

Scale precipitation on HDPE pipe by degassing of CO₂ dissolved in water

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ABSTRACT

In Algeria, high-density polyethylene (HDPE) is widely used in drinking water pipes. This study is focused on the precipitation of calcium carbonate, a major constituent of scale, from calcocarbonically pure (CCP) water in HDPE pipe. Studying scaling in natural conditions is very difficult because it occurs over many years. For this, accelerated scaling is caused by the degassing CO₂ dissolved in water. The kinetic study has shown that the germination time and the critical pH decrease with the hardness (30, 40 and 50 °f) and temperature (30, 40 and 50 °C) of water. On the other hand, scaling process efficiency (η) and the supersaturation coefficient (Ω_{cal}) of CaCO₃ increase with these parameters. The CaCO₃ precipitation occurs both in solution and on walls of HDPE. By the weighing method, it is shown that the deposit mass increases with hardness and temperature. Calcium carbonate precipitates much more in homogeneous phase than in heterogeneous one. The study also showed that heterogeneous nucleation on HDPE is much less important than on PA, PVC, chrome and Inox. These measurements are supported by the characterization of X-ray diffraction deposits and by scanning electron microscopy, which recognizes that the precipitate obtained consists mainly of calcite.

Key words: calcium carbonate, degassing CO₂, HDPE, scale, water

HIGHLIGHTS

- Investigation of scale deposit on HDPE drinking water pipes.
- Accelerated precipitating CaCO₃ by degassing CO₂ of water.
- Increase of scaling process efficiency η with hardness and temperature.
- Scale precipitates much more in flow water phase than on walls of HDPE.
- The precipitate obtained consists mainly of calcite.

INTRODUCTION

The formation of calcium carbonate (CaCO₃) (i.e., scale) in drinking water systems has long been a concern for the treatment and distribution of water. The increasing frequency of scaling, coupled with lack of knowledge about CaCO₃ formation in water supply systems, makes reconsidering this topic timely. A scale deposit formed in domestic and industrial water pipes is a problem that has mainly been the subject of many studies and discussions. A literature review reveals recurring issues related to the CaCO₃ scale (Ghizellaoui *et al.* 2007; Larsen *et al.* 2008; Ketrane *et al.* 2010; Sousa *et al.* 2016; Zhang *et al.* 2018; Zhou *et al.* 2018; Zotzmann *et al.* 2018).

Precipitation of calcium carbonate is influenced by calcium ions, bicarbonate ions, pH, flow rate, temperature and saturation index. In addition, different temperatures may cause different crystal morphology of calcium carbonate. Based on the theory of crystal growth kinetics, Larsen *et al.* (2008) carried out laboratory experiments to study the calcium carbonate scale mechanism (Sousa *et al.* 2016; Zhang *et al.* 2018).

Prediction, monitoring and consequences of CaCO₃ formation has long been a key issue in drinking water treatment. An initial concern was that water strongly undersaturated with CaCO₃ would be corrosive to metal and concrete pipe infrastructure (Baylis 1935). On the other hand, for water highly supersaturated with CaCO₃, these are problems concerning scaling.

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Numerous factors lead to the deposition of scale, such as water pH, total dissolved solids' concentration, pressure systems and temperature (Li *et al.* 2017).

The increased propensity of CaCO₃ to precipitate at higher temperatures makes scaling problematic, especially in water heaters. The scale layers formed on the water pipes control the heat transfer and reduce the efficiency of the system. In the worst cases, the scale formed leads sometimes to the shutdown of an industrial plant (Shakkthivel *et al.* 2004).

In the case of petroleum industries, the contribution of fouling to the loss of profitability is a major source of concern. The refining capacity loss, due to preheat train fouling in one year, was estimated at 25,400 m³/day. In 2003, the total cost of fouling in refineries was estimated to be \$1.5 million within a period of three months (Bories & Patureaux 2003). In 2009, another 31,800 m³/day capacity UK refinery reported that 1 °C loss of preheat temperature (that is oil temperature) cost the operator some £250,000 per year (Macchietto *et al.* 2009). In addition, recent studies have shown that heat exchanger fouling may be responsible for 1%–2.5% of global CO₂ emissions. Considering that there are currently 750 refineries worldwide, the total amount of emitted CO₂, due to fouling, is approximately 88 million tons per year. CO₂ emissions will result in environmental penalties (Ogbonnaya & Ajayi 2017).

As with all systems undergoing crystallization, different stages are distinguished by crystallogenesis. The first phase is obviously germination. When nucleation occurs within the solution or when the process begins in contact with a wall or a solid suspension, this nucleation is said to be homogeneous. After this stage, the crystalline growth occurs (Li *et al.* 2017).

Due to the multiplicity of these allotropic varieties (calcite, aragonite, vaterite, calcium carbonate mono and hexahydrate, amorphous precipitates), the study of the precipitation mechanisms of CaCO₃ is of exceptional interest, both theoretical and practical (Li *et al.* 2017). In order to control this scale formation and according to Ben Amor *et al.* (2004), various studies have been carried out to study the influence of the composition of the water, the temperature and the pH of the water on the calcocarbonic system (CaCO₃-CO₂-H₂O). The role of these parameters in shifting the equilibrium of the calcocarbonic system towards the precipitation of CaCO₃ has been demonstrated.

The scaling is a complex system, so it is difficult to predict the sensitivity to scaling of a solid surface in contact with calcareous water. Scale deposition kinetic is generally lengthy under natural conditions. Therefore, different techniques have been proposed to accelerate the phenomenon in the laboratory (Hui & Lédion 2002). Many physical techniques have been proposed, such as effect of magnetic (Alimi *et al.* 2006) and high-frequency electric fields on water treatment. Many works have been devoted to study calcium carbonate scaling using electrochemistry techniques (Hui & Lédion 2002; Ketrane *et al.* 2009). These techniques consist of increasing the pH near an electrode by an electrochemical reaction. However, electrochemistry techniques are not suitable for studying scale precipitation on non-metallic materials. The chemical methods make it possible to precipitate scale as well on metallic and non-metallic materials such as polymers.

Various experiments have been designed to precipitate CaCO₃ by dipping the wall to be studied in supersaturated water. The critical pH technique proposed by Feitler in 1972 (Hui 1972) consists of increasing the rate of supersaturation of the water to be studied by adding OH⁻ ions until a precipitation of calcium carbonate is obtained. Roques *et al.* (1994) describe very well the technique of controlled degassing of CO₂ dissolved in water. This accelerated technique is to increase the solution pH and cause the scale formation. The degassing of dissolved CO₂ from water displaces the calcocarbonic system towards that of calcium carbonate precipitation.

