

Reconsidering Water Scaling Tendency Assessment

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Evaluation methods of the CaCO₃ scaling risk are still far from being well understood and in many cases lack accuracy. Most of the saturation indices and models used so far for predicting scaling are based on the thermodynamic data of calcite, which is considered to be the most stable form of the different calcium carbonate varieties. However, surpassing the solubility product of anhydrous calcium carbonate forms (calcite, aragonite, and vaterite) is not sufficient to induce spontaneous precipitation. The solubility product of the CaCO₃·H₂O constitutes a lower limit for spontaneous germination. Based on the thermodynamic data of the monohydrate form, a novel scaling index is established and referred to as the Monohydrated form of the Langelier Scaling Index (MLSI). The ability of the MLSI to correctly predict the scaling phenomenon was verified and compared to that of the well-known Langelier Scaling Index (LSI) for several experimental results gathered from the available literature in the scaling field. Unlike the LSI, the MLSI was able to predict the instantaneous CaCO₃ precipitation in scaling water. For water in the temperature range between 25 and 60°C, a classification of scaling/equilibrium state according to MLSI values is presented. © 2006 American Institute of Chemical Engineers AIChE J, 52: 3583–3591, 2006

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Introduction

CaCO₃ scaling is a complex phenomenon that is still far from being well understood. Water treatment and desalination practices have shown that all available scaling risk evaluation methods have some weaknesses. Since the early work of Langelier,¹ the scaling phenomenon was at the heart of much of the research effort on water and related problems. Limited fresh water resources and the increase in water usage have boosted

the ongoing interest on scaling investigations. Many scaling prediction models and indices are currently being developed and verified.^{2–7} Sheikholeslami⁷ carried out a recent review of the most important scaling indices in use.

In most investigations, water scaling assessments were established by comparing water properties to that at a thermodynamic equilibrium state. This allowed defining several scaling saturation indices, of which the Langelier Saturation Index (LSI) is the most famous. LSI is calculated from the water pH, Ca²⁺ concentration, and alkalinity. Despite its weaknesses, this famous scaling assessing method is still being used in many academic investigations^{8,9} and by practitioners.¹⁰ Conscious of limitations of the LSI scaling model, many researchers have

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developed alternative saturation models and indices such as the Ryznar Index,¹¹ the Stiff and Davis Saturation Index,¹² the Poirier and Legrand's model,¹³ and the equilibrium pH method.¹⁴ Because of the limitation of these fundamental models in evaluating the scaling risk, several empirical approaches have also been developed.^{6,15} Whether empirical or fundamental, all the available models have limitations for predicting the scaling risk.^{7,16,17} These limitations in the models can be linked to the following three major weaknesses:

(1) Only equilibrium relations in the liquid phase and at solid/liquid interface were considered. The gas/liquid interface equilibria were totally neglected. As pointed out by Roques,¹⁸ the CO₂ present in the gas has a strong influence on the "CO₂-H₂O-CaCO₃" system.

(2) The thermodynamic equilibrium considerations caused a deadlock on the kinetic problems. In particular, because calcite is thermodynamically the most stable form, only the calcite thermodynamic data were considered in the previous index expressions. However, saturation relative to calcite (aragonite and vaterite) is often largely surpassed without any precipitation occurring.¹⁹⁻²¹

(3) The lack of reliable thermodynamic equilibrium data and their variation with respect to temperature and solute concentrations for all solid phases that can precipitate in hard water containing several solutes.⁷

Despite the fact that a total of six distinct calcium carbonate precipitate phases have been identified, most scaling investigations have focused on the most stable form, the calcite. Whereas three calcium carbonate phases are anhydrous crystalline polymorphs (calcite, aragonite, and vaterite), the other three phases are hydrated forms²² [amorphous calcium carbonate (ACC); monohydrate calcium carbonate (MCC), CaCO₃·H₂O; and hexahydrate calcium carbonate (HCC), CaCO₃·6H₂O]. According to several recent experimental investigations, one of these hydrated forms constitutes a precursor to CaCO₃ germination.¹⁹⁻²³ In their recent work, Elfil and Roques²⁴ delimited the metastable zone in the CO₂-H₂O-CaCO₃ system between 25 and 60°C. This metastable zone was located between the calcite and the MCC equilibrium curves.

All these recent works converge to the same conclusion that scaling prediction solely based on the calcite form reveals some weaknesses and a limited understanding of the CO₂-H₂O-CaCO₃ system. In this article, we will introduce a novel index for CaCO₃ scaling prediction, based on the MCC thermodynamic equilibrium data. This novel index will be compared to the famous LSI.

