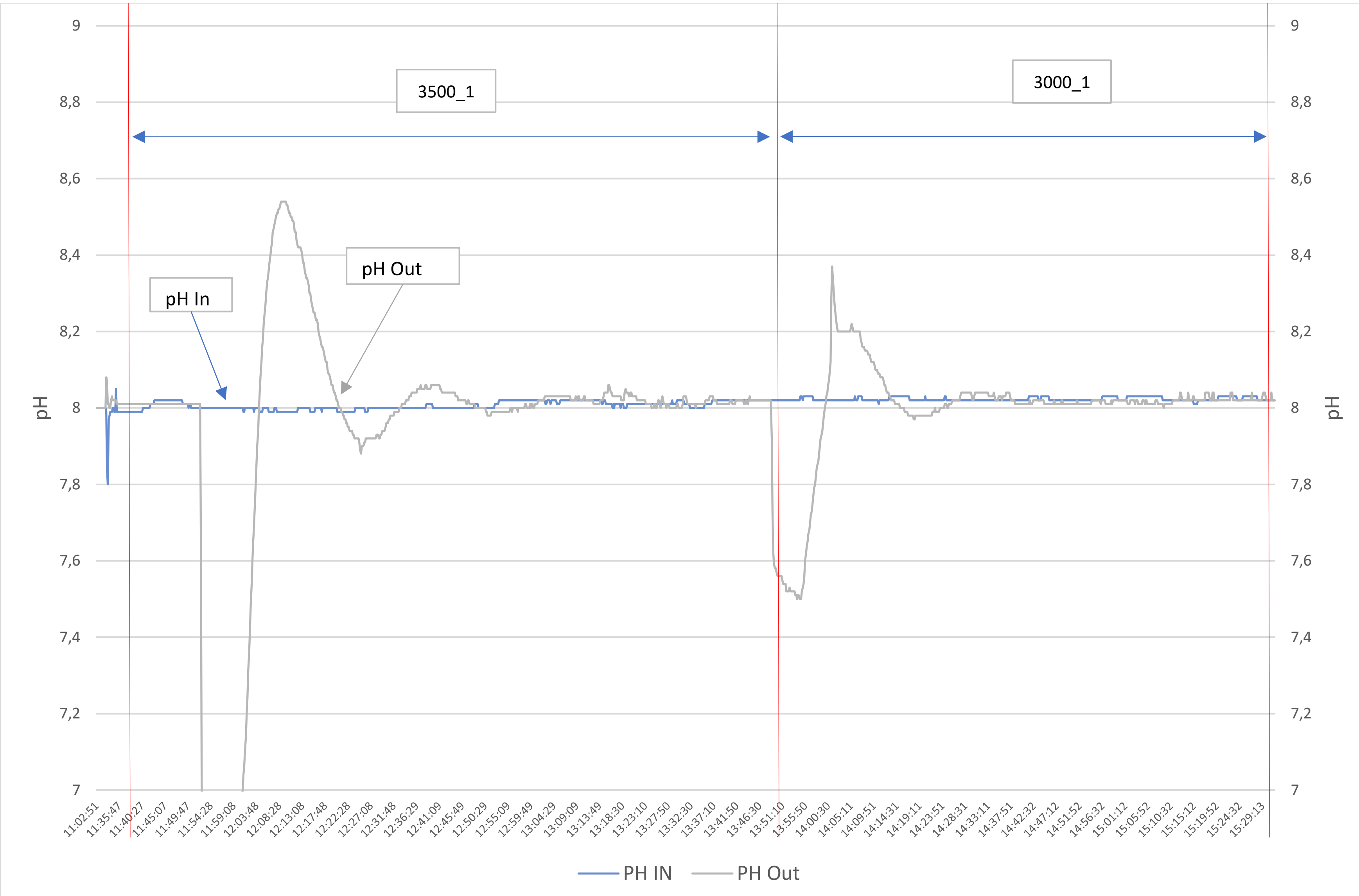


Figure 5 Details of pH stabilization after a step change in CO_2 injection flow in the seawater stream . This is due to the used PID parameters (21-22/09/2022).

2.2.3 Initial results

The results of the analyses carried out on the different samples (2000:1, 3000:1 and 4000:1) are given from Figure 6 to Figure 14.

2.2.3.1 Measurements

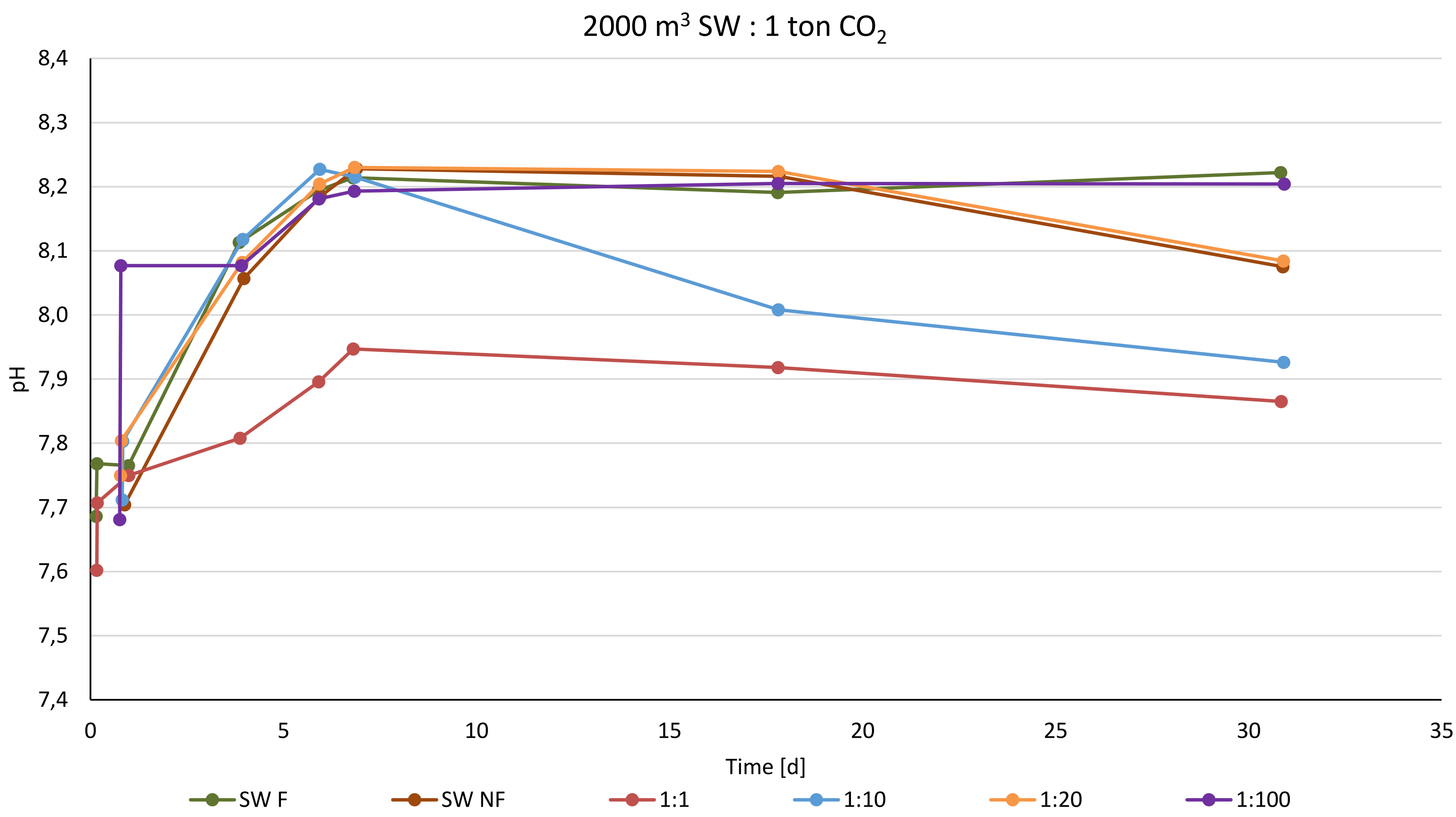


Figure 6 pH analysis. 2000_1 SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

