Journal of Materials and Environmental Sciences
ISSN : 2028-2508
CODEN : JMESCN

J. Mater. Environ. Sci., 2018, Volume 9, Issue 5, Page 1582-1587

https://doi.org/10.26872/jmes.2018.9.5.175

http://www.jmaterenvironsci.com

Study of thermodynamic predictions of scaling of sanitary waters in the tourist area of Agadir

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Received 21 Sep 2017,
Revised 10 Nov 2017,
Accepted 17 Nov 2017

Keywords
- ✓ Physico-chemical
- ✓ Analyzes
- ✓ Hardness
- ✓ Thermodynamic study
- ✓ Scaling

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Abstract

This work evolves around two objectives as its main focus of concern, on one hand, to study the physico-chemical quality of sanitary waters of the tourist area of Agadir and on the other hand, to study the thermodynamics predictions of the scaling by these waters.The follow-up of the physic-chemical quality of the water was realized at various points of the study area. It was carried out during one year. The concerned parameters are: The temperature, pH, electrical conductivity, total hardness, calcium hardness, magnesium hardness and the concentrations of the ions (HCO_3^-, CO_3^{2-}, SO_4^{2-}, NO_3^-, Cl^-, OH^-, Na^+, K^+ ...).The obtained results show that the calcium and magnesium contents are high. The hardness ranges between 25 and 55.63 °F. The complete alkalimetric title ranges from7.5 to 34 °F. The hardness values show that 85 % of waters are very hard. Based on the obtained results of the physico-chemical analyzes, a study of the thermodynamic predictions of scaling was carried out using the Legrand-Poirier-Leroy (LPL) method.

1. Introduction

The dynamic impact of the tourism sector on the main macroeconomic variables and on the other sectors of the regional economy enabled Agadir region to occupy an important position in national tourism. However, the water consumption in the hotel sector is identified by the clogging problem of sanitary hot water pipes. Indeed, the precipitation of calcium carbonate is largely favored by the rise in temperature which, by releasing carbon dioxide, accelerates the precipitation of tartar [1]. The large Agadir is supplied with water from underground and superficial resourceshaving a high hardness. This one engendered the formation of hard deposits adhering to the internal walls of pipes and structures that carry water. The identification and characterization of these deposits of scale formed in hot water pipelines in the south of the touristic area of Agadir were carried out according to standard methods [2].

The objective of our study is to find an effective solution to the problem of scaling. Therefore, we have studied the quality of the sanitary waters in the tourist area. This study is concerned with four points in the touristic seaside area. At each point, the sampling was carried out at the entrance and exit of each of the reservoirs that feed the water tourist units. The physico-chemical quality of these waters was followed along the year 2015. The thermodynamic predictions of scaling by these waters were studied by theLegrand-Poirier-Leroy method [3].

2. Material and Methods

2.1. Sampling

The Water samples analyzed were taken from four well-distributed points in the study area. At each point, the sampling was carried out at the entrance and exit of the reservoirs. The taken samples were placed in polyethylene bottles of 5 L with labels indicating the date and time of collection.

2.2. Methods of physico-chemical analysis

The pH, electrical conductivity and temperature were measured in situ by the device INTERFACE Xplorer GLX PASCO PS-2002. The bottles were then placed in isothermal containers and transported to the laboratory for determination of other parameters, using standardized methods [4]. The contents of calcium, magnesium and total hardness were determined by the complexometry method with EDTA, in the presence of the indicator Black-Eriochrome T and the carboxylic acid. The flame atomic absorption spectroscopy (FAAS), type Perkin

Elmer Model 3110, was used for the determination of the contents of the ions Na^+ and K^+. The chloride ions were analyzed by the volumetric method using mercuric nitrate in the presence of the diphenylcarbazone indicator. The contents of nitrate ions NO_3^- were determined by UV / visible spectrophotometric in the presence of sodium salicylate. Nitrate ions give sodium paranitrosalicylate, colored in yellow and susceptible to a colorimetric titration. The concentrations ofhydroxide carbonate and hydrogen carbonate ions were determined by the volumetric method in the presence of a specific pH indicator (phenolphthalein, methyl orange). The sulphate ions were determined by the gravimetric method.

2.3. LPL method

The calculations of calco-carbonic equilibrium were conducted using the Legrand-Poirier-Leroy method. The latter allows to determine the type of the examined water (calcifying, balanced or aggressive). The graphical representation of Legrand-Poirier-Leroy is done in a two-dimensional space (Figure 1) represented by [5]:

- On the y-axis, total carbon dioxide concentration $[CO_{2\ Total}]$.
- On the x-axis, the calcium ion concentration $[Ca^{2+}]$.

