Evaluation of the irrigation water quality in Biougra circle along with highlighting the effectiveness of a scaling inhibitor

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Abstract: Localized irrigation is characterized by localized frequent and continuous water supply. It ensures the efficient use of water. However, this fertigation system suffers from the problem of clogging of the distributors. The present study aims to study the physico-chemical quality of the water of irrigation within the Biougra circle; analyze of the type of scale deposited in the water pipes and the highlight of the effectiveness of an inhibitor of calcium carbonate precipitation. This study was carried out at a temperature of 25°C, using the technical "LCGE". Indeed, the classification of irrigation water, according to Piper, revealed that the analyzed waters are characterized by calcium and magnesium bicarbonate facies with a slight tendency to migrate to the calcium and magnesium chloride and sulfate facies. The characterization of the scale collected in the irrigation water pipes of Biougra circle by X-ray fluorescence, X-ray diffraction and thermal analysis (ATD-ATG) made it possible to prove that the scale is mainly formed of calcium carbonate with calcite variety. The inhibition of calcium carbonate precipitation by a food inhibitor was obtained with a concentration of 0.6 mg/L.

Keywords: Scale; localized irrigation; water; physico-chemical quality; calcium carbonate.

Introduction

Chtouka Plain is characterized by a particularly well-developed agricultural activity and even constitutes the first primeurist region of Morocco. The high level and quality of modern agriculture in this region ensure its growing importance worldwide. It is export-oriented agriculture.

The intense agricultural activities in this area require considerable water resources given the semi-arid to a sub-desert climate that characterizes the area. It is a climate that promotes agricultural development in the region, but that requires substantial water resources. Today, this area suffers from a recurrent lack of water and from over-exploited groundwater which reaches its limits. The available data shows that the pressure on aquifers to meet the agricultural needs of water in this region has involved a shortage of water resources of about 270 million cubic meters per year. This increased shortage of groundwater resources year after year. It has also led to a serious deterioration of the aquifer. In some areas, there is a total depletion of the aquifer [1].

Aware of this situation, Morocco launched the National Program of Water Economy in Irrigation (NPWE-II). It focuses on two components: economizing and valuing the water of irrigation and aims at the conversion of the existing (traditional) irrigation systems in localized irrigation systems [2].

Micro-irrigation or localized irrigation is done drop-by-drop. It is a very economical technique since it consumes only what the plant needs. Indeed, the water is channelled to the root of the plant. It is appropriate for most of the agricultural cultures.

However, this irrigation system faces the drippers clogging problem. Indeed, clogging leads to poor water distribution in the soil, which directly affects the growth and development of plants [3]. According to studies conducted in Morocco, more than 80 % of micro-irrigated farms suffer from this problem [4].

Considering the major problems caused by scale formation in irrigation water pipes and the absence of relevant studies on fertigation systems, the importance of this study is obvious. This research has three objectives: studying of the physico-chemical quality of the irrigation water of this region; analyzing the type of scale formed in water pipes and highlighting the efficiency of an inhibitor of calcium carbonate precipitation using the controlled degassing technique known as "LCGE" [5-8].

The studied inhibitor is a food product phosphate based. Indeed, phosphate-containing additives have

been used in water treatment practice for several decades. The main purposes of using these chemicals are to control pipe corrosion and inhibit calcium carbonate scale formation [9].

Recent surveys indicate that more than half of the water treatment utilities in the United States have adopted the use of phosphate-containing additives [10,11]. These additives include orthophosphate, zinc orthophosphate, polyphosphate and various phosphate blends [11]. The use of phosphate-containing additives also prevents the deposition of calcium carbonate scale on pipe walls in the distribution system, in boilers, and hot water lines by sequestering calcium and inhibiting calcium carbonate (calcite) precipitation, even under conditions of calcite oversaturation.