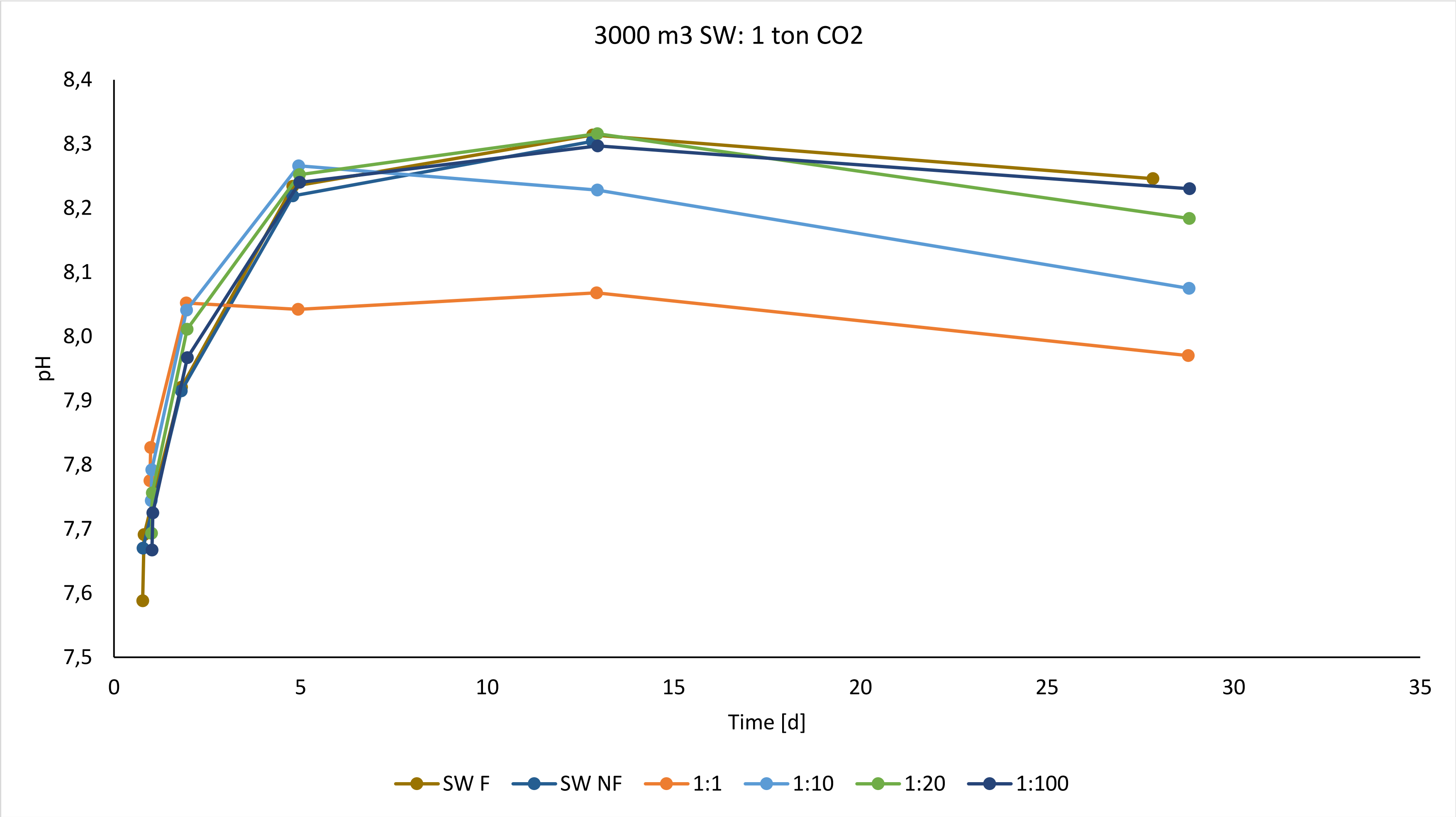


Figure 7 8 pH analysis 3000_1 SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