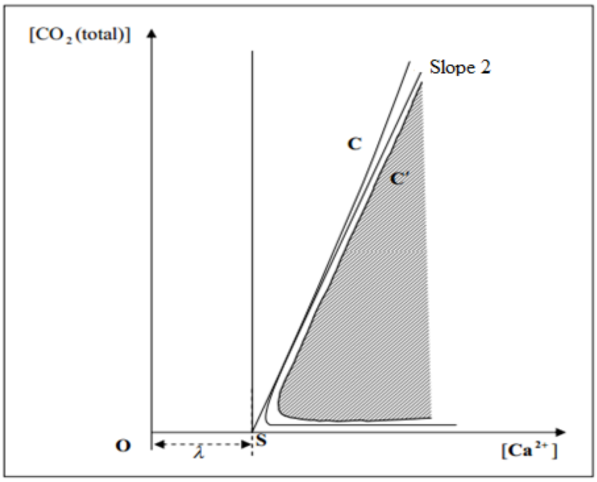


Figure 1: Representative points of a water in calco-carbonic equilibium in the Legrand-Poirier-Leroy diagram

The ion concentrations are linked by the following fundamental relations:

$$[H^+] + 2[Ca^{2+}] + P = [OH^-] + 2[CO_3^{2-}] + [HCO_3^-] + N$$

With $N = 2[SO_4^{2-}] + [Cl^-] + \ldots$ et $P = 2[Mg^{2+}] + [Na^+] + [K^+] + \ldots$

The abscissa λ is given by the relation:

$$\lambda = \frac{N - P}{2}$$

The curve C which comprises an ascending branch and a descending branch is a calco-carbonic equilibrium curve. It separates the schema into two domains: that of the aggressive waters and that of the calcifying waters, which are respectively to the left and to the right of this curve. When water is very scaling, its figurative point is situated to the right of the curve C'.

3. Results and discussion

3.1. Physico-chemical analysis of water

The physico-chemical parameters involved in the analysis of water samples are as follows: pH, temperature, electrical conductivity, hardness, calcium, magnesium, bicarbonate, potassium, sodium, nitrates, sulphates, Chlorides and the dry residue. The results of the physico-chemical analysis are reported in Table 1 in the form of a range Minimum value-Maximum value. The chemical composition of the water shows that the pH values fluctuate from 7.06 to 8.2. The pH is one of the most important factors in water quality [4]. It proved to be neutral to slightly alkaline. The electrical conductivity is relatively high by the presence of chloride which reaches 284 mg/L. These waters are highly mineralized and have a hardness reaching 55.63 °F due to the contents of the cations Ca^{2+} and Mg^{2+} which reached 112.22 mg/L and 69.56 mg/L, respectively. Sodium and potassium concentrations are high and respectively range from 7.45 to 115.15 mg/L and 2.36 to 4.62 mg/L. These waters are charged in hydrogen carbonate. The complete alkalimetric title ranges between 7.5 and 34 °F. However, these hydrogen carbonate ions are in sufficient concentrations to involve the precipitation of calcium carbonate scale [6].

Table1: Results of the physico-chemical analysis of waters

	T	*pH*	*EC at 25°C*	*Dry Residue*	*TAC*	*Cl^-*	*NO_3^-*	*SO_4^{2-}*	*TH*	*Ca^{2+}*	*Mg^{2+}*	*Na^+*	*K^+*	*HCO_3^-*
	°C		*µS/cm*	*mg/L*	*°F*	*mg/L*	*mg/L*	*mg/L*	*°F*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
Minimum value	15.7	7.06	687	295	7.5	21.3	0.2	148.51	25	72.24	11.72	7.45	2.36	91.5
Maximum value	26.2	8.02	1586	1072	34	284	21.96	300.02	55.63	112.2	69.56	115.1	4.62	414.8

3.2. Classification of water according to their hardness

Before beginning to study the thermodynamic predictions of the sanitary waters of the Agadir tourist zone, we proceeded to classify these waters according to their hardness. Table 2 illustrates the chemical quality of water according to the total hardness [7]. When it exceeds 25 °F, water is considered very hard.

Table 2: Chemical quality of water according to the hardness

Water hardness (°F)	**Water type**
0 to 5	Very soft
5 to 12	Water of low hardness
12 to 25	medium hard
>25	Very hard

More the content of calcium carbonate is raised in water, more the risk of chemical clogging of the water pipelines is important.

We carried out 84 samples periodically during one year (from January to December 2015). According to the results of the total hardness (TH) of these samples, 15 % of the waters of the Agadir tourist zone are moderately hard and 85 % are very hard waters, which explain the chemical clogging of the pipes in this zone. The results obtained from water hardness are compatible with the results of the previous work [8-11].

