



# Mechanisms of scale formation and carbon dioxide partial pressure influence. Part II. Application in the study of mineral waters of reference

Jean-Yves Gal\*, Yannick Fovet, Nathalie Gache

*Laboratoire de Chimie Analytique, Université Montpellier II, CC 029 Place E Bataillon, 34095 Montpellier Cedex 5, France*

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## Abstract

In the first part, we have designed a new model of evolution for the calco-carbonic system which includes the hydrated forms of  $\text{CaCO}_3$ :  $\text{CaCO}_3$  amorphous,  $\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$  (ikaite) and  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  (monohydrate) (J. Eur. Hydr. 30 (1999) 47). According to this model, it is the precipitation of one or other of these hydrated forms which could be responsible for the breakdown of the metastable state. After this first step, the precipitates evolve to dehydrated solid forms. Through the elaboration of computer programs in which the  $\text{CaCO}_3^0(\text{aq})$  ion pair formation was considered, this model was compared to experimental data obtained by the critical pH method applied to synthetic solutions.

In the present article, the same method was applied for four French mineral waters, at 25°C under study. Three samples formed a precipitation during the sodium hydroxide addition. For these three cases, this precipitation began for the  $\text{CaCO}_3 \cdot \text{H}_2\text{O}$  saturation. The added volume of sodium hydroxide was more than what was required for neutralizing free  $\text{CO}_2$  initially in solution. These results indicate that during a spontaneous scaling phenomenon, the pH rises at the same time by loss of the initial free  $\text{CO}_2$  and of the one produced by the hydrogen carbonate ions decomposition. Then we calculated, at various temperatures for the three studied scaling waters:  $\text{CO}_2$  partial pressures and loss of total carbon corresponding to the solubility products of  $\text{CaCO}_3$  hydrated forms. The results show that the partial pressure monitoring of the carbon dioxide is important in managing the behavior of scaling waters. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** Limescaling; Calcium carbonate; Hydrated forms; Thermodynamic; Metastable state;  $\text{CO}_2$  partial pressure

## 1. Introduction

Due to heating in most cases, the pH rise caused by the carbon dioxide loss, involves calcium carbonate precipitation according to an homogeneous or heterogeneous process. When the precipitate forms a deposit on the sides, the term “scaling” is used. Numerous works were published on the calcium carbonate precipitations which were caused by the loss of  $\text{CO}_2$ . It is, in particular, the LCGE method [1–4]. These works did not

consider the existence of  $\text{CaCO}_3^0$  complex, and also the interpretation of the measures did not consider the model which is proposed here. In each case, the provoked reaction was of the heterogeneous type.

Although scaling rarely results from the addition of sodium hydroxide, we finalized a method of study whose principle is to raise the pH by continuous addition of sodium hydroxide according to the pH critical method [5,6]. The results were then compared with thermodynamic calculations [7]. This method allowed us to verify the model credibility and to compare various methods generally adopted in predicting scaling risks [6].

The set of various analytical methods, which permit to estimate the scaling risks in circuits, still does not allow

\*Corresponding author. Tel.: +33-4-67-14-35-33; fax: +33-4-67-14-30-31.

E-mail address: jean-yves.gal@wanadoo.fr (J.-Y. Gal).

us to obtain results which can offer the possibility of defining precisely the functioning rules. Each of these methods allows, at the most, comparison of several waters, placed in the same conditions of disturbance; these conditions being mostly very different from usage conditions. For these reasons, the authors tried to test the same waters, to be able to compare their results. Due to their high composition stability, they chose to work with mineral waters, which are easily obtained: they are in France, waters of Contrexéville, Vittel, Evian and Volvic. We studied them with the same methodology as that already applied to synthetic solutions.

In this article, experimental results obtained by the addition of sodium hydroxide in these four mineral waters were described and discussed. They allowed estimating the scaling risks when the pH rises in fact, by the loss of  $\text{CO}_2$ .

## 2. Materials and methods

### 2.1. Experimental device

The four mineral waters were titrated at  $25^\circ\text{C}$  using sodium hydroxide. Assembly was established with a Tacussel TT-Procasseur 2 titration unit that commands a Tacussel EBX3 electronic burette. To registrate the data, it was necessary to use TTP2-PC-01 software. The pH electrode was a Radiometer XC100 electrode calibrated at  $25^\circ\text{C}$  by Radiometer buffers (pH 4 and 7). The concentration of the sodium hydroxide solution was  $5 \times 10^{-2} \text{ mol L}^{-1}$ : the solution was prepared from a  $0.1 \text{ mol L}^{-1}$  titrated Merck solution. 100 mL of studied water was placed in a 150 mL Pyrex glass erlenmeyer. The speed of sodium hydroxide addition was 0.1 mL per minute. The erlenmeyer was covered by a parafilm to limit the evolution of the solution by  $\text{CO}_2$  loss during the titration. Agitation was assured by a Teflon magnetic stirrer. Each titration was triplicated to validate the curves. For each of the four studied waters, references of the corresponding batch were specified in Table 1 and compositions indicated on labels were regrouped in Table 2.

