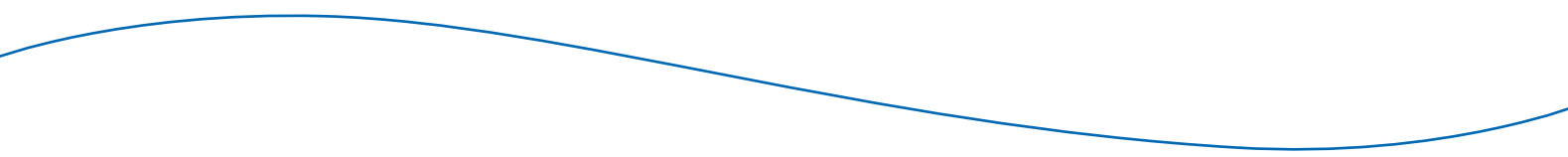


Using carbon dioxide gas to lower  
the pH of tunnelling waste  
water – laboratory test and  
assessment of toxic potential

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<p>Abstract</p> <p>Building of tunnels produces waste water that often is highly alkaline. Such water can be toxic to aquatic organisms, and pH should be lowered before discharge to recipient. A reactor tank was built to test the use carbon dioxide (CO<sub>2</sub>) gas for this purpose. Small scale experiments were conducted with three synthetic solutions prepared by diluting acids and bases, and one sample of tunnelling waste water from Gran, National road 4 (rv. 4). The pH decreased rapidly to pH 8.0 when CO<sub>2</sub> gas was added to alkaline solutions. The rate of pH decrease was markedly slower below pH 7.0. The CO<sub>2</sub> concentration was low (&lt;40 mg/L) at pH values higher than 8.0, but increased rapidly as pH dropped below 8.0. Initially, the pH dropped faster and the CO<sub>2</sub> concentrations increased faster at 4 °C than at 15 °C, but there were no clear differences when the experiments were terminated. The aqueous CO<sub>2</sub> concentration in tunnelling waste water at pH 8.0 is probably not acutely toxic to fish, but can rapidly rise to toxic levels if pH declines further.</p>
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Using carbon dioxide gas to lower the pH of tunnelling  
waste water – laboratory test and assessment of toxic  
potential

## Preface

NORWAT (Nordic Road Water) is a four-year research and development programme (2012 - 2015) under the Norwegian Public Roads Administration (NPRA). The purpose of the agency programme is that the NPRA shall plan, build and operate the road network without causing unacceptable harm to the aquatic environment. This entails implementing the right measures in the right place.

Tunnelling waste water can be so alkaline that it is necessary to lower the pH before release to recipient. In Norwegian tunnelling projects, pH is normally adjusted using mineral acids. These strong acids are potentially dangerous to handle for the operators and pose a risk of over acidification which may cause massive death of aquatic organisms downstream of the discharge. NPRA is therefore considering alternative methods to reduce pH. A literature review concerning chemical and engineering principles of using CO<sub>2</sub> gas for this purpose was performed in 2013 (Torp and Vikan, 2013). The report also highlighted potential toxicity associated with dissolved CO<sub>2</sub> and that there is a lack of knowledge concerning CO<sub>2</sub> concentrations in the water at desired pH for representative Norwegian tunnelling waters.

In this study commissioned by the NPRA, NIVA researchers have conducted small scale laboratory tests using CO<sub>2</sub> gas to reduce pH in both synthetic and real tunnelling water. The potential toxicity of CO<sub>2</sub> in the pH adjusted solutions is assessed by comparing aqueous CO<sub>2</sub> concentrations with levels reported in the literature to be toxic for fish.

Hamar, February 25

*Oyvind Garmo*

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## Summary

Building of tunnels produces waste water that is often highly alkaline. Such water can be toxic to aquatic organisms, and pH should be lowered before discharge to recipient. For this purpose strong acid is normally used in Norway. The weak acid carbon dioxide (CO<sub>2</sub>) could be a good alternative because it eliminates the risk of obtaining very low pH in the treated water and the health risk associated with handling strong acid. It could, however, lead to elevated levels of aqueous CO<sub>2</sub> downstream. In this study, small scale experiments using CO<sub>2</sub> to lower the pH of synthetic and real tunnelling waste water were conducted, and the toxic potential of elevated aqueous CO<sub>2</sub> was assessed.

A reactor tank prototype was built to lower the pH of alkaline solutions using CO<sub>2</sub> gas. Small scale laboratory experiments were conducted with three synthetic solutions prepared by diluting acids and bases, and one sample of real tunnelling waste water from Gran, National road 4 (rv. 4). The pH decreased rapidly to pH 8.0 when CO<sub>2</sub> gas was added to alkaline solutions. It only took a few minutes, depending on initial pH, with the experimental conditions applied in the present study. The rate of pH decrease was markedly slower below pH 7.0. The CO<sub>2</sub> concentration was low (<40 mg/L) at pH values higher than 8.0, but increased rapidly as pH dropped below 8.0. Initially, the pH dropped faster and the CO<sub>2</sub> concentrations increased faster at 4 °C than at 15 °C, but there were no clear differences when the experiments were terminated. The transfer of CO<sub>2</sub> from gas to solution was more efficient and pH dropped faster in the turbid tunnelling waste water compared to the synthetic solutions.