From the physico-chemical analysis of the water, we selected four most calcifying samples from 84 samples. These four selected samples represent different sampling points, to study the thermodynamic predictions of scaling of these waters. Table 3 shows the results of the physico-chemical analysis of the most calcifying waters of the four sampling points.

Table 3: Results of the physico-chemical analysis of the selected waters

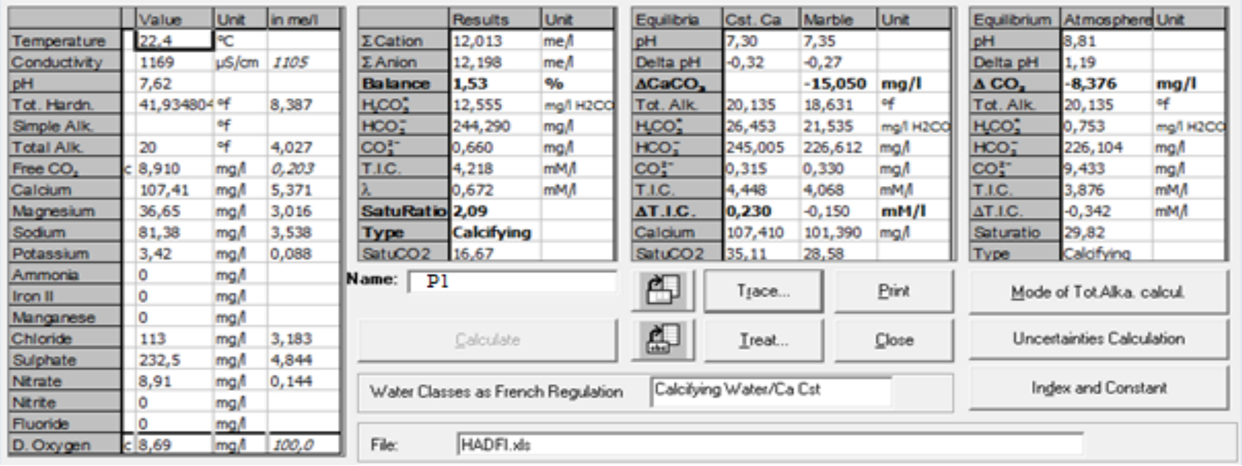
	T	*pH*	*EC à 25 °C*	*Dry Residue*	*TAC*	*TH*	*Ca^{2+}*	*Mg^{2+}*	*Na^+*	*K^+*	*Cl^-*	*SO_4^{2-}*	*NO_3^-*
	°C		*µS/cm*	*mg/L*	*°F*	*°F*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*	*mg/L*
P1	22.4	7.62	1169	820	20.13	41.93	107.41	36.65	81.38	3.42	113.00	232.50	8.91
P2	23.5	7.62	1130	824	21.06	46.01	107.24	46.65	52.40	3.88	89.10	221.60	7.66
P3	22.5	7.5	1296	1029	30.00	45.27	101.20	48.52	99.52	3.53	146.25	185.70	7.20
P4	16.9	7.8	769	482	12.50	31.06	99.39	15.10	30.13	3.40	50.35	167.88	3.73

It is noted that the calcium ion contents of the four samples are important compared with the contents of the magnesium ions and a low concentration of hydrogen carbonate ions is recorded in the sample P4 compared to the other samples. The concentrations of hydrogen carbonate ions of these waters are also very crucial to lead to the precipitation of calcium carbonate, a very sparingly soluble salt, which is the origin of the most common scaling problems [12]. Consequently, the tartars potentials of these waters will be very important because the precipitation reaction of calcium carbonate is directly related to the calcium and hydrogen carbonate contents [13].

3.3. Thermodynamic predictions by the Legrand-Poirier-Leroy method

This method allowed us to determine the position of the selected waters compared to calco-carbonic equilibrium [5]. Then, we determined, using this method, the potential quantity of calcium carbonate that should precipitate a liter of water to reach equilibrium. It is therefore sufficient to carry out a complete analysis of the water so that by means of thermodynamic considerations we can determine if a calcifying or aggressive water. Leroy has shown that calcifying waters free of calcium carbonate germs can be classified into two categories [14].Waters of supersaturation (coefficient of supersaturation lying between 1 and 40) are metastable waters, for which precipitation of calcium carbonate may possibly be caused by external factors. The supersaturation waters (supersaturation coefficient greater than 40) are unstable waters for which spontaneous germination occurs inevitably. However, this was contested by Roques [15] who considers that even for supersaturation coefficient values of 500, the calcium carbonate may not precipitate spontaneously. The homogeneous precipitation is spontaneous massive precipitation, which occurs when a critical supersaturation threshold is reached by the system. This value of the supersaturation coefficient is denoted δ limit. Indeed, the thermodynamic equilibrium can be largely exceeded (δ> 1) without there being this massive precipitation.We can then consider that, the water is under metastable conditions. These phenomena have been amply explained in previous works [16-19]. Tables 4, 5, 6 and 7 illustrate the physico-chemical characteristics and the results of the thermodynamic predictions of water sampling points P1, P2, P3 and P4.