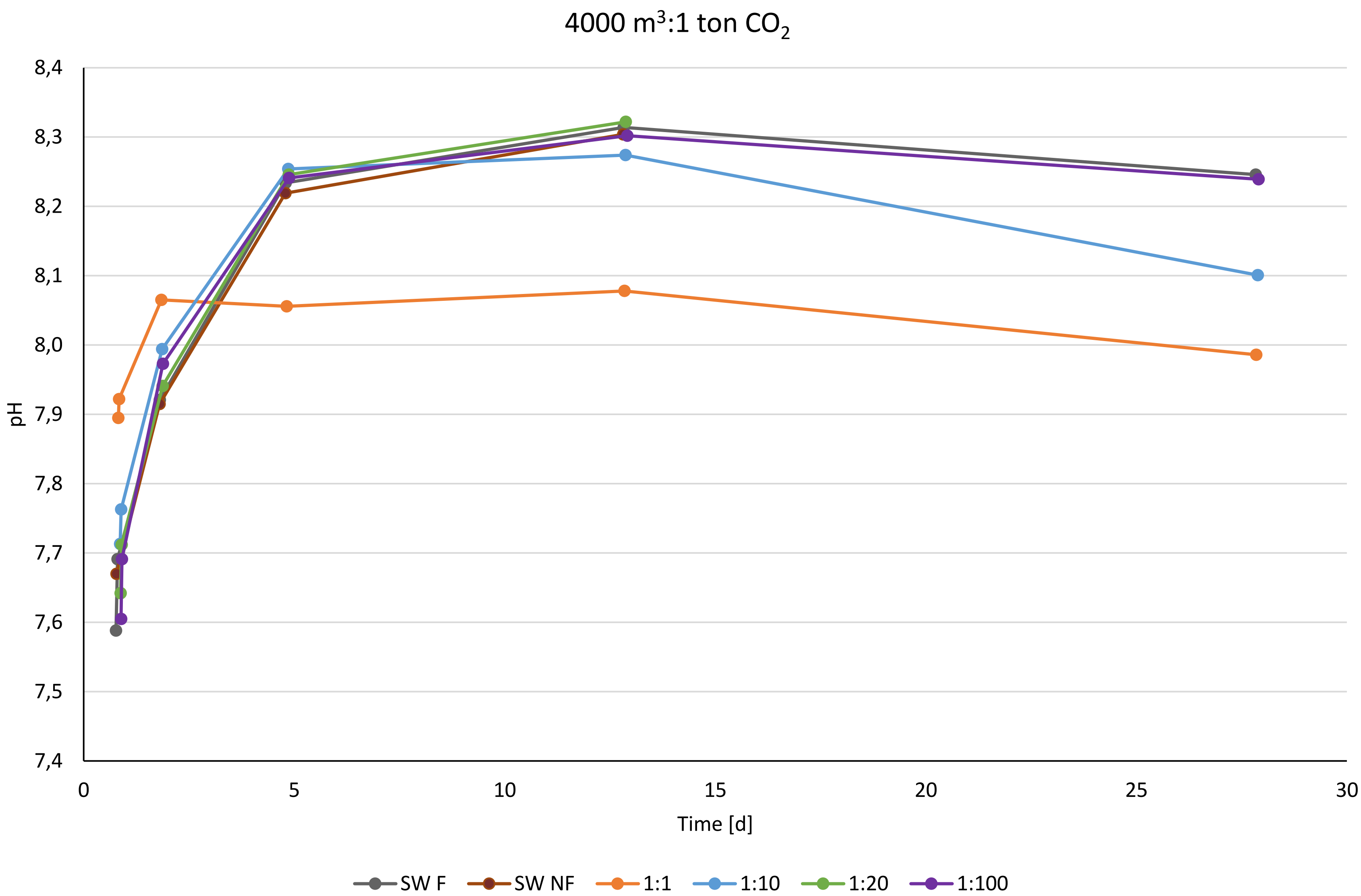


Figure 9: pH analysis 4000_1. SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

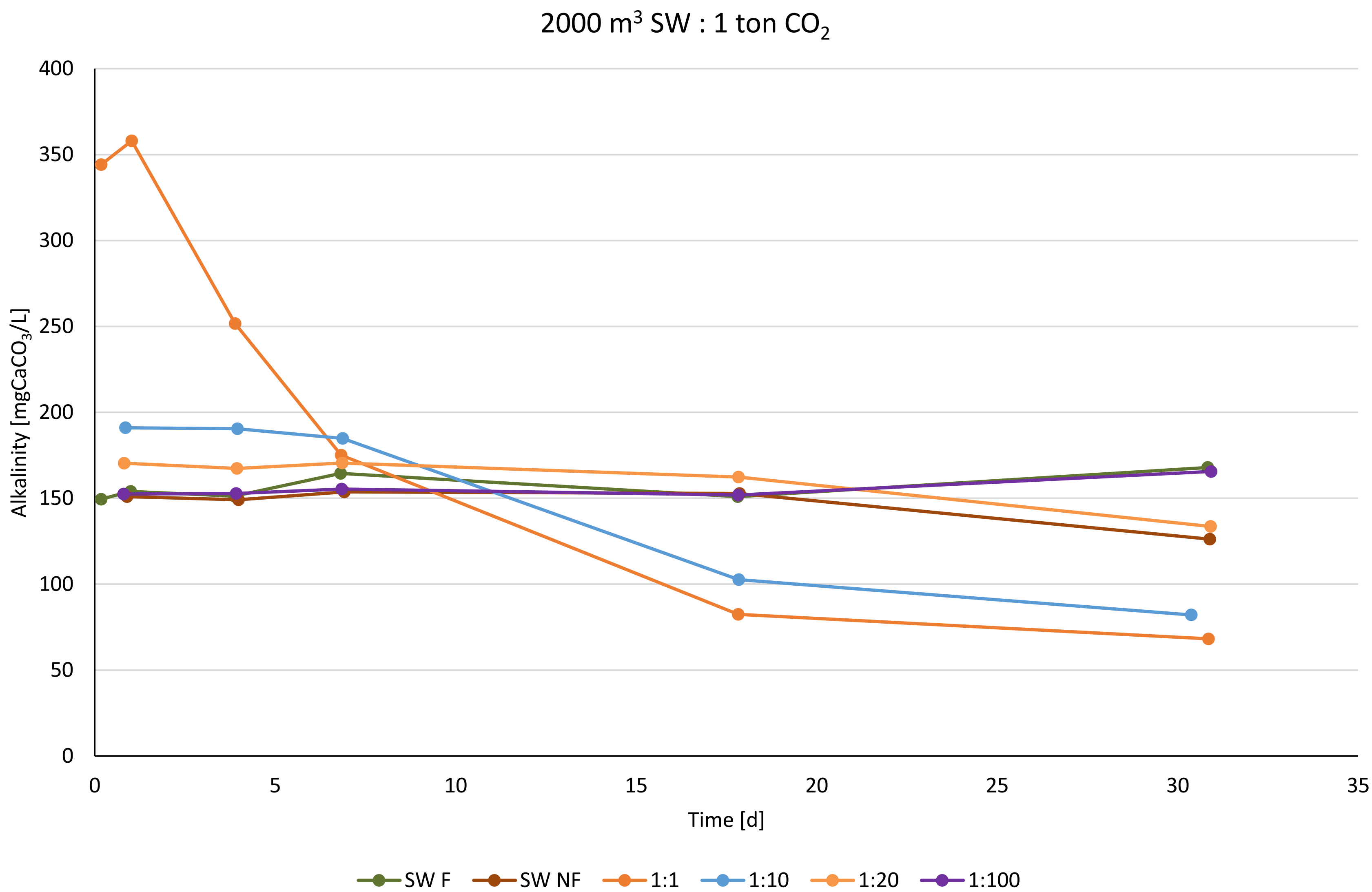

2000 m3 SW : 1 ton CO2
Alkalinity [mgCaCO3/L]
400
350
300
250
200
150
100
50
0
0
5
10
15
20
25
30
35
Time [d]
SW F
SW NF
1:1
1:10
1:20
1:100

Figure 10 Alkalinity analysis 2000_1. SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

