Ca and Mg extraction from rocks: laboratory tests

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1. Introduction

Properties of drinking water influence the health of residents in respective regions; thus, an increase in the biogenic elements in drinking water is of utmost importance.

The development of processes and equipment for effectively increasing the content of biogenic elements requires quantitative data on the possibilities of drinking water recarbonization in real conditions, on available materials suitable for the process as well as on the economy and process sustainability in a suitable type of equipment. Methods used so far are not sufficiently effective and increasing their efficiency requires an innovative approach.

To obtain quantitative data on recarbonization, experimental measurements in suitable laboratory equipment and under suitable conditions have been proposed, allowing for long-term testing of the process and providing material consumption data necessary for the equipment design. The equipment has to be robust, responsive to periodic changes in drinking water flow and with minimal material and operating time consumption.

The experiments were proposed to obtain data for the design and operation of a fluidized bed reactor system for drinking water enrichment with Ca and Mg. The aim was to carry out laboratory tests on rock materials: half-calcined dolomite (HCD), dolomite, gypsum, lime hydrate or their mixtures, to enrich water with Ca and Mg under system carbonization.

Original calcium content of the treated water is ca 25 mg.l^{-1}, that of Mg is ca 5 mg.l^{-1} and mineralization is ca 250 mg.l^{-1}.

Objectives of the presented work can be described in more detail as follows: selection of the most suitable materials or their mixtures for water enrichment with Ca and Mg; obtaining data for the determination of reagents consumption for a defined drinking water amount in a given locality; and carrying out a long-term experiment for selected rock material to verify the data obtained under laboratory conditions.

Drinking water quality requirements

Drinking water from a natural, surface or underground, source must comply with the prescribed health and technical requirements. Drinking water quality indicators and their limits are set in Annex 1 of Government Regulation No. 496/2010 Coll., amending and supplementing Government Regulation No. 354/2006 Coll. for requirements and quality control of water intended for human consumption. The limit and recommended values for selected indicators are summarized in Tab. 1.

According to STN 75 7151 Requirements for water quality transported by pipeline (for steel, cast iron and concrete piping):

Ca^{2+} : above 0.5 mmol.l^{-1} $\quad$ $ANC_{4,5}$: above 0.8 mmol.l^{-1}

Tab. 1. Limit and recommended values for selected drinking water indicators.

Magnesium	Mg^{2+}	10.0 – 30.0	$mg.l^{-1}$	Recommended value
		125.0	$mg.l^{-1}$	Limit value
Calcium	Ca^{2+}	> 30.0	$mg.l^{-1}$	Recommended value
Calcium and magnesium	$Ca^{2+} + Mg^{2+}$	1.1 – 5.0	$mmol.l^{-1}$	Recommended value

Source: Annex 1 to Government Order 496/2010 Coll.

Regulation of the Ministry of Environment of the Slovak Republic 636/2004 Coll. on requirements for raw water quality and monitoring of water quality in public water supply systems also recommends $ANC_{4,5}$ in terms of chemical stability of water to be above 0.8 $mmol.l^{-1}$.

Recarbonization possibilities: materials, equipment, conditions

Lime and carbon dioxide recarbonization

This recarbonization method is relatively simple and one of the most widely used. It is suitable for large water treatment plants. Lime reacts with carbon dioxide to form calcium bicarbonate according to the following chemical reaction:

$$Ca(OH)_2 + 2\ CO_2 \rightarrow Ca(HCO_3)_2$$

The dependence of lime solubility on water pH and temperature has to be considered. Lime may not dissolve easily, increasing the turbidity in water (Olejko, 2007; Rodriguez and Estruch, 2009; Birnhack et al., 2011). This approach is effective only at low operating costs (WHO, 2007).

Carbonates and carbon dioxide recarbonization

This method consists in passing water through a filter filled with carbonates. The use of carbonates is economically advantageous as their natural sources, e.g. dolomite, are cheap (Olejko, 2007).

The process follows chemical reactions:

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

$$MgCO_3 + CO_2 + H_2O \rightarrow Mg(HCO_3)_2$$

which proceed optimally only in excess of CO_2, while the process is controlled so that no water with aggressive effects, resp. with a significant excess of CO_2 is produced.

It is also necessary to include recarbonization before the coagulation unit (Olejko, 2007).

Carbonates and strong acids recarbonization

In this method, ground limestone or dolomite is used as the alkalizing agent. Hydrochloric or sulfuric acid can be used to adjust pH, which leads to increased mineralization due to strong acids and calcium or magnesium bicarbonate is formed (Olejko, 2007):

$$2\ CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + Ca(HCO_3)_2$$

$$2\ CaCO_3 + 2\ HCl \rightarrow CaCl_2 + Ca(HCO_3)_2$$

Similar reactions were observed also for $MgCO_3$. This method is not recommended due to a one-sided increase in hardness; the acid neutralization capacity (ANC) value does not increase (Olejko, 1999).

Half-calcined dolomite and carbon dioxide recarbonization

Half-calcined dolomite (HCD) is a specially pre-treated alkaline material made from dolomite consisting of 50 % of $CaCO_3$ and 50 % of $MgCO_3$. Annealing at 650-800 °C leads to $MgCO_3$ decomposition into MgO while $CaCO_3$ does not change:

$$MgO + 2\ CO_2 + H_2O \rightarrow Mg(HCO_3)_2$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2$$

HCD is mostly used as a granular material in filters where water flows from top to bottom and while chemical reaction between carbon dioxide and HCD occurs according to the above reactions. HCD is gradually consumed and thus it has to be replenished. Moreover, the filters have to be equipped with HCD washing fitting. Washing should be carried out regularly as the filter filling tends to sinter with excreted $CaCO_3$. Also, dust particles from the breakdown of HCD grains are removed during washing (Olejko, 1999).

2. Laboratory batch reactor experiments

To study recarbonization with various materials, conditions leading to fast determination of the material suitability, consumption, biogenic elements concentration and process conditions had to be set. Therefore, a stirred batch reactor (Fig. 1) with the volume of 2 l was employed to test the selected materials and their combinations for water recarbonization. The processes were monitored for five hours while the reaction mixture was carbonated by 0.48 $l.min^{-1}$ carbon dioxide.

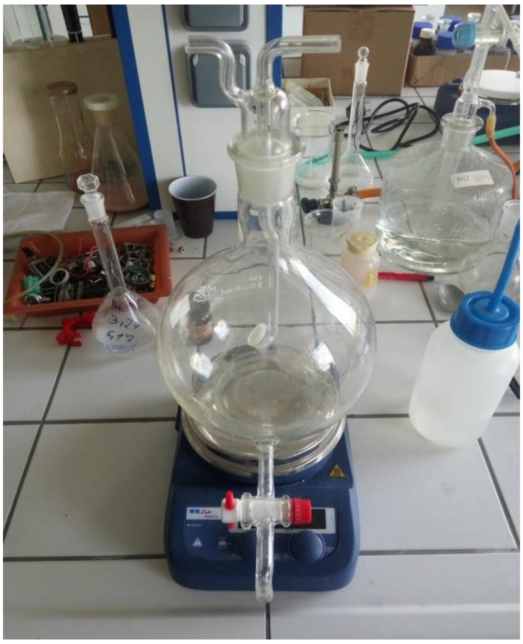

Fig. 1. Stirred recarbonization batch reactor.

Results obtained for the selected materials for recarbonization in the stirred batch reactor show that the highest concentrations of magnesium in drinking water was obtained using half-calcined dolomite (HCD) after five hours of experiments and the highest calcium concentration was obtained for gypsum (Fig. 2).