Table 4: Physico-chemical characteristics and results of the thermodynamic predictions of water at point P1



		Value	Unit	in me/l
Temperature		22,4	°C	
Conductivity		1169	µS/cm	*1105*
pH		7,62		
Tot. Hardn.		41,934804	°f	8,387
Simple Alk.			°f	
Total Alk.		20	°f	4,027
Free CO_2	c	8,910	mg/l	*0,203*
Calcium		107,41	mg/l	5,371
Magnesium		36,65	mg/l	3,016
Sodium		81,38	mg/l	3,538
Potassium		3,42	mg/l	0,088
Ammonia		0	mg/l	
Iron II		0	mg/l	
Manganese		0	mg/l	
Chloride		113	mg/l	3,183
Sulphate		232,5	mg/l	4,844
Nitrate		8,91	mg/l	0,144
Nitrite		0	mg/l	
Fluoride		0	mg/l	
D. Oxygen	c	8,69	mg/l	*100,0*

	Results	Unit
Σ Cation	12,013	me/l
Σ Anion	12,198	me/l
Balance	**1,53**	**%**
$H_2CO_3^*$	12,555	mg/l H2CO
HCO_3^-	244,290	mg/l
CO_3^{2-}	0,660	mg/l
T.I.C.	4,218	mM/l
λ	0,672	mM/l
SatuRatio	**2,09**	
Type	**Calcifying**	
SatuCO2	16,67	

Equilibria	Cst. Ca	Marble	Unit
pH	7,30	7,35	
Delta pH	-0,32	-0,27	
$\Delta CaCO_3$		**-15,050**	**mg/l**
Tot. Alk.	20,135	18,631	°f
$H_2CO_3^*$	26,453	21,535	mg/l H2CO
HCO_3^-	245,005	226,612	mg/l
CO_3^{2-}	0,315	0,330	mg/l
T.I.C.	4,448	4,068	mM/l
ΔT.I.C.	**0,230**	-0,150	**mM/l**
Calcium	107,410	101,390	mg/l
SatuCO2	35,11	28,58	

Equilibrium	Atmosphere	Unit
pH	8,81	
Delta pH	1,19	
Δ CO_2	**-8,376**	**mg/l**
Tot. Alk.	20,135	°f
$H_2CO_3^*$	0,753	mg/l H2CO
HCO_3^-	226,104	mg/l
CO_3^{2-}	9,433	mg/l
T.I.C.	3,876	mM/l
ΔT.I.C.	-0,342	mM/l
Saturatio	29,82	
Type	Calcifying	

Name: P1

Water Classes as French Regulation: Calcifying Water/Ca Cst

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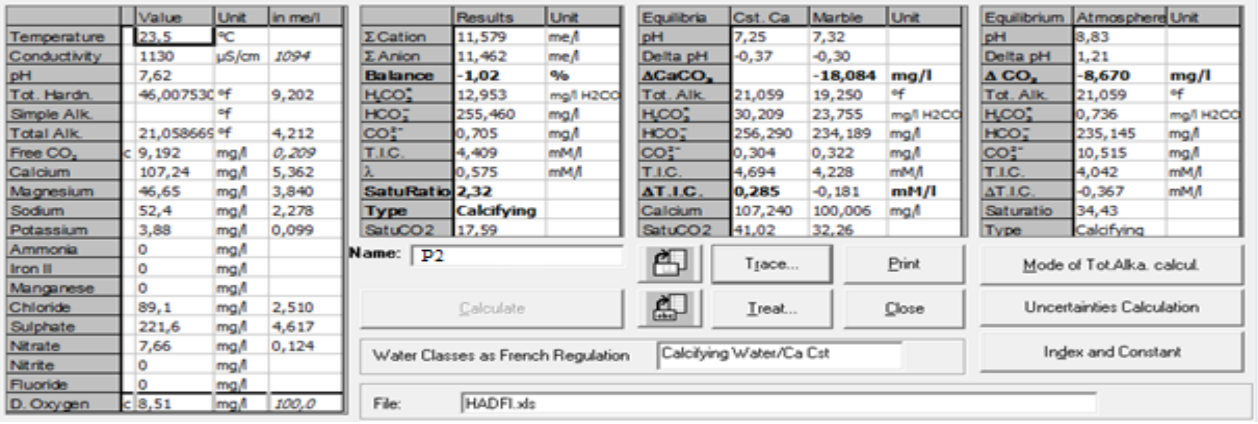
Table 5: Physico-chemical characteristics and results of the thermodynamic predictions of water at point P2