Theory

Most scaling indices were directly or indirectly derived from Langelier's early work,²⁴ which led to the conclusion that water is scaling for positive Langelier saturation indices (LSIs), where LSI is given by

$$LSI = pH - pH_S \quad (1)$$

In Eq. 1, pH is the effective pH of the solution and pH_S is the saturation pH, relative to calcite, where pH_S is defined as follows:

$$pH_S = pK'_2 - pK'_S - \log[Ca^{2+}] - \log[Alc] \quad (2)$$

In Eq. 2, Alc is the solution alkalinity, pK'₂ and pK'_S are the apparent equilibrium constants at a given ionic strength, for calcite solubility product and the second carbonic acid dissociation, respectively.

In following the same approach, it is possible to consider the activities instead of concentrations to derive the water saturation pH from the CaCO₃ solubility product and the carbonic acid second dissociation:

$$pH_S = pK_2 - pK_S - \log[Ca^{2+}] - \log[HCO_3^-] - \log \gamma_{HCO_3^-} - \log \gamma_{Ca^{2+}} \quad (3)$$

The γ_i is the activity coefficient relative to ion *i*.

Given that the solution alkalinity is given by

$$[Alc] = 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] \quad (4)$$

For pH < 9, the OH⁻ and CO₃²⁻ concentrations can be neglected when compared to that of HCO₃⁻, which can be confounded with the solution alkalinity. Then, pH_S can be written as

$$pH_S = pK_2 - pK_S - \log \gamma_{HCO_3^-} - \log \gamma_{Ca^{2+}} - \log[Ca^{2+}] - \log[Alc] \quad (5)$$

pH_S is the saturation pH of the appropriate form of calcium carbonate, which has many allotropic varieties.

As stated earlier, a total of six distinct phases have been recognized. Three of them are anhydrous crystalline polymorphs (calcite, aragonite, and vaterite), the solubility products of which are given by Plummer and Busenberg.²⁵ The other three are hydrated forms as follows:

(1) CaCO₃·6H₂O: Both in nature and in the laboratory the mineral readily crystallizes at temperatures near 0°C and rapidly decomposes to anhydrous forms at warmer temperatures. Because of its instability above 6°C, the hexahydrated form was not considered in this study.²⁶

(2) Amorphous calcium carbonate: Often described in spherical shapes with small diameters (<1 μm), the ACC is the most unstable form. Within a few minutes, the initially formed ACC crystals transform to a mixture of several calcium carbonate crystalline forms.²⁷ The amorphous form constitutes a key precursor for CaCO₃ precipitation at high supersaturations,^{21,28} with an instantaneous and homogeneous germination^{20,27,29} when the ACC solubility product is surpassed.

(3) CaCO₃·H₂O: Monohydrate calcium carbonate (MCC) crystallizes in a hexagonal system with spheroidal shapes. Synthesis of this mineral required the presence of magnesium and some other ions (seawater constituents) as well as organic material.³⁰ The MCC is a precursor for CaCO₃ germination at low supersaturation.²³ Its solubility product constitutes, between 25 and 60°C, a lower limit that must be exceeded to obtain a spontaneous germination.^{20,24}

Surpassing the calcite (also aragonite and vaterite) solubility product is not sufficient to induce spontaneous precipitation. The existence of a metastable zone is an experimental fact. In

the temperature range between 25 and 60°C, the metastable zone in the CO₂-H₂O-CaCO₃ system is located between the equilibrium curves of calcite and CaCO₃·H₂O.²⁴ In this zone the solution is supersaturated with respect to calcite and under saturated in relation to the monohydrated form. This means that the solution could be oversaturated relative to the anhydrous forms (vaterite, aragonite, and calcite) without any possibility of spontaneous precipitation.

Given these facts, the saturation pH will be calculated using the CaCO₃·H₂O solubility product instead of that relative to calcite. Then, Eq. 5 will be rewritten as

$$pH_{S/MCC} = pK_2 - pK_{S/MCC} - \log \gamma_{HCO_3^-} - \log \gamma_{Ca^{2+}} - \log[Ca^{2+}] - \log[Alc] \quad (6)$$

where pH_{S/MCC} and pK_{S/MCC} are the monohydrate calcium carbonate saturation pH and solubility product, respectively.

The idea is to replace pH_S, in the LSI expression (Eq. 1), by that of the monohydrate calcium carbonate (pH_{S/MCC}). The newly defined saturation index, which could be referred to as the Monohydrated form of the Langelier Scaling Index (or MLSI), is given by the following expression:

$$MLSI = pH - pH_{S/CCM} \quad (7)$$

As previously hinted, CaCO₃ germination occurs only if the calco-carbonic solution is supersaturated with respect to MCC. Thus, the solution pH should be greater than pH_{S/MCC} (pH - pH_{S/MCC} > 0) to induce scaling. On the other hand, if the solution is undersaturated with respect to CaCO₃·H₂O (pH - pH_{S/MCC} < 0), there is no spontaneous precipitation. It follows that:

- If MLSI > 0, CaCO₃ has a tendency to precipitate and water is scaling.
- If MLSI < 0, there is no spontaneous precipitation and water is not scaling.

