



## Research article

## Efficiency of one scale inhibitor on calcium carbonate precipitation from hot water sanitary: effect of temperature and concentration

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## ABSTRACT

The scaling of hot water transport pipes has become one of the major problems encountered in Agadir's region, which exploits water of underground origin with very high hardness (40°F). Several methods can be used to prevent this phenomenon. Among these methods, the use of chemical inhibitors remains one of the processes to stop or retard the formation of scale deposits.

In this study, we tested the inhibitor with the trade name "Aquatreat601" at different temperatures such as 30, 40 and 60 °C. This inhibitor was tested at different concentrations for each temperature in order to find the efficiency concentration to prevent the precipitation of scale, which consists mainly of calcium carbonate CaCO<sub>3</sub> of the aragonite variety with a percentage of 88 %, and also the Mg-calcite Mg<sub>0.06</sub>Ca<sub>0.94</sub>(CO<sub>3</sub>) with a percentage of 12 %. These results obtained by method X-ray diffraction (XRD) analysis.

We carried out this study on pure calco-carbonic water, of hardness equal to 40°F, using the "LCGE" method. The quantity of inhibitor is added before the research gas is introduced. In all cases, the presence of chemical inhibitors does not alter the initial pH of the solution or the concentration of calcium (TCa) value measured before the experiment begins.

The results obtained show that the "Aquatreat 601" contents of 100, 180 and 300 ppm allowed total inhibition of calcium carbonate precipitation at temperatures of 30, 40 and 60 °C respectively.

## 1. Introduction

The formation of scale deposits in the circuits supplied by water in Agadir's region is a major concern for water production, treatment and distribution plants in this region [1, 2, 3]. This scaling phenomenon is more accentuated in hot water because the solubility of carbon dioxide decrease when the water temperature rises and consequently generates the deposition of calcium carbonate [4]. In our previous studies on the phenomenon of sanitary hot water in the tourist sector of Agadir city, we have highlighted the characterization of accumulated tartar adhering to the internal sides of the installations of this water. These solid deposits are essentially made up of calcium carbonate of the aragonite variety [3, 5]. The characterisation of the scaling power of this water has also been carried out and has highlighted the highly scaling nature of this water [6].

This present study is the logical continuation of our preceding study of scaling observed in the hot's water sanitary transport pipes in

the tourist area of Agadir city. We investigated the inhibitor with the trade name "Aquatreat 601" is a liquid, non-toxic, colourless and water-soluble product. Its density is 1.05 and its boiling point is above 100 °C, at different temperatures such as 30, 40 and 60 °C. This inhibitor was tested at different concentrations for each temperature in order to find the efficiency concentration that prevents the precipitation of calcium carbonate. The inhibiting of development of aragonite crystals by "Aquatreat 601" can be explained by the obstruction of surface crystal growth sites. The growth sites are then blocked, resulting in the elimination of any deposition of calcium carbonate under the conditions of the test.

This study was performed using the "LCGE" method [7, 8]. The amount of inhibitor is add before the research gas is introduced. Whatever the case, the presence of inhibitor does not modify the initial pH of the solution or the TCa value calculated before the experiment began.

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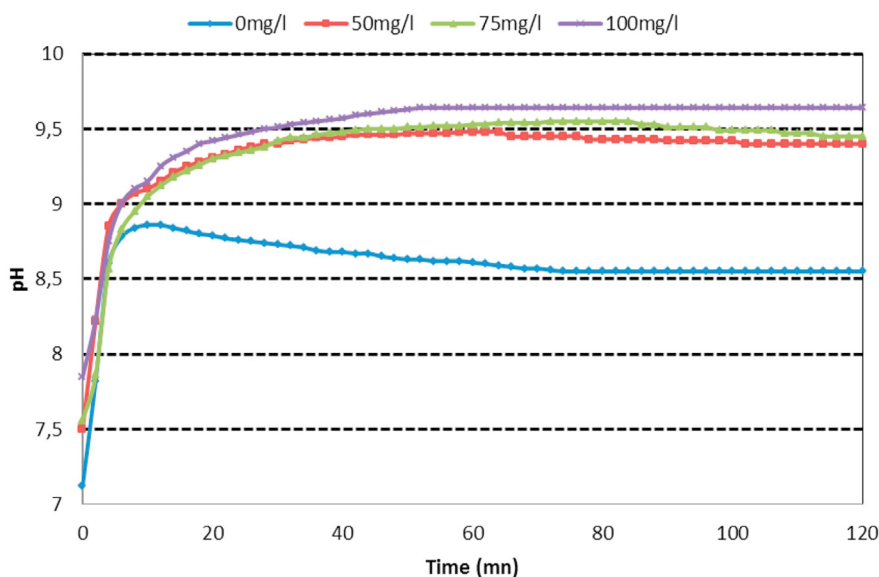


Figure 1. Variation of pH as according to time of the tests with inhibitor “Aquatreat 601” at 30 °C.