Different types of materials used in hydraulic systems have been tested. However, few works are devoted to the influence of the nature of the wall on the precipitation of calcium carbonate (Ben Amor *et al.* 2004; Zhou *et al.* 2018). In addition, it has been shown that nature and surface condition material affects the susceptibility of the liquid/solid interface to be covered by scale.

Polyethylene is a semi-crystalline polymer widely used in packaging, interior coatings, sporting goods and the biomedical field. The use of high-density polyethylene (HDPE) in applications requiring a long service lifetime such as for pressurized pipes for water and gas has dramatically increased in the last years. For the new generation of pipe materials, a lifetime as long as 100 years is expected under normal operation conditions (Sun *et al.* 2014). Currently, in Algeria, HDPE is increasingly used in drinking water pipelines (Ketrane *et al.* 2016). It should be noted that the literature consulted does not report any work relating to the study of scaling by controlled degassing of CO₂ dissolved in water in HDPE pipes.

The purpose of this research is to study the effect of water hardness and its temperature on the scale formation on HDPE walls. The accelerated precipitation of calcium carbonate from calcocarbonically pure water (CCP) is studied by the controlled degassing of CO₂ dissolved in water technique. The combined effect of water hardness and temperature on kinetic precipitation of CaCO₃ is studied. The supersaturation coefficient Ω_{cal} of CaCO₃ under these conditions is also calculated.

The weighted method is used to estimate the percentage of two types of precipitation: a homogeneous one in solution and a heterogeneous one on the walls. The morphology of the precipitate obtained is examined by scanning electron microscopy (SEM) and the formed deposits are characterized by X-ray diffraction (XRD).

METHODS

Water preparation

The experimental solution is CCP water containing only Ca^{2+} , CO_3^{2-} and HCO_3^- ions in order to avoid any side effect by foreign ions. The CCP water was prepared by dissolving CaCO_3 reagent grade in deionised water and the unit of the hardness of this water is °f (1 °f corresponds to $10 \text{ mg}\cdot\text{L}^{-1}$ of dissolved CaCO_3 or to $4 \text{ mg}\cdot\text{L}^{-1}$ of Ca^{2+}). To ensure complete dissolution of CaCO_3 in water, the pH of the solution should be approximately 5.7. For this, it is necessary to bubble the CCP water with CO_2 during 10 hours, depending on Reaction (1):



Controlled degassing CO_2 dissolved in water technique

Controlled degassing CO_2 dissolved in water technique was developed for the first time in 1994 by Roques (Roques *et al.* 1994) and has been used in many studies (Menzri *et al.* 2017). Its principle is based on the displacement of the calcocarbonic equilibrium in the direction of the precipitation of CaCO_3 by degassing the CO_2 dissolved in water by air as shown in Reaction (1).

The CO_2 partial pressure of the stripping gas is lower than the equilibrated P_{CO_2} of the calcocarbonic solution. In this way, supersaturation is created. The amplitude of the supersaturation can be adjusted according to the initial concentration of the solution, the P_{CO_2} of the stripping gas and to the temperature. The evolution of pH and free calcium ions [Ca^{2+}] in CCP water is followed during the experiment.

Conduct of a trial

Controlled degassing CO_2 dissolved in water technique is used to explore systematically the range of supersaturation in the equilibrium plane $\{P_{\text{CO}_2}, [\text{Ca}^{2+}]\}$ shown in Figure 1. On the graph, the TCa is the calcium concentration expressed in French degrees (°f).

The plan of this graph can be divided into two zones:

- area of supersaturation below
- area of subsaturation above.

The starting point M_0 (in the subsaturation area) corresponds to an initial concentration $[\text{Ca}^{2+}]_0$ and the partial pressure (P_1) of CO_2 gas dissolved in water. After changing CO_2 gas by another gas (air), the representative point of the system evolves very rapidly in a vertical direction of the target point noted M_c , which is located in the supersaturation area. Experimentally, precipitation starts at the point M_r noted, before degassing is complete.

After a residence time near the point M_r equal to the germination time, the rate of formation of CO_2 induced by the precipitation reaction of calcium carbonate exceeds the rate of elimination of CO_2 dissolved in water by degassing. This explains the increase of partial pressure of CO_2 (P_{CO_2}) in the solution on the experimental curve (point A), and then, decreases to the point C, corresponding to the equilibrium value $[\text{Ca}^{2+}]$.

Thus, it is necessary to define the degree of supersaturation Ω changing from low values (<1) in the area of subsaturation, to much larger values, when moving into the area of supersaturation.

The supersaturation Ω is defined as follows: $\Omega = ((\text{Ca}^{2+}) \cdot (\text{CO}_3^{2-}))/K_s$

where K_s is solubility product of calcite.

Description of the experimental device

The experimental device of the controlled CO_2 degassing technique (Figure 2) was designed and implemented in our laboratory.