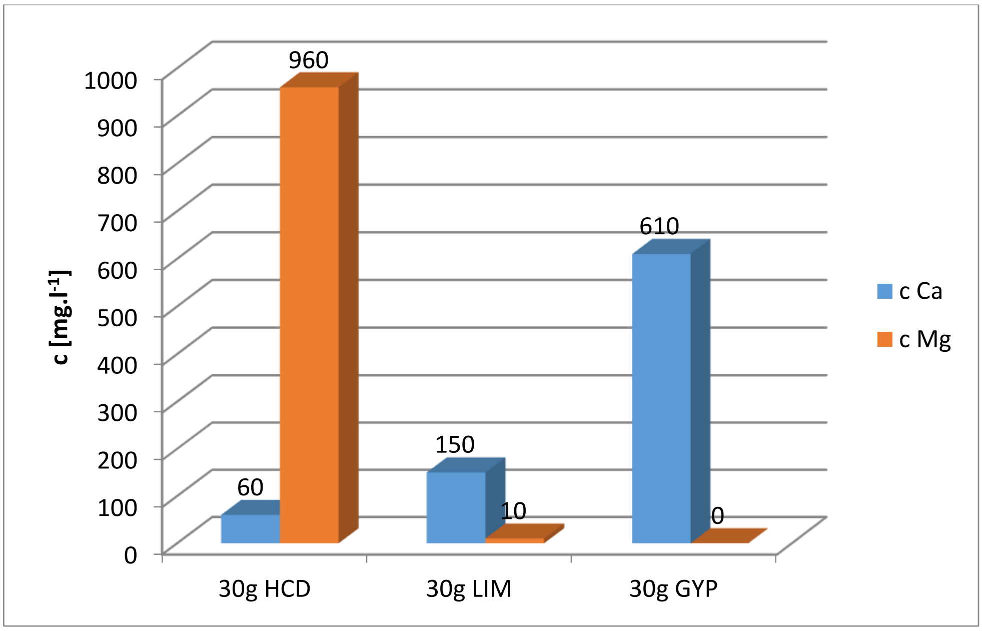

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Fig. 2. Ca and Mg concentrations from HCD, limestone and gypsum dissolution.

Also the effect of HCD, limestone and gypsum combinations on the drinking water Mg and Ca content was observed; a summary of the measurements is provided in Fig. 3.

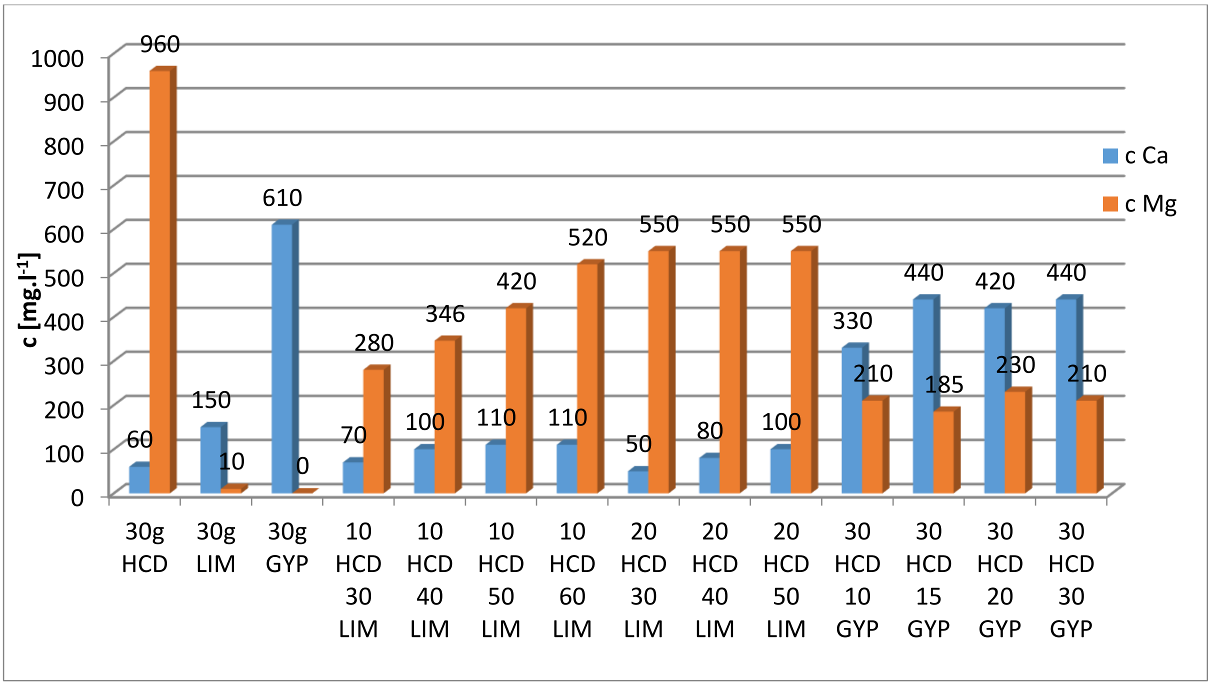

Fig. 3 Mg and Ca concentration using different materials and their combinations in water recarbonization in a stirred batch reactor after 5 hours.

Experimental measurements after five hours of material exposure to water clearly confirm that HCD is the best Mg ion donor. VAP and SAD additions led to a different ratio of Mg and Ca ions in water. If necessary, increase in Ca ion content can be achieved but, as the results indicate, at the expense of the Mg ion content.

If the structure of the solid phase particles changes over time, these results do not apply. Particle diameter and surface conditions change as well as the structure of the porous material. Gradual dissolution of magnesium salts causing the pores to open and the ions inside the pores more accessible. Due to the better magnesium salt dissolution, calcium salts become gradually more accessible and the Mg / Ca ratio, which was not the best in these experiments, may vary.

Laboratory results clearly showed that HCD is the best material for drinking water recarbonization. It was also confirmed that the smaller the HCD particles, the more efficient and faster the process. However, water applications require particles of adequate size, both in terms of pressure loss in the layer (and the associated cost of liquid pumping), handling (large fraction of dust in the solid phase) and material loss when fluid flows through the grain material (material loss and higher process costs).

3. Continuous systems for drinking water recarbonization

In industrial applications, filter-based flow devices filtering the entire amount of water are used. Linear flow velocitites are determined by the size of the filters (mainly the diameter) and the flow rate of water to be treated. If treated water is introduced directly to the water distribution system, these devices operate periodically, as the flow through the filter varies according to water consumption, which fluctuates considerably throughout the day; thus, water recarbonization conditions also change. At low flow rates, a very uneven flow through the layer of solid material used in the filter is presumed; channels are likely to form (lower resistance) which decreases the contact between water and the surface of the solid material in the filter. In addition, at low flow rates, water remains in the solid material layer for a longer time, and a concentrated solution may be formed locally, containing insoluble products of dolomite decomposition and filter material sintering with precipitated calcium carbonate at high pH conditions. These aspects of recarbonization processes in filters require periodic filter washing with large space and operation requirement.

Fluidization is an alternative method to fix bed liquid-solid contact processes; it is a process in which solid particles of suitable size are floating and moving creating fluidized bed in the reaction column employing the flow of fluid against gravity (upwards). Such an arrangement creates conditions for good mass transfer due to the large interface area between the solid and liquid phases. Large interphase, respectively reaction interface, results in significantly higher volumetric reaction rates than conventional packed bed reaction systems. Intense movement of the solid particles is accompanied by abrasion of their surface, removing a part of the unreacted solid and thus constantly renewing the particle surface. In case of half-calcined dolomite, proven to be the most suitable material, this phenomenon also has another effect. During MgO dissolution from the solid phase, pore size in the solid phase changes, the internal surface of the particles becomes more accessible for contact with water, and due to the change of the solid phase structure, even the "old surface" becomes more brittle and easier to remove. The resulting fine particles of the solid phase have large interfacial surface, which improves the conditions for mass transfer and hence recarbonization rate. Small particles can be entrained by the liquid from the layer and thus create conditions for reactions outside the main volume fluidized bed. The particles are removed from the liquid in a subsequent cyclone.

