IMPROVEMENTS TO THE QUALITY OF UNDERGROUND WATER BY INTRODUCING CARBON DIOXIDE

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Abstract

The presented research work is focused on the development of an innovative way of economically improving the quality of underground water by the application of carbon dioxide.
The basic pilot plant was developed with the idea of applying carbon dioxide in order to maintain the carbonate equilibria in water, pumped from under the ground. The optimal content of this natural component in underground water, used in urban areas for different purposes (e.g. drinking water, heating systems etc), simultaneously prevents corrosion and precipitated mineral deposits.
The adaptation of an existing pilot plant started with operational testing and preliminary measurements. An appropriate sensor system for the online monitoring of the tap water's heating process measuring parameters such as the temperature, the concentration of dissolved carbon dioxide, the conductivity and the pH value was built in. Different amounts of carbon dioxide were applied during the two experimental stages. The composition of the water was regularly analysed using automatic titration and ionic chromatography. The gas-dosing control in the first phase was volumetric. Due to an observed inaccuracy in the gas-dosing system, the volumetric dosing control was replaced with a system for the mass control of the introduced gas. Closing the system was considered to be suitable, as the water composition remained almost constant during the entire experiment. Improvements to the gas-dosing control and the closing of the system were carried out in the final phase of the pilot plant's adaptation. Further measurements were made in different seasons to test the seasonal influences on underground water's composition and the efficiency of the carbon dioxide supply.

keywords

underground water, drinking water quality, pilot plant, carbonate equilibria, carbon dioxide, precipitation, scale

1 INTRODUCTION

Underground water, percolating through different geological structures, dissolves certain minerals. The behaviour of this underground water is most interesting in areas that consist of carbonate rocks, e.g. limestones and dolomites. The main minerals in these rocks are calcium and magnesium carbonates, which dissolve easily in underground water and give the water its hardness. The quality of the water depends significantly on its hardness. In urban areas underground water is widely used as a source of water for various purposes, e. g. as drinking water, sanitary water and communal water [1].

Municipal companies that manage distribution systems for underground water and wastewater are constantly confronted by the necessity to invest large amounts of money in maintenance programmes with regard to water installations and canalizations in order to prevent the

consequences of limestone deposits and corrosion [2].

Healthy water for human consumption should not be corrosive in waterworks with either form limestone deposits. Therefore, the water has to be kept in a thermodynamic balance with the mineral phases of calcite or aragonite in order to fulfil this condition [3]. The natural water content depends on a combination of the geochemical and biological processes, in addition to the water's pH and alkalinity, which are two of the most important parameters affecting the composition of natural water [4].

Conventional drinking-water preparation as well as cooling and boiling feed-water preparation is based on softening and demineralization. Softening units are designed to replace of multiply charged positive ions (Ca^{2+}, Mg^{2+}) with sodium (Na^{+}) ions and demineralization units are designed to remove a fraction of all the ions from water [5]. A more recently developed alternative method for preventing waterworks from developing lime scale is introduction of electromagnetic water conditioning. An electromagnetic conditioner works by creating a magnetic field around the pipework, which alters the ions' crystallization behaviour, so removing their ability to form scale [6].

Drinking water pre-preparation, based on the subsequent addition of CO_2 gas as a natural component of healthy drinking water is a low-cost process for improving the quality of drinking water and, simultaneously, not altering the natural water's mineralogical composition. It represents an innovative and environmentally friendly method, as no unwanted by products or pollution arises. The aim of the presented research work was to develop a pilot plant and to test different methods for increasing the efficiency degree of the CO_2 supply. To our knowledge, the presented pilot plant and such an application of carbon dioxide are original and have never been published before.

To date a similar application of CO_2 has been developed by the Messer Company but this one is related only to wastewater neutralization. The advantage of using carbon dioxide rather than sulphuric acid is reflected in simplifying the technological process, while at the same time reducing the costs [7].

2 CARBONATE SPECIES IN NATURAL WATERS

Sedimentary rocks, such as limestones and dolomites represent the most extended rocks of aquifers and their main minerals, calcium and magnesium carbonates dissolve easily in groundwater. Consequently, calcium is found to be the highest concentration of totally dissolved solids in average river compositions from different continents [8].

With regard to the composition of natural waters, 90% of the impurities come from just eight inorganic species i.e., Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^-, SO_4^{2-}, and Cl^-. Some of them are inert, e.g. Na^{+}, K^{+}, NO_3^- and Cl^-, meanwhile the components of the carbonate equilibria are involved in numerous chemical reactions (1), which results in variations in their concentrations [9].

$$\begin{array}{l} CO_2(g) \\ \updownarrow \\ CO_2(aq) + H_2O \longleftrightarrow H_2CO_3 \\ \qquad\qquad\quad \updownarrow \qquad\quad \updownarrow \\ \qquad\qquad OH^- + H^+ \quad H^+ + HCO_3^- \\ \qquad\qquad\qquad\qquad\qquad \updownarrow \\ \qquad\qquad\qquad\qquad H^+ + CO_3^{2-} + Ca^{2+} + CO_3^{2-} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad \updownarrow \\ \qquad\qquad\qquad\qquad\qquad\qquad CaCO_3(s) \end{array} \tag{1}$$

The slowest reaction in this dynamic system is the gas transfer into the aqueous phase, which is slower than other reactions that produce or consume carbon dioxide during the aqueous phase, e.g. calcite dissolution and precipitation. The formation of carbonic acid is reported to equilibrate within 20-200 s in a stirred solution, while the dissociation of bicarbonate and carbonate ions equilibrates within seconds [10].