2. Materials and methods

Roques and collaborators developed The LCGE method [9, 10, 11, 12]. The principle consists in causing the deposition of calcium carbonate by degassing the CO<sub>2</sub> dissolved in the tested solution with a research gas, which is usually the atmospheric air, following the reaction:



The 500 cm<sup>3</sup> of solution to be studied is placed in the working cell of cylindrical shape, with a capacity of 1000 cm<sup>3</sup>, containing in its lower part a diffuser allowing to disperse the working gas in a homogeneous way. This gas is brought to the working temperature by passing it through a copper coil, then through a humidifier and then through the droplet separators. The copper coil and the humidifier are immersed in a bath at a precise temperature. The defrosters and the cell are in a second bath at the working temperature. This ensures that there is no variation in temperature and concentration of the liquid phase by evaporation or dilution, and then a precise amount of the inhibitor to be tested is added.

The monitoring of pH evolution and the concentration of calcium (TCa) of the water tested as a function of time thereafter permits a complete description of the precipitation kinetics of calcium carbonate.

From the curves TCa = f (t) and pH = f (t) we record the experimental germination time (T<sub>g</sub>) and the experimental germination pH (pH<sub>g</sub>) respectively. Subsequently, the kinetic modelling of these same curves provides us with the values of the different kinetic constants and the associated correlation coefficients.

3. Results and discussion

The name commercial inhibitor “Aquatreat 601” is a liquid, non-toxic, colourless and water-soluble product. Its density is 1.05 and its boiling point is above 100 °C. It contains phosphates and used in the food industry.

The effect of “Aquatreat 601” on the deposit of calcium carbonate (CaCO<sub>3</sub>) has been demonstrated at temperatures of 30, 40 and 60 °C.

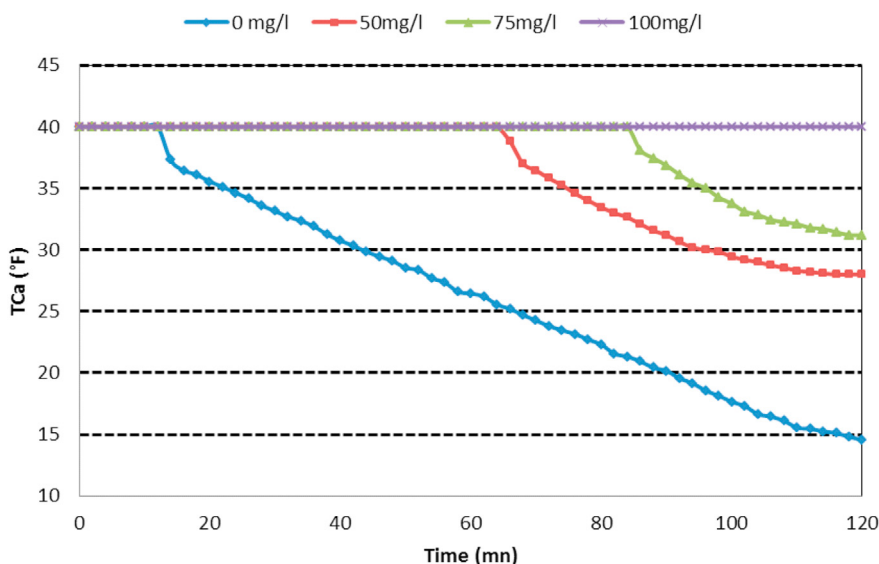


Figure 2. The evolution of TCa according to time in the tests with inhibitor “Aquatreat 601” at 30 °C.

**Table 1.** Germination time ( $T_g$ ), germination pH ( $pH_g$ ) and precipitation rate of the calcium carbonate solution at 40 °F adding increasing amounts of “Aquatreat 601” at 30 °C.