For Contrexéville water, Lin et al. [8] indicated slightly different values of hydrogen carbonates and total calcium concentrations: 377 and  $467 \text{ mg L}^{-1}$ . By

atomic absorption, Callot et al. [9] verified Contrexéville's calcium concentration (from  $1.23$  to  $1.26 \times 10^{-2} \text{ mol L}^{-1}$ ) and Evian's calcium concentration (from  $1.93$  to  $2.13 \times 10^{-3} \text{ mol L}^{-1}$  plus a value of 1.66).

### 2.2. Titration curves

The program used was a development of the program intended for synthetic solutions. On the basis of matter balances, thermodynamic calculations were made by considering the formation of every compound which was able to form during the titration. The program allowed us to ensure the possible formation of an insoluble compound other than calcium carbonate. For calculations, we used data given by Plummer and Busenberg [10] and Gache [11] for the calco-carbonic system. The other values were chosen in various databases: [12–14]. After correction of the initial carbon dioxide content by pH measure of the tested water, it was possible to simulate the titration curve  $\text{pH}=f$  (volume of added sodium hydroxide) by supposing that the calcium carbonate was soluble for any pH. Critical pH could then be determined easily when simulated and experimental curves did not superimpose any more. This point was determined even when the solution did not become cloudy, because of a heterogeneous precipitation which was not immediately observable on the sides. Ionic activity product values, the critical pH as well as the pH and volumes at saturation of various forms were calculated for a pH rise caused by the addition of sodium hydroxide and by  $\text{CO}_2$  stripping.

## 3. Results

Apart from Volvic, the waters had a constant tendency to lose gas because they were strongly supersaturated with carbon dioxide. For each type of water from the same bottle, we have obtained with difficulty the same initial pH.

For the same water, the pH decrease beyond the breakdown was not strictly the same for each test, but it did not depend on deviations already observed on the first part of the curve. However, it was always possible to make simulated and experimental curves coincide rather well up to the beginning of precipitation. Figs. 1–4 show couples (simulated curve/experimental curve) which were chosen for the four water titrations. The characteristic values of the breaking point were indicated on the curves (critical pH, critical volume, corresponding ionic activity product, delay between the moment where the IAP was equal to the monohydrate solubility product and the breaking point).

No precipitation was observed for Volvic. The theoretical precipitation pH of the various forms of calcium carbonate was indicated on the simulated

Table 1  
Batch references of the mineral water

Water	Batch
Contrexéville	02.11.01/15/20: 49
Vittel	12.01/N1/06 21: 17
Evian	23.12.01/J17: 49
Volvic	L796851027

Table 2  
Composition of the mineral waters

		Contrexéville	Vittel	Evian	Volvic
NO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	2.7	6	3.8	6.3
	mol L <sup>-1</sup>	4.35E-05	9.68E-05	6.13E-05	1.02E-04
Cl <sup>-</sup>	mg L <sup>-1</sup>	8.6	7	4.5	8.4
	mol L <sup>-1</sup>	2.43E-04	1.97E-04	1.27E-04	2.37E-04
SO <sub>4</sub> <sup>2-</sup>	mg L <sup>-1</sup>	1187	306	10	6.9
	mol L <sup>-1</sup>	1.24E-02	3.19E-03	1.04E-04	7.18E-05
F <sup>-</sup>	mg L <sup>-1</sup>		0.28		
	mol L <sup>-1</sup>		1.47E-05		
HCO <sub>3</sub> <sup>-</sup>	mg L <sup>-1</sup>	403	402	357	65.3
	mol L <sup>-1</sup>	6.61E-03	6.59E-03	5.85E-03	1.07E-03
Ca <sup>2+</sup>	mg L <sup>-1</sup>	486	202	78	9.9
	mol L <sup>-1</sup>	1.21E-02	5.04E-03	1.95E-03	2.47E-04
Mg <sup>2+</sup>	mg L <sup>-1</sup>	84	36	24	6.1
	mol L <sup>-1</sup>	3.46E-03	1.48E-03	9.87E-04	2.51E-04
Na <sup>+</sup>	mg L <sup>-1</sup>	9.1	38	5	9.4
	mol L <sup>-1</sup>	3.96E-04	1.66E-04	2.18E-04	4.09E-04
K <sup>+</sup>	mg L <sup>-1</sup>	3.2	2	1	5.7
	mol L <sup>-1</sup>	8.18E-05	5.1E-05	2.56E-05	1.46E-04
SiO <sub>2</sub>	mg L <sup>-1</sup>			13.5	30
	mol L <sup>-1</sup>			2.25E-04	5.00E-04
pH		n.i. <sup>a</sup>	n.i. <sup>a</sup>	7.2	7

<sup>a</sup>n.i.: not indicated by the distributor.

curves. Before titration, Contrexéville and Vittel were already saturated in calcite, aragonite and vaterite. Evian was just saturated with calcite and aragonite. Table 3 gives the pH values at the breakdown, the added volume of sodium hydroxide corresponding and the saturation degrees reached for the various hydrated forms.