Under all pH conditions, most of the dissolved CO_2 exists as CO_2 (aq) and only a small amount of the dissolved CO_2 (aq) is hydrated to produce carbonic acid [9]. Various ratios of CO_2 (aq)/H_2CO_3 (aq) have been reported e.g. 385/1 or 250/1 [11]. It is conventional to express the total dissolved carbon dioxide as H_2CO_3*, which represents the sum of the CO_2 (aq) and the H_2CO_3 (aq) [9].

The dissolved carbon dioxide in an aqueous solution is distributed among three species, H_2CO_3* (dissolved CO_2), HCO_3^- (bicarbonate) and CO_3^{2-} (carbonate). Table 1 shows the equilibrium equations and the corresponding constants over different pH ranges [8, 9, 12]:

Table 1. The carbonate equilibria equations and the corresponding equilibrium constants over different pH ranges.

pH range	Equilibrium equation	Equilibrium constant
pH < 4.3	$CO_2\,(g) + H_2O \rightleftarrows H_2CO_3^*$	$K_{CO2} = 10^{-1.47}\ atm^{-1}$
4.3 > pH < 8.2	$H_2CO_3^* + H_2O \rightleftarrows HCO_3^- + H_3O^+$	$K_{H2CO2} = 10^{-6.35}$
pH > 8.2	$HCO_3^- + H_2O \rightleftarrows CO_3^{2-} + H_3O^+$	$K_{HCO3^-} = 10^{-10.38}$

The reaction between calcite ($CaCO_3$) and carbon dioxide (2), derived from biological processes, is the fundamental reaction for understanding the dissolution and precipitation of $CaCO_3$ in nature [8]:

$$CO_2(g) + H_2O(lq) + CaCO_3(s) \rightleftarrows Ca^{2+}(aq) + 2HCO_3^-(aq) \qquad (2)$$

The redundancy of the dissolved CO_2 causes the formation of a weak carbonic acid, a decrease of pH value and dissolution of $CaCO_3$. The acidic pH of drinking water has harmful influence on humans' physiological environment and causes corrosive damage to pipelines (Figure 1).

The deficit of dissolved CO_2 (degassing of water) causes the precipitation of non-soluble crystalline structures (e.g. $CaCO_3$) and results in the obturation of mechanical parts (filters, valves), flow hindrance due to limestone precipitates, and the loss of energy (Figure 2).

Rocks formed from sediments cover 93% of the Slovenia's land area. Among them limestone (25%) and dolomite (10%) are the most extensive. In Slovenia, over 95% of the water used for public supplies is drawn from groundwater, while, for example, in the United States the quantity is only 40% [3, 14].

The Drava basin, located in the Northeast of Slovenia, represents a source of potable water for the wide Maribor area. A geological map in Figure 3 shows the ground composition of the aquifer along the River Drava in the wider area of the City of Maribor. The

Figure 1. Corrosive damage to pipe lines.

Figure 2. Noxious consequences of limestone deposits.