Presentation of the study area

The geographical situation

The plain of Chtouka constitutes an extension of the plain of Souss towards the South-West. It is located at 30° 1072' North of latitude and at -9° 2786' of longitude. It covers an area of 940 Km². It is limited to the North by the prefecture of Inezgane-Ait Melloul, to the East by the outcrops of the primary formations of the Anti-Atlas, to the South by Oued Massa and to the West by the Atlantic Ocean.
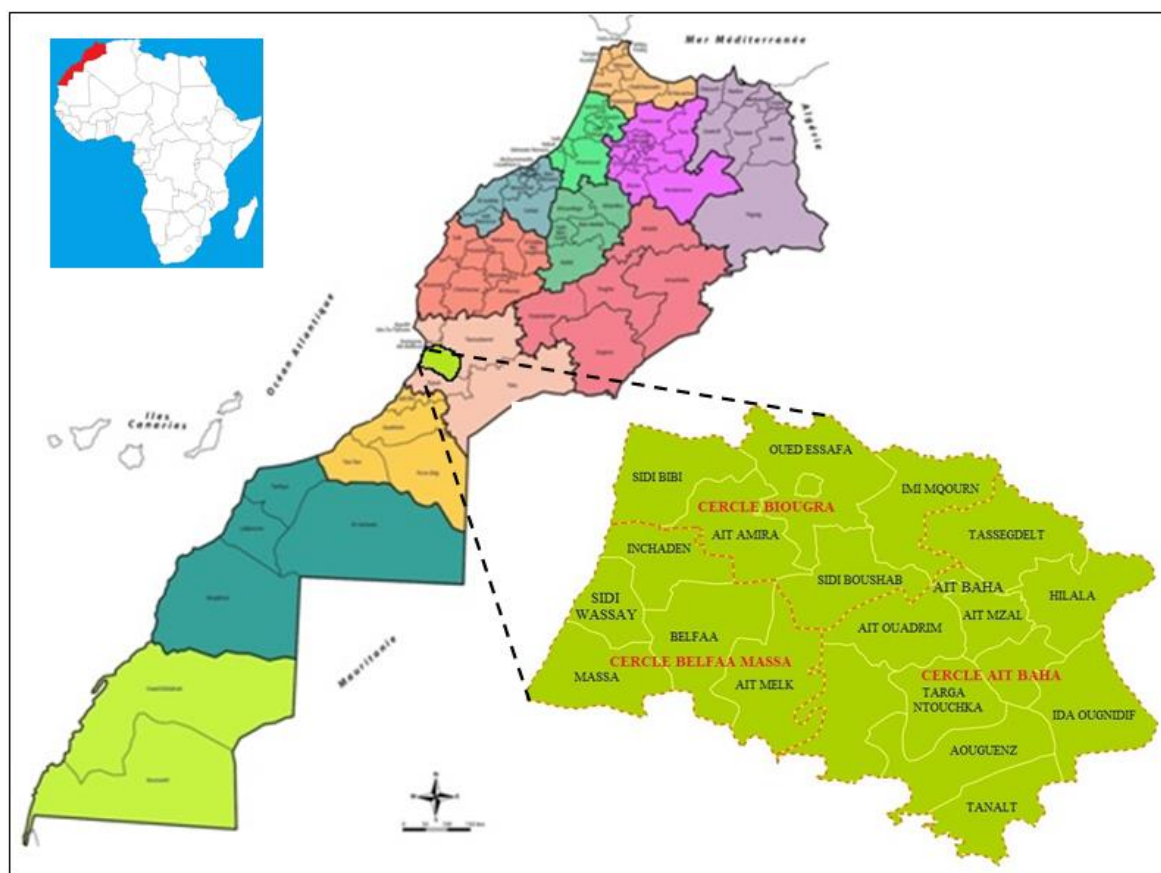

Figure 1. Map of the geographical location of the study area

Climatology

The Chtouka region is located near the desert areas of the northern hemisphere. It is characterized by a semi-arid climate with a desert tendency. It has low and irregular annual rainfall (20 to 30 days/ year), averaging 140 to 214 mm/year. The temperatures are moderate and average 19 °C with an average maximum of 27 °C and a minimum of 11°C. Warm winds (Chergui) are recorded during the spring and summer seasons. The softening current of the ocean and the mountain range of the Anti-Atlas constitute a barrier against the desert influence and promote the agricultural development in this region.

Sampling of irrigation water

To spot the effect of the physico-chemical quality of water intended for irrigation in the Biougra circle on the clogging of the distribution organs, a sampling network was chosen to allow the acquisition of representative data on the spatial variability of the groundwater quality of the studied aquifer. This network consists of 40 boreholes spread over the entire study area. The campaigns were conducted in March and July 2017.

The sampling of water includes the preparation of the sample, the sampling itself, the conditioning of the sample, as well as its storage until the water is

analyzed. Each of these steps is important to guarantee the reliability of the analysis results.