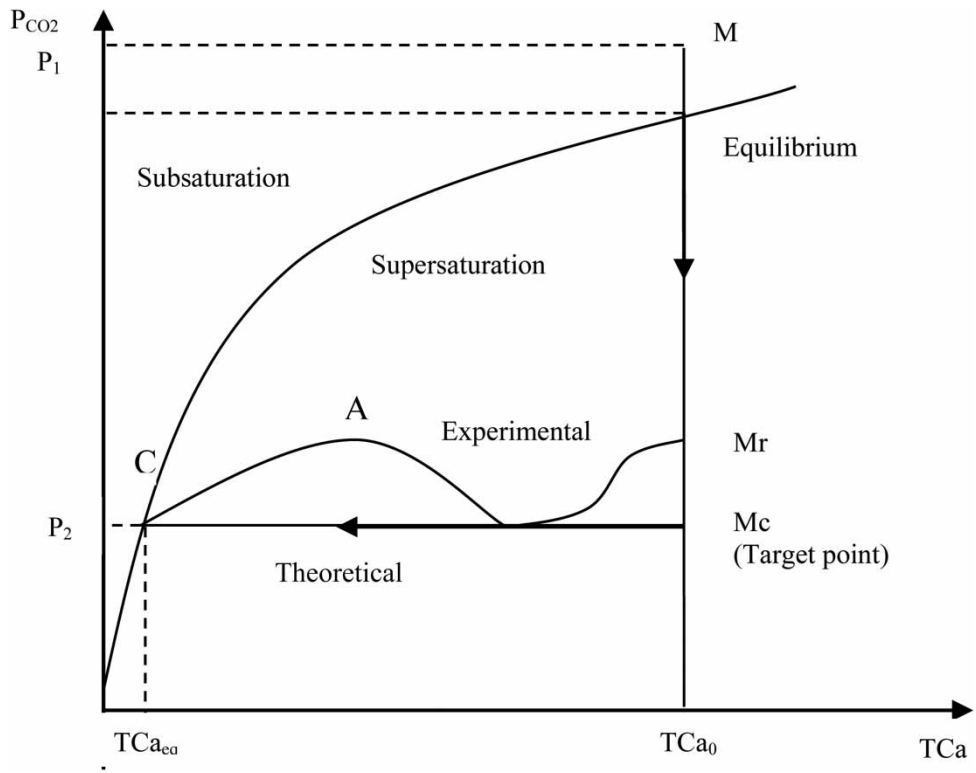


Figure 1 | Representational viewpoint of the solution during a test (Roques et al. 1994).

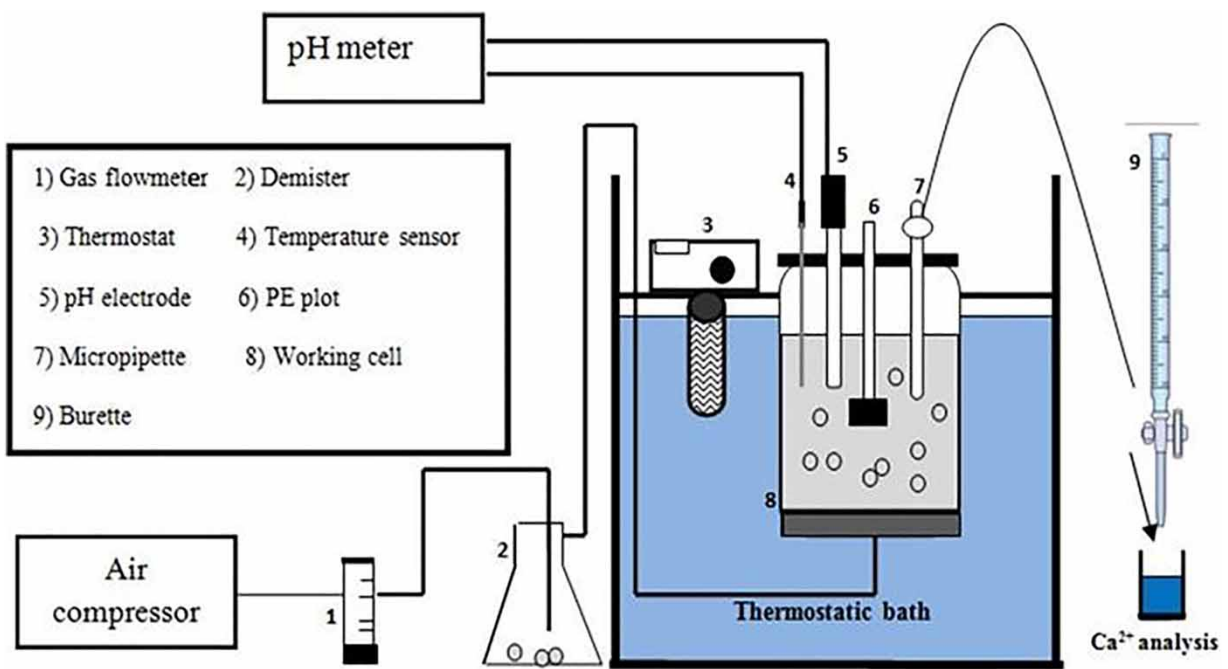


Figure 2 | Experimental device of the controlled CO₂ degassing technique.

The material to be studied in the form of a cylindrical cell made of HDPE is immersed in a thermostatic bath to set the temperature of the CCP water. A dry air inlet is provided at the bottom of the reactor, and thus, its uniform dispersion in the liquid mass is ensured thanks to its perforated bottom. In order to prevent a drop in water temperature after the arrival of the degassing air, this one is preheated beforehand in the thermostatic bath. The evolution of pH and the concentration of free calcium ions $[Ca^{2+}]$ in CCP water is monitored during the experiment. The concentration of Ca^{2+} is determined by EDTA at pH = 10 titrimetric assay in the presence of NET.

Experimental conditions

Experimental conditions are as follows:

- Air flow: 8 L.min⁻¹ (Ben Amor *et al.* 2004)
- CCP water hardness: 30, 40 and 50 °f corresponding respectively to 120, 160 and 200 mg.L⁻¹ of Ca^{2+}
- CCP water temperature: 30, 40 and 50 °C (± 1 °C)
- CCP water volume: 1,000 mL
- Experiment duration: 120 minutes.

Experimental procedures

Once all devices are connected, the thermostat temperature is set to the desired temperature. Thanks to a compressor, high-flow air (8 L.min⁻¹) is introduced into the reactor to degas the dissolved CO₂ of the CCP water.

The passage of the compressed air through the demister eliminates the water droplets present in the air used for degassing the CO₂ dissolved in the water. A volume of 1 mL of CCP water sample is taken throughout the experiment to determine the remaining free Ca^{2+} ions in the water. In addition, the pH of the solution is noted at each water sample.

EDTA (ethylene diamine tetra acetic acid) which has the property of complexing with calcium ions to form soluble compounds carries out the determination of the remaining free Ca^{2+} ions. This test is carried out by adding two to three drops of NET colour indicator and two drops of pH = 10 buffer. The end of the test is detected by the blue colour of the solution.

To remove the scale deposited on the walls of the HDPE reactor at the end of each test, the working cell is treated with sulfuric acid at 0.05 M for 20 minutes and then washed with distilled water.

To ensure the reproducibility of the results, all the experiments are repeated three times.

Weighing method

At the end of the experiment, the suspended CaCO₃ particles, which precipitated in bulk from the solution, were quickly separated from the stock solution by vacuum filtration, using a cellulose nitrate filter with a pore size of 0.45 mm. The scale deposit thus formed is washed with deionized water at 30 °C and then dried in the open air for 24 hours. Subsequently, this scale deposit is dried in an oven for 1 hour 30 minutes at 50 °C to ensure that it does not contain moisture. The mass of scale formed in the solution (homogeneous precipitation) is obtained by weighing.