The CO<sub>2</sub> concentration in tunnelling waste water at pH 8.0 is probably not acutely toxic to fish, but can rapidly reach toxic levels if pH declines further. Based on literature data for fish, it seems that the CO<sub>2</sub> concentration should probably not exceed 40 mg/L for more than a few hours to minimise the risk of toxic effects. For longer term exposures, the concentration should not exceed 20 mg/L.

In a full scale CO<sub>2</sub> treatment plant, pH-controlled dosing seems appropriate in order to minimise the use of gas and the need for degassing or dilution before discharge. It is also advisable to monitor pH and CO<sub>2</sub> concentrations at the outlet.

## Sammendrag

Tunnelbygging produserer spillvann som ofte er svært basisk. Slikt vann kan være giftig for vannlevende organismer, og pH bør senkes før utslipp til resipient. Til dette formålet blir det vanligvis brukt sterk syre i Norge. Den svake syren karbondioksid ( $\text{CO}_2$ ) kan være et godt alternativ fordi den eliminerer risikoen for svært lav pH i behandlet vann og helseisikoen forbundet med håndtering av sterke syrer. Det kan imidlertid gi økte nivåer av løst  $\text{CO}_2$  nedstrøms. I dette studiet ble det gjennomført småskalaeksperimenter med bruk av  $\text{CO}_2$ -gass for senkning av pH i syntetiske og ekte tunneldrivevann. Det toksiske potensialet forbundet med økt nivå av løst  $\text{CO}_2$  ble også vurdert.

En prototype reaktortank ble bygget for å senke pH i basiske løsninger med  $\text{CO}_2$ -gass. Det ble gjennomført eksperimenter med tre syntetiske løsninger laget ved å fortynne syrer og baser, og med en prøve av ekte tunneldrivevann fra Gran, rv.4. pH sank raskt til 8,0 når  $\text{CO}_2$  ble tilsatt til de basiske løsningene. Det tok bare noen få minutter, avhengig av start-pH, med de eksperimentelle betingelsene som ble brukt her. pH sank betydelig saktere under pH 7,0.  $\text{CO}_2$ -konsentrasjonen var lav (<40 mg/L) når pH var høyere enn 8,0, men økte raskt når pH sank under 8,0. Til å begynne med sank pH raskere og  $\text{CO}_2$ -konsentrasjonene økte fortere ved 4 °C enn ved 15 °C, men det var ingen klare forskjeller når eksperimentene ble avsluttet. Overføring av  $\text{CO}_2$  fra gas til løsning skjedde mer effektivt og pH sank raskere i det grumsete tunneldrivevannet sammenlignet med de syntetiske løsningene.

Konsentrasjonen av løst  $\text{CO}_2$  som trengs for å senke pH i tunneldrivevann til 8,0 er trolig ikke akutt toksisk for fisk, men kan raskt nå toksiske nivåer hvis pH fortsetter å falle. Ifølge litteraturdata for fisk, bør  $\text{CO}_2$ -konsentrasjonen trolig ikke overskride 40 mg/L i mer enn noen få timer for å minimere risikoen for toksiske effekter. Ved lengre eksponering, bør konsentrasjonen ikke overstige 20 mg/L.

I et fullskala anlegg for  $\text{CO}_2$ -behandling vil det være hensiktsmessig med pH-kontrollert dosering for å minimere gassbruken og behovet for avgassing eller fortynning før utslipp. Det anbefales også at løst  $\text{CO}_2$  og pH måles i vannet ved utløp fra renselanlegg.

# 1. Introduction

## 1.1 Background

Currently, about 20-30 km of new tunnel is built annually in Norway (Vikan and Meland, 2012). Building of tunnels requires substantial amounts of water. The water use imply a risk of releasing pollutants such as trace metals, radionuclides, particles, oil and nitrogen compounds to the aquatic environment (Åstebøl et al., 2011). Another potential environmental problem is high pH in waste water from tunnelling where cement-based packing and sprayed concrete is used. pH-values as high as 11-12 is not uncommon in untreated tunnelling waste water. Very high pH is toxic to aquatic organisms and especially in combination with a high level of ammonia (see e.g. Torp and Vikan, 2013). For Norwegian road tunnelling projects an upper pH limit between 8 and 9 is usually set for the discharge water. It may also be required that pH in the discharge water is similar to pH in the recipient. The pH is lowered and ammonia is transformed to the less toxic ammonium ion through addition of acid. Strong acid (hydrochloric or sulphuric acid) is normally used for this purpose in Norway, while carbon dioxide (CO<sub>2</sub>) is in use in other countries (Torp and Vikan, 2013). An advantage of using a weak acid such as CO<sub>2</sub> compared to strong acids is that owing to self-buffering, the pH will not drop to very low levels even if accidental overdosing should occur. High concentrations of aqueous CO<sub>2</sub> can, however, be toxic for aquatic organisms. As tunnelling activity is performed during all seasons, temperature and solubility of CO<sub>2</sub> in the waste water can vary. The purpose of the present work was to measure the CO<sub>2</sub> concentrations obtained when the gas was used to lower the pH of synthetic and real tunnelling waste water, and assess whether these concentrations are likely to be toxic. The effect of temperature on the concentrations of aqueous CO<sub>2</sub> in the synthetic waters at different pH-levels was also tested. Use of CO<sub>2</sub> has not previously been tested in Norwegian road projects, and there is a lack of information regarding the concentrations of CO<sub>2</sub> in tunnelling water following pH-adjustments in other countries