For the three waters that precipitated, the breakdown appeared for an ionic activity product included between the solubility product of the monohydrate and that of the ikaite. In Table 4, volumes of sodium hydroxide added at the breakdown were compared with the volume corresponding to the only CO<sub>2</sub> titration initially present at free state in the solution.

It seemed that it was necessary to neutralize a fraction of hydrogen carbonate ions to provoke the breakdown (small for Contrexéville and Vittel but more significant for Evian). Table 5 presents the extreme values corresponding to the beginning of monohydrate precipitation: pH, volume of sodium hydroxide, saturation

degree with regard to the monohydrate, the necessary time to reach the beginning of precipitation. The saturation degrees of the various tests were included between 2 and 3.4.

#### 4. Discussion

According to the thermodynamic calculations, the four mineral waters that were studied were classified, from the most scaling to the least, as follows:

Contrexéville > Vittel >> Evian >>> Volvic

The same classification was found for sodium hydroxide titration with the observed breakdown pH values. In fact, if Volvic did not precipitate in our experimental conditions, in the other cases, the breakdown of the metastable state corresponded to the heterogeneous precipitation of a solution saturated with monohydrated calcium carbonate. The saturation degree was not

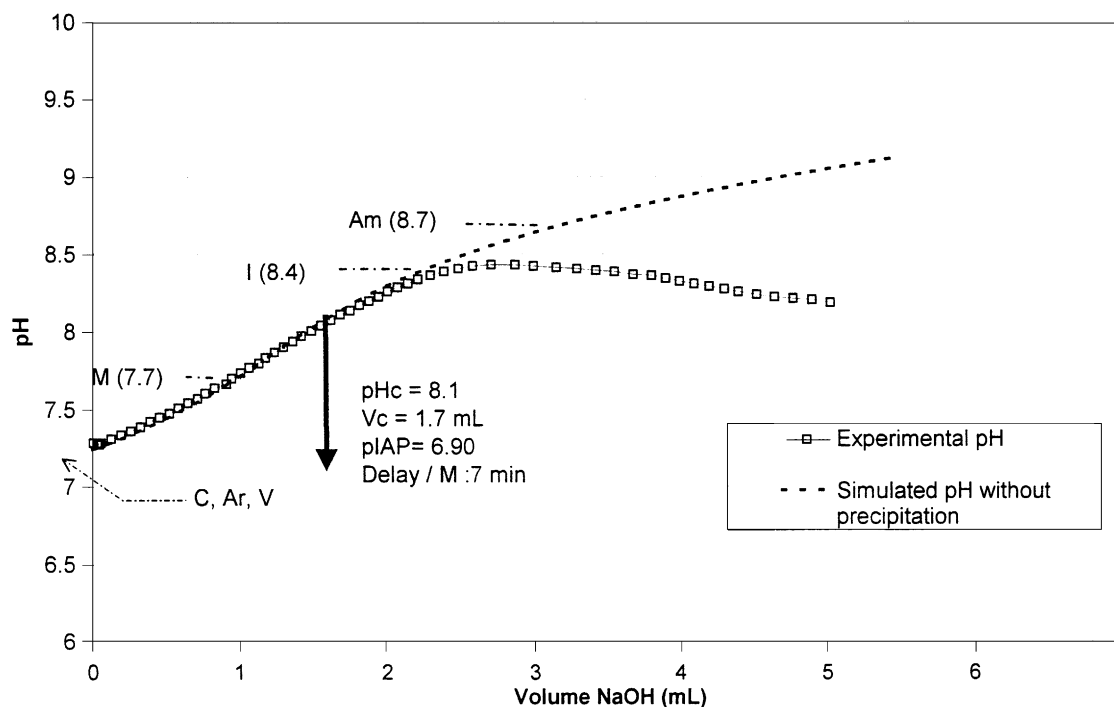


Fig. 1. Titration curves using the critical pH method for 100 mL of Contrexéville water by  $5 \times 10^{-2} \text{ mol L}^{-1}$  sodium hydroxide at  $25^\circ\text{C}$ . (Am: Amorphous, I: Ikaite, M: Monohydrate, C: Calcite, Ar: Aragonite, V: Vaterite, Delay/M: delay according to monohydrate precipitation).

constant for several successive tests and depended on the studied water (Table 5). For the assembly used, a supersaturation in the order of 3 was sufficient to observe the breakdown. This result is in accordance with our model which implies that the solution must be saturated in precursor of a solid given form (here the monohydrate) and not simply in  $\text{CaCO}_3^0$  complex, to observe a precipitation. It is logically necessary to form more complex than the thermodynamic solubility limit so that hydrated forms, through their evolution, have time to reach the real saturation with monohydrate.