The gas/liquid interface equilibrium involving CO₂ exchange was not explicitly considered in the derivations, although the MLSI expression implicitly takes into account the dissolved CO₂, the activity of which in calco-carbonic solutions at equilibrium with their ambient atmosphere is closely linked to pH, (HCO₃⁻), and (CO₃²⁻) through Eq. 8 established from the first and the second carbonic acid dissociation equilibrium constants:

$$(CO_3^{2-}) = (HCO_3^-) \times 10^{pH-pK_2} = (CO_2) \times 10^{2pH-pK_1-pK_2} \quad (8)$$

Results and Discussion

MLSI, the novel index introduced in this article, was evaluated and compared to the equivalent LSI values for several experimental results found in the literature related to the Ca-carbonic system. The individual ion activity coefficients (γ_i) were calculated using a modified form of the Debye-Hückel equation given by the Truesdell and Jones model³¹ available for solution with ionic strengths < 0.2.

Evaluation of the novel saturation index for some experimental results

To delimit the calcium carbonate metastable region in which there is no spontaneous germination, Tai et al.³² carried out more than 50 experiments where CaCl₂ and Na₂CO₃ solutions, with various concentrations and a pH of 8.5, were mixed and stirred for 2 h at 25°C.

Comparison between experimental results and those predicted by the novel index (MLSI) is presented in Table 1. Part of this table is borrowed from Tai et al.³² The authors used the letters "T" and "C" to refer to the occurrence and the lack of precipitation, respectively. The Modified Langelier Saturation Index of these solutions was computed and is reported in the same table.

As previously stated, for MLSI < 0, no spontaneous nucleation is to be expected. Comparing the predicted results to the experimental results of Tai et al., there were only nine cases out of 50 where the predictions seem to be in disagreement with the experimental results of Tai et al.³² These differences can be classified into two categories:

(1) MLSI > 0, and solutions did not show any evidence of precipitation in the 2 h mixing time (C).

(2) MLSI < 0, and solutions revealed the occurrence of some precipitation (T).

For the first type of discrepancies (values in bold font), although the MLSI values are slightly >0 (0 < MLSI < 0.12), there was no evidence of precipitation. This could be explained by the fact that nucleation would be delayed beyond the 2-h mixing time fixed by Tai et al.³² in their experiments. Indeed, for low supersaturated solution (in those cases Ω_{CCM} < 1.3), the germination time would be long and can easily exceed 2 h.²⁰ Besides the uncertainty for calculating the MLSI, this mismatching could also be explained by the experimental errors. Indeed, although Tai et al. did not report any experimental errors, one may consider inaccuracies in the reported pH values of 0.1, as well as inaccuracies in CaCl₂ and Na₂CO₃ concentrations of 2%, and accounts for the actual contribution of CO₃²⁻ ions in the solution alkalinity; the inaccuracy on the MLSI value would be around ±0.11.

For the second category of disagreements (underlined values), which appeared just for two experiments despite the fact that the MLSI values are slightly <0 (0 > MLSI > -0.08), the authors reported a precipitation occurrence. Unlike the first type of discrepancies, this second type of disagreements could be attributed only to the error on the MLSI value. In fact, as stated earlier, if one considers the same inaccuracies, the MLSI value for both cases would have an error of ±0.11.

After considering the error margins previously defined on the MLSI calculation arising from experimental errors, only one case apparently could not be correctly predicted perhaps as a result of the delay in precipitation occurrence for very low supersaturated solution. It is worth mentioning that even when the same experimental error is considered, the LSI, whose values were >0.75, is unable to correctly predict 20 out of 48 experiments (that is, almost 42% failure).

Comparison of the novel index with LSI for scaling and nonscaling cases

Scaling Cases. Scaling indices (LSI and MLSI) were calculated for the experimental results reported by Elfil and

Table 1. Demarcation of the Metastable Region for Calco-Carbonic Solutions and MLSI Values for Various Concentration Levels (pH = 8.5 and T = 25°C)*