## 1.2 CO<sub>2</sub> in water

The following reactions and equilibrium constants are relevant for describing the process where CO<sub>2</sub> gas dissolves in water (**Table 1**). The CO<sub>2</sub> gas is highly soluble in water. For pure water in equilibrium with a partial pressure of one atmosphere of CO<sub>2</sub>, the solubility is about 1.5 g/L at 25 °C, corresponding to a pH of 3.9. However, it takes time to achieve equilibrium and the efficiency that can be achieved by a practical treatment set up will be constrained by reaction kinetics.

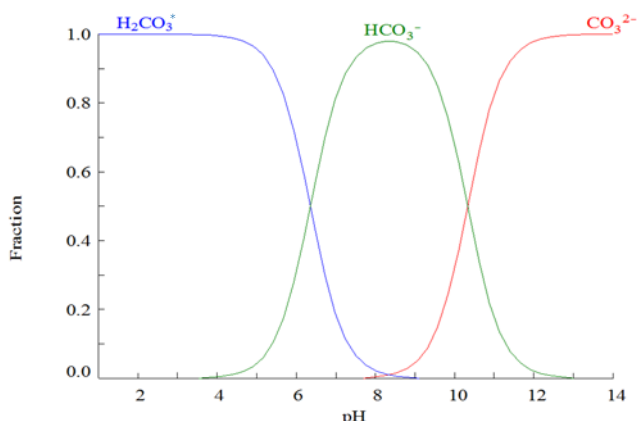
**Table 1.** Equilibrium constants (K) (from Stumm and Morgan, 1996) for carbonate equilibria and the dissolution of calcite (aqueous phase is not indicated in the notation).

Equation	Reaction	-log K (ionic strength = 0)	
		5 °C	15 °C
1	CO <sub>2</sub> (g)+H <sub>2</sub> O=H <sub>2</sub> CO <sub>3</sub> *	1.20	1.34
2	H <sub>2</sub> CO <sub>3</sub> *=H <sup>+</sup> +HCO <sub>3</sub> <sup>-</sup>	6.52	6.42
3	HCO <sub>3</sub> <sup>-</sup> =H <sup>+</sup> +CO <sub>3</sub> <sup>2-</sup>	10.56	10.43
4	CaCO <sub>3</sub> (s)=Ca <sup>2+</sup> +CO <sub>3</sub> <sup>2-</sup>	8.35	8.37
5	H <sub>2</sub> O=H <sup>+</sup> +OH <sup>-</sup>	14.73	14.34

*H<sub>2</sub>CO<sub>3</sub>\* comprise both aqueous CO<sub>2</sub> and true H<sub>2</sub>CO<sub>3</sub>, i.e. the first acidity constant above reflect both hydration and protolysis reactions.*

**Figure 1** demonstrates how the dominating species change with pH.





**Figure 1.** Relative species distribution versus pH.

## 2. Materials and methods

A tank reactor prototype with stirring was built to conduct the experiments (**Figure 2**). The reactor was built in polycarbonate and was shaped as a cylinder of 98.5 cm height and 19.0 cm internal diameter. Neutralization experiments were carried out with 20 L of alkaline water by using a gas cylinder to add  $\text{CO}_2$  with a constant flow rate of 456 mL/min through a fine bubble diffuser installed in the bottom of the reactor. With the configuration described here, a surface volumetric gas flow of 1.61 mL  $\text{CO}_2/\text{cm}^2/\text{min}$  was achieved. Gas-liquid mixing was carried out mechanically by using a spiral propeller blade at 1800 rpm. The tank was partly covered by a lid, implying that the partial pressure of  $\text{CO}_2$  did not significantly exceed 1 atm at the surface. With 20 L of sample in the tank, the partial pressure of  $\text{CO}_2$  at the bottom should be about 7 % higher than at the surface.

The pH was continuously monitored with a glass electrode in the reactor. Aqueous  $\text{CO}_2$  was also monitored frequently by withdrawing 5 mL samples from the reactor and immersing a selective electrode (Mettler Toledo) in the solution (the accuracy of sensor measurements was verified with acidified standard solutions prepared by dissolving pure sodium carbonate and adding hydrochloric acid to pH 3). Samples for determination of alkalinity were taken at different stages in the process of lowering the pH of the alkaline test water: (i) start, (ii) when pH reached 8 and 6.4 and (iii) when the rate of pH change stagnated. Alkalinity was measured by titrating the sample to pH 4.5 with hydrochloric acid (NS EN-ISO 9963-1. Determination of alkalinity. Part 1, Ed 1, 1996 (in Norwegian)).