The influence of the inhibitor presence on the formation of a precipitate by addition of sodium hydroxide has already been studied [15]. In the same experimental conditions as those described in the present publication, the influence of the Nitrilotris (methylene)-triphosphonic acid (ATMP) was specified [11]. ATMP's presence delays the breakdown of the metastable state. This effect is more pronounced if the quantity of inhibitor increases. This observation is important because it cannot be explained by an adsorption phenomenon as usual [15]. When precipitation finally begins, ATMP's presence slows down the precipitation speed by influencing the speed of the growth of crystals. According to its concentration, ATMP can stop evolution on an intermediate form. In the experimental

conditions described,  $0.5 \text{ mg L}^{-1}$  of ATMP concentration stabilizes the monohydrated form. Beyond  $0.75 \text{ mg L}^{-1}$ , ikaite can even be obtained at room temperature. This point is largely described in the literature [16].

Natural inhibitor content can also partially explain the observed deviation in the saturation in an irregular way, for three scaling waters studied. Here in particular, different silica concentrations whose inhibitor role has already been described, can be responsible for this phenomenon [17]. It can also explain why the beginning of precipitation for Volvic water was never put in evidence, despite having widely exceeded the pH of theoretical precipitation of the monohydrate.

The same authors noticed also that in practice, often precipitation occurred for a critical ionic activity product equal to 40 times the calcite solubility product [18]. At  $25^\circ\text{C}$ , it corresponds to  $\text{IAPc} = 10^{-6.9}$ . It is less than 2.8 times the value of the monohydrate solubility product at this temperature. We think that there is a coherence between these results. The hypothesis of the preliminary monohydrate formation during the scaling phenomena with heterogeneous kinetics is thus consolidated.

During a spontaneous scaling phenomenon, Table 4 indicates that the stripping of the free  $\text{CO}_2$  present in

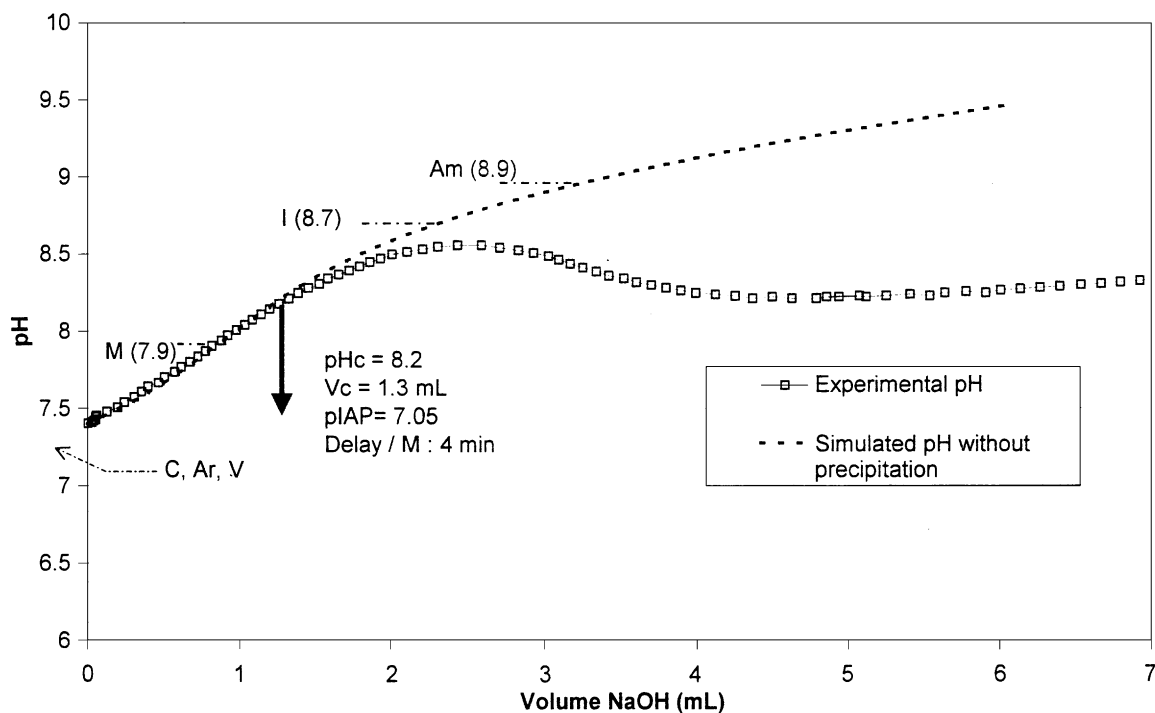


Fig. 2. Titration curves using the critical pH method for 100 mL of Vittel water by  $5 \times 10^{-2} \text{ mol L}^{-1}$  sodium hydroxide at 25°C.