Sampling area

Given a large number of boreholes in the study area, and faced with the impossibility of analyzing the water from all these boreholes, we proceeded to the selection of 40 boreholes uniformly distributed throughout the circle of Biougra.

Selection of sampling points

For good representativeness of samples, we chose the sampling boreholes according to the following criteria:

- Good spatial distribution of boreholes
- Water use for irrigation
- Accessibility of the water points to be sampled.

Execution of samples

After the choice of sampling points, it is necessary to open the valve sufficiently to renew the water contained in the piping until it becomes representative of the aquifer portion to be sampled. To disinfect the valve, it must be passed under a flame.

The water samples must be taken in clean bottles, rinsed with distilled water and then with the water to be analyzed. After the samples have been bottled, the bottles must be hermetically sealed without leaving air bubbles in the bottle.

The bottles must be identified with labels indicating the sample number.

Storage of samples

All waters are likely to change more or less rapidly as a result of physical, chemical or biological reactions that may occur in the bottle in the lapse of time between sampling and analysis.

For that, samples must be brought to the laboratory as soon as possible (less than 24 hours). The temperature of the sample must never exceed that of the groundwater sampled. The bottles should be stored in a cool and away from light (cooler or refrigerator). In the laboratory, samples should be stored in a refrigerator between 3 and 5 °C [12].

Physico-chemical analyses

The field-measurements include electrical conductivity (EC), pH and temperature. The chemical analyses carried out in our laboratory concern: Cations: Ca^{2+}, Mg^{2+}, Na^+ and K^+, Anions: Cl^-, SO_4^{2-}, HCO_3^-, CO_3^{2-} and NO_3^- and the dry residue (DR).

The results of chemical analyses of water must imperatively be subjected to a validity test which consists of the calculation of the ionic balance. This parameter is used to verify the accuracy of the analytical methods used and the validity of chemical determinations. If it is less than 5 % the analyses are considered as correct when its value is between 5 % and 10 %; the analyses can be rigorously retained. However, above 10 % the analyses must be repeated [13].

Results and Discussion

The analysis results of irrigation water

The aim of this hydrochemical study is to determine the physico-chemical characteristics of water and dissolved elements in order to determine their origins, to define the chemical facies of groundwater, to compare them and to follow their evolution in space.

Table 1 summarizes the results of the physico-chemical analyses of the water samples in this study. The electrical conductivity (EC) oscillates between 447 µS.cm^{-1} and 1376 µS.cm^{-1} with an average of 865 µS.cm^{-1}. The pH is close to neutrality. Their dry residues are moderately accentuated, ranging between 320 mg/L and 1043 mg/L with an average of 641 mg/L. The complete alkalimetric title (CAT) in the water samples analyzed was essentially due to bicarbonate ions. The CAT ranged from 212.28 to 396.5 mg/L with an average concentration of 338.81 mg/L. However, about 94 % of the waters have a CAT above 20 °F, which results in high concentrations of bicarbonate ions. The average concentrations of calcium and magnesium are respectively 74.99 and 49.48 mg/L.

Table 1. Average physico-chemical characteristics of sampled waters.

Variable	pH	Cond (µS/cm à 25 °C)	RS (g/l à 105°C)	TH (°F)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)
Min	6,89	447,50	320,37	28,40	0,00	212,28	23,53	12,40	1,69	40,90	24,19	11,73	0,60
Max	8,21	1376,00	1043,76	67,50	6,00	396,50	297,49	240,17	55,38	136,32	98,53	155,17	9,77
Average	7,43	865,57	641,82	37,69	0,15	338,81	121,21	60,66	22,03	74,99	49,48	60,49	2,92
Standard deviation	0,32	241,46	194,48	7,32	0,96	39,24	69,52	53,56	11,35	19,08	15,01	38,43	2,10

Table 2 summarizes the physico-chemical analyses of water samples taken is the circle of Biougra. The samples are taken from about forty boreholes.