Four water qualities were tested: 1) Tap water adjusted to pH 11.0 with sodium hydroxide. 2) A solution with ion concentrations resembling tunnelling waste water from Frodeåsen was prepared by diluting sulphuric and hydrochloric acid, and dissolving calcium and sodium hydroxide to concentrations indicated in **Table 2**. 3) Simulated “Lofast” water was prepared correspondingly and 4) real waste water sampled from a tunnel drilling point in Gran (National road 4 (rv. 4)) on January 28, 2014 (**Figure 3**). At the time of sampling, concrete had been sprayed inside the tunnel, but injection of cement based packing into bore holes to reduce the influx of water had not been done in the Gran tunnel. Injection produces smaller and more mobile particles than the mixture used for spraying of walls (Malin Torp personal communication). The sample was taken from a pond collecting water pumped out of the tunnel. The pond acted as a reservoir feeding water to the treatment plant. The tunnelling water had a high concentration of suspended particles, and these were not removed before the experiment. For water qualities 1-3, duplicate experiments were carried out with freshly prepared solutions at temperatures of 4 and 15 °C in thermostatic chambers. The experiment with real water was performed at 10 °C, i.e. in the range that the experiments with synthetic solutions were conducted, shortly after sampling. The experiments were terminated when the rate of dissolution of  $\text{CO}_2$  had decreased considerably. After the Lofast experiment

at 15 °C, the solution was left stirring, with no CO<sub>2</sub>-addition and open lid to re-equilibrate with the atmosphere for a time span of 18 hours.

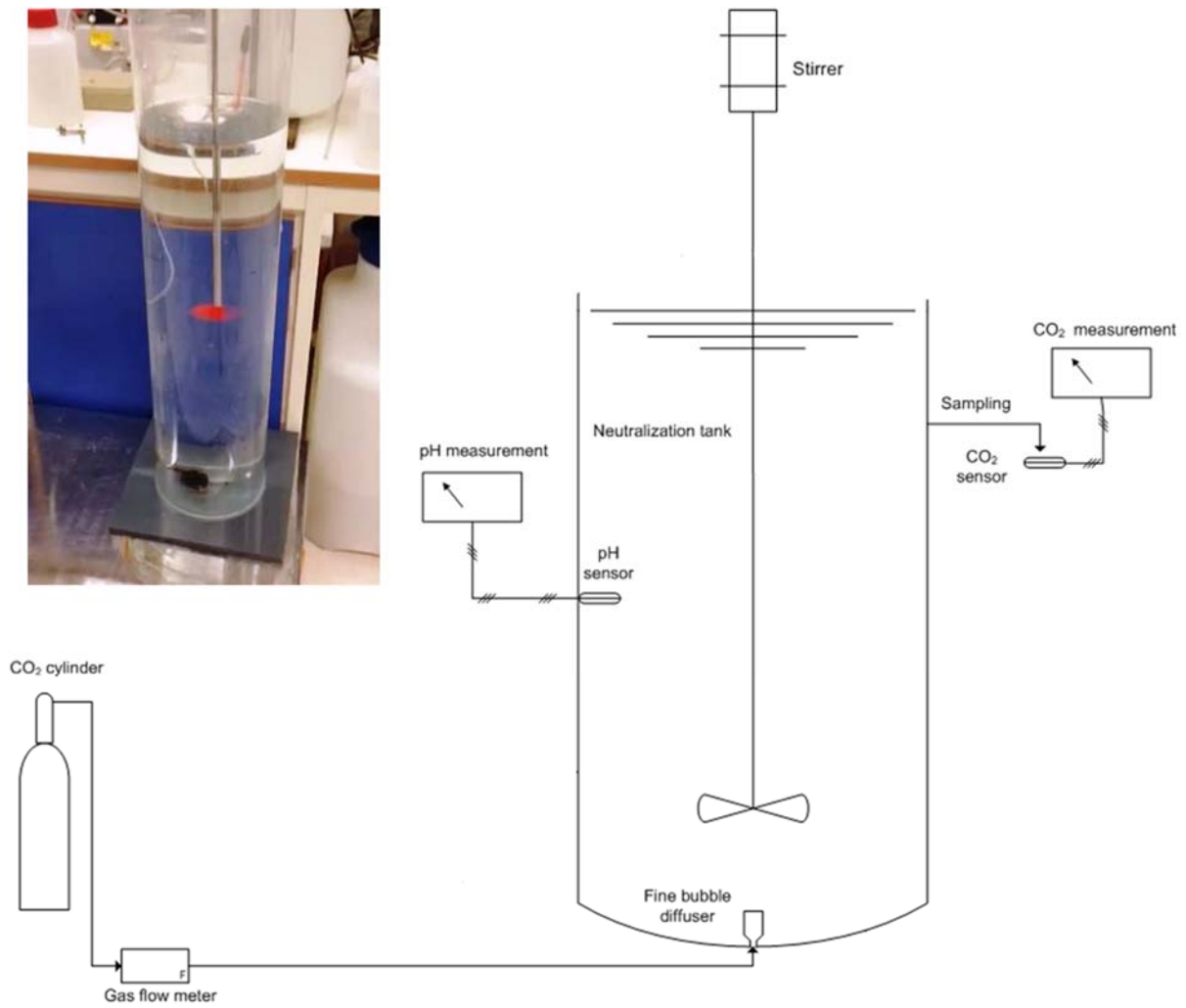
**Table 2.** Nominal concentrations of ions (mg/L) and initial pH in the synthetic water qualities.