Thus, fluidized bed reactors enable intensification of processes at the solid-liquid interface. Such processes are applied in various branches of the chemical industry, in anaerobic and anoxic wastewater treatment processes as well as in the denitrification process in the treatment of drinking water. However, to our knowledge, this reaction technique has not been used in the chemical treatment of water, including the recarbonization process. With aim to process large flow rates of treated water and to minimize the investment costs of the recarbonization process, a fluidized bed recarbonization reactor was proposed to investigate this process.

The process has been designed to prepare a concentrate of biogenic elements to be mixed in suitable proportions into drinking water supplied to consumers. This idea stems from the real rate of ion release into water and the resulting size of the device. In addition, the system where the ion concentrate is prepared is more stable in terms of ion concentration and the required elements in the drinking water are supplied to the consumer more evenly.

3.1. Fluidized bed reactor

Unlike HCD filters, a fluidized bed recarbonization reactor (FBRR) with moving bed has been designed. Such an arrangement of the device creates conditions for good mass transfer due to the large interface area between the solid and liquid or gas phase. Large interphase /

reaction area results in significantly higher volumetric reaction rates than in conventional packed reaction columns. Moreover, moving solid phase is not sintered by $CaCO_3$.

Basic design parameters of a fluidized bed reactor include the particle size and density, which influence the hydraulic conditions in the reactor and thus the superficial velocity necessary to achieve the desired bed expansion in the reactor. Considerable part of the operating costs of the fluidized bed reactor is related to the required internal particle circulation and water recirculation in the reactor.

Minimum fluidization fluidization velocity is a limit value of the fluid flow rate at which particles in the bed begin to move. At a higher flow rate, the particle bed expands and the dissipated mechanical energy is reflected in the increase in the volume of the bed.

The minimum fluidization velocity (w_p) can be determined from the experimental dependence of the pressure loss (ΔP) on the superficial liquid velocity (w) (Fig. 4).

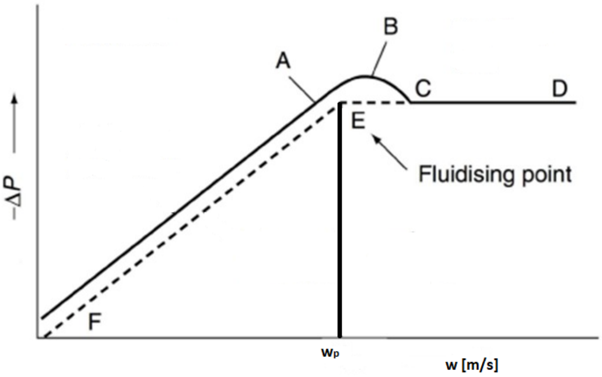

Fig. 4. Pressure loss dependence on the superficial velocity.

Fluidized bed expansion and bed voidage can also be experimentally determined using a similar procedure and similar apparatus as for determination of minimum fluidization velocity. Both the minimum fluidization velocity and expansion depend on the properties of the solid particles (diameter, density, shape) and on the fluid properties (density, viscosity). If properties of both the particle (e.g. diameter and shape) and the fluid (density and viscosity change due to the salt content) change during the process, also the minimum fluidization velocity and the bed expansion change during the process. These facts have to be considered in the equipment design.

Fig. 5 shows the course of pressure drop (ΔP) in the particle bed in dependence on the fluid velocity (w). For this experiment, 360 g of HCD was used and a graphical method was employed to determine the minimum fluidization velocity (w_p). The results indicate a minimum fluidization velocity for the 2.0-4.0 mm particle fraction to be $w_p = 0.0475$ m.s^{-1}.

Experimental data were obtained under the following conditions:

- Particle mass in the bed: $m_c = 0.36$ kg Voidage of fixed bed: $\varepsilon = 0.4217$
- Volume of fixed bed of solids: $V_s = 0.266.10^{-3}$ m^3
- Cross-sectional area of the column: $A_p = 1.8.10^{-3}$ m^2.

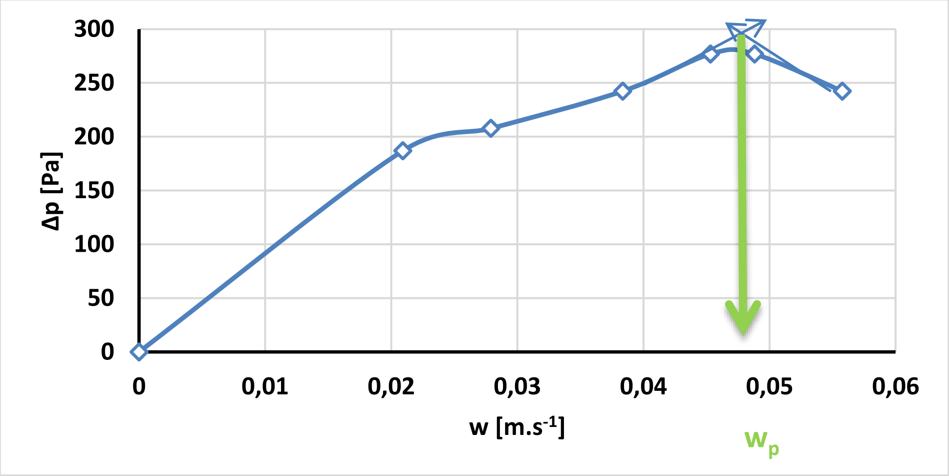

Fig. 5 Dependence of pressure loss (ΔP) on superficial velocity (w) and minimum fluidization velocity (w_p) for half-calcined dolomite Magno Dol (Akdolit) fraction of 2.0-4.0 mm.

Drinking water recarbonization experiments were performed in a laboratory fluidized bed reactor.

A glass recarbonization fluidized bed reactor (FBRR) was used. HCD particles (d = 2.0 – 4.0 mm) were washed with water. Water from the supply network was fed to buffer tank (2) at suitable flow rate and through a rotameter by pump (4) to fluidized bed reactor (5).

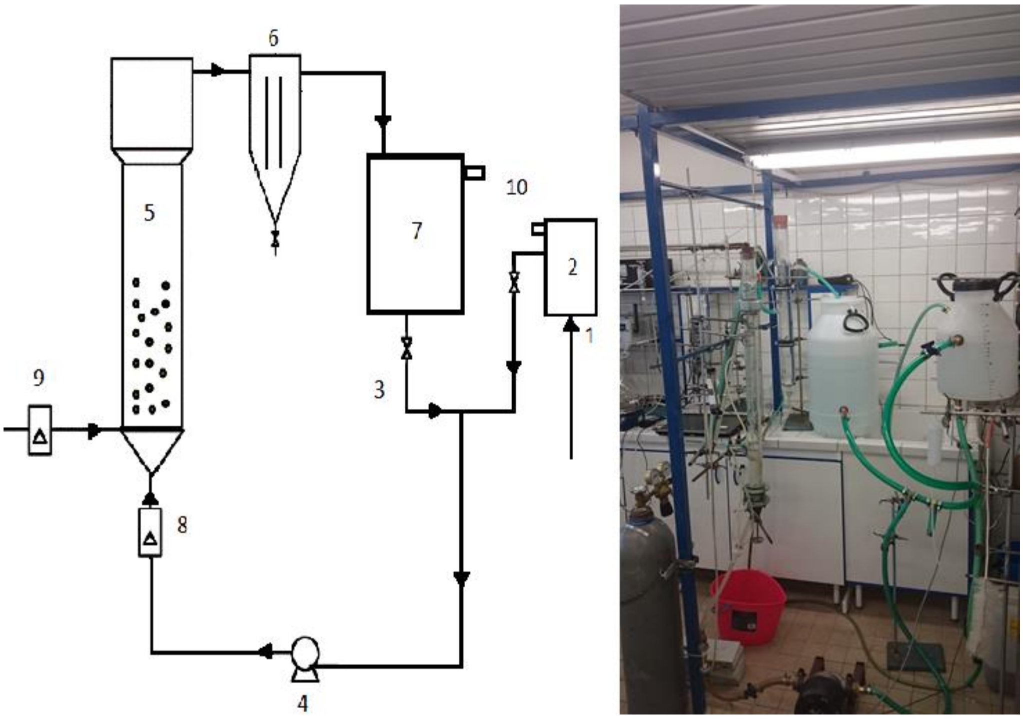

Fig. 6 Schematic diagram of the recarbonization system.

