Use of a stable carbon isotope to assess the efficiency of a drinking water treatment method with CO₂

M. Poberžnik, A. Leis and A. Lobnik

ABSTRACT

CO₂ gas with a special isotopic signature (δ¹³C = −35.2‰ vs. VPDB) was used as a marker to evaluate the efficiency of a drinking water treatment method and the effect of an ultrasonic (US) stirrer. This treatment was developed to prevent precipitation and corrosion effects in water-supply systems. The research work was performed using a laboratory-scale pilot plant that was filled with tap water. The stable isotope analyses of δ¹³C-DIC (Dissolved Inorganic Carbon) in the water samples indicated that the maximum content of added CO₂ gas in DIC was in the range of 35 to 45%. The use of the US stirrer during the entire experiment decreased the method’s overall efficiency by 10%, due to degassing at a late stage of the experiment but accelerated the dissolution process in the early experimental stage.

Key words | ¹³C stable isotope, carbon dioxide, carbonate equilibrium, corrosion, drinking water, limestone

INTRODUCTION

Natural water can have, depending on origin, a high content of dissolved carbonate minerals (e.g. calcium carbonate). These minerals have a tendency to precipitate if the mineral content of the water becomes oversaturated. The resulting insoluble mineral deposits can then lead to a number of problems, such as, the clogging of pipes and heat exchangers, and damage to valves. It is also possible that an excess of CO₂ can create serious corrosion problems, resulting in increased concentrations of certain, often toxic, metal ions, such as lead, cadmium, nickel and iron, in tap water (Lahav et al. 2009). Corrosion products accumulated as sediments in water-supply systems can also reduce the effect of disinfectants and affect the tap water’s microbiological quality (Melidis et al. 2007). Insoluble mineral deposits and corrosion are the cause of the majority of the maintenance costs in water-supply systems (Sander et al. 1996). Moreover, such problems invariably mean an increase in energy consumption (Alimi et al. 2007). For these reasons, water of optimal quality for human consumption should not be corrosive in water systems, nor should it lead to the formation of calcium carbonate deposits. To meet these conditions the water should be, as far as possible, in thermodynamic equilibrium with respect to the mineral phases of calcite or aragonite (Poberžnik et al. 2008).

Drinking water pre-conditioning, based on a subsequently controlled addition of carbon dioxide (CO₂) gas as a non-toxic, natural component of healthy drinking water, represents an environmentally friendly and low-cost process to improve the quality of drinking water (Linde 2003). The reaction (1) between calcium carbonate (CaCO₃) and carbon dioxide (CO₂) is fundamental to an understanding of the dissolution or precipitation of calcite and indicates that the optimal CO₂ concentration is critical to maintaining equilibrium conditions (Szaran 1997; Fitts 2002):

\[
\text{CO}_2(g) + \text{H}_2\text{O}(lq) + \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq) \tag{1}
\]

The application of carbon dioxide as it relates to drinking-water conditioning has often been studied in the context of desalination plants, where the gas is used for recarbonation in the limestone/carbon-dioxide method (Marangou & Savvides 2001; Glade et al. 2005), while a method for introducing CO₂ into well water in...
full-scale distribution systems is only in early implementation phase.

Stable isotope analyses in hydrogeology have developed rapidly since the 1950s and nowadays represent the most common technique in surface and groundwater studies (Edmunds 2009). However, there are only a few studies in the field of civil engineering where stable isotopes are used to assess technical problems such as sinter formation in tunnelling and drainage systems (Dietzel et al. 2008, 2009) or mortar and plaster investigations (Dietzel et al. 1992; Kosednar-Legenstein et al. 2008).

Light stable carbon isotopic analyses are a well-proven tool for identifying the source of carbon, especially when it comes to distinguishing between isotopically lighter and isotopically heavier carbon. The stable carbon isotope ratio $^{13}$C/$^{12}$C is widely used in natural sciences to study processes in atmospheric, terrestrial, marine and freshwater environments (Boutton et al. 1991; Sharp 2007). However, the use of stable isotopes in technical solutions represents an advanced approach to evaluating the efficiency of drinking-water treatment with CO$_2$.