		Value	Unit	in me/l
Temperature		23,5	°C	
Conductivity		1130	µS/cm	*1094*
pH		7,62		
Tot. Hardn.		46,007530	°f	9,202
Simple Alk.			°f	
Total Alk.		21,058669	°f	4,212
Free CO_2	c	9,192	mg/l	*0,209*
Calcium		107,24	mg/l	5,362
Magnesium		46,65	mg/l	3,840
Sodium		52,4	mg/l	2,278
Potassium		3,88	mg/l	0,099
Ammonia		0	mg/l	
Iron II		0	mg/l	
Manganese		0	mg/l	
Chloride		89,1	mg/l	2,510
Sulphate		221,6	mg/l	4,617
Nitrate		7,66	mg/l	0,124
Nitrite		0	mg/l	
Fluoride		0	mg/l	
D. Oxygen	c	8,51	mg/l	*100,0*

	Results	Unit
Σ Cation	11,579	me/l
Σ Anion	11,462	me/l
Balance	**-1,02**	**%**
$H_2CO_3^*$	12,953	mg/l H2CO
HCO_3^-	255,460	mg/l
CO_3^{2-}	0,705	mg/l
T.I.C.	4,409	mM/l
λ	0,575	mM/l
SatuRatio	**2,32**	
Type	**Calcifying**	
SatuCO2	17,59	

Equilibria	Cst. Ca	Marble	Unit
pH	7,25	7,32	
Delta pH	-0,37	-0,30	
$\Delta CaCO_3$		**-18,084**	**mg/l**
Tot. Alk.	21,059	19,250	°f
$H_2CO_3^*$	30,209	23,755	mg/l H2CO
HCO_3^-	256,290	234,189	mg/l
CO_3^{2-}	0,304	0,322	mg/l
T.I.C.	4,694	4,228	mM/l
ΔT.I.C.	**0,285**	-0,181	**mM/l**
Calcium	107,240	100,006	mg/l
SatuCO2	41,02	32,26	

Equilibrium	Atmosphere	Unit
pH	8,83	
Delta pH	1,21	
Δ CO_2	**-8,670**	**mg/l**
Tot. Alk.	21,059	°f
$H_2CO_3^*$	0,736	mg/l H2CO
HCO_3^-	235,145	mg/l
CO_3^{2-}	10,515	mg/l
T.I.C.	4,042	mM/l
ΔT.I.C.	-0,367	mM/l
Saturatio	34,43	
Type	Calcifying	

Name: P2

Water Classes as French Regulation: Calcifying Water/Ca Cst

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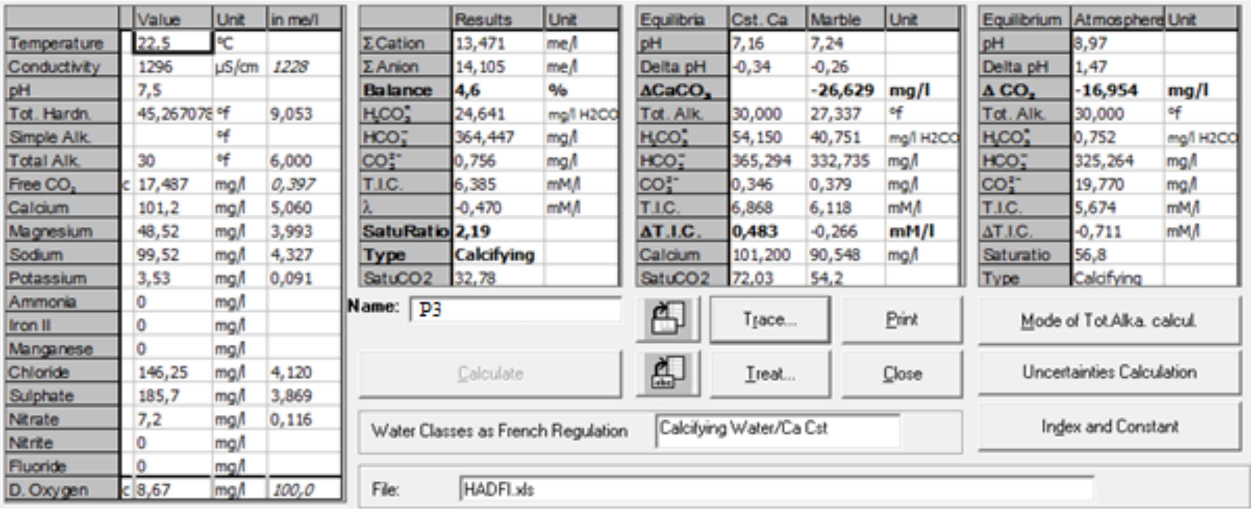
Table 6: Physico-chemical characteristics and results of the thermodynamic predictions of water at point P3