1 – water feed, 2 – buffer tank, 3 – recirculation valve, 4 – pump, 5 – fluidization reactor, 6 – sedimentation tank, 7 – storage tank, 8 – rotameter, 9 – CO_2 *feed, 10 – buffer and sedimentation tank outlet, reactor height: 90 cm and diameter: 4.8 cm.*

Water enriched with Ca and Mg flowed from the reactor to the sedimentation tank (6) and then into the storage tank (7). From there water flows through recirculation valve (3) into the water pipe from buffer tank (2) and then it was fed to the reactor bottom. Treated water (concentrate) was discharged from the system through outlet (10) at the top of the tank. CO_2 was continuously fed below the reactor distributor through rotameter (9).

Recarbonized drinking water at the system outlet (10) was analyzed for Ca and Mg ions concentration. Also, solution conductivity, temperature, volumetric flow rate of water circulating through the fluidized bed reactor and CO_2 flow into the reactor were continuously measured.

3.2. Experimental results

Experimental results obtained in a fluidized bed reactor indicate higher efficiency of recarbonization than in fixed bed reactor.

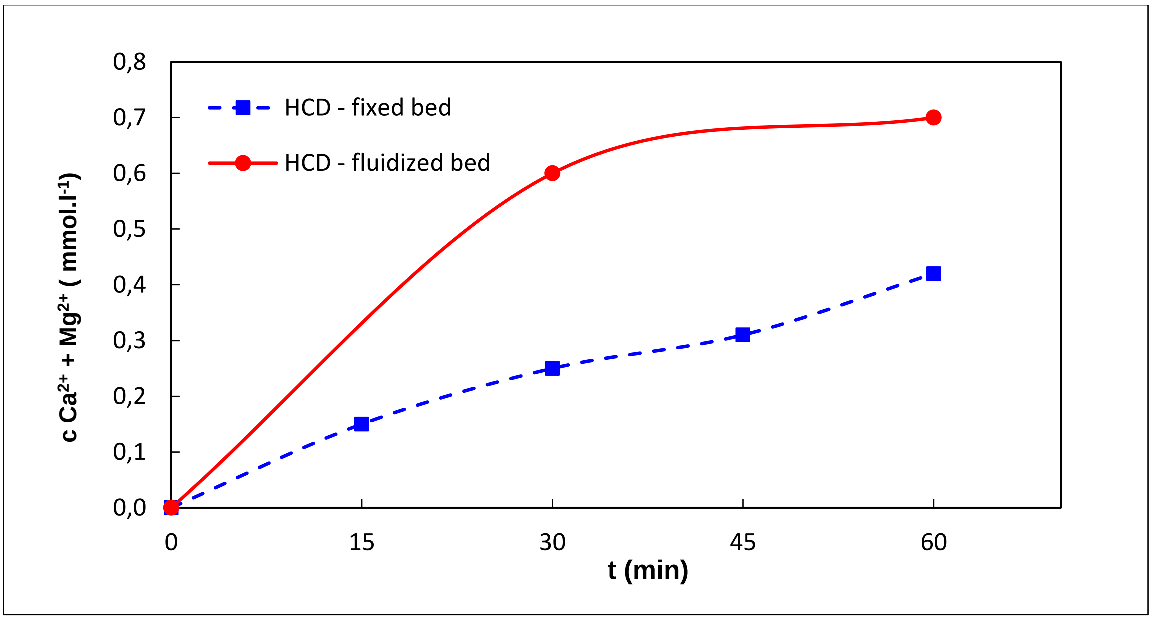

Fig. 7 Time dependence of Ca^{2+} + Mg^{2+} concentration for fixed HCD and fluidized bed (at minimum fluidization velocity)

Experiments also confirmed positive effect of CO_2 on recarbonization (Fig.8).

In the fluidized bed reactor, the effect of a combination of different materials on the biogenic elements content in drinking water was studied. The water flow rate was $Q_{H2O} = 3.03$ l.min^{-1} and the reaction mixture was saturated with CO_2 at the flow rate $Q_{CO2} = 0.48$ l.min^{-1}
Also experiments in fluidized bed clearly show HCD to be the most suitable recarbonization material.

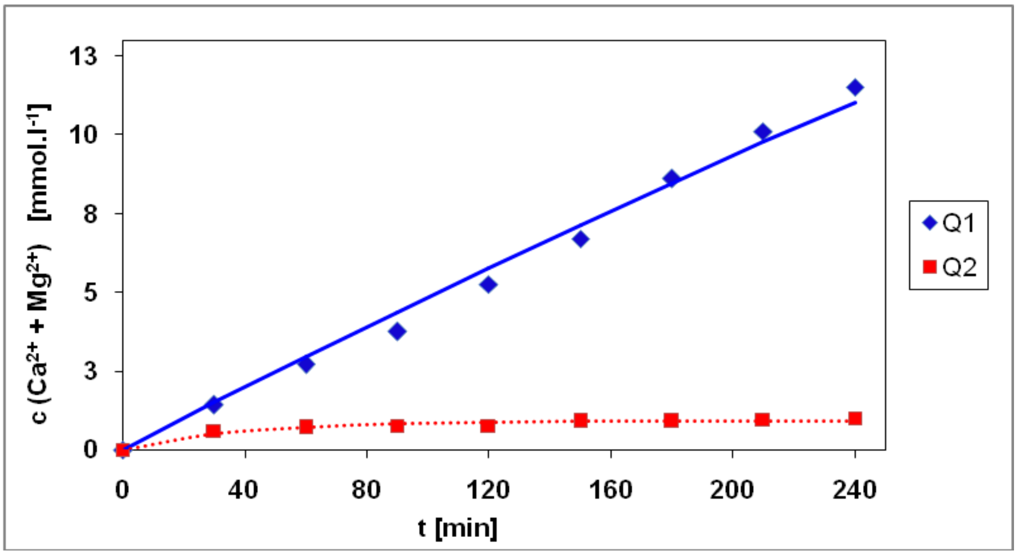

Fig. 8 Ca^{2+} + Mg^{2+} content increase using HCD without ($Q_{CO2,2}$ = 0 $l.min^{-1}$) and with carbonation ($Q_{CO2,1}$ = 0,09 $l.min^{-1}$) in the fluidized layer (minimum fluidization velocity w = 0.0147 $m.s^{-1}$)

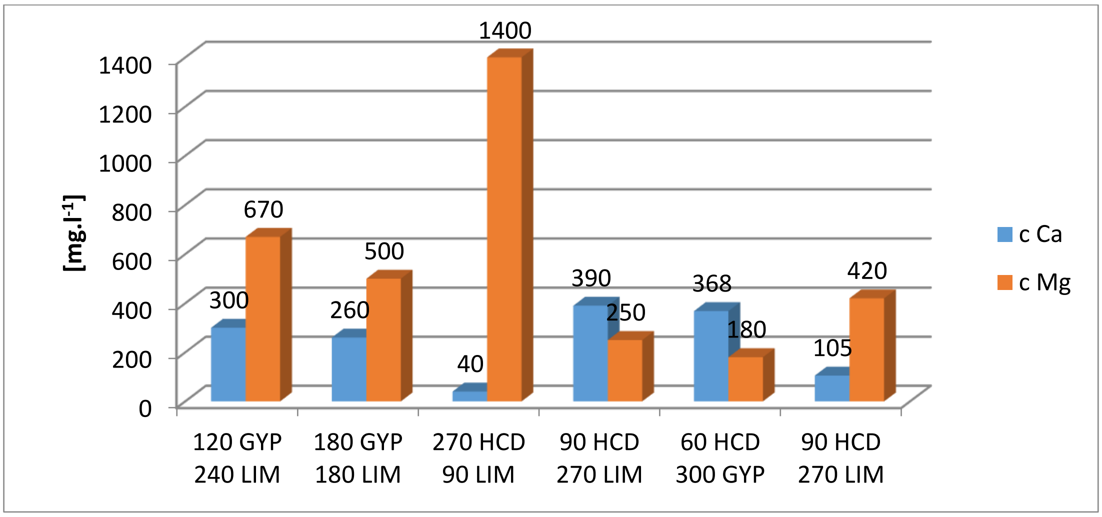

Fig. 9 Ca and Mg concentration after 20 hrs of recarbonization in a fluid bed reactor at different HCD/limestone and HCD/gypsum ratios.