The same procedure is followed to obtain the mass of scale deposited on the HDPE walls (heterogeneous precipitation) recovered by washing with sulfuric acid.

The determination of the total mass of scale formed (in solution and on HDPE wall) after drying leads to calculation of the percentage of scale precipitation both homogeneous (in solution) and heterogeneous (on HDPE wall).

SEM and XRD characterization of calcium carbonate particles

Ex-situ characterization of scale formed after drying is performed with a FEI Quanta 200 scanning electron microscopy (SEM). X-ray diffraction analysis is also carried out on the same scale using Rigaku (MiniFlex) diffractometer.

RESULTS AND DISCUSSION

In order to study the phenomenon of scaling on an HDPE wall, a wall used for drinkable water, calcium carbonate precipitation is induced by controlled degassing of CO₂ dissolved in CCP water.

The calcium carbonate precipitation using controlled degassing of CO₂ dissolved in CCP water technique on HDPE wall consists of supersaturating the CCP water by blowing in a gas at low pressure in CO₂ which is atmospheric air ($PCO_2 = 3.10^{-4}$ atm) (Ben Amor *et al.* 2004) with a flow rate of 8 L.min⁻¹.

By this accelerated technique, the scaling kinetic study is carried out by following simultaneous evolution of the CCP water pH and the $[Ca^{2+}]$ (free Ca^{2+} concentration in water) versus time (Figure 3).

Figure 3(a) represents the evolution of CCP water pH versus time. There is a regular rise in pH, which begins at around 5.65 until a peak of pH equal to 8.56 is observed. This peak obtained after 34 minutes is followed by a fall and then a slight rise, to finally stabilize at around pH of 8.2. Indeed, the rise in pH shows an instantaneous response of the kinetics of transfers at the gas-liquid interface and chemical reactions in the liquid phase which are due to the large surface/volume ratio created by the gas bubbles and the relative speed of the reactions in the liquid phase. This indicates a progressive degassing of CO_2 dissolved in water induced by the passage of air (Coto *et al.* 2012; Zhaoa *et al.* 2018).

Under usual working conditions, the stock solution has a pH below $(pK_1 + pK_2/2)$ (average 8.4 at room temperature). Under these conditions, the HCO_3^- ions are very predominant over the CO_3^{2-} ions, which suggests that crystallization takes place between Ca^{2+} and HCO_3^- ions and not between Ca^{2+} and CO_3^{2-} ions. This is the necessary transformation of HCO_3^- ions into CO_3^{2-} before they can be included in the crystal according to the reaction:



Reaction (2) releases the protons responsible for the pH drop observed. This release is also necessary for stoichiometric reasons. In order to keep the electronic neutrality, a Ca^{2+} cation is associated with two HCO_3^- anions that means two carbon atoms in the solution, whereas in the crystal, which results therefrom, a Ca^{2+} ion is associated with a CO_3^{2-} ion, that is to say, a single carbon atom. It is necessary to eliminate the other carbon atom according to this reaction:



It is this release of CO_2 in Reaction (3) which is responsible for the rise in the equilibrium PCO_2 pressure immediately after the start of precipitation, that is to say, at the time when the rate of release of the protons H_3O^+ is the largest. This leads to a rate of accumulation of CO_2 greater than its elimination rate by degassing. The precipitation rate decreases thereafter, while the degassing rate linked to the gas flow remains constant. There comes a time when degassing rate becomes faster than CO_2 formation rate according to Reaction (3). This clearly explains the pH water rise (Coto *et al.* 2012; Zhaoa *et al.* 2018).

Figure 3(b) represents the calcium concentration variation (corresponding to the $[Ca^{2+}]$ free) versus time for CCP water at $120 \text{ mg}\cdot\text{L}^{-1}$ hardness and at 30°C . The $[Ca^{2+}]$ remains unchanged from the start of the experiment up to 34 minutes. After

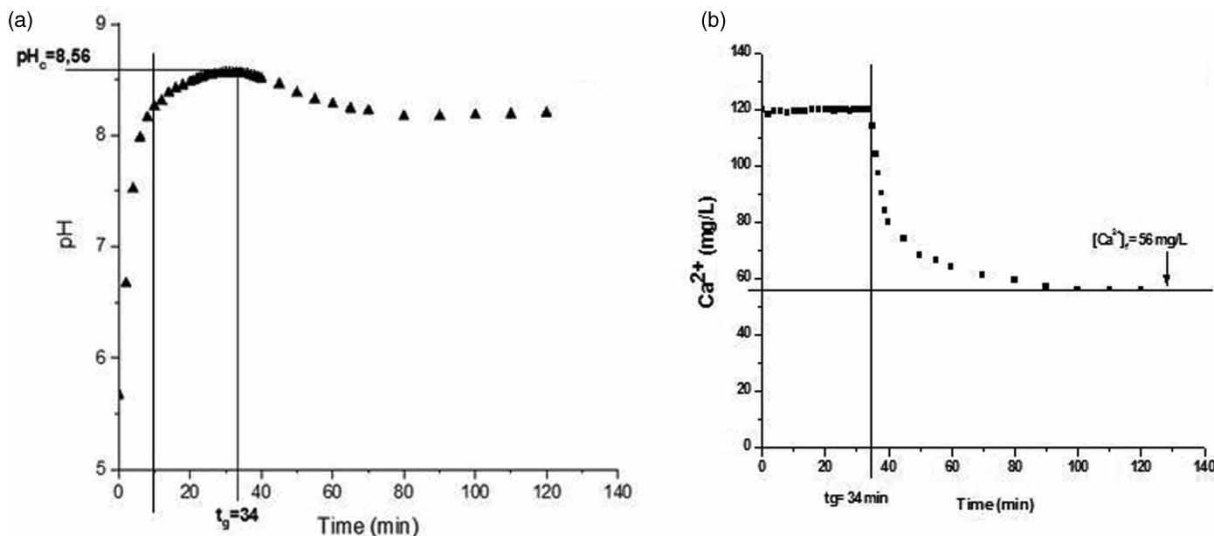


Figure 3 | Temporal evolution of CCP water pH (a) and concentration of Ca^{2+} (b) ($[Ca^{2+}]_0 = 120 \text{ mg}\cdot\text{L}^{-1}$ and $T = 30^\circ\text{C}$).

this time, a sudden and regular fall in $[\text{Ca}^{2+}]$ is recorded and then stability after 85 minutes until the end of the experiment. The final value of $[\text{Ca}^{2+}]_f$ is equal to $56 \text{ mg}\cdot\text{L}^{-1}$.