[Na ₂ CO ₃] (mol/L)	[CaCl ₂] (mol/L)						
	0.05	0.025	0.015	0.005	0.0025	0.0015	0.0005
0.05							0.48 T
0.025							0.27 T
0.0175							0.17 T
0.015							0.12 C
0.005	1.42 T			0.67 T	0.41 T	0.21 T	-0.24 C
0.004						0.13 T	
0.0035						0.08 T	
0.00325						0.05 C	
0.003					0.22 T	0.02 C	
0.0025	1.12 T			0.40 T	0.15 T	-0.05 C	
0.00225					0.11 C		
0.002					0.06 C		
0.0015				0.19 T	-0.06 C		
0.00125	0.82 T						
0.001				0.02 C			
0.000875	0.67 T						
0.0005	0.43 T	0.22 T	0.07 T	-0.28 C	-0.52 C		
0.00045	0.38 T						
0.0004	0.33 T	0.13 T	-0.03 T	-0.37 C			
0.000375			-0.05 C				
0.00035	0.27 T	0.07 T					
0.0003			-0.15 C				
0.00025	0.13 T	-0.08 T	-0.23 C				
0.000225	0.08 T	-0.12 C					
0.0002	0.03 C	-0.17 C					
0.00015	-0.10 C						
0.00005	-0.57 C						

*With respect to calco-carbonic solutions see Tai et al.³² T, Turbid (precipitation); C, Clear (no precipitation after 2 h).³² Numerical values: MLSI (Eq. 7).

Roques.²⁰ In these experiments, CO₂ and air gas mixtures were allowed to bubble in Ca-carbonic solutions and the germination time was tracked. The operating conditions and the obtained results are summarized in Table 2. The cases corresponding to calcium concentrations ([Ca]) ranging between 1.8 and 5.0

mM, where spontaneous germinations occurred, are well predicted by the two scaling indices (LSI and MLSI).

For the [Ca] of 1.5 mM, where the solution is slightly supersaturated, germination starts after 2 h. The related MLSI value is slightly <0, which seems to be in disagreement with

Table 2. MLSI and LSI Values for Scaling and Nonscaling Cases and for Geothermal Water

	Tries	T (°C)	[Ca] (mM)	[Alc] (mM)	pH _G	t _G (min)	MLSI	LSI	
Scaling cases	1		5	10	8.51	11	0.83	2.15	
	2		4	8	8.59	16	0.74	2.06	
	3		3	6	8.68	22	0.61	1.93	
	4		30	2.5	5	8.67	32	0.51	1.83
	5			2	4	8.60	44	0.21	1.53
	6			1.8	3.6	8.62	70	0.15	1.47
	7			1.5	3	8.56	120	-0.05	1.26
Nonscaling cases	8		4	8	7.40		-0.45	0.87	
	9		4	8	7.54		-0.31	1.01	
	10		4	8	7.60		-0.25	1.07	
	11			5	10	7.71		0.04	1.35
	12		30	4	8	7.75		-0.10	1.22
	13			2.5	5	7.90		-0.27	1.05
	14			1.5	3	8.50		-0.12	1.20
	15			1	2	8.50		-0.44	0.87
	16			1	2	8.60		-0.34	0.97
Geothermal water	17	65			6.8		-0.77	0.32	
	18	65			8.0	8	0.43	1.52	
	19	60			8.39	10	0.70	1.85	
	20	50	10	2	8.23	16	0.33	1.54	
	21	40			8.40	26	0.29	1.57	
	22	30			8.40	>120	0.11	1.40	

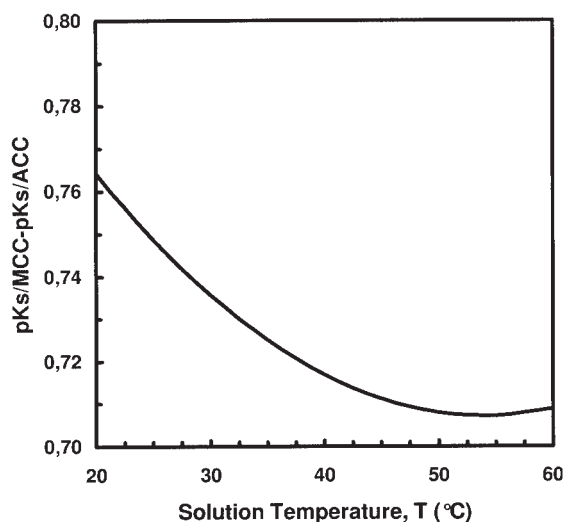


Figure 1. pKs/MCC-pKs/ACC (MLSI_{inst}) as a function of temperature.

the experimental results. Nonetheless, considering that the pH was fixed within ± 0.05 , and relative experimental errors on [Ca] and [Alc] of 2%, the uncertainty on the novel scaling index will be about $\Delta \text{MLSI} = \pm 0.05$. The negative MLSI value for Trial 7 could then be included in the experimental error range. As expected, the germination time decreases with the MLSI value. The positive values of LSI are in agreement with experimental results.

Nonscaling Cases. The saturation indices were also calculated for calco-carbonic solutions, where no germination occurred after a long period well exceeding 2 h.²⁴ The experimental conditions as well as the corresponding scaling indices are reported in Table 2.

The negative MLSI values are in agreement with the obtained results because germination did not occur. This was true for all experiments but one (Trial 11 for which $\text{MLSI} = 0.04$) that can be justified by the experimental error because, as stated earlier, the MLSI is given with an accuracy of ± 0.05 .