For continuous processes is common to monitor quality of the process continuously. It was found that the conductivity of the solution is directly proportional to the ion content in the water, can be measured continuously and it allows on-line monitoring of the process. The results indicated that it is simple and reliable method with very good correlation with the Ca^{2+} + Mg^{2+} content.

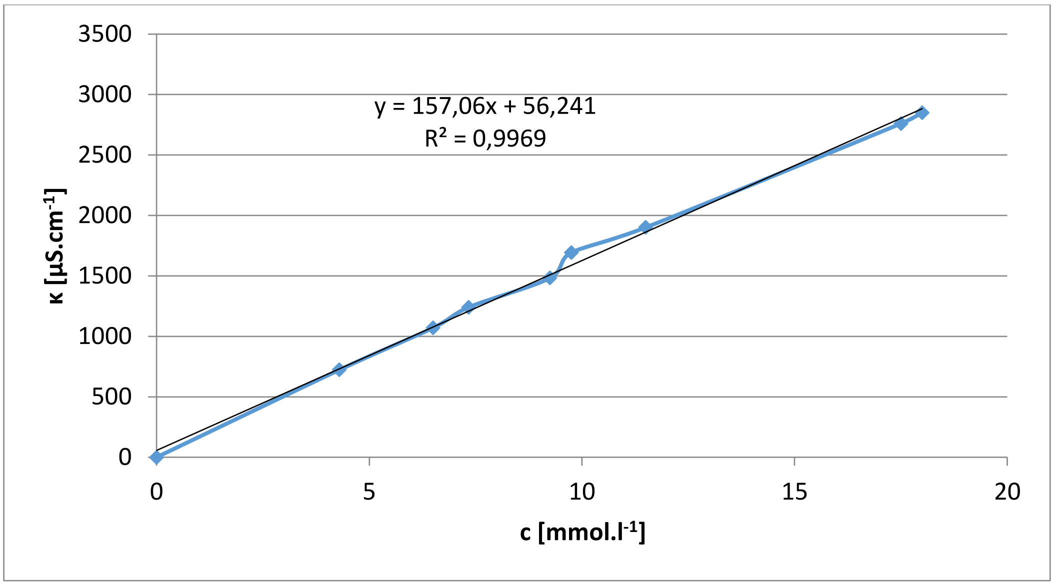

Fig. 10 Dependence of experimental (points) and calculated (line) Ca^{2+} + Mg^{2+} concentration on experimental conductivity measurement with real water (Q_{CO2} = 0.48 $l.min^{-1}$; w = 0.0147 $m.s^{-1}$).

3.3. Continuous drinking water recarbonization

According the proposed process design it is necessary to determine the time required to saturate the solution with biogenic elements. Therefore, the laboratory system was initially operated in the batch mode (water was recirculated from the storage tank through the reactor). Concentration of the elements was monitored in the storage tank. Conductivity with increase with time is presented in Fig.11. and indicates increase in salt content in water.

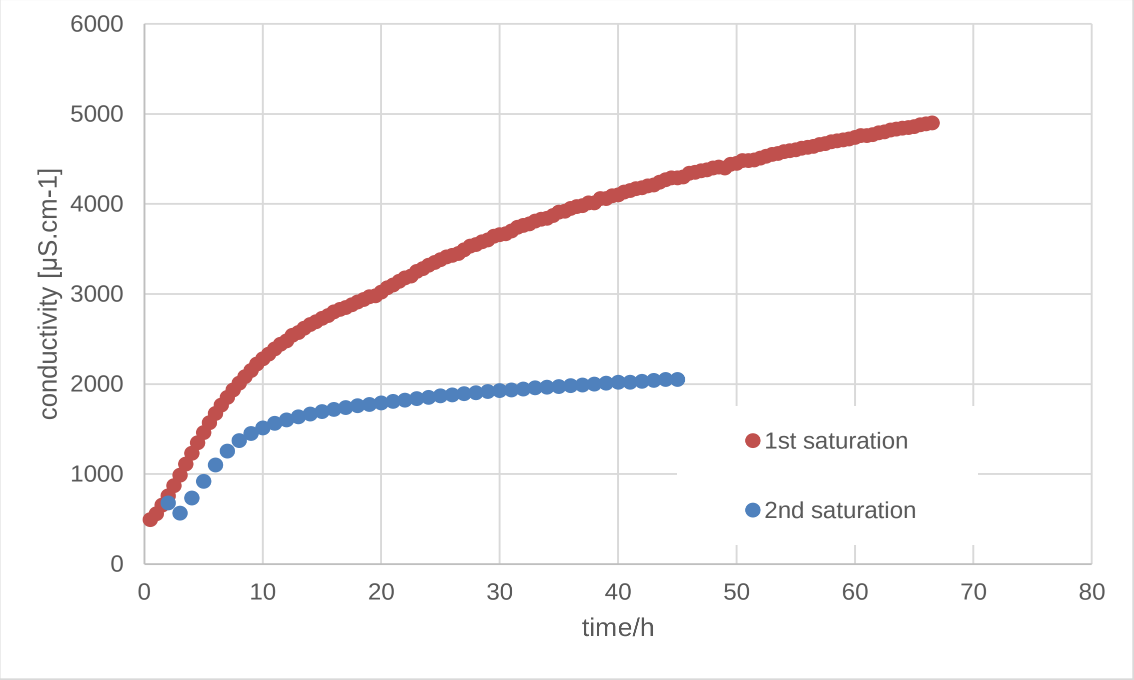

Fig. 11 Solution conductivity vs. time during water saturation with biogenic elements.

Data for "first saturation" were obtained with fresh HCD in a fluidized bed reactor. The second saturation was performed after addition of fresh water to the storage tank, and saturation in the batch mode was repeated ("second saturation").

Final Mg concentrations after water saturation are provided in Tab. 2

	pH [-]	κ [µS.cm^{-1}]	c_{Ca+Mg} [mmol.L^{-1}]	c_{Ca} [mmol.L^{-1}]	m_{Ca} [mg]	c_{Mg} [mmol.L^{-1}]	m_{Mg} [mg]	c_{Ca}/c_{Mg} [-]
1st sat.	7.147	5350.0	34.5	1.5	60.1	33.0	801.9	0.1
2nd sat.	6.413	2060.0	13.3	1.4	56.11	11.9	289.2	0.1

At the beginning of the first saturation, the bed height was 18 cm, while at the beginning of the second saturation it was only 12.6 cm, HCD was used for a relatively long time, indicating that not only the amount but also the quality of the recarbonization decreased, since MgO is dissolved preferably. This should be taken into account when designing real equipment.

Another part of the experiments was performed in the continuous mode. Water recirculation from the feed to the reactor was 6 L.min^{-1} and the water flow rate to and from the system was 50 mL.min^{-1}. The height of the fluidized bed decreased to L_t = 6.4 cm before this series of experiments started (ZERO time in the results) and therefore, 240 g of fresh HCD were added increasing thus the fluidized bed height to 21 cm.