The stability of the $[\text{Ca}^{2+}]$ at $120 \text{ mg}\cdot\text{L}^{-1}$ at the start of the experiment shows that the precipitation of calcium carbonate does not yet occur. This period corresponds to the germination phase which makes it possible to define a practical germination time, noted t_g (Hui & Lédion 2002). Germination is followed by crystal growth. As the solution is supersaturated, precipitation begins, therefore the concentration of Ca^{2+} ions decreases, transforming according to Reaction (1) up to a $[\text{Ca}^{2+}]_f$ value, which cannot be exceeded. The value of $[\text{Ca}^{2+}]_f$ reached at the end of the experiment corresponds to $[\text{Ca}^{2+}]_{\text{eq}}$ obtained when the equilibrium is reached. Indeed, beyond this value $[\text{Ca}^{2+}]_{\text{eq}}$, the calcocarbonic system goes theoretically to the subsaturation zone where precipitation is obviously impossible.

The calculated supersaturation coefficient, noted Ω_{cal} , of CaCO_3 , which is an indicator of the scaling power of water, is obtained by a laborious calculation developed on Excel. This calculation is based on analytical chemistry notions and on the equations governing the calcocarbonic system.

The calculated supersaturation coefficient Ω_{cal} evolution versus time is represented in Figure 4. At the start of the experiment, the value of supersaturation coefficient Ω_{cal} starts from zero and increases rapidly until it reaches a maximum value ($\Omega_{\text{cal}} = 23$) corresponding to the germination time deduced previously (34 minutes). Subsequently, the supersaturation coefficient drops rapidly, indicating a decrease in the ionic product $(\text{Ca}^{2+})\cdot(\text{CO}_3^{2-})$ as a consequence of CaCO_3 precipitation. After 100 minutes of experiment, the value of Ω_{cal} stabilizes until the end of the experiment.

Influence of water hardness and temperature

Temporal evolution of the pH

Figures 5(a) and 6(a) show, respectively, the temporal evolution of CCP water pH at different hardness and at different temperatures. The pH evolution versus time follows the same trend for all cases, whatever the hardness and temperature of the water. First, a sharp increase in water pH is observed until it reaches a critical value (pHc), which is inversely proportional to the temperature and hardness of the CCP water. From the pHc, the CaCO_3 precipitation occurs and the pH of the water decreases slowly. Towards the end of the experiment, the water pH stabilizes.

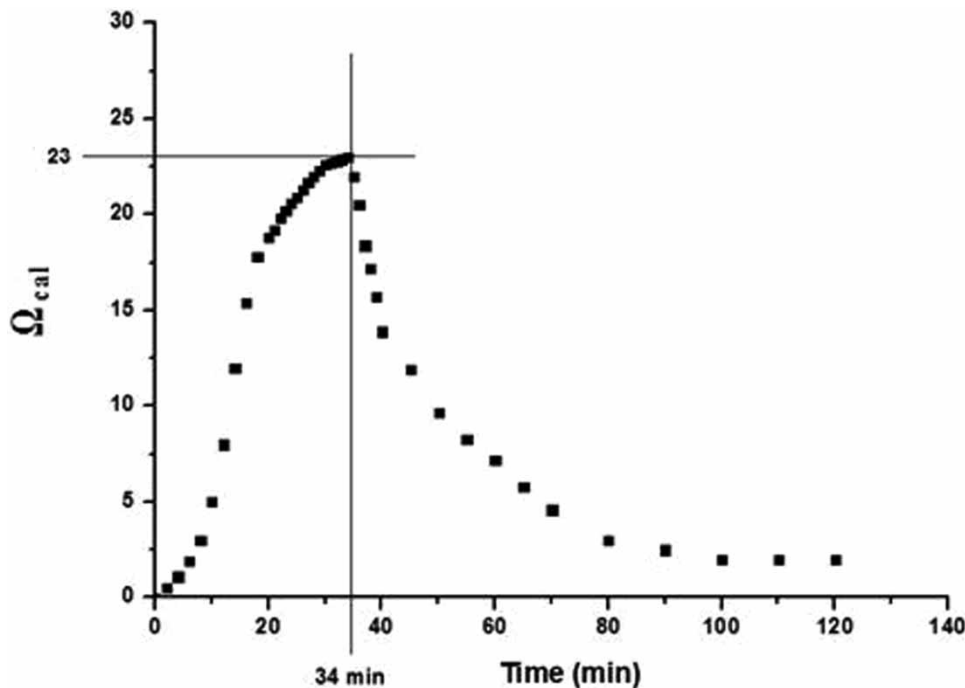


Figure 4 | Temporal evolution of supersaturation coefficient Ω_{cal} in CCP water ($[\text{Ca}^{2+}]_0 = 120 \text{ mg}\cdot\text{L}^{-1}$ and $T = 30 \text{ }^\circ\text{C}$).