		Value	Unit	in me/l
Temperature		22,5	°C	
Conductivity		1296	µS/cm	*1228*
pH		7,5		
Tot. Hardn.		45,267078	°f	9,053
Simple Alk.			°f	
Total Alk.		30	°f	6,000
Free CO_2	c	17,487	mg/l	*0,397*
Calcium		101,2	mg/l	5,060
Magnesium		48,52	mg/l	3,993
Sodium		99,52	mg/l	4,327
Potassium		3,53	mg/l	0,091
Ammonia		0	mg/l	
Iron II		0	mg/l	
Manganese		0	mg/l	
Chloride		146,25	mg/l	4,120
Sulphate		185,7	mg/l	3,869
Nitrate		7,2	mg/l	0,116
Nitrite		0	mg/l	
Fluoride		0	mg/l	
D. Oxygen	c	8,67	mg/l	*100,0*

	Results	Unit
Σ Cation	13,471	me/l
Σ Anion	14,105	me/l
Balance	**4,6**	**%**
$H_2CO_3^*$	24,641	mg/l H2CO
HCO_3^-	364,447	mg/l
CO_3^{2-}	0,756	mg/l
T.I.C.	6,385	mM/l
λ	-0,470	mM/l
SatuRatio	**2,19**	
Type	**Calcifying**	
SatuCO2	32,78	

Equilibria	Cst. Ca	Marble	Unit
pH	7,16	7,24	
Delta pH	-0,34	-0,26	
$\Delta CaCO_3$		**-26,629**	**mg/l**
Tot. Alk.	30,000	27,337	°f
$H_2CO_3^*$	54,150	40,751	mg/l H2CO
HCO_3^-	365,294	332,735	mg/l
CO_3^{2-}	0,346	0,379	mg/l
T.I.C.	6,868	6,118	mM/l
ΔT.I.C.	**0,483**	-0,266	**mM/l**
Calcium	101,200	90,548	mg/l
SatuCO2	72,03	54,2	

Equilibrium	Atmosphere	Unit
pH	8,97	
Delta pH	1,47	
Δ CO_2	**-16,954**	**mg/l**
Tot. Alk.	30,000	°f
$H_2CO_3^*$	0,752	mg/l H2CO
HCO_3^-	325,264	mg/l
CO_3^{2-}	19,770	mg/l
T.I.C.	5,674	mM/l
ΔT.I.C.	-0,711	mM/l
Saturatio	56,8	
Type	Calcifying	

Name: P3

Water Classes as French Regulation: Calcifying Water/Ca Cst

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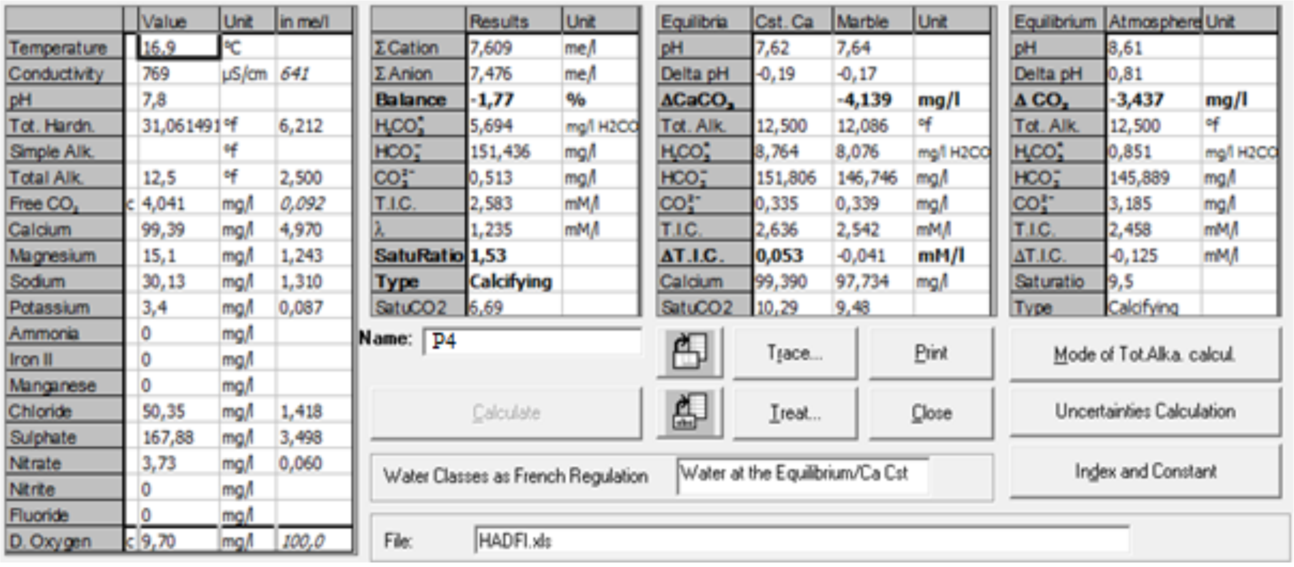
Table 7: Physico-chemical characteristics and results of the thermodynamic predictions of water at point P4