The course of Mg concentration vs. time obtained over further 180 h of experiment (Fig. 11) indicates significant changes. At 31 h, CO_2 feed was interrupted and the pH value increased while Mg release rate decreased. After the reintroduction of CO_2, the Mg release rate returned to its original value. Later, HCD was added to the reactor and the rate of Mg ion production increased as expected to more than 300 mg.l^{-1}.

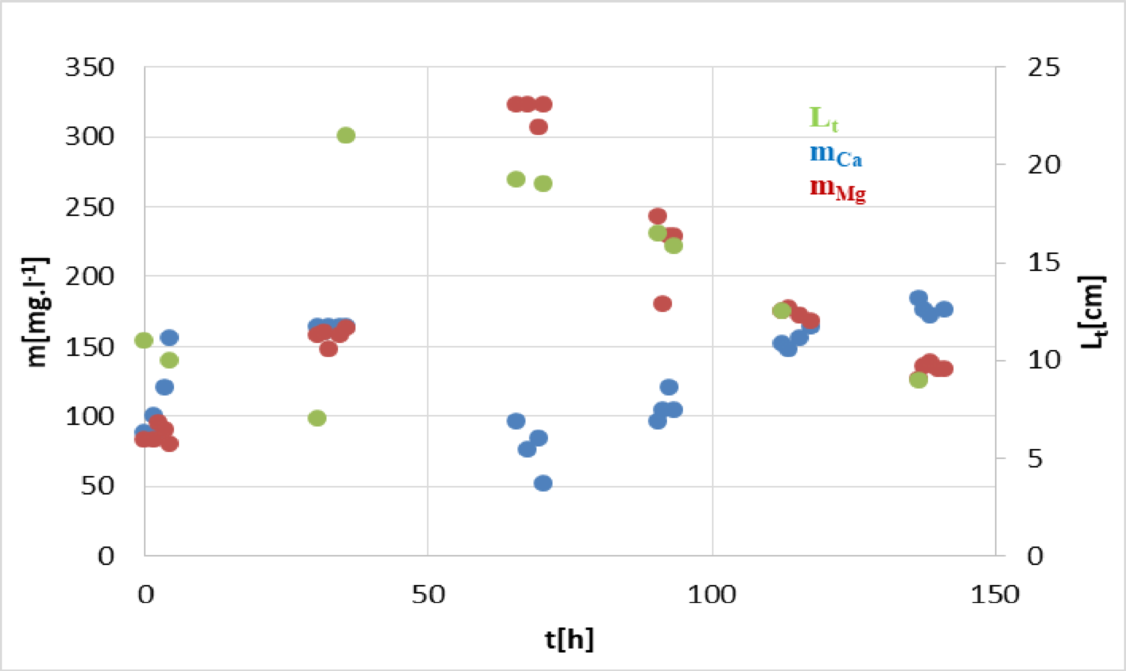

Fig. 12 Process characteristics in a 141 h experiment.

From Fig 12 it follows that concentrations of the studied components are related to the amount of HCD in the system. However, changes in Ca concentration show the opposite trend compared to those in Mg concentration and in fluidized bed height. Given the volume of water in the system (43 L), the shift between the increasing concentration of the components and the height of the fluidized bed is also evident.

An important parameter in the recarbonization with half-calcined dolomite in FBRR is the characteristic particle size and data on its change. These data play an important role in the design and operation of such a reactor. For the half-calcined HCD fraction of 1.00 - 1.25 mm, the characteristic particle size values are:

- Sauter diameter - d_s = 1.14 mm
- equivalent diameter - d_e = 1.09 mm.

Longer experiments have shown that HCD particles are not rounded but take a pyramid shape. This can be explained by the layered structure of dolomite, which is characterized by sharp-edged disintegration (Galvánek, 2004).

Fig. 13 shows particle diameter values measured at different water flow rates i.e. at different superficial velocities (w_1 = 0.0147 m.s^{-1}, w_2 = 0.0295 m.s^{-1}, w_3 = 0.0460 m.s^{-1}) and the flow rate of Q_{CO2} = 0. 09 l.min^{-1}.

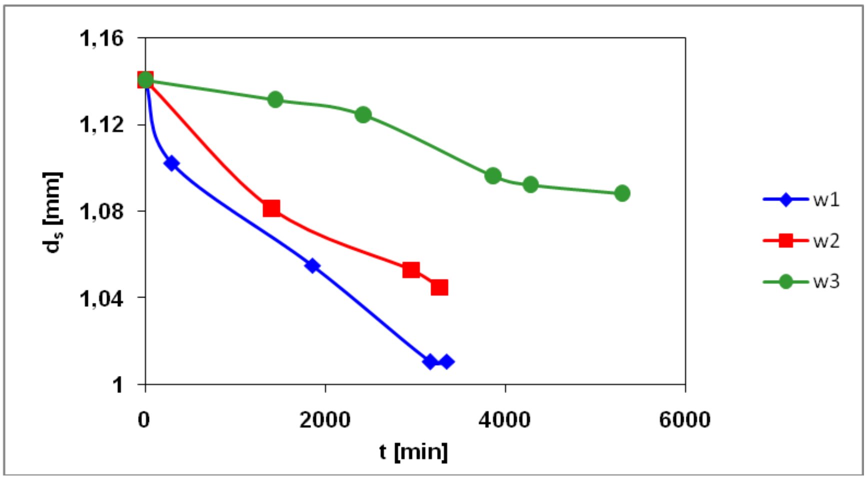

Fig. 13 Time dependence of particle size changes.

Measured HCD particle sizes at different water flow rates indicate that at lower flow rates, near the minimum fluidization velocity, interparticle contact is very intense and mechanical particle abrasion is more significant than at higher liquid flow rates, where particle circulation is higher.

3.4. **Long-term test results**

The main aim of the first series of measurements was to obtain basic information about the behavior of the system in Fig. 6. Basic prerequisite for the development of a drinking water recarbonization plant was to produce a concentrate to be added in appropriate proportions to the drinking water distribution network to achieve the desired biogenic element content. Therefore, it was necessary to determine the conditions for water saturation with the desired ions in the batch mode (water from the storage tank was circulated through the fluidization reactor and returned back to the storage tank).

Experimental conditions: HCD with the particle diameter of 2-4 mm was used, initial fluidized bed height was 18 cm, water flow rate through the reactor was about 6 $l.min^{-1}$ and CO_2 flow rate was from 0.1 to 0. 5 $l.min^{-1}$. Volume of the whole system was 43 l.

Long-term experiments were designed to verify the assumptions from laboratory measurements. The following parameters were changed: HCD amount and "age" in the system, water flow in the circulating loop, CO_2 flow, freshwater flow rate to and from the system, and also the plant layout. Concentrations of Mg and Ca, solution conductivity and fluidized bed height were experimentally determined. Total operating time was above 2000 hours

Dependences of Mg concentration, CO_2 flow rate, fluidized bed height and treated water flow on time are shown in the individual sub-figures in Fig. 14. The height of the fluidized bed depends on the HCD amount added into the reactor as well as on the HCD consumption during recarbonization.

These dependencies indicate opposite trends of Mg concentration and CO_2 flow for the predominant measurement time period. The course of Mg concentration shows a certain delay compared to the time course of the fluidized bed height, which can be explained by the reaction time required to release Mg and Ca ions from the HCD matrix into treated water.

Values of fluidized bed height correlate well with those of treated water flow rate, especially at longer reaction time. However, it should be noted that the flow rate of treated drinking water is by about two orders of magnitude lower compared to the total water flow rate through the reactor (internal water recirculation), which forms the fluidized bed hydraulics.

Time dependence of freshwater flow rate into the system contributes to a better assessment of the parameters effects on the process. In a real drinking water recarbonization system, water abstraction is periodic and the means of influencing equipment performance should be considered.