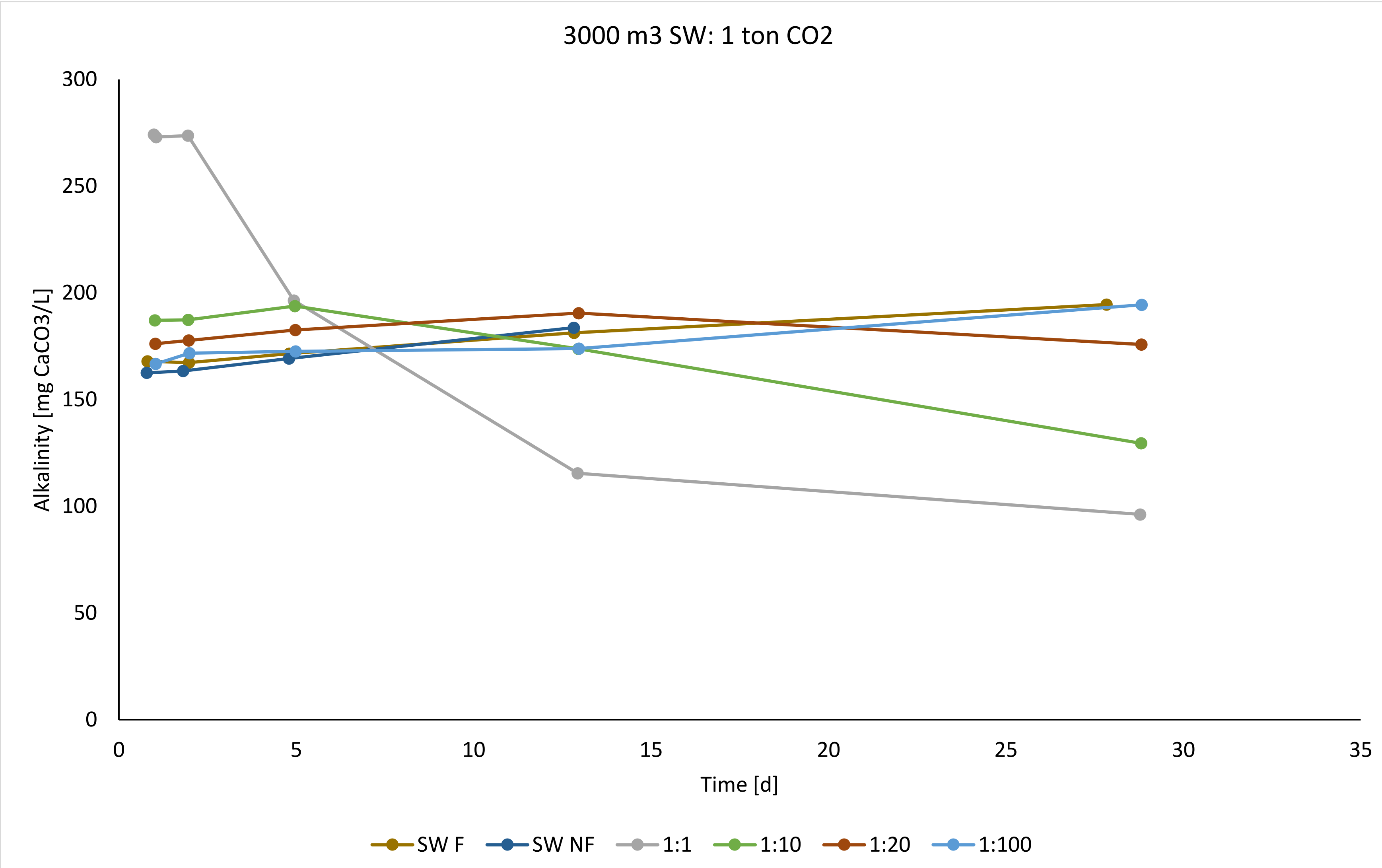

3000 m3 SW: 1 ton CO2
Alkalinity [mg CaCO3/L]
300
250
200
150
100
50
0
0
5
10
15
20
25
30
35
Time [d]
SW F
SW NF
1:1
1:10
1:20
1:100

Figure 11 Alkalinity analysis 3000_1. SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

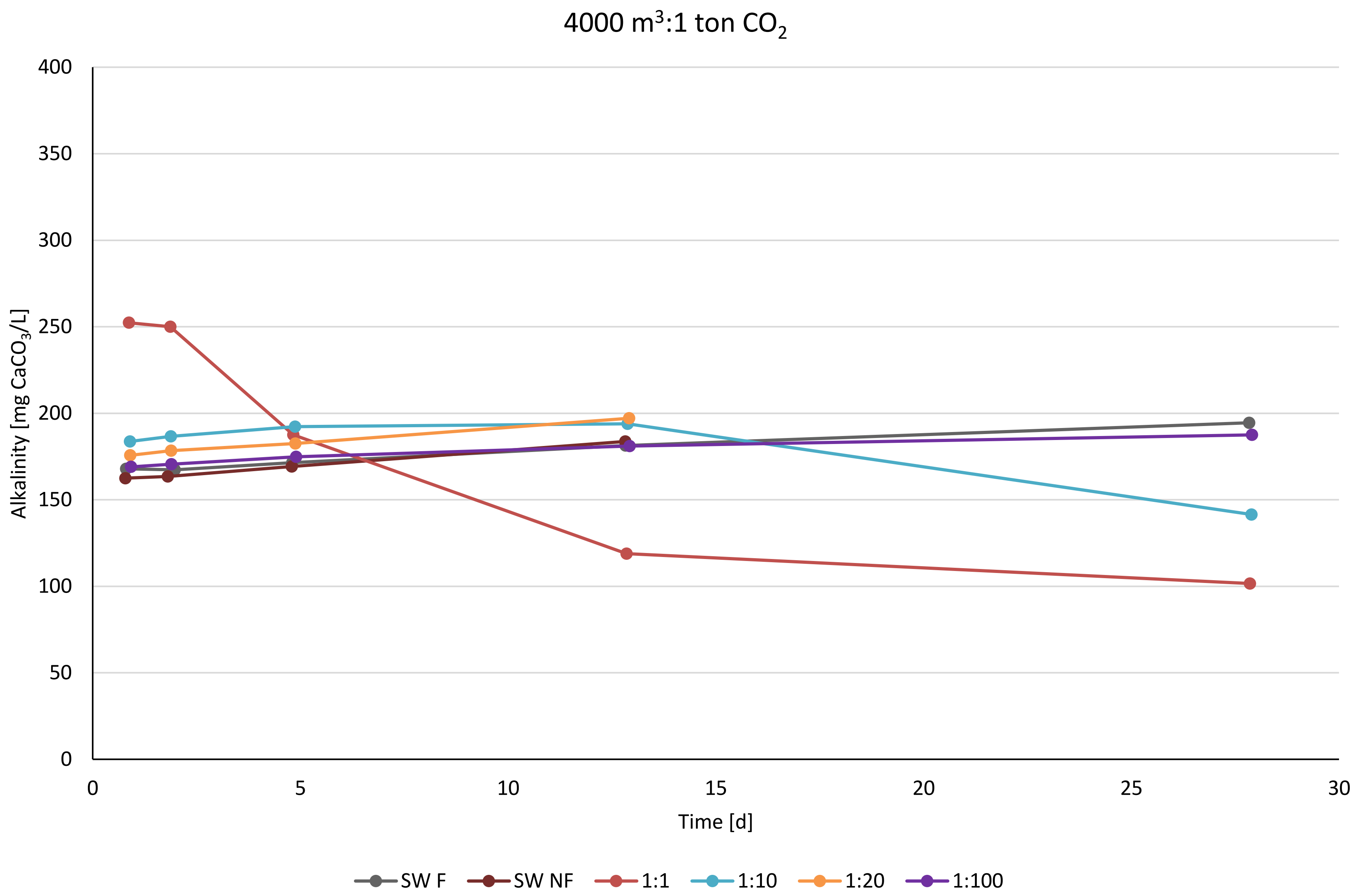
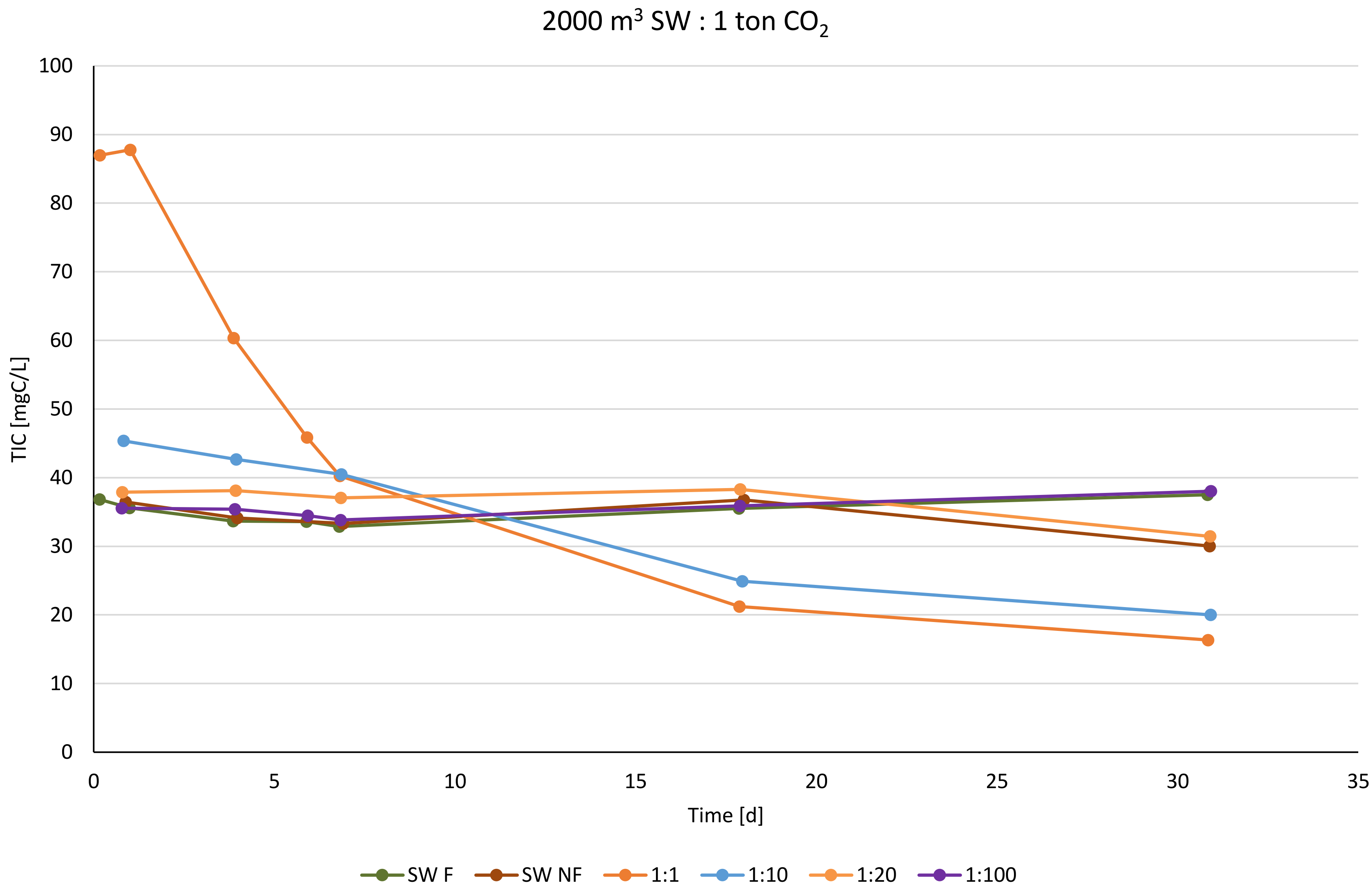