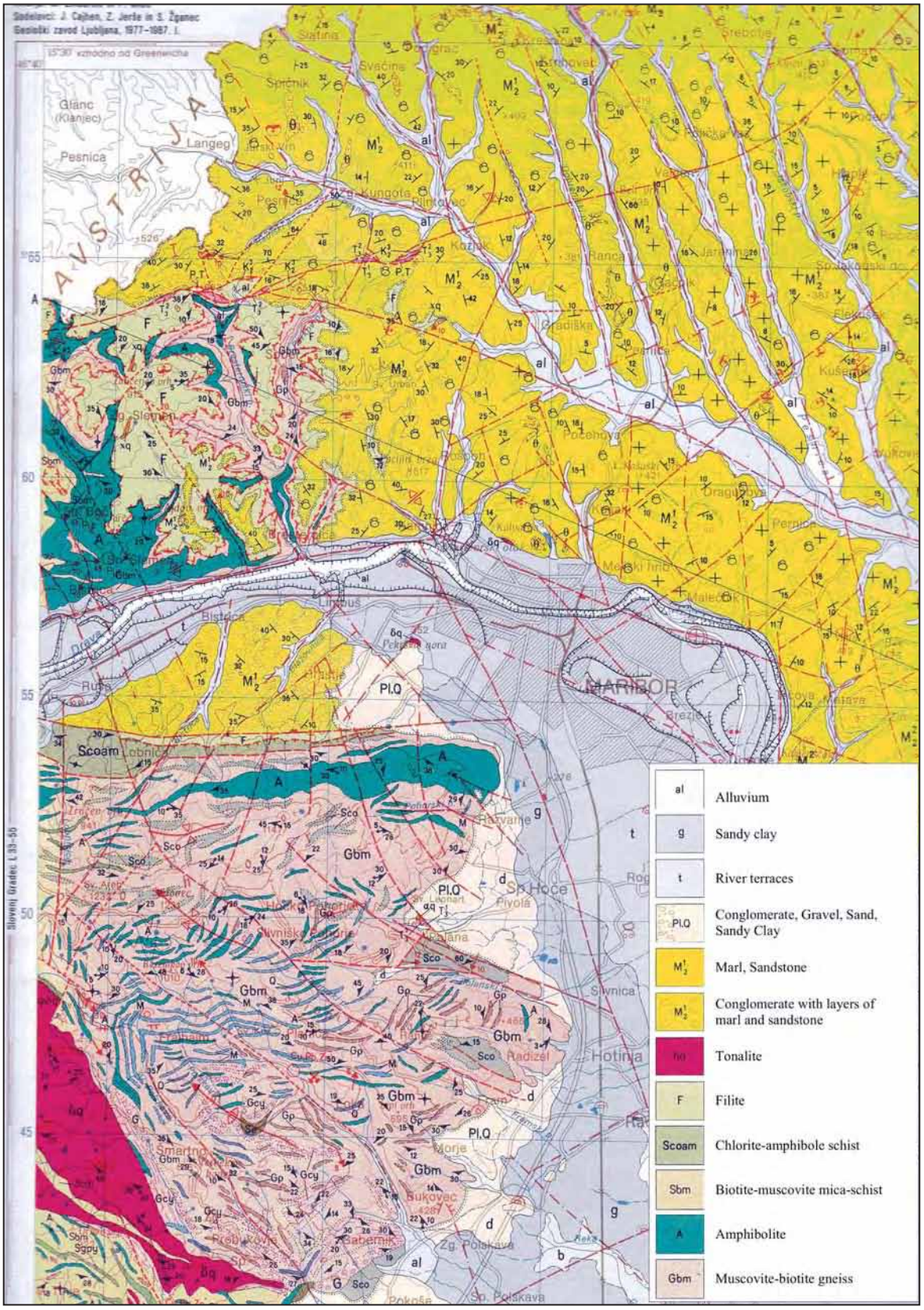

Figure 3. Geological map of the underground water area in Maribor.

underground water levels (UWL) around the pumping station at Vrbanski plateau are presented in Figure 4. The underground water level variations over the period 2004 to 2008, considering water flow and the quantity of pumped water are shown in Figure 5.

The presented international research work that discusses the optimization of underground water quality by introducing carbon dioxide was performed within the K-Net Centre of Water Resources Management (WRM).

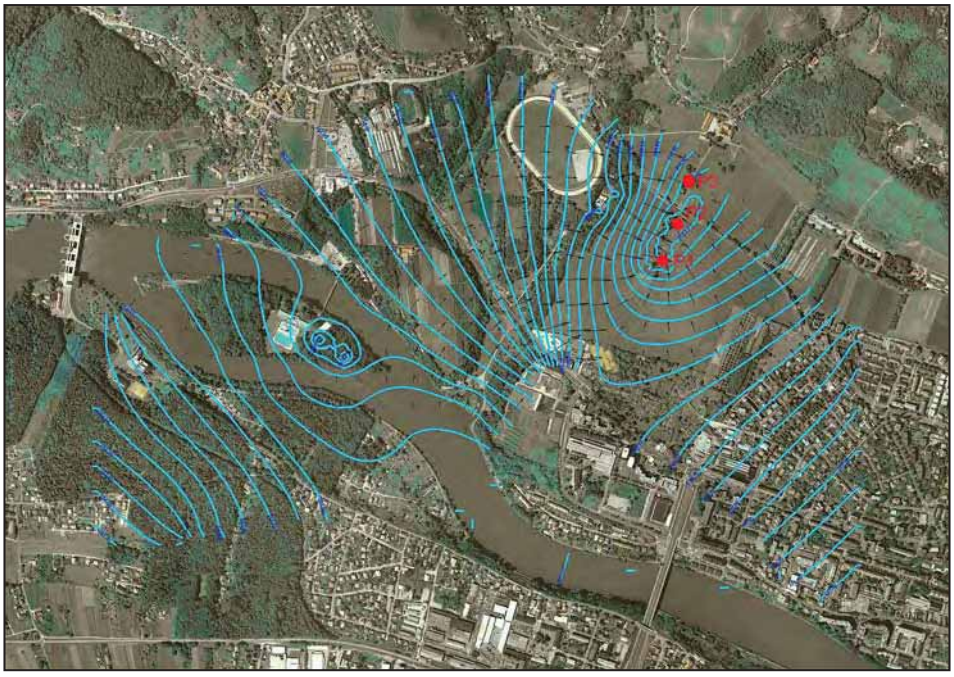

Figure 4. Underground water levels (UWL) in the area of Vrbanski plateau, the pumping station for Maribor waterworks.