Sample identity	Sulphate (mg/L)	Calcium	Sodium	Chloride	pH (start)
pH adjusted tap water	2.1	20.0	1.87	9.4	11.0
“Frodeåsen”	42.8	65.5	80.3	44.8	9.4
“Lofast”	78.9	13.1	20.3	7.6	11.8

**Calculations:**

The CO<sub>2</sub> sensor measures the partial pressure of CO<sub>2</sub>. The CO<sub>2</sub> concentration in solution was calculated by means of Henry’s law.

The total concentration of dissolved carbonate species, C<sub>T</sub> (sum CO<sub>2</sub>(aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>), was calculated from measured alkalinity and the equilibrium constants (Eqs 2-5) given in **Table 1** according to the procedure described by Stumm and Morgan (1996). The concentration of aqueous CO<sub>2</sub> can also be estimated from alkalinity and pH, resulting in somewhat higher values than the sensor at the lowest pH values; the estimated concentrations are not presented in the following as we believe the sensor measurements are more accurate.



**Figure 2.** Schematic illustration and picture of the tank reactor.



**Figure 3.** Sampling of tunnelling waste water from a pond collecting water pumped out from the tunnel in Gran, rv. 4.

### 3. Results and discussion

#### 3.1 Experiments with synthetic solutions

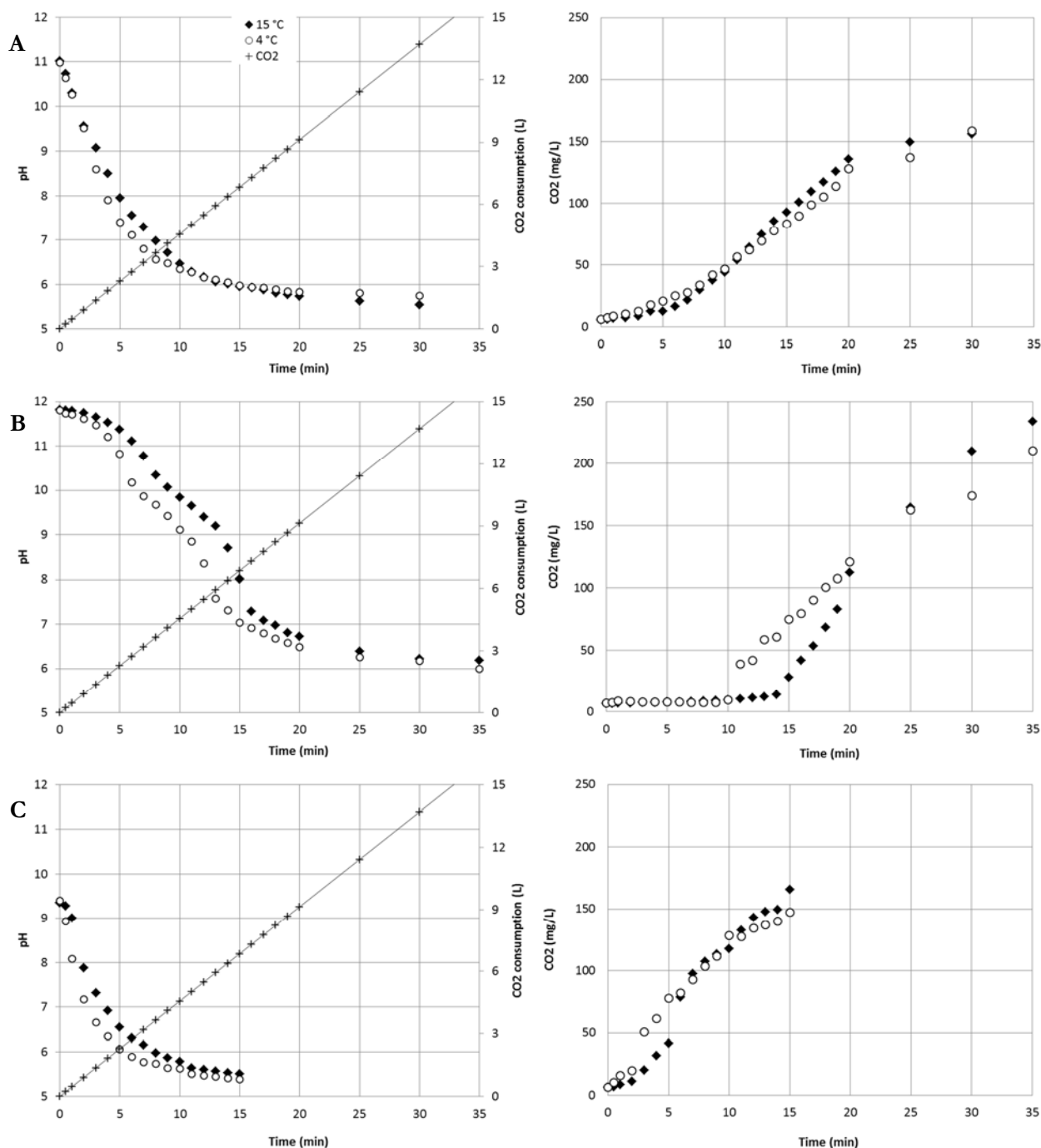
In the synthetic solutions that were prepared without using carbonate, the initial rate of pH decrease depended on the starting pH, as the rates of dissolution and/or hydration of CO<sub>2</sub> are limited (**Figure 4, Table 3**). It took about 4, 13 and 1.5 minutes to reach pH 8.0 in the pH-adjusted tap water, “Lofast” and “Frodeåsen” water, respectively, and about 10, 24 and 5 minutes to reach pH 6.4. At about pH 7.0 the rate of pH decrease slowed down. The equilibrium pH depends on the initial pH of the solution, i.e. it is higher in a solution that starts at pH 12 than a solution that starts at pH 9. This was reflected in the results, and the experiments with pH adjusted tap water, “Lofast” water and “Frodeåsen” water was terminated at about pH 5.6, 6.1 and 5.4, respectively. The difference between results from replicate experiments was small.