Figure 12: Alkalinity analysis. SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).


2000 m3 SW : 1 ton CO2
TIC [mgC/L]
100
90
80
70
60
50
40
30
20
10
0
0
5
10
15
20
25
30
35
Time [d]
SW F
SW NF
1:1
1:10
1:20
1:100

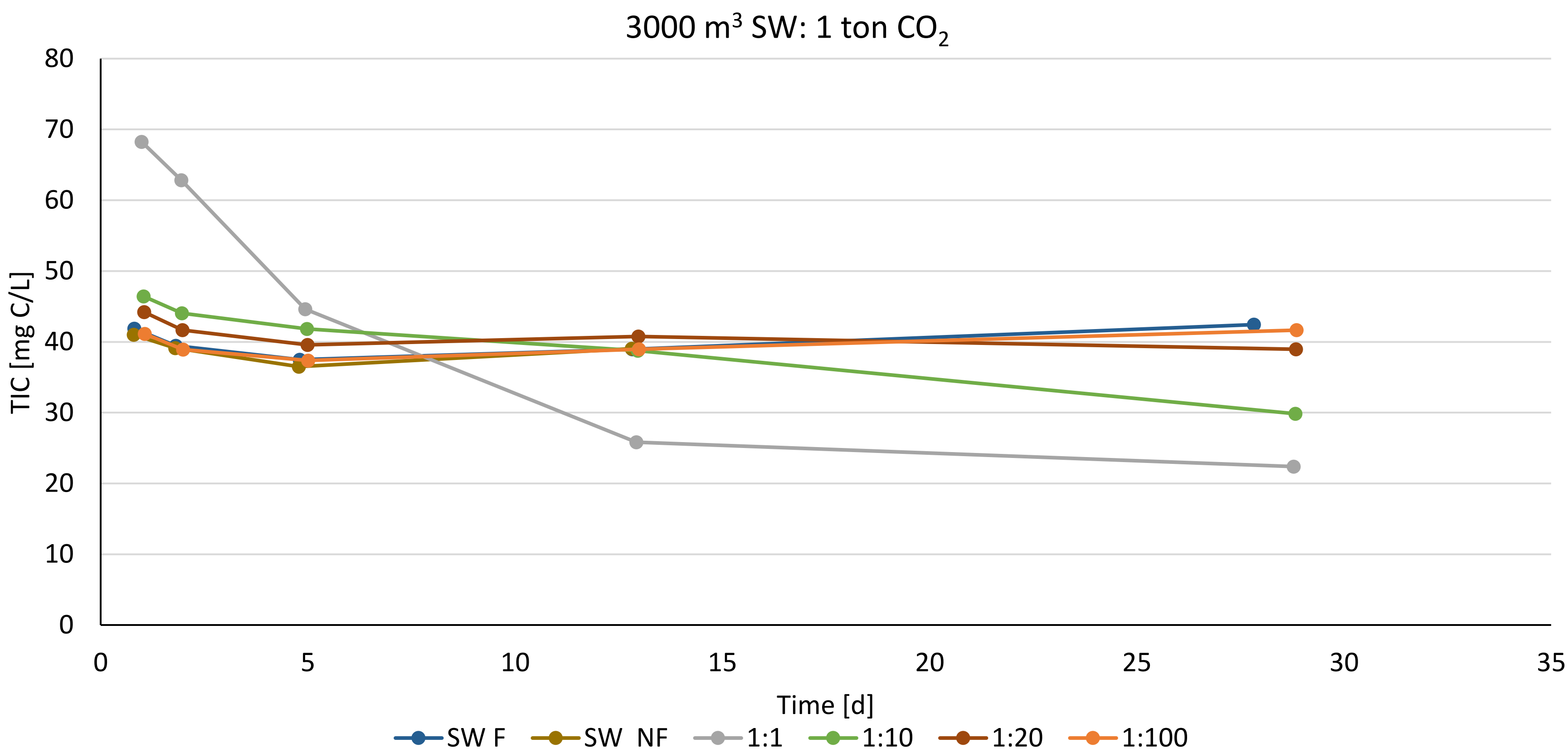


Figure 13 TIC analysis. 3000_1 SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