Table 2. Physical-chemical parameters of irrigation water from the circle of Biougra.

boreholes	pH	Cond µS/c à 25 °C	D.R. g/l à 105°C	TH (°F)	CO_3^{2-} (mg/l)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	Ca^{2+} (mg/l)	Mg^{2+} (mg/l)	Na^+ (mg/l)	K^+ (mg/l)	Ionic balance
1	6,89	1130,00	857,15	48,60	0,00	341,60	199,94	62,90	22,46	80,96	98,53	37,95	1,95	0,04
2	7,24	750,00	536,94	40,60	0,00	348,00	106,50	17,43	24,10	80,16	50,09	46,00	1,56	0,04
3	7,25	1298,00	984,59	39,10	0,00	262,30	297,49	131,84	11,58	98,88	35,07	145,97	3,19	0,05
4	7,24	870,00	659,93	39,00	0,00	366,00	76,57	90,57	30,13	81,76	45,93	39,79	1,95	0,04
5	7,85	712,00	509,74	38,40	0,00	335,00	128,00	20,00	27,00	66,00	53,50	47,15	5,85	0,00
6	8,11	545,00	390,18	38,19	0,00	356,85	71,00	45,05	10,96	66,96	52,22	19,48	1,70	0,02
7	7,76	930,00	705,45	37,80	0,00	317,20	94,30	106,75	13,06	78,55	44,26	50,02	3,51	0,02
8	7,10	943,00	715,31	37,60	0,00	353,80	60,86	34,86	27,26	79,35	43,25	32,43	1,36	0,02
9	7,07	920,00	697,86	37,00	0,00	292,80	111,67	109,27	17,74	80,16	41,34	50,02	3,51	0,04
10	7,27	955,00	724,41	35,58	0,00	212,28	269,80	146,36	7,87	86,80	33,84	155,17	3,19	0,01
11	7,15	830,00	594,21	34,40	0,00	305,00	49,98	144,85	7,17	68,13	42,28	44,39	3,51	0,03
12	8,21	574,00	410,94	33,88	0,00	359,90	44,38	25,76	18,20	78,88	34,51	19,92	1,40	0,02
13	7,55	700,00	501,14	33,40	0,00	355,50	39,35	17,61	23,14	64,93	41,79	18,17	2,34	0,01
14	7,45	731,00	523,34	33,40	0,00	347,70	52,60	13,92	23,26	75,35	35,50	22,40	1,56	0,01
15	7,52	503,70	360,61	33,00	0,00	359,90	57,30	13,60	33,30	68,70	38,70	23,50	1,40	0,04
16	7,07	700,00	501,14	32,80	0,00	335,50	38,28	30,55	21,92	60,12	43,95	17,94	2,34	0,01
17	7,70	447,50	320,37	32,00	0,00	329,40	45,50	12,40	20,60	40,90	53,00	13,30	1,95	0,02
18	7,30	1240,00	940,59	31,83	0,00	219,60	281,85	131,64	4,49	87,68	24,19	150,39	3,48	0,05
19	7,15	835,00	633,38	30,40	0,00	370,00	85,08	38,40	21,91	86,20	45,00	35,30	1,33	0,00
20	7,24	612,00	438,14	30,00	6,00	305,00	23,53	13,11	1,69	65,73	33,05	11,73	1,95	0,05
21	7,30	760,00	544,10	30,00	0,00	326,35	61,68	37,02	20,40	59,33	36,93	37,49	8,34	0,02
22	7,40	960,00	728,20	29,00	0,00	356,00	119,00	22,80	17,38	80,20	58,00	24,50	1,48	0,00
23	7,90	413,00	295,67	21,91	0,00	100,65	26,63	128,00	1,19	72,08	9,55	8,08	2,93	0,03
24	7,17	1285,00	974,73	67,50	0,00	344,65	214,78	240,17	8,12	136,32	81,41	85,01	2,88	0,01
25	7,42	774,00	554,12	45,20	0,00	390,00	142,00	34,50	23,00	41,70	84,63	52,90	7,80	0,00
26	6,99	1100,00	834,40	44,80	0,00	359,90	192,95	18,69	33,48	82,56	58,80	95,45	1,95	0,04
27	7,57	800,00	572,74	44,00	0,00	384,00	131,00	34,50	35,00	104,20	43,77	51,77	7,02	0,00
28	8,16	1300,00	986,11	43,60	0,00	390,00	122,00	64,00	19,00	87,00	53,00	81,00	3,51	0,04
29	7,42	700,60	501,57	43,20	0,00	329,40	148,20	28,00	11,00	63,30	66,60	51,80	2,73	0,03
30	7,13	1230,00	933,01	40,80	0,00	338,55	188,26	95,61	55,38	73,74	54,43	101,20	1,95	0,04
31	7,85	653,00	467,50	38,00	0,00	366,00	128,00	29,00	18,44	83,36	41,83	62,00	9,77	0,00
32	7,61	659,30	472,01	37,60	0,00	341,60	128,00	19,60	19,10	42,50	65,70	69,00	0,60	0,03
33	7,54	663,70	475,16	37,20	0,00	341,60	112,80	21,20	39,40	54,50	57,40	62,10	1,95	0,02
34	7,57	1052,00	797,99	37,20	0,00	347,70	164,84	52,60	31,26	65,73	50,54	110,40	1,56	0,01
35	7,31	900,00	682,69	35,60	0,00	372,10	94,75	80,20	23,37	66,53	46,17	66,70	2,34	0,04
36	7,57	920,00	697,86	34,40	0,00	336,00	115,00	45,00	32,27	64,00	45,00	85,00	2,34	0,02
37	7,64	754,00	539,80	33,20	0,00	347,70	141,40	35,60	50,00	51,30	49,60	110,40	0,60	0,01
38	7,70	633,60	453,61	31,20	0,00	326,35	74,09	53,40	17,17	62,10	38,20	53,50	2,30	0,01
39	7,25	1376,00	1043,76	28,40	0,00	346,00	221,00	60,00	23,70	114,00	39,70	110,00	1,71	0,01
40	6,98	1010,00	766,13	52,00	0,00	396,50	93,59	186,91	13,97	96,19	68,10	67,85	3,90	0,01