Concentration (mg/L)	$T_g$ (mn)	$pH_g$	Diffusional Calcite		Reddy Calcite	
			$K_D$ ( $mn^{-1}$ )	$R^2$	$K_R$ ( $F^{-1}.mn^{-1}$ )	$R^2$
0	12	8.86	1.08E-02	0.9858	5.74E-04	0.9303
50	64	9.48	6.93E-03	0.9450	2.46E-04	0.9646
75	84	9.55	7.29E-03	0.9380	2.38E-04	0.9530
100	-	-	-	-	-	-

### 3.1. Study of inhibition by “Aquatreat 601” at 30 °C

#### 3.1.1. Study by monitoring the evolution of pH

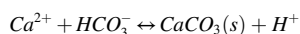
The Figures 1 and 2 respectively show the results of pH and concentration of calcium (TCa) content as a function of time in tests with inhibitor “Aquatreat 601” at 30 °C.

According to this graph, we notice that the pH decline is obvious in the test without inhibitor, but with rising concentrations of inhibitor, the decline becomes less observable. A bearing is observed before precipitation, which confirms that the duration of the germination phase surpasses that of degassing. The pH rises with the concentration of inhibitor at the germination point of the treated calco-carbonic solution, and it moves from 8.86 for 0 mg/L to 9.55 for 75 mg/L. This reveals a delay in precipitation and also slower growth kinetics [13].

#### 3.1.2. Study by monitoring the evolution of TCa

With the concentration of the scale inhibitor “Aquatreat 601”, we notice that the germination time rises. It increases from 12 mn for the test without inhibitor to 84 mn at a concentration of 75 mg/L.

At the beginning of the degassing phase, no change is observable in the  $Ca^{2+}$  concentration. During this period, defined as the time of germination. The fall in TCa is observed for concentrations up to 75 mg/L of “Aquatreat 601”. This decline is caused by the deposit of calcium carbonate with the liberation of proton  $H^+$  following this equation:



Roques and his collaborators have demonstrated the formation of calcium carbonates  $CaCO_3$  from  $HCO_3^-$  and  $Ca^{2+}$  [14].

We do not observe any precipitation of carbonate calcium starting from 100 mg/L of “Aquatreat 601”. So, inhibition becomes total.

The results of kinetic modelling and analysis of these curves is shown in Table 1.

It's noted that the germination time  $T_g$  and the germination  $pH_g$  increase with concentration of inhibitor up to 75 mg/L. Under the circumstances of the experiment, the precipitation of calcium carbonate is no longer noticed at a concentration of 100 mg/L.

The kinetic of precipitation follow the diffusional style for the test without inhibitor and the Reddy model for the tests in the presence of the inhibitor “Aquatreat 601” [15, 16, 17].

The obtained experimental results (Figures 1 and 2) at 30 °C, enable to conclude that the germination time in the case of the calco-carbonic solution at 40 °F is obtained at 12 mn without inhibitor. The addition of 100 mg/L of “Aquatreat601” to the solution stops the precipitation of calcium carbonate under the circumstances of the experiment.

### 3.2. Study of inhibition by “Aquatreat 601” at 40 °C

#### 3.2.1. Study by monitoring the evolution of pH

The obtained results when monitoring the pH and TCa content according to time in tests with “Aquatreat 601” inhibitor at 40 °C are shown in Figures 3 and 4 respectively.

The pH at the germination point of the treated calco-carbonic solution rises with the concentration of the inhibitor from 9.05 for 0 mg/L to 10.10 for 150 mg/L [18].

The germination time goes up with the concentration of “Aquatreat 601”. It rises from 10 min for the test without inhibitor to 92 min at 150 mg/L.

#### 3.2.2. Study by monitoring the evolution of TCa

From concentration superior or equal to 180 mg/L (efficiency concentration), no inhibition is occurred and no further deposition is observed under the conditions of the experiment during the test.

This efficiency concentration is confirmed from the TCa curve according to time, which does not show a drop for this concentration.