The aim of the present study is to assess the efficiency of drinking-water treatment with CO$_2$ by using stable-isotope signatures of carbon as an internal tracer. The experimental work included an efficiency evaluation of the water-conditioning method using gas with a special carbon isotopic ratio value *CO$_2$ ($\delta^{13}$C = $-35.2$‰ vs. VPDB) and assessing the effect of an ultrasonic (US) stirrer on the gas dissolution. The results of the carbon isotopic composition are reported in terms of delta notation (2), as recommended by the IUPAC, referring to the Vienna Pee Dee Belemnite (VPDB) calcite standard (Hut 1987; Coplen et al. 2006).

$$\delta^{13}\text{C}_{\text{sample}} = \left(\frac{^{13}\text{C}/^{12}\text{C}_{\text{sample}}}{^{13}\text{C}/^{12}\text{C}_{\text{VPDB standard}}} - 1\right) \times 1,000$$

(2)

The $\delta^{13}$C values of dissolved carbonate species in nature, among which hydrogen carbonate ($\text{HCO}_3^-$) is prevalent, are various, but are typical with respect to different sources (Drever 1997; Sharp 2007).

EXPERIMENTAL SET-UP

The experiments were performed using a pilot plant (Figure 1) for the controlled introduction of the CO$_2$ gas into the water. The plant was constructed to observe the limestone precipitation in the pipeline and gasketed plate heat exchanger. The pilot plant consists of a closed primary pipeline with adjustable temperature of heating fluid (water) and closed secondary line, supplied with tap water. The volume of the secondary line, where the gas is introduced, is approximately 180 L. The pilot plant is equipped with a sensor system with the corresponding software package for online monitoring of the dissolved carbon dioxide, the pH, the temperature and the conductivity, and a US stirrer (27 kHz, 4 W).

The experimental set-up, the pilot plant and the experiments performed with commercial CO$_2$ gas ($\delta^{13}$C = 3.41‰) are described in detail in Poberžnik et al. (2008). To evaluate the method’s efficiency, the experimental work was carried out using a gas with a special carbon isotopic value *CO$_2$ ($\delta^{13}$C = $-35.2$‰ vs. VPDB, Messer). The system was closed with regard to freshwater inflow and the operating conditions were as follows: temperature, 60 ± 5 °C; pressure, 2 bars; water flow, 2 L/min, and the maximum amount of added *CO$_2$. Experiments were performed with and without the US stirrer. The maximum amount of added *CO$_2$ turned out to be dependent on the use of the US stirrer, i.e. 273 g without the US stirrer, and 240 g with the US stirrer.

The system was filled up with fresh tap water and heated to the working temperature before we began the procedure.
of adding the gas. The experiments lasted until the system was in the steady state, i.e. the pH and the conductivity were constant. Some samples of water were then removed from the system at a defined measuring point, marked as MP in Figure 1. The initial sample (1) was taken before the heating started, and the second sample (2), when the system was heated to the operating temperature, before any gas was added. The subsequent samples (3 to 13) were taken after different amounts of added gas 1, 3, 5, 10, 15, 20, 25, 50, 100, 150 g and the maximum values, 273 and 240 g.

In the next step the chemical composition of the water was analyzed. The concentrations of cations, such as Na\(^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), and anions, such as Cl\(^-\), NO\(_3^-\), SO\(_4^{2-}\), were determined with ion chromatography (Dionex ICS-3000/DX-500). The hydrogen carbonate ion (HCO\(_3^-\)) concentrations, i.e. the alkalinity of the investigated water samples, were determined using automatic titration (Metrohm, 736 GP Titrino).

The samples for stable carbon isotopes of DIC (\(^{13}\)C/\(^{12}\)C) were collected in 10 mL Na-glass vials (Labco exetainer) preloaded with six droplets of phosphoric acid, capped with air-tight caps and flushed with helium. The isotopic composition of the DIC was analyzed using a fully automated peripheral continuous-flow gas-preparation device (Gasbench II), which was connected to a Finnigan Deltaplus XP mass spectrometer. The declared and experimentally proven overall precision of the method is 0.1‰.

### RESULTS

The hydrochemical composition as well as the electrical conductivity of the treated water samples (Table 1) indicates only minor, but expected changes (Ca\(^{2+}\), HCO\(_3^-\)) during heating and *CO\(_2\) gas addition. The concentrations of the other monitored dissolved ions were not significantly affected during the *CO\(_2\) gas addition and heating process.