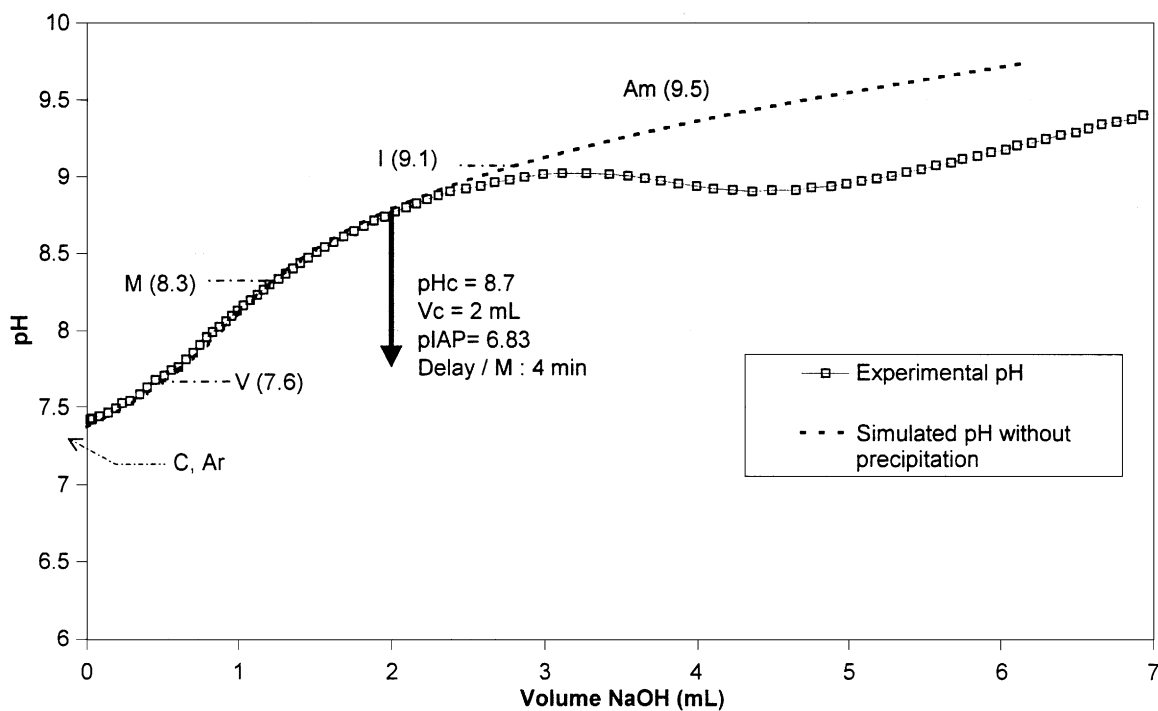


Fig. 3. Titration curves using the critical pH method for 100 mL of Evian water by  $5 \times 10^{-2} \text{ mol L}^{-1}$  sodium hydroxide at 25°C.