The CO<sub>2</sub> concentrations were low in all synthetic waters at pH above 8 (< 40 mg/L in all experiments) because CO<sub>3</sub><sup>2-</sup> and HCO<sub>3</sub><sup>-</sup> were the dominating species, but increased rapidly as pH dropped below 8 (see also **Figure 1**). The CO<sub>2</sub> concentrations started to plateau and were between 150-200 mg/L when the experiments with synthetic waters were terminated.

Initially, the pH dropped faster and the CO<sub>2</sub> concentrations increased faster at 4 °C than at 15 °C. There was, however, no clear difference between the CO<sub>2</sub> concentrations or the pH values at the two temperatures when the experiments were terminated, which is surprising considering the temperature dependence of the equilibrium constant (**Eq 1, Table 1**). The calculated total concentration of dissolved carbonate species (C<sub>T</sub>) indicate that more CO<sub>2</sub> was dissolved at 4 °C than at 15 °C, but still well below the solubility limit (about 45 mM at 15 °C). Presumably, the experiments were terminated somewhat early, so that the data did not reflect true equilibrium situations.

**Table 3.** Measured alkalinity and calculated total carbonate concentration, C<sub>T</sub> (sum CO<sub>2</sub>(aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) in samples from the experiment with pH adjusted synthetic solutions.

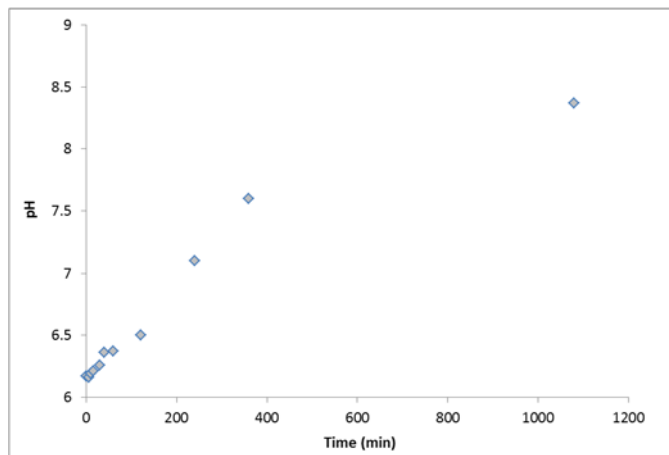
Sample identity	pH	Temperature 4 °C		pH	Temperature 15 °C	
		Alk. (mM)	C <sub>T</sub> (mM)		Alk. (mM)	C <sub>T</sub> (mM)
Tap water	11.0 (start)	1.55	0.9	11.0 (start)	1.78	1.0
	8.0	2.16	2.2	8.0	1.82	1.9
	6.4	2.18	5.1	6.4	1.83	3.7
	5.7 (end)	2.19	17	5.5 (end)	1.83	17
“Lofast”	11.8 (start)	5.50	3	11.8 (start)	7.31	4
	8.0	5.54	6	8.0	7.35	8
	6.4	5.54	13	6.4	7.52	15
	6.0 (end)	5.62	24	6.2 (end)	7.71	21
“Frodeåsen”	9.4 (start)	0.89	0.8	9.4 (start)	0.88	0.8
	8.0	0.92	0.9	8.0	0.90	0.9
	6.4	0.91	2.1	6.4	0.90	1.8
	5.4 (end)	0.92	13	5.5 (end)	0.90	8.3



**Figure 4.** Average results from two replicate experiments with synthetic solutions at 4 and 15 °C. The difference between replicates was small and not indicated in the plots. The panels show pH (left) and CO<sub>2</sub> concentration (right) versus time after addition of CO<sub>2</sub> gas started for the experiment with **A** Tap water adjusted to pH 11, **B** “Lofast” water, and **C** “Frodeåsen” water. The straight lines represent accumulated consumption of CO<sub>2</sub>.