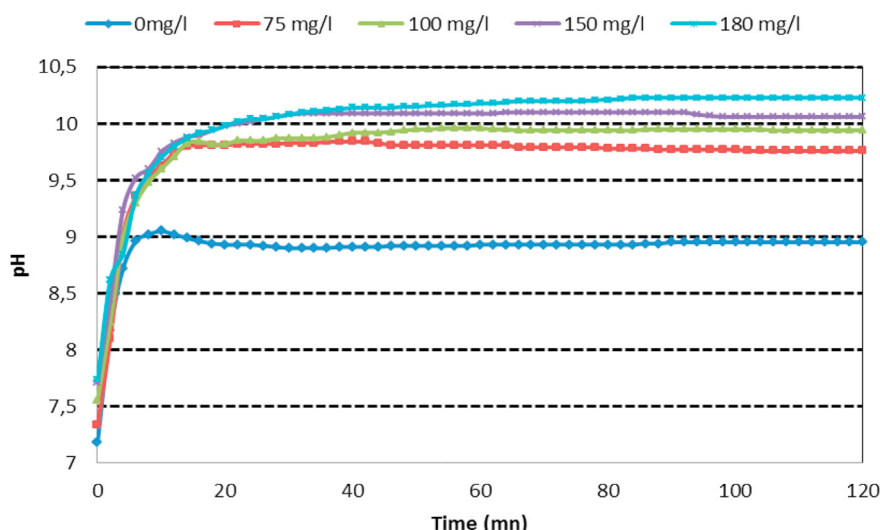


Figure 3. pH according to time in the tests with “Aquatreat 601” at 40 °C.

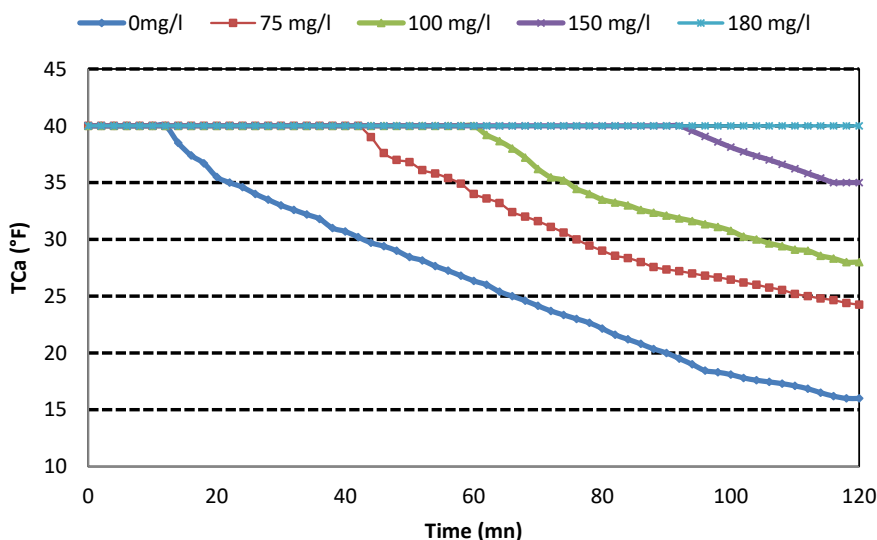


Figure 4. Variation of the TCa according to time in the tests with “Aquatreat 601” at 40 °C.

The examination of these curves and kinetic modelling is illustrated in Table 2.

Germination time and germination pH increase with inhibitor concentration up to 150 mg/L. The concentration of 180 mg/L is the efficiency concentration under the conditions of the experiment since no further calcium carbonate precipitation is observed for this test. It should be noted that the efficiency concentration of “Aquatreat 601” at 40 °C is higher than in the case of 30 °C since its only 100 mg/L in the latter case.

The kinetic of precipitation follow the diffusional model for the test without inhibitor and the Reddy model for the tests with the inhibitor “Aquatreat 601”.

The obtained experimental results (Figures 3 and 4) at 40 °C, enable to conclude that the germination time in the case of the calco-carbonic solution at 40 °F is 10 mn without inhibitor. 180 mg/L added of the inhibitor “Aquatreat601” to the solution stops the precipitation of calcium carbonate under the circumstances of the experiment.

The inhibition of calcium carbonate of the aragonite variety crystal growth by "Aquatreat601" can be explained by blockage of surface crystal growth sites.

### 3.3. Study of inhibition by “Aquatreat 601” at 60 °C

#### 3.3.1. Study by monitoring the evolution of pH

The results obtained when monitoring the pH and TCa content according to time in the tests with inhibitor “Aquatreat 601” at 60 °C are shown in Figures 5 and 6 respectively.

At the beginning of the experiment, the pH value increases sharply to a maximum and then falls again.

The pH at the germination point of the treated calcium carbonate solution rises with the concentration of the inhibitor from 9.45 for 0 mg/L to 10.48 for 250 mg/L.

The germination time increases with the concentration of “Aquatreat 601”. It rises from 10 min for the test without inhibitor to 100 min for a concentration of 250 mg/L at 60 °C.