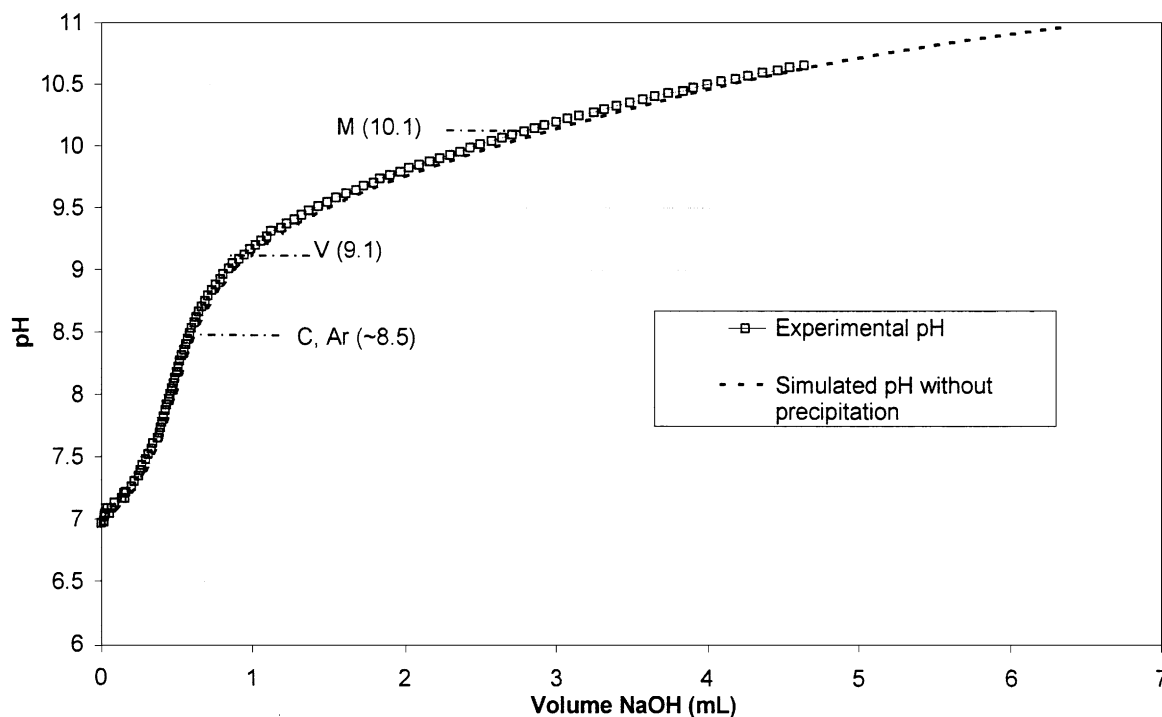


Fig. 4. Titration curves using the critical pH method for 100 mL of Volvic water by  $5 \times 10^{-2} \text{ mol L}^{-1}$  sodium hydroxide at  $25^\circ\text{C}$ .

Table 3

Saturation degree of the mineral waters at  $25^\circ\text{C}$  in comparison with monohydrate, ikaite and amorphous forms

Water	Volume (mL)	pH	Saturation/monohydrate	Saturation/ikaite	Saturation/amorphous
Contrex	1.6	8.1	2.5	0.5	0.3
Vittel	1.2	8.2	1.9	0.4	0.2
Evian	2	8.8	3.2	0.6	0.4

Table 4

Determination of the soda volumes necessary to neutralize the initial carbon dioxide compared with volumes measured at the breaking point

	$\text{CO}_2$ initial theoretical ( $\text{mmol L}^{-1}$ )	$\text{CO}_2$ initial ( $\text{mmol L}^{-1}$ )	Volume NaOH for titration of $\text{CO}_{2\text{aq init}}$ V1 (mL)	Critical volume V2 (mL)	$\square V = V2 - V1$ (mL)
Contrex	7.47	7.12	1.6	1.7	0.1
Vittel	7.15	7.02	1.2	1.3	0.1
Evian	6.50	6.13	1.0	2.0	1.0

Table 5

Scattering of critical point of waters: pH, volume, saturation degree in comparison with monohydrate, ikaite and amorphous forms

	$\text{pH}_c$	Volume NaOH (mL)	Saturation/monohydrate	Time between saturation and critical point (min)
Contrex	8.0–8.1	1.5–1.7	2.3–3.1	15–17
Vittel	8.1–8.2	1.1–1.3	2.0–2.3	11–13
Evian	8.7–8.8	1.9–2.1	2.7–3.4	19–21

water occurs and also, in addition, the one of the  $\text{CO}_2$  formed by decomposition of hydrogen carbonate ions. If the formation of the scaling precursors studied by pH meter method is interesting, it is important also to be able to appreciate the processes speeds which are going to cause the pH rise towards the breakdown domain.

Since it is mostly the  $\text{CO}_2$  loss which is the determining factor, Roques [2], always preferred this way of raising the pH. Recently, Elfil [19] completed this LCGE method. By reducing partial pressure in  $\text{CO}_2$  of the gas used to reach the precipitation pH of its solutions, he has accelerated the formation speed of the precursors without modifying their dehydration speed. In these conditions, a predominant homogeneous germination, whose precursor would be the amorphous calcium carbonate, was revealed at the lowest values of used partial pressures. For higher values, as already described in detail, heterogeneous germination depending on the nature of the vessel was found, but here by specifying that the precursor would be the monohydrated calcium carbonate. These results also verify the model, which we are proposing, according to a totally different experimental approach.

With the aim of estimating the scaling risks, Lédion proposed the PCR method, which is also based on the pH rise by the loss of  $\text{CO}_2$  [20]. This method consists simply in shaking a volume of water and in measuring pH and resistivity regularly. The pH curve had the same aspect as the curves obtained by addition of sodium hydroxide.