All the LSI values are positive (> 0.87), hinting that the CaCO_3 has a tendency to precipitate in those solutions. Thus, the LSI is unable to predict the nonscaling behavior of the Ca-carbonic solutions.

Case of Geothermal Water. The scaling power of real geothermal water, where an extensive scaling takes place in the cooling towers, was also assessed.³³ The geothermal water reaches the surface having a temperature and a pH of about 65°C and 6.8, respectively. Its Ca hardness is around 10 mM with HCO_3^- concentration of about 2 mM and an ionic strength close to 0.07.

At the exit conditions, the geothermal water is not scaling because there was no evidence of scaling in the output piping or at the top of the cooling tower. It is important to note that the MLSI value, reported in Table 2 for Trial 17, is consistent with the observed phenomenon, which is not the case of the LSI. For the experiments with air bubbling carried on the geothermal water at 65, 60, 50, and 40°C, both indices confirmed the scaling tendency of the water as shown in Table 2. At 30°C, the water keeps a calco-carbonic equilibrium state after 2 h, which seems to be in contrast with values of both scaling indices. In

fact, for such a low MLSI, slightly > 0 (0.11, Trial 22), the scaling would be delayed and needs a much longer observation time to be spotted. The delay in the scaling appearance could also be linked to the existence of soluble trace impurities as organic matter, known to induce such effects.³⁴ For the same trial, the discrepancy could also be attributed to the uncertainty in calculating the true MLSI value with respect to the experimental errors for real water, transported and stored, would be much higher than that for synthetic water.

MLSI value for high scaling and instantaneous precipitation

Several experimental investigations confirmed that CaCO_3 nucleation is instantaneous for highly supersaturated calco-carbonic solution and specifically when the ionic activity product (IAP) is higher than the solubility product of the amorphous calcium carbonate.^{20,27,35} Then, if the solution pH is greater than the ACC saturation pH (that is, $\text{pH} > \text{pH}_{\text{S/ACC}}$), the germination will be instantaneous. The $\text{pH}_{\text{S/ACC}}$ expression is obtained by replacing $\text{pK}_{\text{S/MCC}}$ with $\text{pK}_{\text{S/ACC}}$ in Eq. 6:

$$\text{pH}_{\text{S/ACC}} = \text{pK}_2 - \text{pK}_{\text{S/ACC}} - \log \gamma_{\text{HCO}_3^-} - \log \gamma_{\text{Ca}^{2+}} - \log[\text{Ca}^{2+}] - \log[\text{Alc}] \quad (9)$$

By combining Eqs. 7 and 9, the MLSI value from which germination in the Ca-carbonic solution is instantaneous is given by

$$\text{MLSI} = \text{pH} - \text{pH}_{\text{S/MCC}} \geq \text{pH}_{\text{S/ACC}} - \text{pH}_{\text{S/MCC}} = \text{MLSI}_{\text{inst}} \quad (10)$$

The MLSI value for instantaneous germination (MLSI_{inst}) as a function of temperature is given in Figure 1. In the temperature range between 10 and 60°C, the MLSI_{inst} decreases as the temperature increases.

To confirm the results concerning the MLSI_{inst} values, some experimental results, where instantaneous CaCO_3 germination takes place, are taken from the literature. Ogino et al.²⁷ indicated that for high supersaturations (initial concentrations for calcium and carbonate were 19.2 and 9.24 mM, respectively; ionic strength = 0.2), regardless of the used stirring system, the precipitation was instantaneous and took place just at the moment of mixing CaCl_2 and Na_2CO_3 solutions. IAP values at germination points of these solutions vs. temperature are summarized in Table 3 (partially borrowed from Ogino et al.²⁷). The calculated MLSI values of these germination points were added to this table. In agreement with experimental results, all the reported values are higher than MLSI_{inst}, which is consistent with an instantaneous precipitation taking place.

The experimental results of the second set, chosen to confirm

Table 3. MLSI Values for Instantaneous CaCO_3 Germination at Different Temperatures

T (°C)	IAP	pH	MLSI
25	1.0E-6	9.06	1.15
30	2.0E-6	9.31	1.49
40	5.0E-7	8.65	1.00
50	3.3E-7	8.40	0.95
60	2.0E-7	8.17	0.92

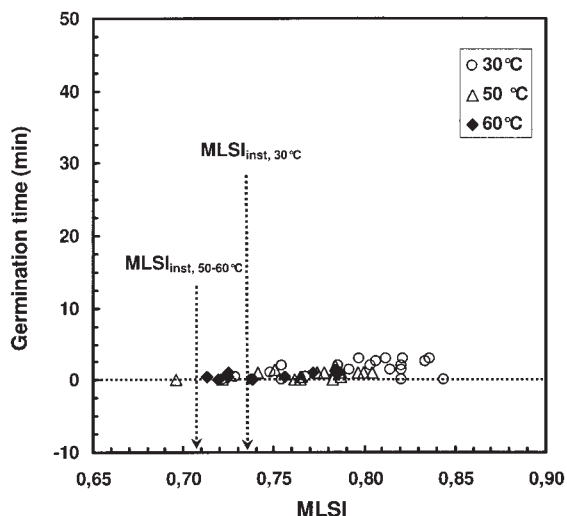


Figure 2. Evolution of the germination time vs. MLSI at the germination moment at 30, 50, and 60°C.