After the experiment with synthetic Lofast water at 15 °C, the CO<sub>2</sub> gas was turned off while stirring continued (**Figure 5**). The pH increased from 6.2 to 7.6 at about constant rate during the first 6 hours as CO<sub>2</sub> degassed. The pH was 8.4 after 18 hours, which is close to the expected pH for this solution at equilibrium with atmospheric CO<sub>2</sub>. The tank leaves a relatively small area of interface between the

solution and the atmosphere, but the experiment demonstrates that the solution remains supersaturated with CO<sub>2</sub> for several hours.

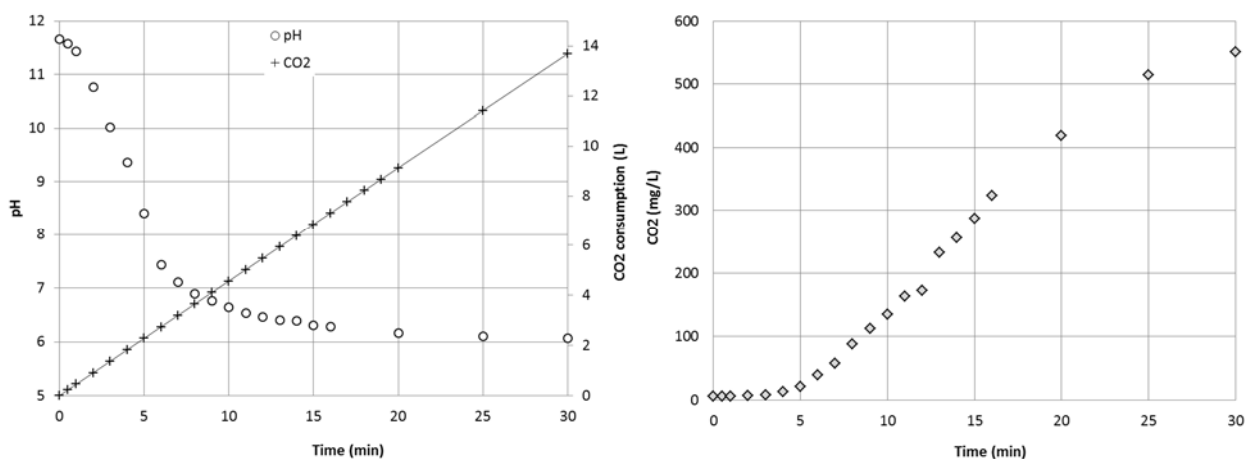


**Figure 5.** pH as a function of time for synthetic Lofast water at 15 °C as CO<sub>2</sub> is degassing

### 3.2 Experiment with tunnelling waste water from Gran

The pH in the real tunnelling water decreased much faster when exposed to pure CO<sub>2</sub> gas than the synthetic Lofast solution that had a similar initial pH. The pH dropped to 8.0 in just 5 minutes (**Figure 6**), which is 2-3 times faster than the “Lofast” solution responded (and consuming only 1/3-1/2 of the gas volume required to lower the pH in the “Lofast” solution to 8.0). The initial alkalinity was relatively low (**Table 4**), but somewhat higher than in the synthetic solutions (**Table 3**). This shows that the transfer of CO<sub>2</sub> from gas to solution was more efficient in the turbid tunnelling waste water compared to the synthetic solutions, probably owing to a high concentration of inert particles (i.e. not acid reactive) in the former. Thus, the particles appeared to improve the efficiency of the pH adjusting process with the experimental set up used here. More CO<sub>2</sub> would have been required to lower the pH of the water if the particles had provided considerable alkalinity.

The CO<sub>2</sub> concentration reached a much higher level in the tunnelling water than the synthetic waters, and was probably close to saturation (calculated  $C_T = 49$  mM) at the end of the experiment. This can be attributed to the more efficient mass transfer as explained above, and, possibly, to some dissolution of solid carbonate particles during the experiment. It is likely that the final CO<sub>2</sub> concentration (after 30 minutes) in the real tunnelling water would have been lower if the particles had been removed prior to the experiment.



**Figure 6.** Tunnelling waste water from Gran at 10 °C. Plot of pH and CO<sub>2</sub> concentration versus time after addition of CO<sub>2</sub> gas started. The straight line represents accumulated consumption of CO<sub>2</sub>.

**Table 4.** Measured alkalinity and calculated total carbonate concentration, C<sub>T</sub> (sum CO<sub>2</sub>(aq), H<sub>2</sub>CO<sub>3</sub>, HCO<sub>3</sub><sup>-</sup>, and CO<sub>3</sub><sup>2-</sup>) in samples from the experiment with tunnelling waste water from Gran.

pH	Temperature 10 °C	
	Alk. (mM)	C <sub>T</sub> (mM)
11.7 (start)	10.0	5
8.0	11.1	11
6.4	12.8	28
6.1 (end)	14.2	49

### 3.3 Assessment of toxic potential

The experiments demonstrate that the CO<sub>2</sub> concentration is relatively low (<40 mg/L) in all the tested solutions at pH above 8.0, but increases to high levels if a lower pH is to be obtained. Effluent with acutely toxic low pH (<4.5), which is an environmental risk when using strong acid to adjust pH, is unlikely when using CO<sub>2</sub> gas at a partial pressure of 1 atmosphere or less. If the raw water is highly alkaline (pH=12), it is difficult to achieve a pH lower than 5.0 using CO<sub>2</sub> (at 1 atm or less). If the raw water is less alkaline (e.g. pH 9.5) it is theoretically possible to attain a pH lower than 4.0. However, the experiments show that this will take long time.