The pH reached by loss of  $\text{CO}_2$  corresponding to the solubility products of calcium carbonate hydrated forms

for Contrexéville, Vittel and Evian, can be calculated. The results are presented in Table 6 for several temperatures.

By comparing these results with Lédion's tests for Vittel [20], the breakdown pH at 8.35 was situated between the saturation pH of the monohydrate and the ikaite, as it is by titration with sodium hydroxide. The final pH equal to 8 corresponded rather well to the equilibrium with calcite (pH calculated as 8.1).

By observing the results of Elfil and Lédion, we noticed that the calculations agree perfectly with the experiments conducted by the loss of  $\text{CO}_2$ . It was the same for the calculation of the breakdown pH of the Contrexéville and Evian waters reached by the loss of  $\text{CO}_2$  (8.1 and 8.2, respectively) in another study [9]. For a scaling water, it therefore seemed justified to use the results in Tables 6 and 7 to discuss the  $\text{CO}_2$  partial pressure influence in the breakdown of the metastable state.

At 25°C, when solution was balanced with air ( $-\log p\text{CO}_2 = 3.5$ ), the value of the amorphous form solubility product can only be reached for Contrexéville. Therefore, the amorphous form precipitation did not seem likely to be observed, while for much higher  $\text{CO}_2$  partial pressures, the monohydrate solubility product was already reached for the three waters studied. The initial formation of monohydrate close to the inner sides of the vessel could therefore be expected. The phenomenon was effectively obtained in the laboratory by wet air bubbling [21]. When the temperature was higher (35°C, 45°C and 55°C), the predicted values in Table 6 were not too much different from those calculated at 25°C.

Table 6

Calculations in opened system. Determination of the pH and the cologarithm of the partial pressure of  $\text{CO}_2$  at the product of solubility of the monohydrate, the ikaite and the amorphous form

T(°C)		Monohydrate		3 × monohydrate		Ikaite		Amorphous	
		pH	$-\log p\text{CO}_2$	pH	$-\log p\text{CO}_2$	pH	$-\log p\text{CO}_2$	pH	$-\log p\text{CO}_2$
25	Contrex	7.7	2.20	8.1	2.65	8.5	3.06	8.8	3.42
	Vittel	7.9	2.36	8.4	2.90	8.7	3.24		
	Evian	8.2	2.74	8.8	3.36				
35	Contrex	7.5	1.97	8.0	2.51	5.6	3.13	8.7	3.29
	Vittel	7.7	2.12	8.3	2.68	9.0	3.50	8.8	3.33
	Evian	8.0	2.50	8.6	3.14				
45	Contrex	7.4	1.77	7.9	2.32			8.4	2.86
	Vittel	7.6	1.91	8.1	2.48			8.5	2.96
	Evian	7.9	2.29	8.5	2.94				
55	Contrex	7.3	1.58	7.8	2.14			8.2	2.56
	Vittel	7.5	1.72	8.0	2.29			8.4	2.73
	Evian	7.8	2.1	8.4	2.74			8.9	3.32

Table 7

Comparison between CO<sub>2</sub> concentration in mineral waters and loss of total carbon necessary to reach 2 and 3 times  $K_s$  of monohydrate in opened system at 45°C<sup>a</sup>

		pH	pCO <sub>2</sub>	[CO <sub>2</sub> ] (mol L <sup>-1</sup> )	Ct (mol L <sup>-1</sup> )	Loss Ct (mol L <sup>-1</sup> )
Contrex	Initial	7.28	1.63	5.02E-04	6.93E-03	
	2 × mono	7.73	2.10	1.70E-04	6.46E-03	4.78E-04
	3 × mono	7.93	2.32	1.03E-04	6.27E-03	6.68E-04
Vittel	Initial	7.4	1.72	4.08E-04	6.90E-03	
	2 × mono	7.93	2.26	1.18E-04	6.44E-03	4.61E-04
	3 × mono	8.13	2.48	7.10E-05	6.27E-03	6.36E-04
Evian	Initial	7.45	1.79	3.48E-04	6.01E-03	
	2 × mono	8.29	2.68	4.48E-05	5.32E-03	6.91E-04
	3 × mono	8.51	2.94	2.46E-05	5.08E-03	9.30E-04

<sup>a</sup> Ct: Total carbon; 2 × (3 ×) mono: 2 × (3 ×) pK<sub>s</sub> monohydrate; Loss Ct = Ct initial – Ct.