the MLSI values for instantaneous germination, were obtained by bubbling calco-carbonic solutions with gas mixture (air-CO₂).^{19,36} The solutions are initially undersaturated in relation to calcite. As the gas mixture is dispersed into the liquid, which initially has a low CO₂ content, the solution pH and IAP increase. After a few minutes of bubbling, the Ca-carbonic solution drifts toward supersaturation. The magnitude of the supersaturation depends on the initial concentration, CO₂ partial pressure of the gas mixture, the temperature, and the bubbling time.

Figure 2 shows germination time vs. MLSI for three different temperatures (30, 50, and 60°C) when quick precipitation was obtained. The germination time ($T_{G/ACC}$) represents the time lapse between the solution saturation with respect to ACC and the instant where germination is detected. As shown in Figure 2, germination is obtained at the moment or just 1 to 3 min after the calco-carbonic solutions reach the $MLSI_{inst}$ (about 7.1 at 60°C and 7.4 at 30°C). The delay of just a few minutes in the appearance of germination can be attributed to experimental errors. Indeed, these experiments were performed using a classical pH electrode, which is known to have a response time between 1 and 2 min. Only few experiments among these were done with a pH-specific electrode¹⁹ with a response time of about 20 s. Then, CaCO₃ germination can be considered as instantaneous when the $MLSI_{inst}$ is exceeded by the Ca-carbonic solutions MLSI.

The $MLSI_{inst}$ can be replaced by LSI calculated relative to amorphous calcium carbonate, which is designated the ALSI (amorphous form of Langelier Saturation Index). In this case, CaCO₃ germination is instantaneous when ALSI is positive.

Evolution of germination time vs. MLSI

Two other experimental series were considered. The first set, borrowed from Hort et al.,³⁷ was carried out at 50°C; the second set, borrowed from Elfil et al.³⁸ and Manzola,³⁹ was performed at 30°C.

For each experiment, the MLSI was calculated at the germination moment and presented vs. germination time ($T_{G/MCC}$)

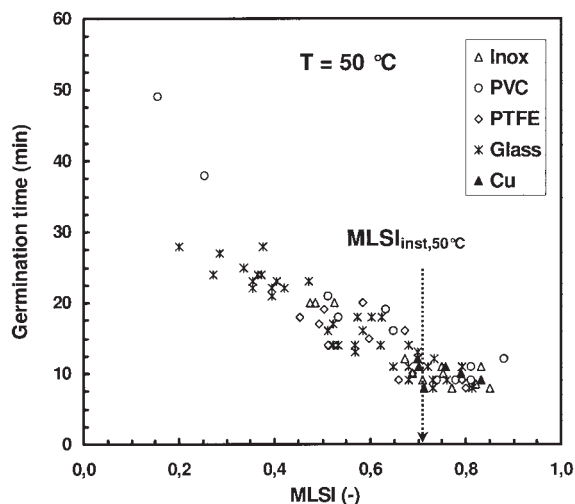


Figure 3. Evolution of the germination time vs. MLSI at 50°C with different reactor wall materials.

in Figures 3 and 4. $T_{G/MCC}$ is the period between the time when the solution was supersaturated with respect to CaCO₃·H₂O and the time when germination was detected. In these two experimental sets, the Ca-carbonic solutions were also supersaturated with the same bubbling technique as that in the previous section with similar reactors but of a different wall material.

The results are analogous to those obtained in the previous section. When the MLSI values are higher than the $MLSI_{inst}$, the germination times are almost constant and independent of the operating conditions. For MLSI values lower than the $MLSI_{inst}$, the germination time decreases with increasing MLSI. Sometimes, at the same MLSI, the germination times are very different. In reality, in this range ($pK_{S/MCC} < IAP < pK_{S/ACC}$), the germination time is highly dependent on the partition nature.²⁰

The driving force for precipitate formation is given by Gibbs free energy variation when going from the supersaturated solution to equilibrium:

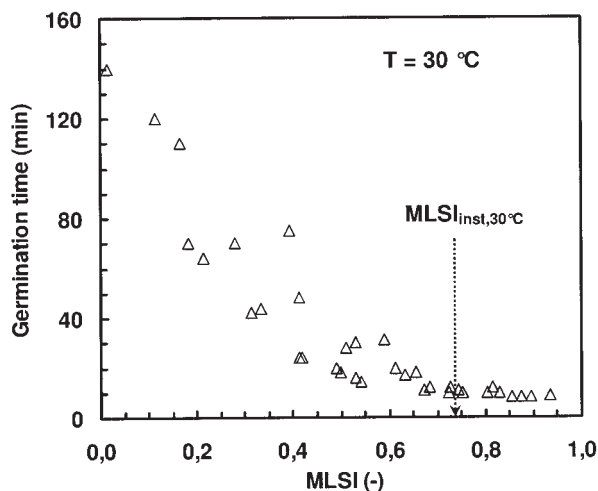


Figure 4. Evolution of the germination time vs. MLSI at 30°C.

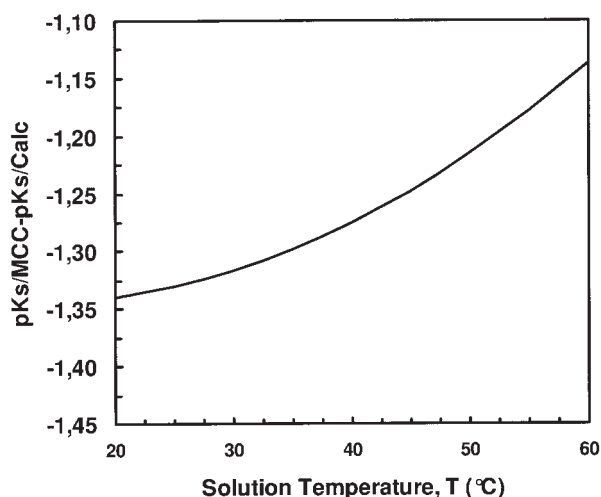


Figure 5. $pK_{S/MCC} - pK_{S/Calc}$ ($MLSI_{agr}$) as a function of temperature.

$$\Delta G = \frac{RT}{2} \ln(\Omega) \quad (11)$$

In the calco-carbonic system, Ω is the supersaturation relative to $CaCO_3 \cdot H_2O$ (Ω_{MCC}):

$$\Delta G = -\frac{RT}{2} \ln\left(\frac{PAI}{K_{S/MCC}}\right) = \frac{RT}{4,6} (pK_{S/MCC} - pIAP) \quad (12)$$

According to Eq. 6, " $pK_{S/MCC} - pPAI$ " is equivalent to " $pH - pH_{S/MCC}$ "; $MLSI$ can then also be considered as a driving force in the calco-carbonic system.

From Figures 3 and 4 it is clear that the $CaCO_3$ germination time depends on the $MLSI$ values. Based on those observations and those of the results obtained with different IAP values,³⁸ the $CaCO_3$ scaling time seems closely dependent on the $MLSI$ values. With $MLSI$ close to zero, scaling is a slow phenomenon. Between zero and $MLSI_{inst}$, the higher the scaling index value, the shorter the scaling time. The germination time eventually tends to zero as the $MLSI$ values exceed $MLSI_{inst}$, that is, for an $ALSI > 0$. As expected, for the same values of $MLSI$, induction times are shorter at 50°C, given that higher temperatures enhance nucleation and growth rates. It is also worth noting that as the temperature increases, CO_2 transfer out of the solution at the air-liquid interface is boosted, favoring the conversion of HCO_3^- into CO_3^{2-} . Thus the scaling is promoted as the global reaction shifts toward the formation of $CaCO_3$.

MLSI values for solutions at calco-carbonic equilibrium

In a recent work, Elfil and Roques²⁴ displayed that a calco-carbonic solution remains in a metastable state for several days when the solution pH is located between the saturation pH values of calcite and $CaCO_3 \cdot H_2O$. This means that the solution maintains a calco-carbonic equilibrium when

$$pH_{S/Calcite} < pH_{Sol-eq} < pH_{S/MCC} \quad (13)$$

In this expression, the index "Sol-eq" indicates that the pH is relative to the solution at a calco-carbonic equilibrium. When arranging the inequality¹³ one obtains

$$pK_{S/MCC} - pK_{S/Calcite} < MLSI_{Sol-eq} < 0 \quad (14)$$

The $pK_{S/MCC} - pK_{S/Calcite}$ values, calculated as a function of temperature,^{25,30} are shown in Figure 5. The solutions are at a calco-carbonic equilibrium state when the $MLSI$ values are located between 0 and those given by " $pK_{S/MCC} - pK_{S/Calcite}$." Under this lower limit, which corresponds to a negative LSI , the solution IAP is lower than $pK_{S/Calcite}$, $CaCO_3$ will be dissolved, and the calco-carbonic solution becomes aggressive.^{1,18} The boundary could be referred to as the aggressive $MLSI$ ($MLSI_{agr} = pK_{S/MCC} - pK_{S/Calcite}$).