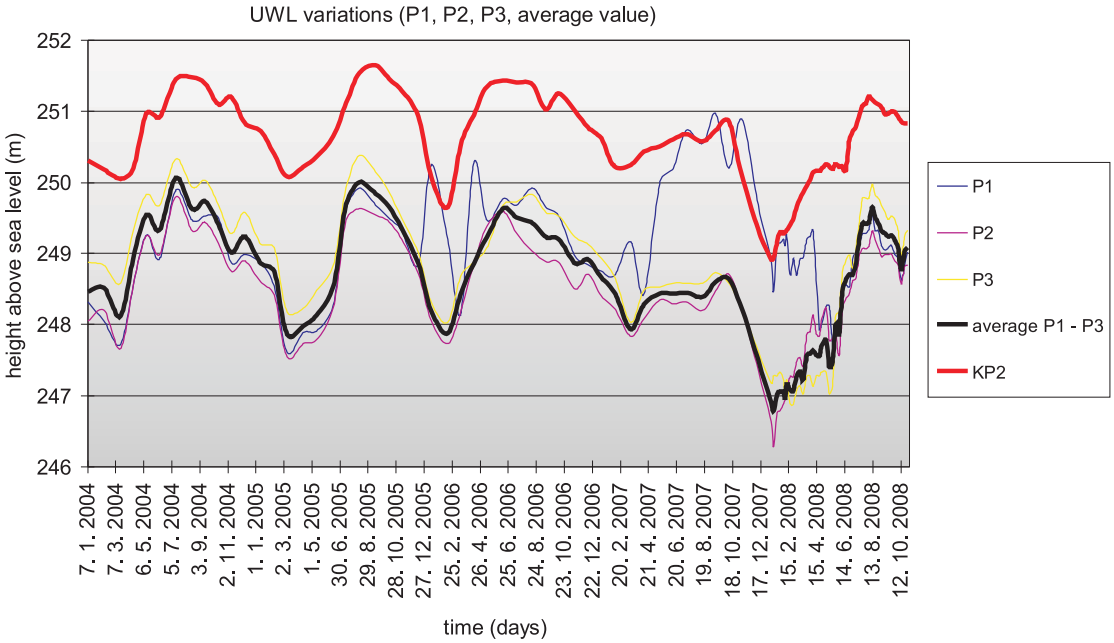

Figure 5. The underground water-level variations over the past four-year period (2004 to 2008) considering the water flow and the quantity of pumped water.

Table 2. The average values of significant carbonate equilibria parameters regarding drinking water over a ten-year (1995 -2005) period in the Maribor area.

	Winter	Spring	Summer	Autumn
Ca^{2+} (mg · L^{-1})	76.17	81.28	54.35	73.81
HCO_3^- (mg · L^{-1})	265	273	248	251
pH	7.52	7.53	7.47	7.57
Conductivity (μS · cm^{-1})	516	511.25	510.62	511.16

The aquifer is classified as a carbonate-silicate type with inter-grained porosity and belongs to the second most extended of the Slovenian aquifers' types (26.2%) [15]. Analytical data, including the averages of the past ten years characterize the tap water in the Maribor region as moderately hard water (12–18 °n) [16]. Comparing the ten-year averages of water composition over different seasons indicates some typical patterns in the most significant parameters of carbonate equilibria (Table 2) [16]. The total dissolved solids concentration (TDS), including the concentration of Ca^{2+}, Mg^{2+} and CO_3^{2-} is increased in the spring and winter seasons due to more intensive rock weathering and washing out. Meanwhile, the pH value does not vary significantly over the year.

3 EXPERIMENTAL

The experiments were performed on a pilot plant constructed for the observation of precipitation in pipe-lines and heat exchanger. The basic pilot plant consisted of a closed primary pipeline with adjustable temperatures of the heating fluid and an open secondary pipeline, supplied by tap water, a heat exchanger, and an ultrasonic stirrer.

An operational test was performed to find out the initial time for the stabilization of the system, and to indicate the scale precipitation in the heat exchanger under the following conditions: 65°C, 2 bars and 2 L/min of water flow, known tap-water composition, applied ultrasound (US, 27 kHz, 4W), and without introducing additional carbon dioxide.

A preliminary set of measurements was carried out on the basic pilot plant, without the sensor system. The samples were taken periodically every hour at five points of the process. The concentrations of free carbonic acid, calcium ions and hydrogen carbonate ions were determined titrimetrically. The temperature and the pH value were measured, while the pressure and water flow were kept constant during the entire experiment. Other experiments were performed using the same pilot plant, operating under the same conditions, but with the application of different amounts of additional carbon dioxide [14].

The new sensor system and the corresponding software package were chosen on the basis of the preliminary results. During the first adaptation phase, a new sensor system (Figure 6) for online monitoring of the dissolved carbon dioxide, the pH, the temperature and the conductivity were built in and calibrated. The disadvantage of this, the only appropriate sensor system, is that it makes it possible to control the mentioned parameters only within a limited temperature range. The CO_2 electrode characteristics make it possible to measure the amount of dissolved CO_2 within a temperature range up to 65°C and within a concentration range from 0 to 4000 mg/L. The heat exchanger was also replaced with a new, gasketed one.

Figure 6. Sensor system with electrodes.

The pilot plant after the first phase of adaptation is presented in Figure 7.