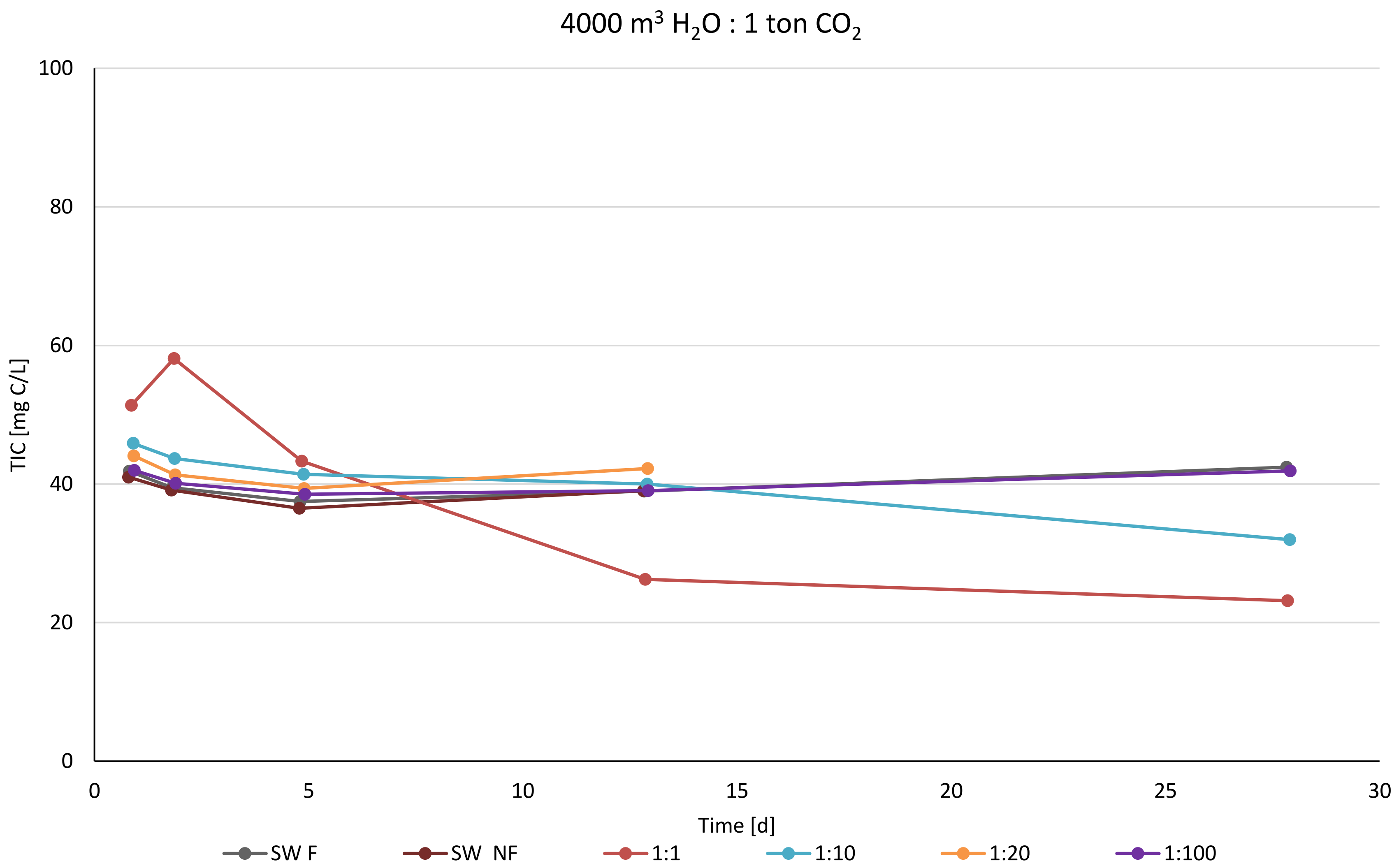


Figure 14: TIC analysis. 4000_1 SW F (SeaWater Filtered); SW NF (SeaWater Not Filtered); 1:1 (Diluition 1 to 1); 1:10 (Diluition 1 to 10); 1:20 (Diluition 1 to 20); 1:100 (Diluition 1 to 100).

2.2.3.2 Remarks

The pH growth observed at the beginning of each analysis could be caused by degassing phenomena during the transportation of the sample.

As shown in the previous figures, the lower stability of TIC occurs for samples with higher bicarbonates concentration. Those are also the ones with higher Ω (See Table 3)

At lower Ω (higher dilutions), alkalinity, pH and TIC follow the trend of natural seawater. The data are insufficient for a comprehensive statistical analysis, but this trend seems to indicate that there are not significant differences between seawater and the most diluted samples (compare, for example, 1:10 to 1:100 for 3000 and 4000 ratios, and 1:100 for 2000 m^3.)

2.2.4 Conclusions after the preliminary phase

The experiments were carried out on a small-scale samples and on statistically limited samples, nevertheless, show that with the right dilution of the buffered water with fresh seawater there is stability of calcium bicarbonates. These results are promising and in agreement with the previous study conducted by Hartmann et al[23] and Moras et al.[24]. These fosters additional studies to be conducted during the second phase of experiments with more systematic and statistically valid samples.

The indications from these preliminary results are useful to start designing the industrial application of LIMENET because it seems that with the right ratio H_2O:CO_2 in the LIMENET process and the right dilution rate in the plume to reach Ω= 5 in few minutes, the precipitation of carbonates is completely avoided.

2.3 Second phase

The second phase is an ongoing project that will starts by mid-October 2022 and will last until January 2023. It will use as sample tanks five swimming pools of 9 m^3 (See Figure 15) in equilibrium with the atmosphere. This volume will be filed by different dilution ratio with the buffered alkaline seawater discharged by the LIMENET process with a H_2O-CO_2 ratio of 4000:1 by weight. As for the preliminary phase, pH, conductivity, alkalinity, and TIC will be analysed though the time.

Those are the five swimming pools parameters:

Table 4 Swimming pools dilution rates.

	Pools 1	Pool 2	Pool 3	Pool 4	Pool 5
buffered seawater : fresh seawater	Fresh water	1:10	1:20	1:50	1:100

[23] Hartmann, J., Suitner, N., Lim, C., Schneider, J., Marín-Samper, L., Arístegui, J., Renforth, P., Taucher, J., and Riebesell, U.: Stability of alkalinity in Ocean Alkalinity Enhancement (OAE) approaches – consequences for durability of CO2 storage, Biogeosciences Discuss. [preprint], https://doi.org/10.5194/bg-2022-126, in review, 2022.

[24] Moras et al. (2021) Ocean Alkalinity Enhancement - Avoiding runaway CaCO3 precipitation during quick and hydrated lime dissolution - https://doi.org/10.5194/bg-2021-330

Figure 15 Swimming pool experiment for calcium bicarbonate stability.

This experiment it is expected to confirm the stability of calcium bicarbonate at different dilution rates and establish what are the Ω limits to avoid abiotic precipitation of $CaCO_3$ and which are the optimal conditions for the most efficient CO_2 storage.

3 Water discharge simulation

In the future implementation of LIMENET technology, large amounts of water will be processed.

After the discharge, the buffered seawater must be diluted to reach the ideal Ω_{ar} that avoids the secondary carbonate precipitation (which is a drawback that would undermine the overall process). From the literature the highest Ω_{ar} that safely avoids precipitation is 5[25].

This dilution is crucial for bicarbonate stability. Using a simple and preliminary water discharge simulation routine realized by Politecnico di Milano (Dip. Aerospace science and technology[26]), with Matlab[27], it is possible to calculate the concentration along a controlled volume of the plume and its respective velocities (along x axis).

The initial conditions of LIMENET future industrial standard plant have a water plume discharging speed of 1 m/s and a discharging pipe diameter of 1 meter. The seawater in which the plume is discharged, is considered without any currents (stable condition). If sea currents or other turbulences will be considered, the dilution will require less time (Condition in which sea is considered infinite).

The following Figure 16 represent the plume dilution respect the centerline x with concentration areas.