		Value	Unit	in me/l
Temperature		16,9	°C	
Conductivity		769	µS/cm	*641*
pH		7,8		
Tot. Hardn.		31,061491	°f	6,212
Simple Alk.			°f	
Total Alk.		12,5	°f	2,500
Free CO_2	c	4,041	mg/l	*0,092*
Calcium		99,39	mg/l	4,970
Magnesium		15,1	mg/l	1,243
Sodium		30,13	mg/l	1,310
Potassium		3,4	mg/l	0,087
Ammonia		0	mg/l	
Iron II		0	mg/l	
Manganese		0	mg/l	
Chloride		50,35	mg/l	1,418
Sulphate		167,88	mg/l	3,498
Nitrate		3,73	mg/l	0,060
Nitrite		0	mg/l	
Fluoride		0	mg/l	
D. Oxygen	c	9,70	mg/l	*100,0*

	Results	Unit
ΣCation	7,609	me/l
ΣAnion	7,476	me/l
Balance	**-1,77**	**%**
$H_2CO_3^*$	5,694	mg/l H2CO
HCO_3^-	151,436	mg/l
CO_3^{2-}	0,513	mg/l
T.I.C.	2,583	mM/l
λ	1,235	mM/l
SatuRatio	**1,53**	
Type	**Calcifying**	
SatuCO2	6,69	

Equilibria	Cst. Ca	Marble	Unit
pH	7,62	7,64	
Delta pH	-0,19	-0,17	
Δ$CaCO_3$		**-4,139**	**mg/l**
Tot. Alk.	12,500	12,086	°f
$H_2CO_3^*$	8,764	8,076	mg/l H2CO
HCO_3^-	151,806	146,746	mg/l
CO_3^{2-}	0,335	0,339	mg/l
T.I.C.	2,636	2,542	mM/l
ΔT.I.C.	**0,053**	-0,041	**mM/l**
Calcium	99,390	97,734	mg/l
SatuCO2	10,29	9,48	

Equilibrium	Atmosphere	Unit
pH	8,61	
Delta pH	0,81	
Δ CO_2	**-3,437**	**mg/l**
Tot. Alk.	12,500	°f
$H_2CO_3^*$	0,851	mg/l H2CO
HCO_3^-	145,889	mg/l
CO_3^{2-}	3,185	mg/l
T.I.C.	2,458	mM/l
ΔT.I.C.	-0,125	mM/l
Saturatio	9,5	
Type	Calcifying	

Name: P4

Water Classes as French Regulation: Water at the Equilibrium/Ca Cst

File: HADFI.xls

It is noted that the ionic balance for each point is between 1 and 5%, which confirms the accuracy of the chemical analysis methods used. According to *Legrand* et al, the ionic balance must be less than 5 % [3]. The coefficient of supersaturation is greater than 1, which proves that the studied waters are saturated with calcium carbonate. They are, therefore, of calcifying type and they must deposit a quantity of $CaCO_3$ to reach the equilibrium.

The curves of the calco-carbonic equilibrium of the waters of the points P1, P2, P3 and P4 according to Legrand-Poirier-Leroy are represented by figures 2, 3, 4 and 5. It is noted in each case that the position of the figurative point is situated between the two ascending parts of the curves which correspond to values of 1 and 40 of the supersaturation coefficient in the zone of the calcifying waters. It is also in agreement with the results of the literature [5, 20].

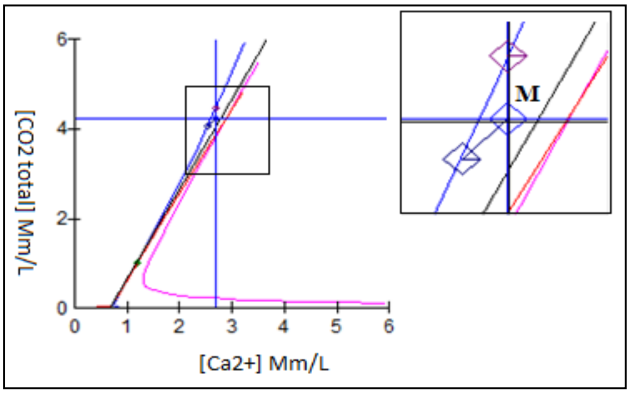


Figure 2 : Representation of the calco-carbonic equilibrium of the water of point P1 according to Legrand-Poirier-Leroy