The concentrations of the Ca\(^{2+}\) and HCO\(_3^-\) ions decreased to maximum values of 95.3 and 97.9%, respectively of the initial value during heating (sample 4), and increased to maximum values of 100% and 102.3%, respectively of the initial value during the addition of the *CO\(_2\) (sample 12). The decrease of the Ca\(^{2+}\) and HCO\(_3^-\) ions in the last water sample indicates the loss of the gas from the solution, when the separation of liquid and gas phases in the system took place. However, the changes in the carbon-isotope composition of the DIC in the water samples reflect the effect of the added gas more clearly (Figures 2 and 3).

Moreover, Figure 2 shows that the \(\delta^{13}\)C DIC values of the water samples approximate to the \(\delta^{13}\)C value of the added gas, which indicates that the introduced special isotopic gas *CO\(_2\) is involved in the formation of hydrogen-carbonate ions. The use of the US stirrer influenced the dynamics of the gas dissolution, as well as the final \(\delta^{13}\)C DIC values of the water samples. The effect of the US stirrer was most significant in the late phase of the experiment. This is reflected in the different \(\delta^{15}\)C values of

### Table 1 | Chemical water composition for the experiment without the use of the US stirrer

<table>
<thead>
<tr>
<th>Sample</th>
<th>(^{13})CO(_2) added (g)</th>
<th>pH</th>
<th>El. cond. (μS)</th>
<th>Na(^+) (mg/L)</th>
<th>K(^+) (mg/L)</th>
<th>Mg(^{2+}) (mg/L)</th>
<th>Ca(^{2+}) (mg/L)</th>
<th>Cl(^-) (mg/L)</th>
<th>NO(_3^-) (mg/L)</th>
<th>SO(_4^{2-}) (mg/L)</th>
<th>HCO(_3^-) (mg/L)</th>
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<td>12.0</td>
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<td>17.3</td>
<td>77.8</td>
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<td>16.6</td>
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the final water samples, i.e. the δ¹³C value of the last water sample from the experiment without the US stirrer was 2.7‰ closer to the δ¹³C value of the added gas (−35.2‰), compared to that from the experiment without the US stirrer.

Based on the measured δ¹³C DIC values of the water samples from the experiments using the special isotopic gas, the corresponding mole fractions of the added gas *CO₂ in the water samples were calculated. The *CO₂ mole fractions in the water samples taken during the experiments with and without the US stirrer are presented in Figure 3.

In the early stage of the experiment (samples 2 and 3) the *CO₂ mole fractions were slightly in the negative range, i.e. −0.9 and −2.4‰ with respect to the initial value without and with the use of US stirrer, respectively. It is clear that the lighter isotopic fraction (δ¹³C = −35.2‰) was leaving the system during heating (ΔT = 41 °C) and the effect was additionally intensified by the use of the US stirrer. In the subsequent experimental phase, while adding an isotopically lighter gas *CO₂, its mole fraction increased and reached a terminal value in the steady state after 23.2 h without and 21.3 h with application of the US stirrer. The final mole fraction value was significantly higher (44.7‰) in the unstirred solution, while the application of the US stirrer in the later stage of the experiment (samples 11 to 13) caused degassing and, consequently, a lower *CO₂ mole fraction (34.7‰). By considering that the DIC concentration
in the experimental pH range (5.5–7.2) mainly corresponds to the concentration of hydrogen carbonate ions (HCO₃⁻). we can state that almost 45 and 35%, respectively, depending on the use of the US stirrer, of hydrogen carbonate ions result from reactions with the added gas.

We can also conclude that the use of the US stirrer negatively influences the dissolution of the added gas in the later phase of the experiment (samples 12 and 13), but it also promotes the dissolution during the middle phase of the experiment (samples 3 to 5).

**CONCLUSION**

The research work was performed on a laboratory-scale pilot plant, filled with tap water and using ¹³C-CO₂ gas with a special isotopic signature (δ¹³C = −55.2‰ vs. VPDB) as a tracer. The experimental results were used to evaluate the efficiency of the drinking water treatment method with CO₂ and the effect of the US stirrer. The use of carbon stable isotopes of DIC as a tracer to assess the efficiency of the investigated water conditioning method results from reactions with the added gas.

We can also conclude that the use of the US stirrer negatively influences the dissolution of the added gas in the later phase of the experiment (samples 12 and 13), but it also promotes the dissolution during the middle phase of the experiment (samples 3 to 5).

**REFERENCES**


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