[25]Ocean Alkalinity Enhancement - Avoiding runaway CaCO3 precipitation during quick and hydrated lime dissolution. Moras at all. https://doi.org/10.5194/bg-2021-330

[26] https://www.aero.polimi.it/

[27]https://it.mathworks.com/products/matlab.html

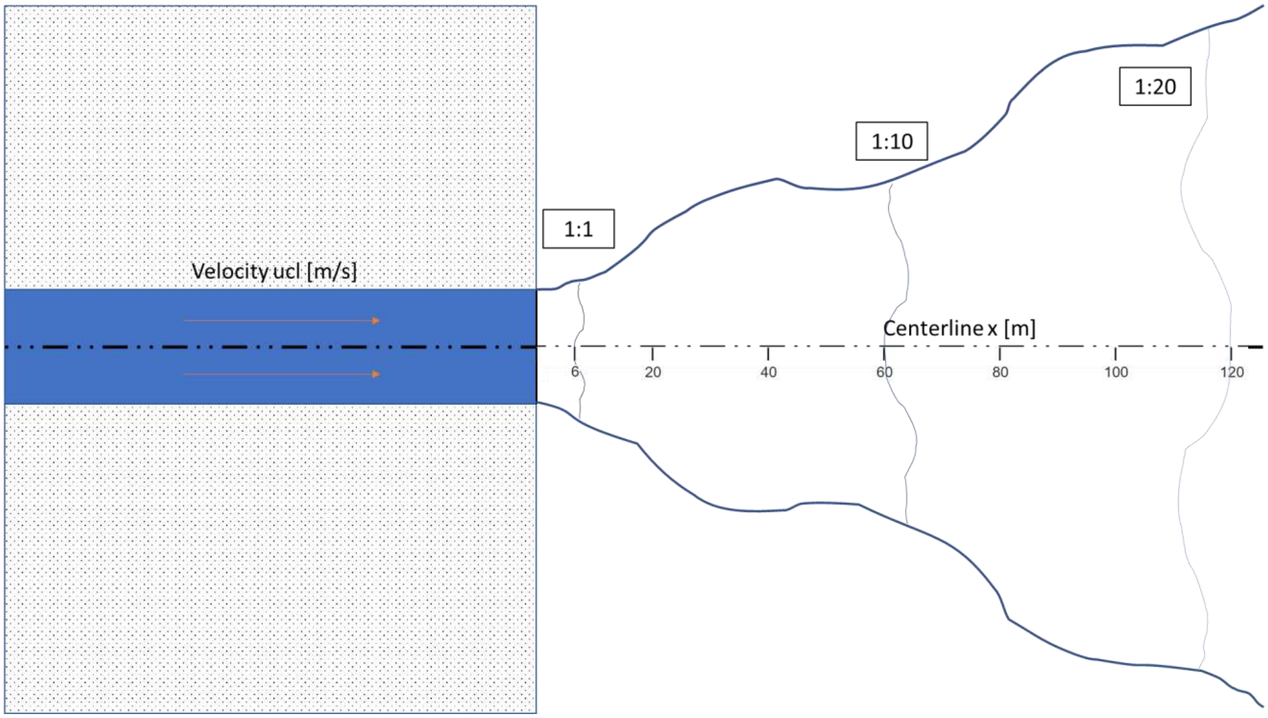
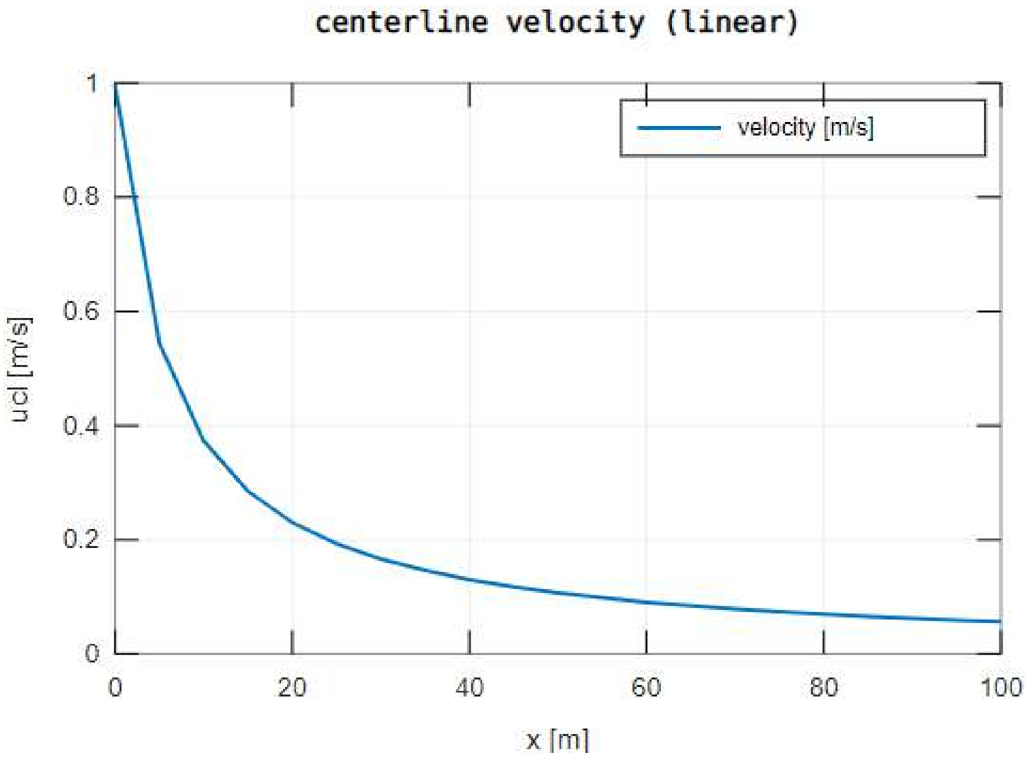


Figure 16 Discharging pipe plume simulation.

Table 5 Time needed for 1/20 dilution.

Ratio	time sec	Time min	meters
1-1	7.57895	00:00:07	6
1-10	343.711	00:05:43	60
1-20	1295.79	00:21:35	120

As evident from Figure 17 and in Figure 18, the concentration reaches the dilution of 1 over 20 in ca. 120 meters. If one calculate the time needed to go from 0 to 120 meters, to 1:20 dilution ratio, the result is less than 25 minutes (See Table 5**Errore. L'origine riferimento non è stata trovata.**). This is ideal for avoiding any precipitation of carbonates within the plume during the dilution phase.