#### 3.3.2. Study by monitoring the evolution of TCa

From a concentration of 300 mg/L or more (efficiency concentration) the inhibition becomes complete and the TCa curve as a function of time no longer falls under the conditions of the experiment.

It should be noted that the efficiency concentration of “Aquatreat 601” rises with temperature, It's 300 mg/L at a temperature of 60 °C, whereas at 40 and 30 °C it's 180 and 100 mg/L respectively. As the temperature raises, the solubility of CO<sub>2</sub> decreases and thus causes the deposition of calcium carbonate [19], and thus the efficiency concentration of inhibitor becomes high.

The examination of these curves and kinetic modeling lead to the values illustrated in Table 3.

The germination time T<sub>g</sub> and the germination pH<sub>g</sub> increase with inhibitor concentration up to 250 mg/L. At a concentration of 300 mg/L, the deposition of calcium carbonate is no longer noticed under the circumstances of the experiment.

The kinetic of precipitation follow the diffusional model for the test without inhibitor and the Reddy model for the tests with the inhibitor “Aquatreat 601”.

The obtained experimental results (Fig.5 and 6) at 60 °C, enable to conclude that the germination time in the case of the calco-carbonic solution at 40 °F is 10 mn without inhibitor. The addition of 300 mg/L of the inhibitor “Aquatreat601” to the solution prevents the precipitation of calcium carbonate under the conditions of the experiment.

The temperature has an important effect on the solubility of calcium carbonate. The latter goes up in the presence of carbon dioxide. Indeed, the rise in temperature decreases the amount of dissolved carbon dioxide

Table 2. Germination time (T<sub>g</sub>), germination pH (pH<sub>g</sub>) and precipitation rate of the pure calcium carbonate solution at 40 °F adding rising amounts of “Aquatreat 601” at 40 °C.

Concentration (mg/l)	T <sub>g</sub> (mn)	pH <sub>g</sub>	Diffusional Aragonite		Reddy Aragonite	
			K <sub>D</sub> (mn <sup>-1</sup> )	R <sup>2</sup>	K <sub>R</sub> (F <sup>-1</sup> .mn <sup>-1</sup> )	R <sup>2</sup>
0	10	9.05	1.04E-02	0.9957	5.49E-04	0.9653
75	42	9.84	7.40E-03	0.9800	2.91E-04	0.9932
100	60	9.96	6.58E-03	0.9777	2.34E-04	0.9900
150	92	10.10	5.80E-03	0.9876	1.78E-04	0.9897
180	-	-	-	-	-	-

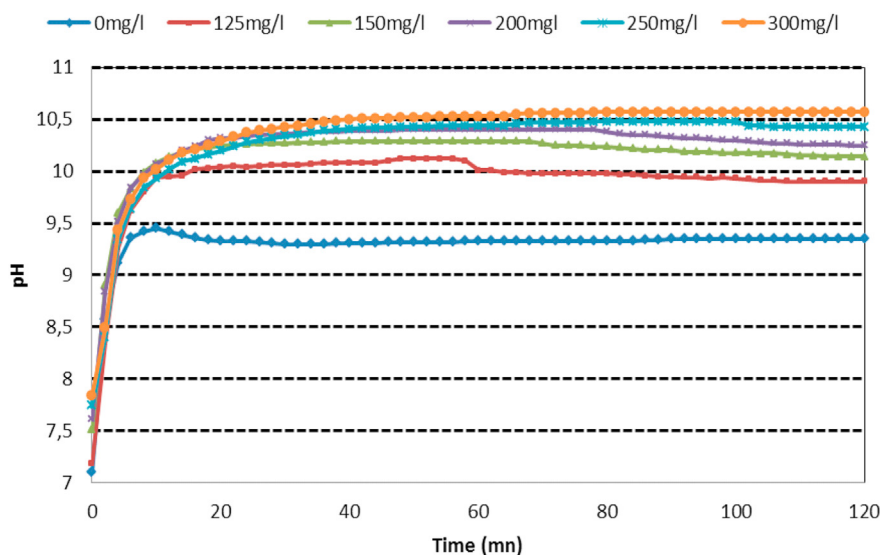


Figure 5. Curves pH according to the time of the tests with inhibitor “Aquatreat 601” at 60 °C.