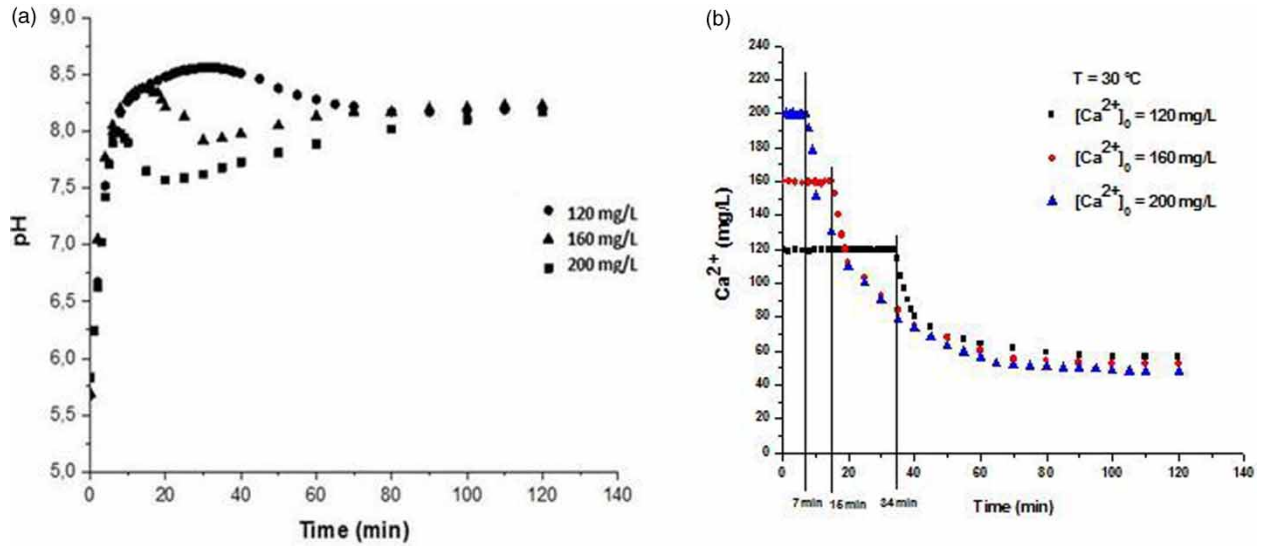


Figure 5 | Temporal evolution of CCP water pH (a) and concentration of Ca²⁺ (b) at different hardness and at T = 30 °C.

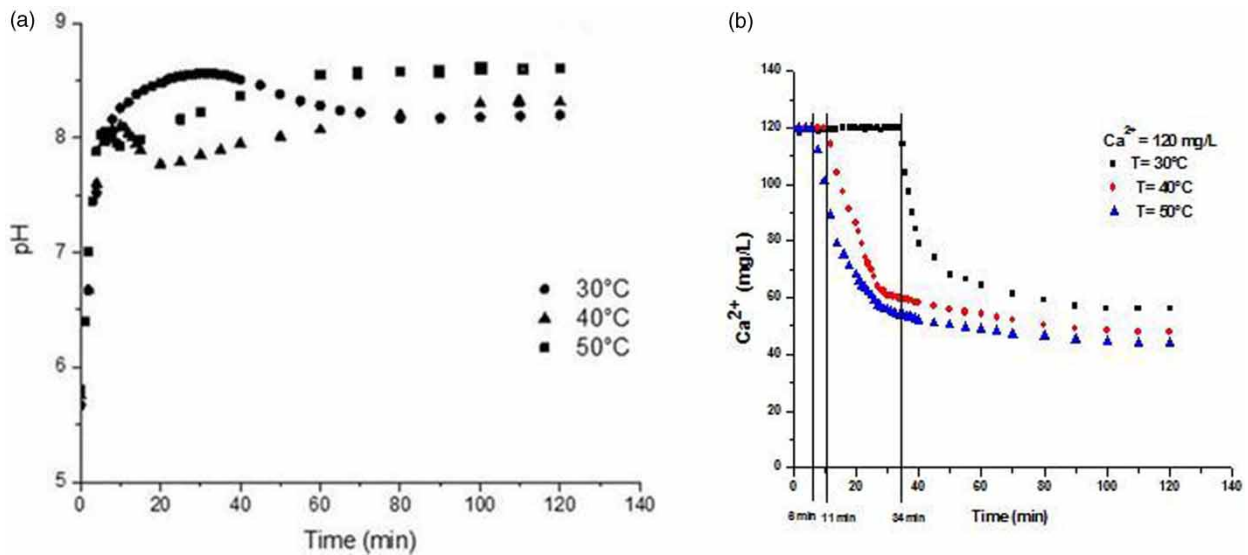


Figure 6 | Temporal evolution of CCP water pH (a) and concentration of Ca²⁺ (b) at different temperatures and at [Ca²⁺]₀ = 120 mg·L⁻¹.

Temporal evolution of the calcium concentration

The different curves obtained at different hardness (Figure 5(b)) and at different temperatures (Figure 6(b)) of the CCP water show that a fall in the calcium content cannot be obtained before the germination time t_g . The latter is inversely proportional to the temperature as well as to the water hardness. Beyond this germination time, a rapid decrease of the calcium concentration is observed at the beginning of the calcium carbonate precipitation. Approaching the end of the experiment, the speed of this precipitation diminishes and eventually stabilizes.

Table 1 summarizes the different parameters characterizing the technique of controlled degassing of CO₂ dissolved in CCP water. The kinetic study on the HDPE wall has shown that germination time t_g , pH_c and calculated supersaturation coefficient Ω_{cal} decrease with the water hardness (120, 160 and 200 mg·L⁻¹) and also with temperature (30, 40 and 50 °C). Moreover, the precipitation rate increases with the water hardness and temperature. As expected, increased hardness and

Table 1 | Different parameters derived from the study of the effect of temperature on the scaling kinetics of CCP water at different hardness

Hardness Ca ²⁺ (mg·L ⁻¹)	Parameters	Temperature (°C)		
		30	40	50
120	t _g (min)	34	11	6
	pH _C	8.56	8.10	8.05
	Ω _{cal}	23	38	41
	Ca _f ²⁺ (mg·L ⁻¹)	56	48	44
	η (%)	53.33	60	63.33
160	t _g (min)	15	9	5
	pH _C	8.38	8.06	8.02
	Ω _{cal}	29	44	51
	Ca _f ²⁺ (mg·L ⁻¹)	52	44	40
	η (%)	67.5	72.5	75
200	t _g (min)	7	5	3
	pH _C	8	7.96	7.59
	Ω _{cal}	32	47	53
	Ca _f ²⁺ (mg·L ⁻¹)	48	44	40
	η (%)	76	78	80

temperature of water accelerates the scale precipitation. The scaling process efficiency η (Reaction (4)) increases also with the hardness and the temperature of the CCP water. This result seems very consistent.

$$\eta(\%) = (([Ca^{2+}]_0 - [Ca^{2+}]_f) / [Ca^{2+}]_0) \cdot 100 \tag{4}$$

where η is process efficiency (%), [Ca²⁺]₀ is initial concentration of free Ca²⁺ ions (mg·L⁻¹) and [Ca²⁺]_f is final concentration of free Ca²⁺ ions (mg·L⁻¹).

Evaluation of the deposited masses of scale

The percentage of scale formed in solution (homogeneous precipitation) and the percentage of scale deposited on HDPE wall (heterogeneous precipitation) are evaluated for all experiments. In Table 2 all the results are summarized.

From the results obtained, it is easy to observe that the total mass deposited of CaCO₃ increased with temperature and hardness of CCP water. This explains the scale formation in hard and hot water pipes. It is also noted that the scale precipitates much more in homogeneous form than in heterogeneous form on HDPE wall. In homogeneous form, the CaCO₃ is formed but it is in the water flow. HDPE seems to be a very interesting wall for water flow because the scale precipitation in the heterogeneous phase (on the walls of the pipes) seems weak.