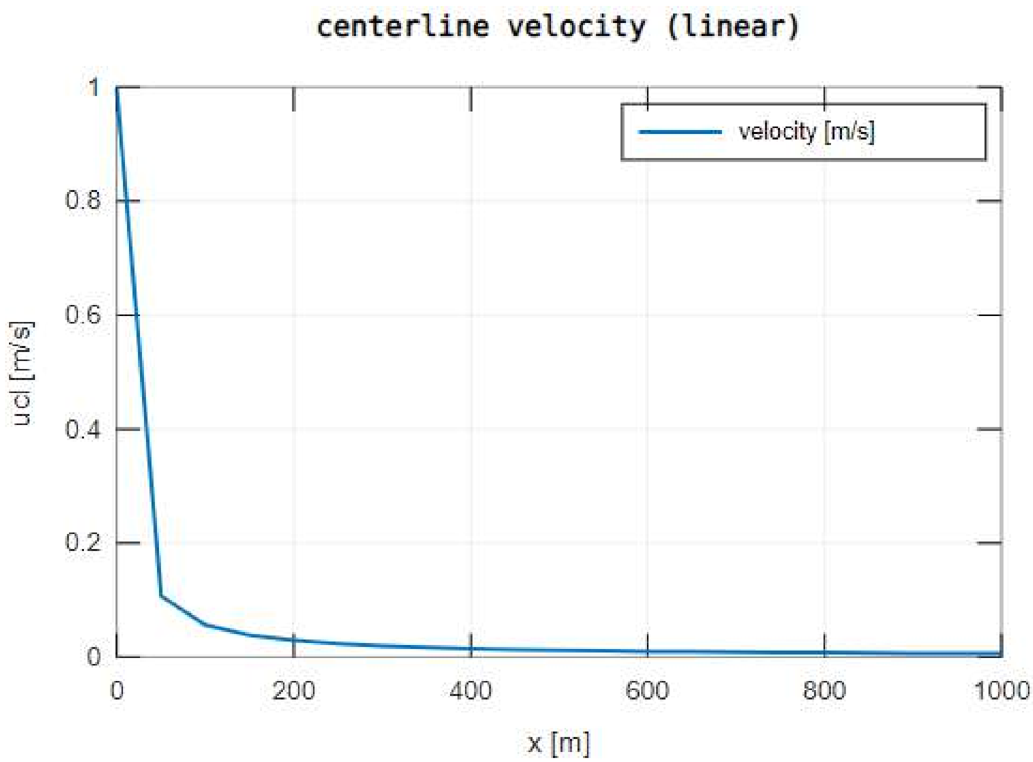
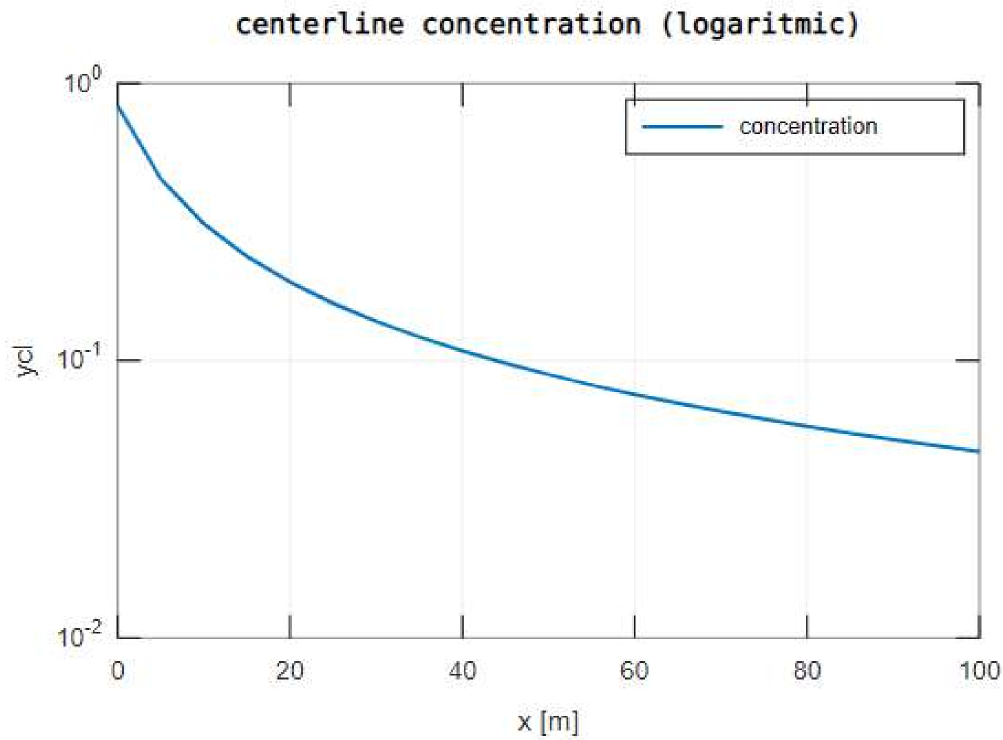


Figure 17 Centerline velocity of the first 100 and 1000 meters of plume.



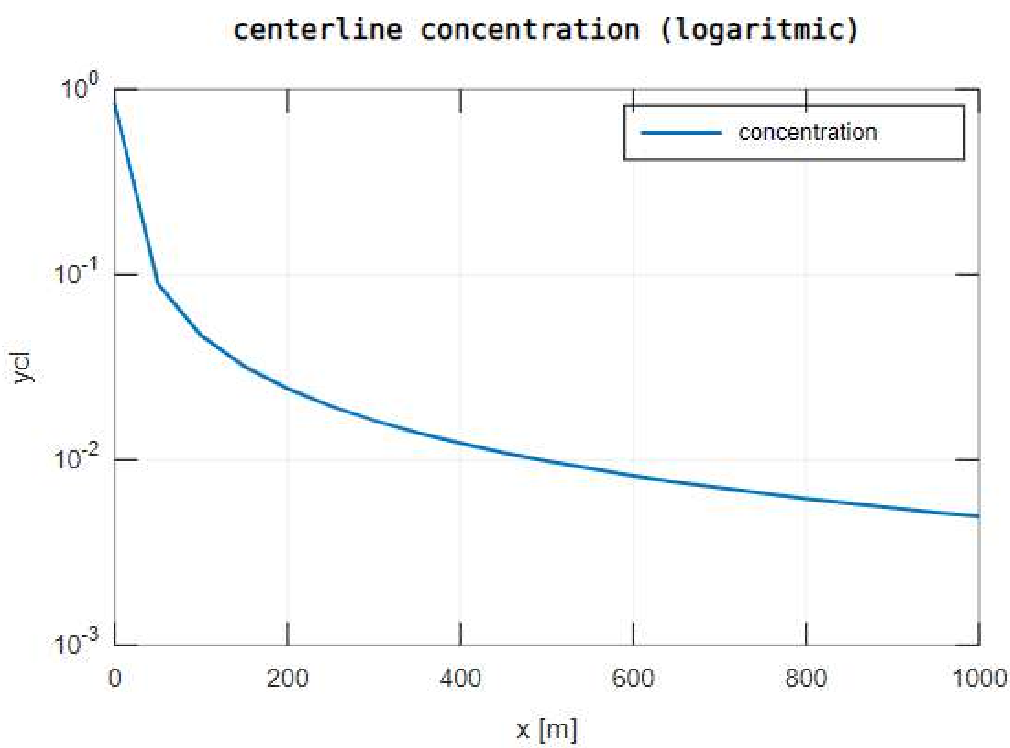


Figure 18 Centerline concentration of the first 100 and 1000 meters of plume.

Appendix 1

It is fundamental to systematically calibrate the analytical instruments to guarantee a high precision and accuracy.

Hanna instruments HI84531 Total Alkalinity Mini titrator & pH Meter:

This instrument requires weakly one calibration of the electrode whereas the pump needs a calibration every time the alkalinity measures are performed.

ELECTRODE CALIBRATION

Three points of calibration are performed, using the three standard buffers at pH 4.01, 7.01, and 8.30.

PUMP CALIBRATION

The calibration of the pump must be performed every time the syringe, pump tube, the titrant bottle or the pH electrode are changed. It is possible to select the optimal range expected for the measurement: low (30.0 to 400.0 mg/L) or high range (300 to 4000 mg/L). We used low range during the first phase.

pH meter, Mettler Toledo Seven Excellence™:

Three points of calibration can be performed, using the three predefined buffers: red (4.01), green (7.00) and blue (9.21).

TIC Analyzer, Analytikjen multi N/C Series

Firstly, TIC analyzer calibration was performed by creating a calibration curve with several standard solutions. Daily, the accuracy is checked by analyzing a standard 20 mgC/L solution.