Groundwater classification according to PIPER

We used Avignon's hydrochemistry software (version 6.51), which allowed us to determine the chemical facies of the irrigation water, and in particular to construct the Piper diagram. This diagram has been used by several authors for data processing and has given satisfactory results [14-16].
The Piper diagram is consisting of two triangles which depict the distribution of anions and cations respectively, and a rhombus is representing the synthetic distribution of major ions (Fig. 2).

Piper Diagram (Fig. 2) consists of two triangular ("trilinear") plots representing cations and anions, and a third diamond-shaped plot onto which the relative cation and anion concentrations are projected. Relative concentrations of the individual cations and anions in meq/L are expressed as percentages of the total cations or total anions (e.g., calcium, divided by the total of calcium, magnesium, and sodium plus potassium). The points are then plotted on the central diamond-shaped field by projection along lines parallel to the axes of the central field. The intersection of these projections represents the composition of the water concerning the combination of ions shown. The central diamond-shaped field is used to show the overall chemical character of the water [17,18]. The circles plotted in the central field have radii proportional to the dissolved solids concentration of each water sample. Back and Hanshaw [19,20] defined subdivisions of the diamond field, which represent water-type categories that form the basis for one common classification scheme for natural waters.

The Piper diagram also allows:

☞ to illustrate the chemical evolution of water in an aquifer as well as the mixtures of waters of different mineralizations,
☞ to have an idea about lithology from chemical analyzes,
☞ to have a relationship between the chemistry of water and the lithological nature of rocks,
☞ the projection of several samples at the same time:

- To follow their evolution in time and space,
- To compare them,
- To get an idea about the concept of mixing,

☞ to follow the physicochemical properties during their spatiotemporal evolution.

The point clouds concentrated in one pole represent for the different samples the combination of cationic and anionic elements.
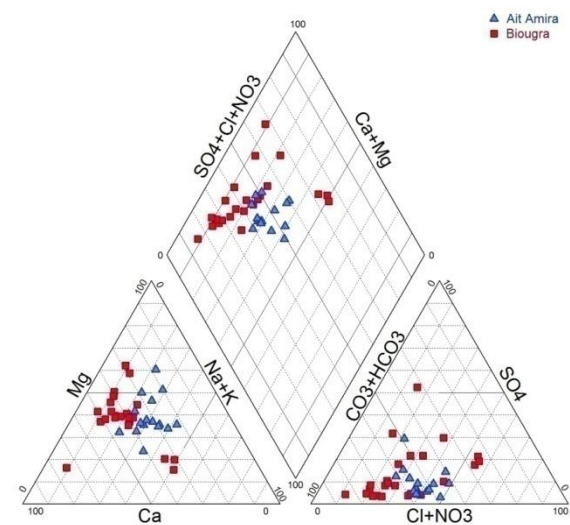

Figure 2. Representation of the Piper diagram

Figure 3. Representation of the waters of Biougra circle on the Piper diagram

Ait Amira is a rural Moroccan municipality in the circle of Biougra.