High aqueous concentration of CO<sub>2</sub> in the effluent is probably a greater risk than low pH when using CO<sub>2</sub> to adjust pH (it should be noted that temporarily high CO<sub>2</sub> concentrations will also occur when strong acid is used to lower the pH of carbonate rich raw water significantly below 8.0). Aqueous organisms produce CO<sub>2</sub> when they respire and excrete CO<sub>2</sub> (or HCO<sub>3</sub><sup>-</sup>) through diffusion from their bodily fluid (e.g., blood, hemolymph, protoplasm) to the external aqueous solution. This net transport of CO<sub>2</sub> is hampered if CO<sub>2</sub> concentration is high in the external solution, causing a disturbance in the acid-base balance within the body. The CO<sub>2</sub> concentration is usually less than 4 mg/L in natural surface waters. Physiological effects of high CO<sub>2</sub> is relevant to topics of current interest such as ocean acidification, CO<sub>2</sub> storage in the ocean floor and high intensity aquaculture. Here we limit the discussion to toxic levels of CO<sub>2</sub> for fish.

In a literature survey Torp and Vikan (2013) compiled a table with concentrations found to be acutely toxic to some marine fish species at various life stages. For young fish, the median lethal concentration (i.e. the concentration causing the death of 50 % of the sample population within a short time span) ranged from 36 mg/L CO<sub>2</sub> for young fish of the species red seabream (*Pagrus major*), to 167 mg/L for olive flounder (*Paralichthys olivaceus*). Eggs and larvae tended to tolerate higher concentrations. Acute exposure to CO<sub>2</sub> concentrations above 67 mg/L caused profound extracellular acid-base disturbances that

led to violent struggling and then anaesthesia within 20 min in rainbow trout, *Oncorhynchus mykiss* (Bernier and Randall, 1998). When Silvercarp (*Hypophthalmichthys molitrix*), bighead carp (*Hypophthalmichthys nobilis*), largemouth bass (*Micropterus salmoides*) and bluegill (*Lepomis macrochirus*) were exposed to 30 mg/L of dissolved CO<sub>2</sub> for 1 h, they showed an elevated stress response, along with alterations to ionic– osmotic balance. Exposure to 70 mg/L of CO<sub>2</sub> caused a reduction in ventilation rates after 1 h, while both silver carp and bighead carp lost equilibrium. Silver carp, largemouth bass, and bluegill also showed avoidance of CO<sub>2</sub> at approximately 100 mg/L (Kates et al., 2012). CO<sub>2</sub> concentrations above 374 mg/L were required to anaesthetise carp, *Cyprinus carpio* (Yoshikawa et al., 1991). Grøttum and Sigholt (1996) found a median lethal concentration of CO<sub>2</sub> of 110 mg/L for the European seabass (*Dicentrarchus labrax*). The European eel, *Anguilla anguilla*, was found to be extremely hardy and could withstand acute exposure to 300 mg/L of CO<sub>2</sub> and chronic (> 6 weeks) exposure to 168 mg/L (McKenzie et al., 2002, 2003). Chronic effects (e.g. reduced growth) in parr of Atlantic salmon, *Salmo salar*, have been documented after exposure to 23-42 mg/L of CO<sub>2</sub> for 7-9 weeks in freshwater (Fivelstad et al., 2007, 1999). In seawater, chronic effects was found after exposure to 44 mg/L of CO<sub>2</sub> (Fivelstad et al., 1998).

Based on this limited review of studies on fish, it seems that the CO<sub>2</sub> concentration should probably not exceed 40 mg/L for more than a few hours to minimise the risk of toxic effects on fish. For longer term exposures, the concentration should not exceed 20 mg/L.

## 4. Conclusion

The pH decreased rapidly to pH 8.0 when CO<sub>2</sub> gas was added to alkaline solutions. It only took a few minutes, depending on initial pH, with the experimental conditions applied in the present study. The rate of pH decrease was markedly slower below pH 7.0. The CO<sub>2</sub> concentration was low (<40 mg/L) at pH values higher than 8.0, but increased rapidly as pH dropped below 8.0. Initially, the pH dropped faster and the CO<sub>2</sub> concentrations increased faster at 4 °C than at 15 °C, but there were no clear differences when the experiments were terminated. The transfer of CO<sub>2</sub> from gas to solution was more efficient and pH dropped faster in the turbid tunnelling waste water compared to the synthetic solutions.

The CO<sub>2</sub> concentration in tunnelling waste water at pH 8.0 is probably not acutely toxic to fish, but can rapidly reach toxic levels if CO<sub>2</sub> is used to further lower the pH. In a full scale CO<sub>2</sub> treatment plant, pH-controlled dosing seems appropriate in order to minimise the use of gas and the need for degassing or dilution before discharge. It is also advisable to monitor pH and CO<sub>2</sub> concentrations at the outlet.

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