Table 2 | Masses of deposits (total, homogeneous and heterogeneous) at different temperatures for different hardness

T (°C)	[Ca ²⁺] (mg·L ⁻¹)	Total mass of CaCO ₃ deposited (mg)	Homogeneous		Heterogeneous	
			Mass of CaCO ₃ deposited (mg)	%	Mass of CaCO ₃ deposited (mg)	%
30	120	160	145	90.63	15	9.37
	160	270	230	85.18	40	14.82
	200	380	302	79.48	78	20.52
40	120	180	153	85	27	15
	160	290	238	82.07	52	17.93
	200	390	307	78.72	83	21.28
50	120	190	154.5	81.32	35.5	18.68
	160	300	242	80.67	58	19.33
	200	400	305	76.25	95	23.75

To further demonstrate the advantage of the HDPE wall over others, comparisons are made between our experimental results and those found by Ben Amor *et al.* (2004), obtained in the same conditions ($[Ca^{2+}]_0 = 160 \text{ mg}\cdot\text{L}^{-1}$ corresponding to $0.4 \text{ mg}\cdot\text{L}^{-1}$ of CaCO_3 , $T = 30 \text{ }^\circ\text{C}$, air flow = $8 \text{ L}\cdot\text{min}^{-1}$).

The following histogram (Figure 7) groups together the scale precipitation parameters on HDPE and on other materials (chrome, Inox, PA and PVC).

The germination times obtained on PA, PVC, chrome and Inox are similar (average 10 minutes) except for HDPE where the germination time t_g is delayed to 15 minutes. Furthermore, the percentage of heterogeneous precipitation scale decreases from PA to HDPE. Indeed, the heterogeneous percentage obtained on PVC, PA and HDPE (polymer materials) is 86, 61 and 14.81%, respectively.

Thus, it is obvious that under the same conditions of hardness ($[Ca^{2+}]_0 = 160 \text{ mg}\cdot\text{L}^{-1}$), temperature ($30 \text{ }^\circ\text{C}$) and air flow ($8 \text{ L}\cdot\text{min}^{-1}$) of CCP water, HDPE has a great advantage over other polymer materials because of its low tendency to form scale on the walls.

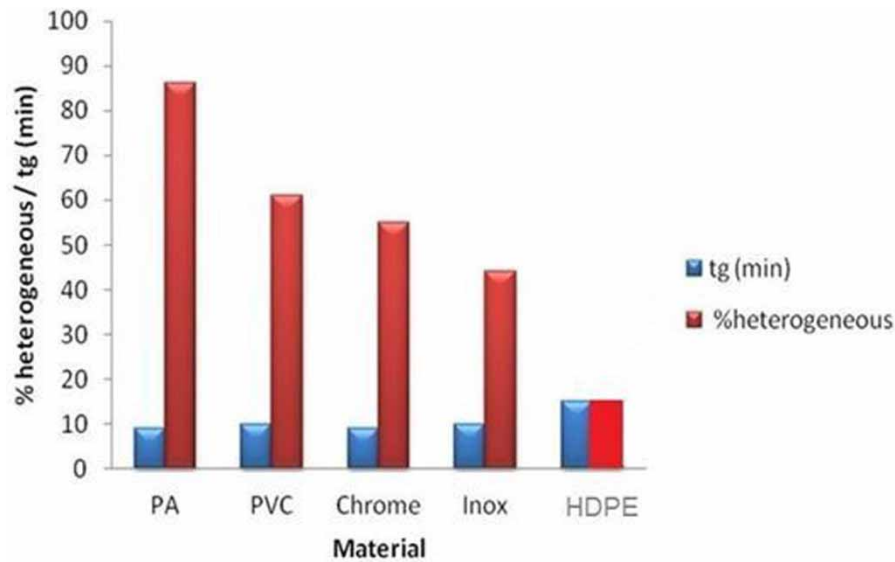


Figure 7 | Scale precipitation parameters on HDPE and on other materials ($[Ca^{2+}]_0 = 160 \text{ mg}\cdot\text{L}^{-1}$, $T = 30 \text{ }^\circ\text{C}$, air flow = $8 \text{ L}\cdot\text{min}^{-1}$).

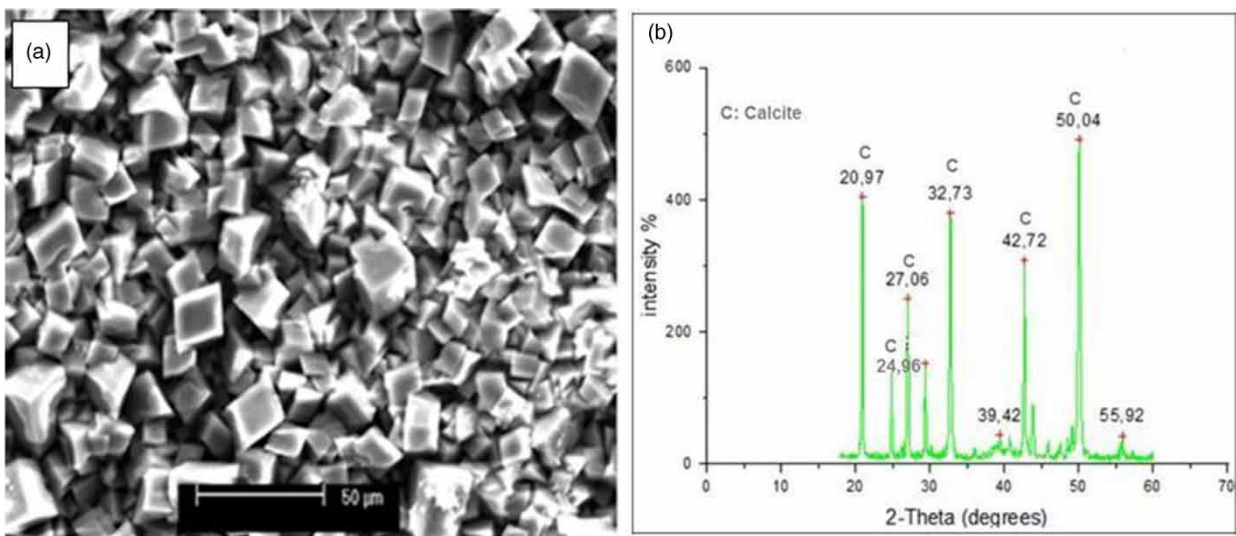


Figure 8 | Scanning electron microphotograph (a) and X-ray diffraction (b) for scale obtained from CCP water at $[Ca^{2+}]_0 = 200 \text{ mg}\cdot\text{L}^{-1}$ and $T = 30 \text{ }^\circ\text{C}$.