The first set of experiments was carried out in the summer season. It comprised 35 measurements: seven at each of five measuring points (MP), with the addition of different amounts of CO_2 (1 L/min, 3 L/min and 5 L/min), and all with and without the application of

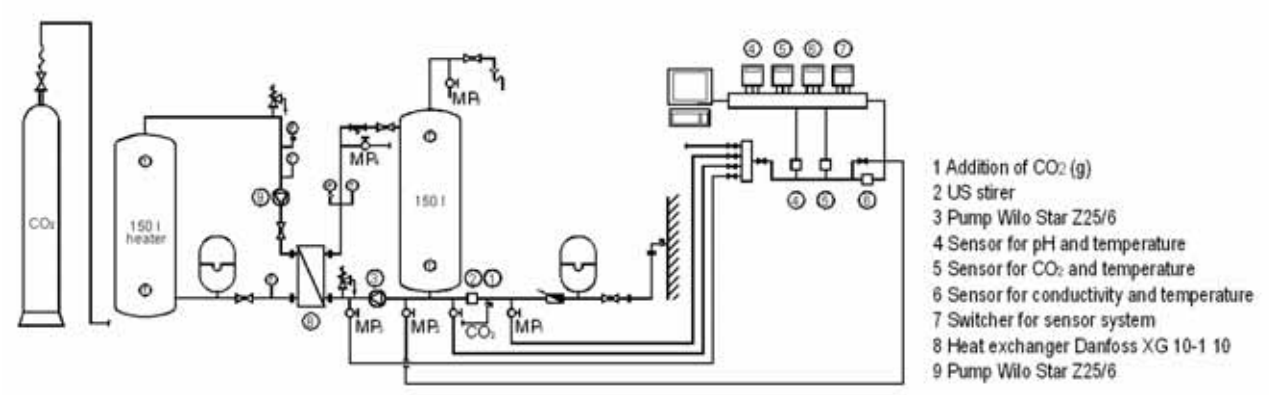

Figure 7. Partially adapted pilot plant.

ultrasound. The temperature, the amount of dissolved carbon dioxide, the conductivity, and the pH value were measured online. During this set of experiments, some inaccuracy was observed in the volumetric dosing control of the carbon dioxide. Therefore, an additional adaptation of the CO_2 dosing system was necessary.

To improve the dosing accuracy of the additional gas into the system, the non-return valve was replaced with a new one and an additional gas reservoir was built in as a buffer (Figure 8). The mass of gas introduced became controllable on the basis of measurements of the gas weight (Figure 9). The reduction valve on the tap line was also changed and an additional overflow valve was built in at the outflow of the experimental line, in order to maintain the pressure in the system at a constant value.

One measuring point in the system became sufficient, operating under close conditions (regarding water). The former measuring point four (MP 4) was chosen as the most appropriate.

The water samples were further analysed using automatic titration (Metrohm GP Titrino 736) and ionic chromatography (Dionix ICS – 3000 DC, DX - 500).

The second, i.e. winter, set of experiments was carried out on the adapted pilot plant, operating as a closed system with mass control of the gas dosing. This set comprised nine experiments: five with and four without the application of ultrasound (US) with the addition of different amounts of CO_2 (25 g, 50 g, 100 g, and the maximum amount, 240 g), which finally resulted in 65 water samples. The maximum amount of introduced gas was determined experimentally and depended on the application of ultrasound. Without ultrasonic stirring the amount of introduced gas corresponded to the solubility limit of CO_2 in water. In the case of applied ultrasound the non-dissolved gas was leaving the aqueous system due to stirring and its introduction did not stop spontaneously. The process temperature during the winter set of experiments was between 60 and 65°C due to working-temperature limitation of the sensor system.

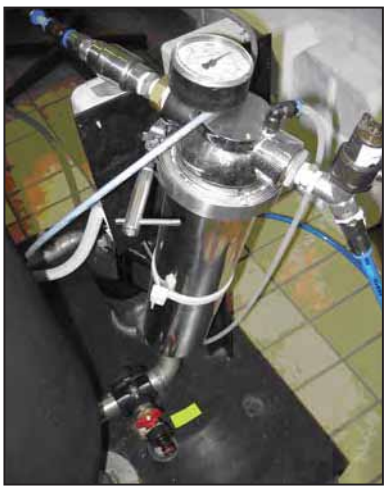

Figure 8. The additional gas reservoir.

Figure 9. Weighting of the introduced gas.

The detailed water-composition analyses for all the water samples followed the work on the pilot plant.

The software package "PHREEQC-2" was selected as the relevant program for the hydro-chemical modelling and Langelier saturation indexes were determined on the basis of the collected experimental data for the second experimental set.

4 RESULTS AND DISCUSSION

Preliminary and test measurements were carried out on the basic pilot plant to test the operating conditions of the plant and the experimental proceedings. The early phase was focused on the adaptation of the plant, and the selection and purchasing of an appropriate sensor system.