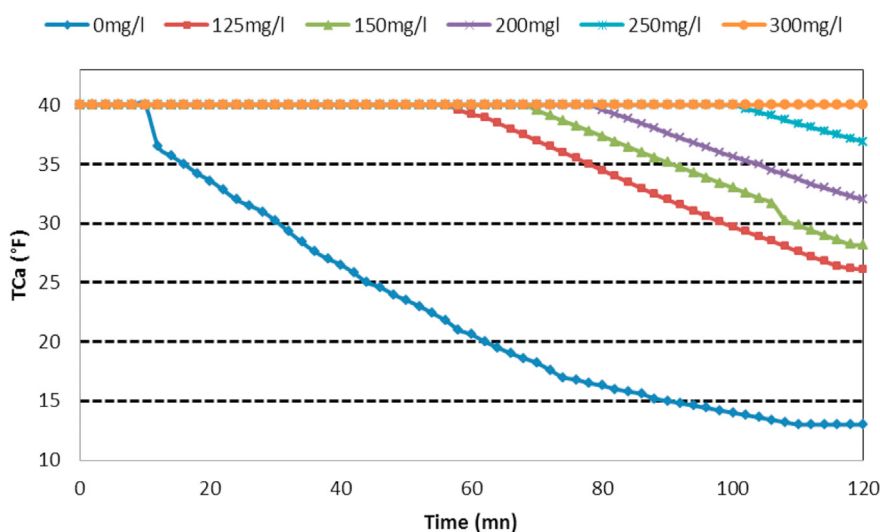


Figure 6. TCa Curves according to the time of the tests with inhibitor “Aquatreat 601” at 60 °C.

and generates the precipitation of calcium carbonate. At higher temperatures, the latter was attributed to a decrease in supersaturation conditions.

4. Conclusion

The chemical inhibition of calcium carbonate precipitation can be considered as a method of choice to fight against the scaling observed in the tourist sector of Grand Agadir (TH~40°F). The chemical inhibitor by

“Aquatreat 601” was tested. This study was carried out on pure calco-carbonic water at 40 °F at temperatures of 30, 40 and 60 °C using the “LCGE” method.

The germination time and the pH value at the germination point of the treated calcium carbonate solution increase with the concentration of “Aquatreat 601” inhibitor at the different tested temperatures. The efficiency concentration of “Aquatreat 601” increases with increasing temperature. It’s 100, 180 and 300 ppm at temperatures of 30, 40 and 60 °C respectively.

Table 3. Germination time (Tg), germination pH (pHg) and precipitation rate of the calcium carbonate solution at 40 °F adding increasing amounts of “Aquatreat 601” at 60 °C.

concentration (mg/L)	T <sub>g</sub> (mn)	pH <sub>g</sub>	Diffusional Aragonite		Reddy Aragonite	
			K <sub>D</sub> (mn <sup>-1</sup> )	R <sup>2</sup>	K <sub>R</sub> (F <sup>-1</sup> .mn <sup>-1</sup> )	R <sup>2</sup>
0	10	9.45	1.47E-02	0.9972	6.83E-04	0.9791
125	56	10.12	8.34E-03	0.9918	2.94E-04	0.9929
150	68	10.29	7.93E-03	0.9723	2.82E-04	0.9725
200	78	10.40	6.04E-03	0.9895	1.98E-04	0.9972
250	100	10.48	4.53E-03	0.9995	1.36E-04	0.9996
300	-	-	-	-	-	-

The kinetic of precipitation follow the diffusional model for the test without inhibitor and the Reddy model for the tests with the inhibitor "Aquatreat 601".

These results will help us to focus our research of suitable efficiency inhibitors of scaling in order to stop the precipitation of scale in the hot water system in the touristic area of Agadir city.

As a result, it is essential to find a new generation of scale inhibitors, which is remarkable, on the one hand, by a good inhibiting effectiveness of calcium carbonate, and, on the other hand, by their ecological effect due to the respect of health and environment norms.

## Declarations

### Author contribution statement

M'barek Belattar: Conceived and designed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Abdallah Hadfi: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Said Ben-Aazza: Conceived and designed the experiments; Analyzed and interpreted the data.

Ilham Karmal, Said Mohareb, Mohamed El Housse: Performed the experiments.

Naima Hafid: Conceived and designed the experiments; Wrote the paper.

Ali Driouiche: Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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### Data Availability Statement

The authors do not have permission to share data.

### Declaration of interests statement

The authors declare no conflict of interest.

### Additional information

No additional information is available for this paper.

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