Characterization of deposits by scanning electron microscopy (SEM) and X-ray diffraction (XRD)

In order to characterize the calcium carbonate precipitate recovered at the end of a test, the scale mass recovered after filtration is analysed by SEM and by XRD.

Micrographies of the scale formed are taken, using SEM at different experimental conditions. Shown in Figure 8(a) is the crystal deposited for 120 minutes from CCP water ($[Ca^{2+}]_0 = 200 \text{ mg}\cdot\text{L}^{-1}$) at 30°C and in Figure 9(a), the one formed for 120 minutes from CCP water ($[Ca^{2+}]_0 = 120 \text{ mg}\cdot\text{L}^{-1}$) at 50°C . The formed crystals present a major regular structure with defined cubic crystal characteristics corresponding to calcite (Plummer & Busenberg 1982). Calcite presence is confirmed by XRD analysis, as when focusing on the crystal deposited, characteristic peaks of calcite are detected (Figures 8(b) and 9(b)). Finally, it can be concluded that CaCO_3 is mainly present as calcite. However, calcite constitutes the most stable and most adherent crystallographic variety of CaCO_3 .

Temperature effect

CaCO_3 precipitation depends mainly on the solubility product value (K_s) which depends on temperature. The K_s value of calcite was determined at several temperatures between 5 and 75°C , using the empirical expression (Dorange *et al.* 1990):

$$\text{p}K_s = 7.8156 + 0.0311111 \cdot T + 1502/T - 5518 \cdot \log(T) \quad (5)$$

where $\log(T)$ is the common logarithm of the absolute temperature $T(\text{K})$.

The different values of K_s of calcite calculated using Reaction (5) at 30 , 40 and 50°C is $10^{-8.38}$, $10^{-8.51}$ and $10^{-8.67}$, respectively. K_s values show that when the temperature increases, CaCO_3 solubility product decreases.

Unlike other salts whose solubility increases with temperature, the solubility of calcite decreases with temperature, as shown by the calculation of K_s . Therefore, precipitation of calcite is favoured at high temperature.

Added to this phenomenon, the experimental results (Table 1) have shown that CaCO_3 precipitation occurs at lower critical pH when the water temperature increases. To conclude, temperature considerably increases the scaling speed and decreases the germination times. This corroborates that scaling occurs more in hot water pipes than in cold water ones.

CONCLUSIONS

The present survey is focused on the study of calcium carbonate CaCO_3 precipitation from calcocarbonically pure water by degassing CO_2 dissolved in water. This accelerated technique allowed us to study the real phenomenon of scaling at the laboratory in record time. The kinetic study of scaling carried out by following CCP water pH and concentration of free ions Ca^{2+} versus time has shown that germination time t_g and pH_c decrease with the water hardness and temperature. However, the calculated supersaturation coefficient Ω_{cal} and total mass of calcium carbonate deposited increase with these two parameters. As expected, an increased hardness and temperature of the CCP water accelerates the scale precipitation and leads to a higher scaling process efficiency η and a great mass of scale. All the results obtained seem very consistent.

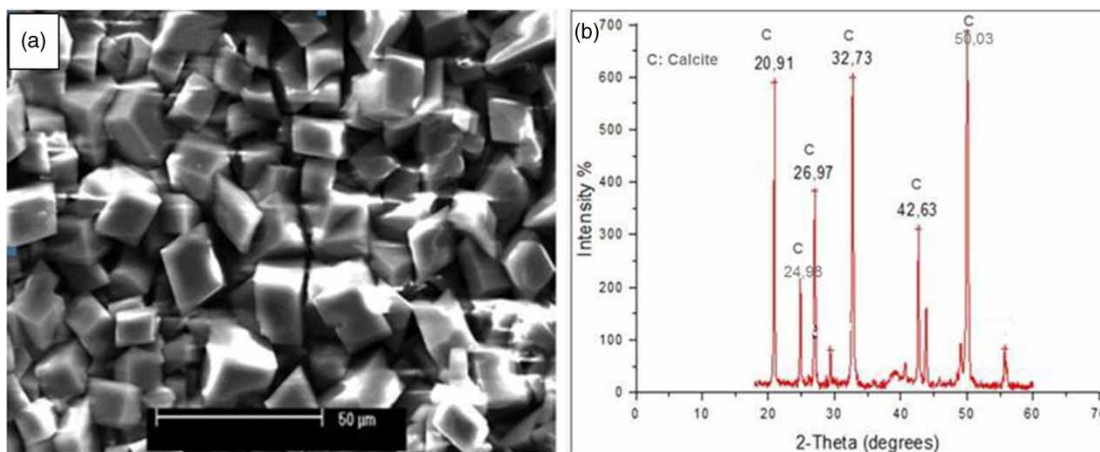


Figure 9 | Scanning electron microphotograph (a) and X-ray diffraction (b) for scale obtained from CCP water at $[Ca^{2+}]_0 = 120 \text{ mg}\cdot\text{L}^{-1}$ and $T = 50^\circ\text{C}$.

The experimentations show that CaCO_3 precipitation occurs both in solution and on the walls of a cell made of HDPE. Calcium carbonate precipitates much more in the homogeneous phase than in the heterogeneous one. The study also showed that heterogeneous nucleation on HDPE is much less important than on PA, PVC, chrome and Inox.

Finally, the characterization of the deposits formed by XRD and by SEM show that the calcium carbonate precipitates mainly in the form of calcite.

Of particular interest is the use of HDPE pipes in the water supply. Indeed, it has been shown that the scale formed precipitates very weakly on the HDPE walls. Scale formed mainly in the flow of the water can be removed easily by filtration. This work is limited to study the parameters which influence scaling in a closed reactor made of HDPE. The degassing of CO_2 dissolved in water caused by high-flow air blowing is not intended to study hydrodynamics. To demonstrate the effect of hydrodynamics on the scaling phenomenon, it is necessary to carry out other experiments by using another experimental device much more suitable than that used in this study.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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