During the preliminary experiments carried out without the sensor system, it was established that the operating conditions are stabilized over a period of two hours. When the system operated without introducing additional carbon dioxide, the measured concentrations of calcium ions at the measuring points MP 1 and MP 3 were about 10% higher than the equilibrium concentrations (evaluated from a thermodynamic diagram of the calcium carbonate solubility vs. temperature and pH). A slight over-saturation was already present at the entrance and this increased during the heating, resulting in abundant scaling on the heated surfaces. The output concentrations were comparable to the equilibrium values. The additional application of carbon dioxide between measuring points MP 1 and MP 2 resulted in an increase in the concentrations of free carbonic acid, and a decrease in the pH value. The results from the next three measuring points (MP 3 to MP 5), which showed a decrease in free carbonic acid concentration and a slight rise in the pH compared to MP 2, are probably related to transferring the gas into the aqueous phase [14].

The extensive experimental work presented in the next paragraphs was performed in summer and winter of 2006 and 2007. Due to large amount of experimental data only some representative data are discussed in this paper.

After the sensor system was built-in and calibrated, the first, summer set of measurements was performed using on-line monitoring of the most relevant carbonate equilibria parameters. Considering the results of the water-composition analyses, the open system, operating at temperatures between 18 and 58°C without the introduction additional carbon dioxide, displayed only slight signs of the expected behaviour. As the temperature increases, the concentration of CO_2 decreased by 12% and the pH value increased by 2%, from the initial values (Figure 10). Based on slight changes in the Ca^{2+} ions content (a decrease of 0.5% at MP 3) it might follow that the over-saturation of the water involved is relatively low.

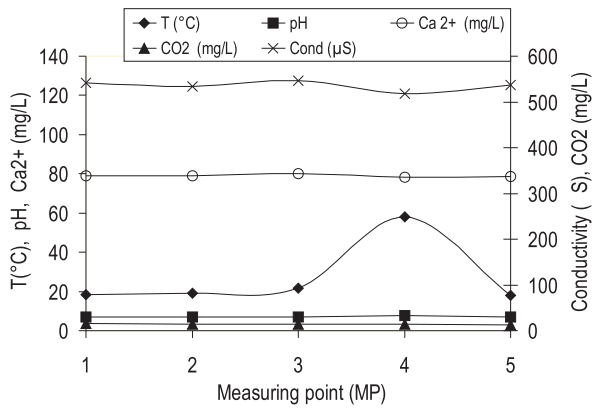

Figure 10. Measurement results without applied US and without introducing additional CO_2 (open system).

The measurement results with 5 L/min of introduced carbon dioxide without the applied ultrasound are presented in Figure 11.

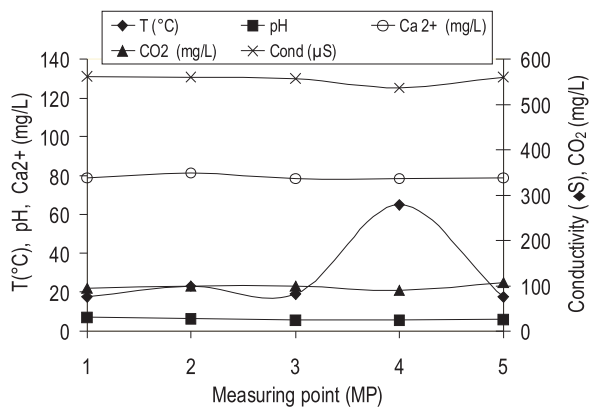

Figure 11. Measurement results without applied US and with introducing 5 L/min of additional CO_2 (open system).

Carbon dioxide was applied between MP 1 and MP 2, which resulted in a 3% increase in the concentration of dissolved carbon dioxide and a 26% decrease in the pH value at MP 3. The calcium- ions content decreased due to precipitation (0.08%). The result from the last measuring point, MP 5, which shows a rise of 0.1 units of pH compared to MP 3, is related to the transferring of the gas into the aqueous phase. The concentration

of calcium ions increased by 2.5%, as the temperature decreased to approximately 50°C and this could indicate that the precipitated calcium carbonate was partly dissolved again. The terminal pH value remained within a slightly acidic range (5.93).

The same experiment was carried out with the application of an ultrasonic stirrer. The application of ultrasound was indicated by the 20% increase in the initial amount of dissolved carbon dioxide at MP 5 as a consequence of the ultrasonic stirring.

Based on the water analyses results and the changes of water composition during the experimental process, a more detailed study and description of the system followed.

They showed that the composition of the water did not alter significantly during the whole of the experimental period. A possible explanation for this in the presented investigation phase was that the kinetic conditions did not allow precipitation in this open system, although the system was over saturated from the thermodynamic point of view. The extracts from wider water composition analyses, carried out by the automatic titration and ionic chromatography, are presented in Tables 3 and 4. It turned out that no significant variations in the calcium content occurred with process temperatures up to 65°C. The maximum analysed variation in the calcium content was only 2.66 mg, i.e. 3.6% of the initial value.

This led to the idea of closing the system (in terms of freshwater inflow) in order to intensify the precipitation process and to examine the effect of different amounts of additionally introduced carbon dioxide.

The second, i.e. winter set of measurements was carried out on the pilot plant, operating as a closed system in terms of fresh water inflow. The overview of the experiments showed that the optimal quantity of applied carbon dioxide for the operating conditions and the used tap-water composition used is 500 mg. The experimental procedure and the measurement data without introduced gas, with the application of 500 mg of carbon dioxide are presented in the following Figures 12 and 13, respectively.