Advantages and Drawbacks of the $MLSI$ /Critical Analysis

The scaling state of a calco-carbonic solution can be classified as follows:

- $ALSI > 0$ or $MLSI > MLSI_{inst}$: Water is highly scaling and the phenomenon is instantaneous.
- $MLSI > 0$ and $ALSI < 0$: Water is scaling; the phenomenon depends on the nature wall and will be slow for $MLSI$ values close to 0.
- $MLSI < 0$ and $LSI > 0$: There is no spontaneous precipitation; water is at a calco-carbonic equilibrium.
- $LSI < 0$ or $MLSI < MLSI_{agr}$: Water is undersaturated with respect to calcite and can be considered as aggressive.

The scaling/equilibrium state of calco-carbonic solutions as a function of temperature and $MLSI$ is displayed in Figure 6. Unlike the previous indices, the $MLSI$ is able to correctly delimit the scaling/nonscaling regions. This feature of $MLSI$ is explained by the fact that it considers the thermodynamic data of the hydrated forms that were shown to be crucial precursors for $CaCO_3$ spontaneous germination. This scaling assessment approach would be useful in rationalizing the use of chemicals (acid and inhibitors) in water treatment processes. This model

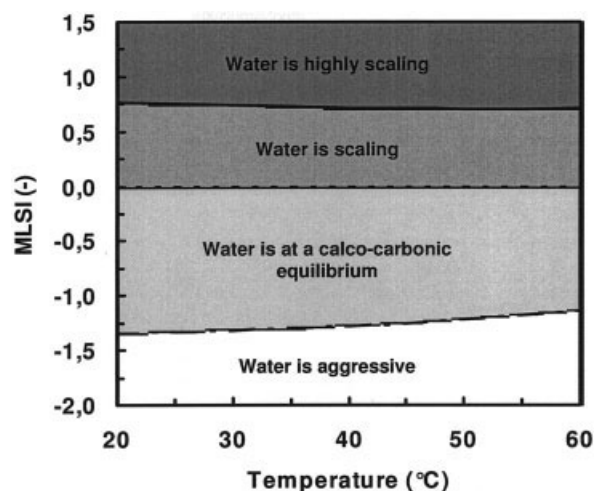


Figure 6. Scaling/equilibrium state of a calco-carbonic solution as function of temperature and $MLSI$.

would also help to predict and avoid highly scaling conditions often encountered at high temperatures.

Nonetheless, like all the previous indices, for low supersaturation cases the MLSI is also sensitive to experimental errors mainly on the solution pH and at a second level on the species concentrations. Another disadvantage that the newly defined scaling index shares with similar indices based on thermodynamic data is related to the fact that very little reliable thermodynamic data are available in the literature for complex calco-carbonic systems. For dynamic situations where the calco-carbonic solution is exchanging material with its environment, mass transfer rates would depend on the prevailing operating conditions and are difficult to obtain, making it extremely complicated to predict the exact moment for scaling occurrence.

Conclusions

In the last few years there has been growing evidence of the role of hydrated forms as necessary precursors for CaCO_3 germination in calco-carbonic water. Several experimental investigations showed that, between 25 and 60°C, there is no spontaneous precipitation if the calco-carbonic solution is undersaturated with respect to $\text{CaCO}_3 \cdot \text{H}_2\text{O}$, and germination is instantaneous if the solution is supersaturated relative to the amorphous form.

Based on the thermodynamic data of the hydrated forms, a novel index for predicting scaling was established. This new saturation index is referred to as the Monohydrated form of the Langelier Saturation Index (MLSI). MLSI values are in agreement with experimental results obtained from the literature with respect to the scaling field. The MLSI was compared to the well-known Langelier Saturation Index (LSI) for scaling and nonscaling conditions. For scaling conditions, both indices were able to predict the scaling phenomena. On the contrary, for nonscaling situations, only MLSI is able to correctly predict the nature of the nonscaling solution. A classification of water scaling/equilibrium state according to MLSI values was performed. For MLSI values greater than $\text{MLSI}_{\text{inst}}$, corresponding to the positive Amorphous form of the Langelier Saturation Index (ALSI), water has a high scaling power and scaling is almost instantaneous. Between zero and $\text{MLSI}_{\text{inst}}$, the germination time is closely dependent on the MLSI values; the scaling power will be low for MLSI values close to zero. Water remains at calco-carbonic equilibrium when the MLSI is located between zero and a lower limit given by MLSI_{agr} , which matches the LSI equal to zero. For MLSI values lower than MLSI_{agr} , that is, for negative values of LSI, water is aggressive relative to calcium carbonate.

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