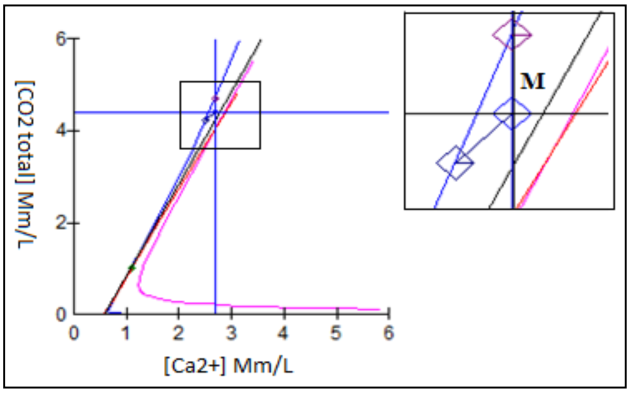


Figure 3 : Representation of the calco-carbonic equilibrium of the water of point P2 according to Legrand-Poirier-Leroy

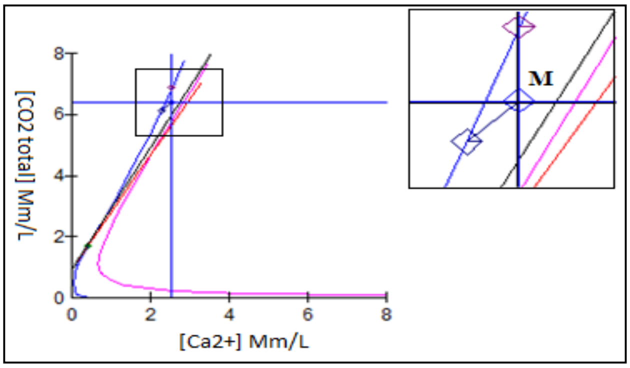


Figure 4: Representation of the calco-carbonic equilibrium of the water of point P3 according to Legrand-Poirier-Leroy

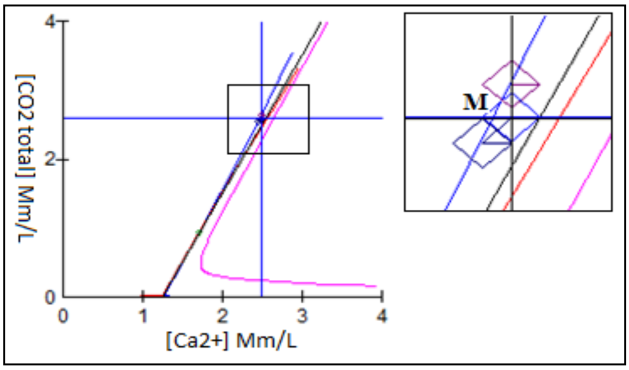


Figure5: Representation of the calco-carbonic equilibrium of the water of point P4 according to Legrand-Poirier-Leroy

Table 8 compiles the main parameters of this study. A high concentration of the hydrogen carbonate ions is observed for point P3 which allows achieving a high quantity of precipitated calcium carbonate, followed by P2 and P1, while the lowest concentration of hydrogen carbonate ions is recorded at the point P4, Resulting in a small quantity of precipitated calcium carbonate. All these results confirm that these waters are calcifying.

Table 8: Assessment of the results obtained in the four sampling points studied

	Ca^{2+} mg/L	*HCO_3^- mg/L*	*Hardness °F*	*Ionic balance %*	*Supersaturation coefficient*	*$CaCO_3$ Precipitatedmg/L*	*Water type*
P_1	107.41	244.08	41.93	1.53	2.09	15.05	Calcifying
P_2	107.24	257.00	46.01	1.02	2.32	18.08	Calcifying
P_3	101.20	366.12	45.27	4.6	2.19	26.62	Calcifying
P_4	99.39	152.55	31.06	1.77	1.53	4.13	Calcifying

Conclusion

The seaside tourist area of Agadir faces the problem of water clogging pipes. To remedy this problem, we have proceeded to the evaluation of the physico-chemical quality of waters. The main physical and chemical parameters were followed for one year. Samples of the water feeding the tourist area were carried out monthly on reservoirs levels of tourist units. The obtained results show that these waters are rich in calcium and hydrogen carbonate. Their hardness varies from 25 to 55.63 °F. The physico-chemical characterization of the waters supplying the seaside tourist area of Agadir allowed to conclude that 85% of these waters are very hard. The Legrand-Poirier-Leroy method allowed us to determine the position of the selected waters compared to calco-carbonic equilibrium. The obtained curves confirm that the selected waters are calcifying. The scaling character of the studied waters requires the use of appropriate ways to stop the phenomenon of scaling.

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