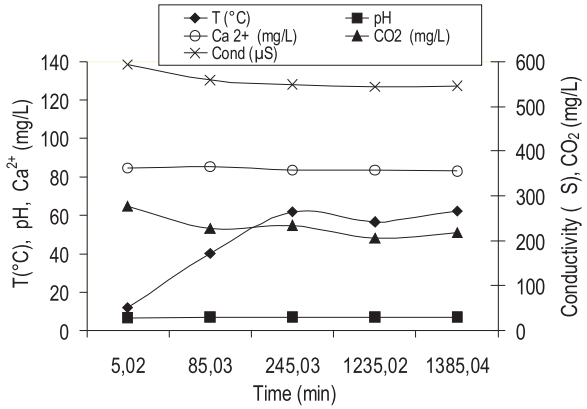

Figure 12. Measurement results without applied US and without introducing of additional CO_2 (closed system).

Table 3. Water composition analyses results without applied US and without additional CO_2.

	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	alkalinity (ml HCl)
MP 1	n. a.	n. a.	n. a.	78.95	19.87	17.24	30.28	281.56	4.61
MP 2	13.28	2.07	15.22	78.88	19.55	15.68	30.31	284.04	4.65
MP 3	14.35	2.20	15.58	80.26	21.16	19.02	32.12	288.49	4.73
MP 4	13.01	2.14	15.37	78.15	19.58	18.23	30.53	282.19	4.62
MP 5	13.01	2.08	15.45	78.58	19.74	17.34	31.06	280.68	4.60

Table 4. Water composition analyses results without applied US and with 5 L/min of additional CO_2.

	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	alkalinity (ml HCl)
MP 1	13.07	2.23	15.37	78.88	20.35	17.74	31.49	282.14	4.62
MP 2	13.68	2.32	15.53	81.38	21.60	17.82	33.01	291.41	4.78
MP 3	13.24	2.23	15.15	78.24	19.91	17.55	30.68	281.18	4.61
MP 4	13.19	4.26	15.00	78.48	22.22	18.11	31.05	282.02	4.62
MP 5	13.24	2.23	15.20	78.80	21.23	19.13	31.60	279.62	4.58

The system was stabilized and the terminal temperature of 62°C was reached in a period of four hours because the initial water temperature was only 11.8°C due to the winter season. During the heating the CO_2 concentration of decreased by 42.8 mg/L (15.4% of the initial value) and consequently the pH value increased by 0.43 units (6.3% of the initial value). The variations in Ca^{2+} concentration during the process were expected, but were not significant. The highest Ca^{2+} concentration (85.1 mg/L) was reached at 40°C, and it decreased by 1.8 mg/L (2.1% of the initial value) until the terminal temperature was reached. The variations in the dissolved species showed

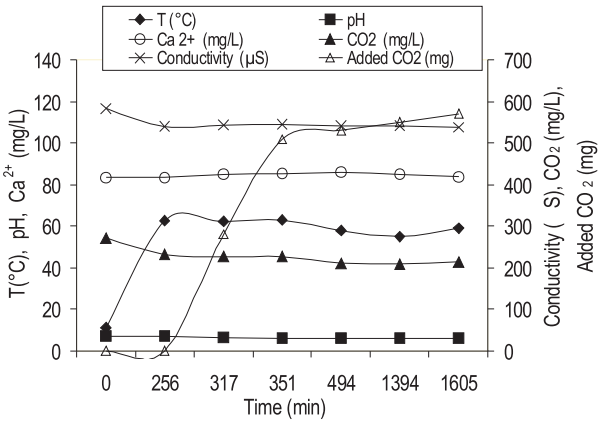

Figure 13. Measurement results without applied US and with introducing 570 mg of additional CO_2 (closed system).

that, also in the closed system, operating at a temperature of 62°C meant that only slight precipitation was present.

In the case of introducing 570 mg of additional CO_2 the initial temperature was 11.1°C (winter season). The system reached the terminal temperature (63.1°C) after 256 minutes of heating, when the introduction of additional gas started. The added gas caused a drop in the pH value, which after the introduction of 280 mg of CO_2 decreased by 0.74 units (10.3% of initial value). The lowest pH value (6.06) was reached after the addition of 550 mg of gas, when the initial value was decreased by 1.11 units (15.3% of initial value). As expected, analyzing the contents of the Ca^{2+} ions, less significant variations were noticed. The content of Ca^{2+} decreased only by 0.2 mg/L (0.25% of initial value), when the system was heated to the terminal temperature (63.1°C). During the introduction of the additional gas, the Ca^{2+} concentration increased and reached a maximum value of 86.2 mg/L (103% of initial value) after 494 minutes, when 530 mg of gas was introduced. The initial Ca^{2+} concentration was exceeded at that point, which showed that the existing mineral deposits were dissolved. The experiment was concluded after 1605 minutes (26.75 hours), when the Ca^{2+} content reached 100.35% of its initial value and the pH value was in slightly acidic range (6.14 or 1.03 units lower than initial value). Taking into account the early phase of the experiment, it could be concluded that despite the closing of the system, the

Table 5. Water composition results without applied US and without additional CO_2 (closed system).