The relatively stable Mg concentration decreases with time despite stable freshwater flow rate (relatively high per system volume) with the decreasing CO_2 flow rate and increasing fluidized layer height due to the addition of HCD to the reactor. After a dramatic increase in the amount of HCD in the reactor, the concentration increased and gradually decreased despite the increase in the CO_2 flow. After freshwater flow (reactor feed) was stopped, Mg concentration increased up to 500 $mg.l^{-1}$ and decreased with the restoration of the fresh water flow even at higher CO_2 flow rates.

From the above it follows that Mg content of the solution is significantly influenced by the amount of HCD, freshwater flow rate and, in a lower extent, also by the CO_2 flow rate. It can also be stated that, despite dramatic changes in process parameters, Mg concentration in the concentrate can be safely maintained in the concentration interval between 100 and 200 $mg.l^{-1}$.

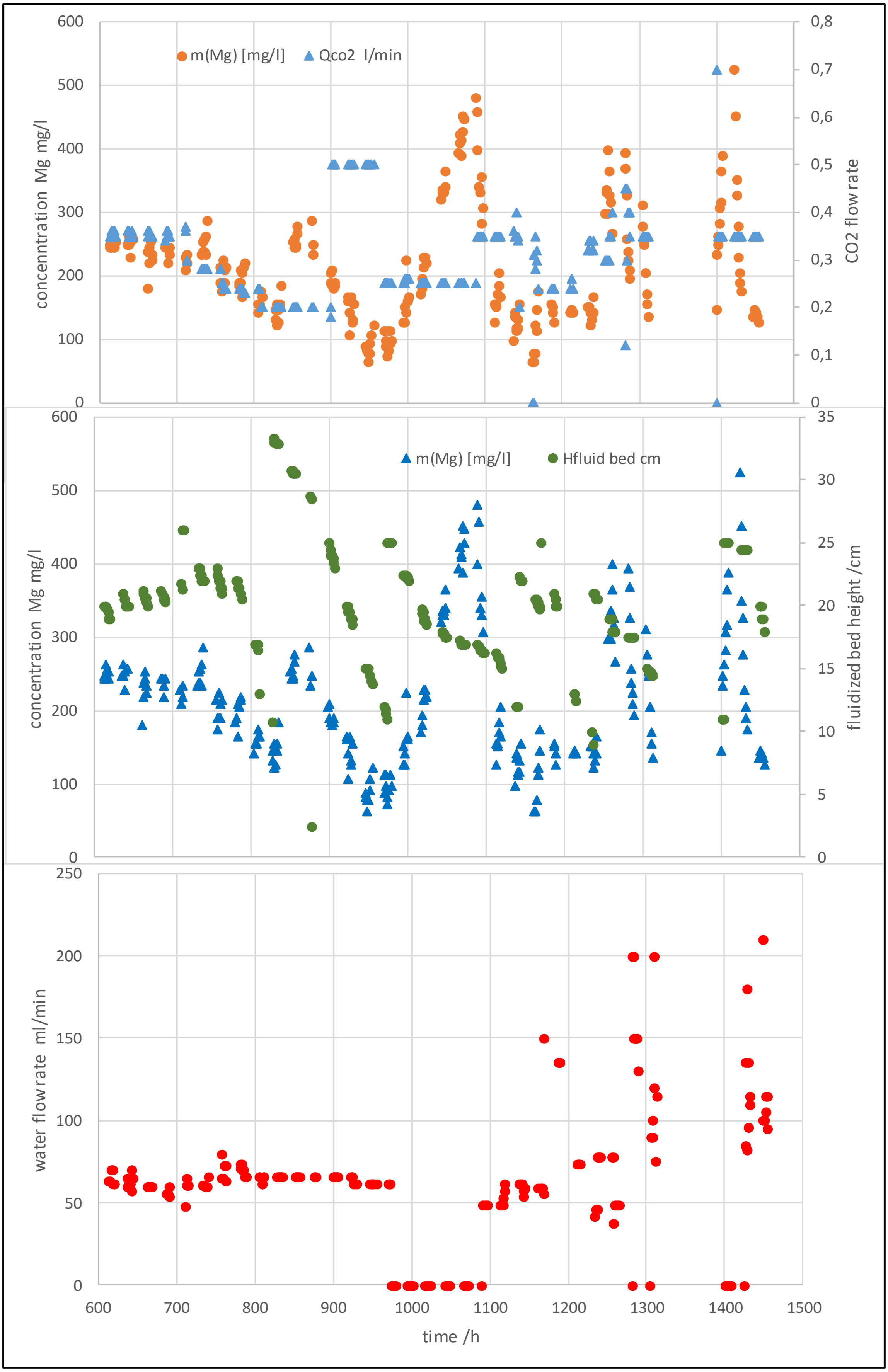

Fig. 14 Time dependence of drinking water recarbonization process characteristics in FBRR.

3.5. Simplified model of industrial system layout

An attempt to adapt the proposed recarbonization system consisting of a reactor, concentrate storage tank, and a concentrate supply to the drinking water distribution network encountered a problem with the complex control and regulation system of plant operation. The reason is that the drinking water supply system in Devičie consists of a well from which water is pumped into a water tank and it is distributed to consumers through the same pipeline. This implies that the same pipeline is used to pump water both in and out of the water tank, which significantly complicates dosing of the concentrate to the distribution system while maintaining the water level in the water tank, in the concentrate storage tank while changing the water flow direction to achieve the necessary concentration of biogenic elements in water. Technical complications related to the condition of the pipelines in the distribution system also contradict the possibility of construction redesign of the distribution system without increasing the risk of installing a recarbonization system on the site.

Therefore, a system to pump water from the water tank through the reactor and back has been designed; thus, conditions in the reactor are significantly different from those investigated in the laboratory experiments. The difference mainly concerns the salt content of water entering the reactor as well as the temperature of water in the reactor

Ca and Mg concentrations obtained in the fluidized bed for direct supply of fresh water to the reactor showed that such direct arrangement is not functional since the enrichment of drinking water in one pass through the HCD bed is not sufficient.

For this reason, recarbonized water was proposed to be fed into the reactor and discharged from the reactor to a settling tank, from which water with the appropriate salt content is led to a water tank. The settling tank is to protect the water tank from possible leakage of particles from the reactor if unexpected flow fluctuations, pump failures etc. occur. In addition, the settling tank serves as a solution reservoir in which the salt concentration is optimal for the recarbonization process (temperature, CO_2 absorption).

Further experiments were aimed at the determination of Ca and Mg concentration in the water circulation stream between the reactor and the settling tank while CO_2 was fed below the distributor in the reactor and in the second case to the storage tank to find Mg concentration in the settling tank needed to minimize the volume of the settling tank (constructional and static constraints at the installation site) and to ensure sufficient Mg concentration in water pumped into the water tank.

In two experiments, the usual amount of HCD (360 g) was used and CO_2 was fed under the distributor of the reactor and into the settling tank. In the second set of data, double amount of HCD in the reactor was used under otherwise maintained conditions and the CO_2 feed below the reactor grid.