In Table 7, for the three waters at 45°C, we compared initial free CO<sub>2</sub> concentration and loss of the total carbon, necessary for reaching two and three times the monohydrate solubility product in opened system. Except for twice the monohydrate solubility product for Contrexéville (lower value than the limit verified at 25°C by addition of sodium hydroxide), loss of carbon was superior to the initial content in free CO<sub>2</sub> and thus partially resulted in the decomposition of hydrogen carbonate ions. Besides the different speeds of the phase transfer, some reaction speeds are also going to occur in the scaling processes: formation and evolution of the different calcium carbonate forms and decomposition of hydrogen carbonate ions.

From these calculations, we highlighted the fact that dealing with the CO<sub>2</sub> partial pressure in the control of the scaling conditions was interesting. In the tests that will be described later, we have put in evidence that not only must the thermodynamic equilibrium conditions be considered but that the stationary state at the water/air interface was particularly important. According to the hydrodynamic conditions and the volumes of water and air put together, the real partial pressure of CO<sub>2</sub> in this zone can be much lower than the equilibrium pressure because of an important loss of carbon at the interface. The pH can reach values much higher than those calculated. This phenomenon can appear in circuits where air pockets can be found. It would be enough to impose a CO<sub>2</sub> partial pressure higher than the pressure corresponding to the limit of monohydrate precipitation in order to avoid scaling.

It is important to specify that the presence of inhibitors, by delaying the breakdown, reduces the influence of the CO<sub>2</sub> partial pressure decrease. As the natural inhibitor content of waters varies throughout the year, it leads to the same variability for the dependence on the CO<sub>2</sub> partial pressure. Fig. 5 (according to Gache [11, p. 210]) shows

that for the water of the French river Seine, the CaCO<sub>3</sub> ionic activity product is always close to the CaCO<sub>3</sub> · H<sub>2</sub>O solubility product. The presence of natural inhibitor thus certainly limits the phenomena of spontaneous precipitation which could appear before even pumping for cooling of nuclear power stations waters.

Moreover, in summer, under the photosynthesis influence, CO<sub>2</sub> partial pressure in surface waters can decrease far lower than balance pressure with air [22]. The spontaneous precipitation of the amorphous form can occur, as well as its consequences on the adsorption phenomena.

From this set of results, it emerges that the partial pressure monitoring of the carbon dioxide is important in managing the behavior of scaling waters.

- (1) During a spontaneous scaling phenomenon, the pH rises at the same time by loss of the initial free CO<sub>2</sub> and of the one produced by the hydrogen carbonate ions decomposition.
- (2) For quick decreases of the CO<sub>2</sub> partial pressure, we observe a predominant homogeneous germination, whose precursor would be the amorphous calcium carbonate. For slower decreases, heterogeneous germination depending on the nature of the vessel occurs, but here the precursor would be the monohydrated calcium carbonate.
- (3) In addition to the thermodynamic equilibrium conditions which must be taken into account, the stationary state at the water/air interface is particularly important.
- (4) The presence of inhibitors, by delaying the breakdown, reduces the influence of the CO<sub>2</sub> partial pressure decrease. As the natural inhibitor content of waters varies throughout the year, it leads to the same variability for the dependence on the CO<sub>2</sub> partial pressure.



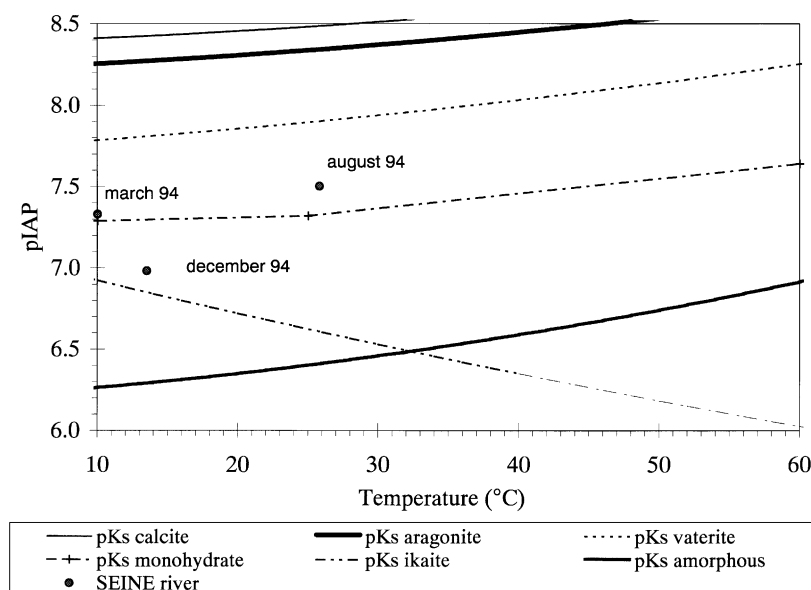


Fig. 5. Representative plots of the calco-carbonic system state of Seine river water in the plan temperature-pIAP.

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