Time of experiment (min)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	alkalinity (ml HCl)	HCO_3^- (mg/L)
5.02	12.4	2.39	17.71	84.4	18.1	16.2	27.60	5.10	311.2
85.03	12.7	2.42	18.03	85.1	18.5	16.4	28.15	5.12	312.4
245.03	12.7	2.40	18.05	83.3	18.7	16.3	28.32	5.00	305.1
1235.02	12.5	2.37	17.73	83.4	18.3	16.0	27.90	5.00	305.1
1385.04	12.5	2.38	17.76	83.2	18.4	16.1	27.98	5.02	306.3

Table 6. Water composition results without applied US and with 570 mg of additional CO_2 (closed system).

Time of experiment (min)	Na^+ (mg/L)	K^+ (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	Cl^- (mg/L)	NO_3^- (mg/L)	SO_4^{2-} (mg/L)	alkalinity (ml HCl)	HCO_3^- (mg/L)
0	12.2	2.27	17.53	83.7	19.6	17.1	30.40	5.03	306.9
256	12.5	2.40	17.85	83.5	n.a.	n.a.	n.a.	5.02	306.3
317	12.4	2.32	17.83	85.1	10.0	9.4	16.78	5.14	313.6
351	12.4	2.33	17.84	85.3	11.0	10.3	18.04	5.18	316.1
494	12.5	2.35	18.04	86.2	11.9	10.9	19.33	4.70	286.8
1394	12.4	2.69	17.79	84.9	12.7	11.4	20.03	4.80	292.9
1605	12.3	2.32	17.58	84.0	12.9	11.7	20.62	5.07	309.4

precipitation process (during heating) was not intensified significantly, because the operational temperature was too low.

The water composition results, presented in Tables 5 and 6, confirmed the above statements. They were made using ionic chromatography and automatic titration. The quantities of cations, such as Na^+, K^+, Mg^{2+}, Ca^{2+} and anions, such as Cl^-, NO_3^-, SO_4^{2-} were defined using ion chromatography. The automatic titration along with the incremental method was used to define the amount of hydrogen carbonate ions (HCO_3^-) and the alkalinity of the investigated water samples.

On the basis of the analyses of the corresponding calcium and magnesium contents it was find out that only slight variation in their quantities occurred during the experiments. These results were relevant for the preliminary hydro-chemical modelling, which showed that a slightly negative Langelier saturation index could be expected at such a process temperature.

Measurements were carried out over different seasons, in summer and winter, to study the seasonal influence on tap-water composition and to test the applied method's efficiency in various conditions. The tap-water composition used for the experiments was regularly analyzed in detail. The data in Table 7 represents the average values of the significant carbonate equilibria parameters regarding the drinking water used over the summer and winter periods.

Table 7. The average values of significant carbonate equilibria parameters regarding drinking water over summer (2006) and winter (2006/07) period in the Maribor area.

	Winter	Summer
Ca^{2+} ($mg \cdot L^{-1}$)	84..05	79.05
Mg^{2+} ($mg \cdot L^{-1}$)	17.62	15.26
HCO_3^- ($mg \cdot L^{-1}$)	309.05	284.16
pH	6.96	7.64

The measured values of all the parameters correlate to the existing data for ten-years' averages (Table 2), except that the values are generally higher than the averages, which could be related to the intensity of the rock weathering or shorter response time due to less precipitation. The calcium ions concentration was 10.3 % higher in winter 2007, and 45.4% higher in summer 2006 season compared to the ten-year (1995-2005) average. The water from the Maribor area also contains 12.2% more Mg^{2+} ions in summer and 15.1% more Mg^{2+} in winter season compared to the ten-year average.

5 CONCLUSION

The water quality optimization by introducing carbon dioxide is a very promising method in terms of reduction the costs of technological process and energy consumption. Another advantage of the described method is that it does not change the original water's mineralogical composition as it does not deplete the water of the minerals in comparison to the conventional methods, i.e. water softening. This should be taken into account especially when the preparation of the drinking water is an issue. The recently developed gas application is environmentally friendly. It does not produce any pollution or waste.

This completely adapted pilot plant with an advanced sensor system and an improved and more accurate gas-dosing system represents a useful technical tool for studying the behaviour of the described system operating under closed conditions with different tap-water compositions, and various seasonal influences.

The used tap water from the Drava basin aquifer in the summer of 2006 and the winter of 2007 generally contained larger quantities of dissolved minerals compared to ten-year averages. The concentrations of all the carbonate equilibria relevant contents correlate to the existing average values and their variations due seasonal influence, which means that the groundwater originating from the alluvial aquifer is richer in minerals in the winter and spring seasons, compared to the summer and autumn seasons.

The results were relevant for preliminary hydro-chemical modelling with a determination of saturation indexes, which confirm our presumptions and shows in most cases only a slightly negative Langelier saturation index ($-0.3 < LSI < -0.2$) at such an experimental temperature. The modelling will be continued and regularly updated with new data from experiments planned on the pilot plant at higher process temperature but without the online monitoring.

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