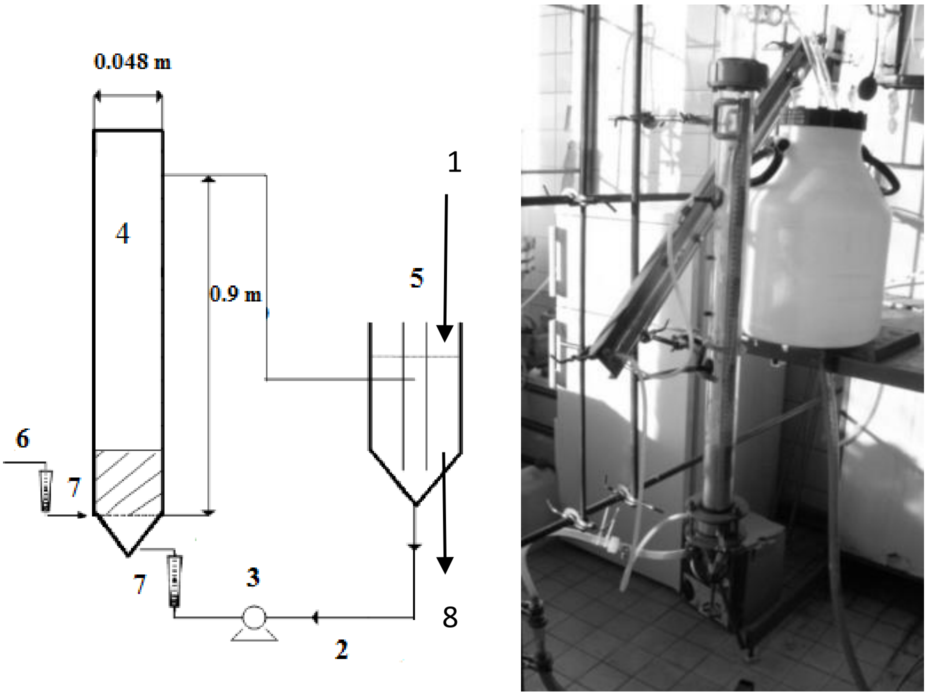

Fig.. 15. Scheme of the laboratory equipment – fluidized bed reactor
1 – fresh water feed, 2 – recirculation stream, 3 - pump, 4 – fluidized bed reactor, 5 – settling and storage tank, 6 – gas feed (CO_2), 7 – flowmwter, 8 – water outlet

Higher increase in Mg concentration at twice the HCD amount is logical and is initially caused mainly by low Mg concentration in water (below 200 mg.l^{-1}). At higher concentrations, the rate of Mg formation decreases due to the reaction kinetics. To better compare the obtained results, the dependence of Mg ion formation rate on Mg concentration was calculated with respect to the amount of HCD in the reactor (Fig. 16).

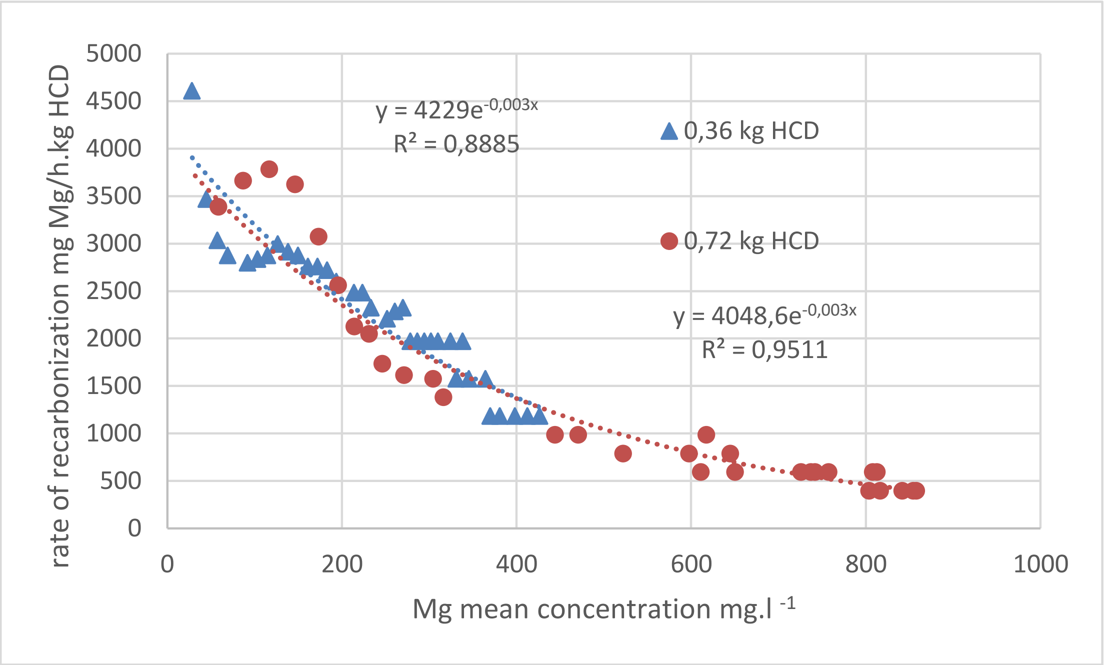

Fig. 16 Rate of recarbonization process *vs.* Mg mean concentration.

It is apparent from the course of the dependencies that the specific Mg release rates at different amounts of HCD are very similar, which indicates that a process scale-up is possible. In addition, the rate of Mg release from HCD decreases with the Mg concentration in the solution, showing that an optimal Mg concentration interval where the release rate is advantageous and further increase of the solution concentration is not necessary. Concentrations of about 200 $mg.l^{-1}$ are considered as the optimal concentration interval. Volume of the settling tank also depends on this value as well as on the water flow to consumers from the water tank. Appropriate settling tank volume ensures that the water flow rates in the tank caused by the inflow of reactor solution and water from the water tank do not interfere with particle settling and protect the water tank from fine particles leaching from the settling tank.

4. Conclusion

Preliminary results of drinking water recarbonization by biogenic elements have shown that the process can be carried out in both batch and continuous systems, with a fixed (filter) or fluidized bed of a suitable recarbonizing material. Experimental data obtained with various Ca- and Mg-containing materials have clearly shown that half-calcined dolomite (HCD) is the most appropriate of the studied materials and their combinations. The results obtained also confirm that a fluidized-bed system is preferable to a fixed bed. It has also been experimentally confirmed that the process is more efficient if the system produces an Mg and Ca ion concentrate (with a concentration higher than required in the drinking water used) and mixes it in a suitable proportion with the drinking water from the water source.

Long-term experiments in the fluidized-bed system were aimed at the verification of the recarbonization process robustness under laboratory conditions and at the determination of the main process parameters impact on the recarbonization efficiency to enable equipment design for specific drinking water recarbonization conditions at the given average drinking water consumption under real conditions. They were performed in two series between March and August 2019. The total time of the experiments was more than 2000 hours.

HCD (Magno Dol (Acdolite), Rheinkalk Acdolite, Germany) with the particle size of 2-4 mm is considered to be used for the recarbonization of drinking water in the proposed location. Preliminary laboratory tests have shown its suitability for recarbonization under fluidized bed conditions both in terms of the recarbonization process efficiency and in terms of fluidization characteristics.

Long-term experiments in a fluidized bed reactor and concentrate storage system operated continuously have shown that the HCD recarbonization process is sufficiently robust, even at significant changes in the process parameters (stopping CO_2 or fresh water feed), it can return to the steady state providing enough Mg and Ca ions to achieve the desired concentration of these biogenic elements in drinking water. The process is dependent on the suitable amount of HCD and therefore it is necessary to carry out pilot experiments to optimize the process conditions considering the required parameters. Also, the optimal amount of CO_2 required to achieve maximum process efficiency is to be checked under pilot plant conditions. The effect of temperature will also be the subject to verification under pilot conditions.

Based on the experimental results, production rates of Mg ions required to achieve the desired Mg concentration in drinking water were determined. It also enabled the determination of the HCD amount needed in a real plant. Parameters of the circulation pump (flow, discharge, etc.) can be determined from the water flow rate in the circulation loop. From the water consumption, known Mg concentration increase and water tank volume, water flow between the water tank and the settling tank at a given Mg concentration in the settling tank can be determined. Thus, pump parameters for pumping water from the water tank to the settling tank can be estimated.

Based on experimental data in the continuous system, the main process parameters were determined (minimum fluidization velocity, pressure drop in the bed versus water flow rate, fluidized bed height, particle diameter reduction, etc.). Optimum conditions of the recarbonization process and the hydrodynamic characteristics of the fluidized bed have shown that a pilot plant fluidized bed reactor can be designed to verify all findings under laboratory conditions and to treat soft water in real plant operation conditions. The proposed methodology of the recarbonization process intensification in a fluidized bed reactor can be used for further enlargement of the recarbonization reactor under real conditions.

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