The representation of the chemical results of the groundwater samples on the Piper diagram shows that the chemistry of the analyzed waters is characterized by the calcium and magnesium bicarbonate facies with a slight tendency to migrate to the calcium and magnesium chloride and sulfate facies (Fig. 3). Thus, the chemical composition of water from the natural environment is highly variable. It depends on the geological nature of the soil from which it originates and the reactive substances it encountered during the flow [21].

- Purely calcium-bicarbonate groundwater path, having a short runtime in the formations of the calcareous dorsal;
- Bicarbonate-calcic groundwater path, having a long run time in the formations of the calcareous dorsal.
- Purely Chlorinated and sulfated calcic groundwater path,

- Chlorinate-calcic groundwater path influenced by the contact with water with bicarbonate calcic and magnesian predominance, revealing a high bicarbonate rate.

Characterization of scale deposits

X-ray fluorescence, X-ray diffraction and thermal analysis (DTA/TGA) are used to identify scale deposits collected on irrigation water pipes in Biougra Circle.
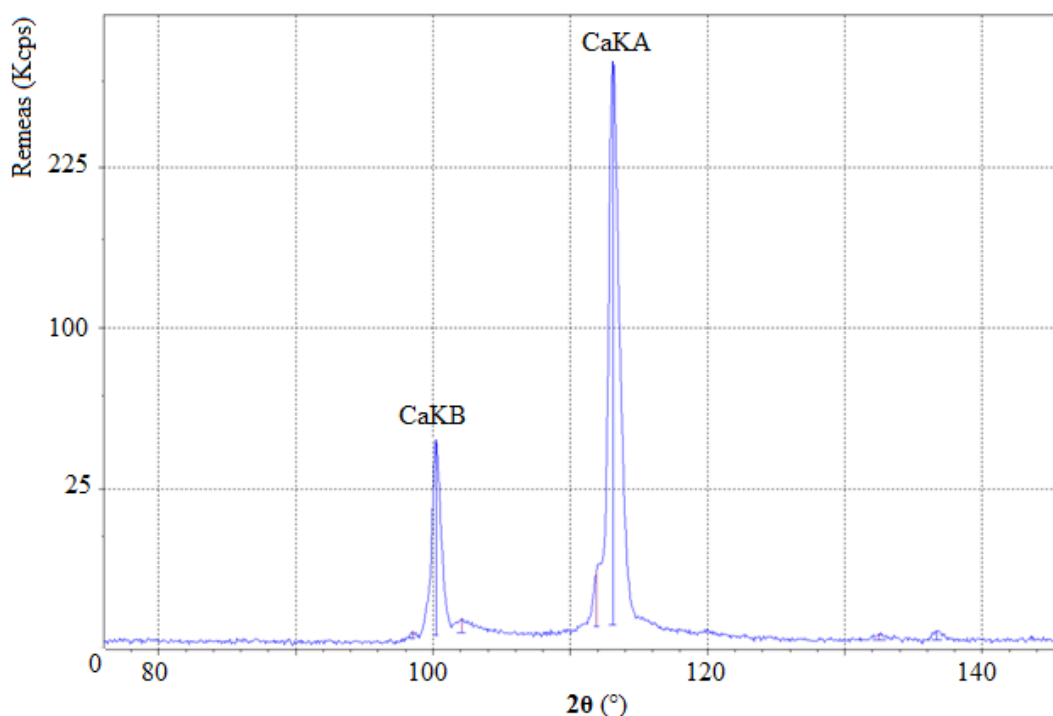
X-ray fluorescence analysis

Qualitative chemical analysis

For more detailed characterization of the various scales collected and to highlight elements present in the trace state, we are led to use the X-ray fluorescence analysis (Axiosm AX Spectrometer) which proves to be the best method to use since it is at the same time sensitive, fast and more or less non-destructive. Using this technique, the scale constituents collected in the irrigation water pipes can be identified.

Fig. 4 shows the spectrum of the main elements found in the irrigation water scale samples. According to this figure, calcium is the major element. It has an intense peak at $2\theta = 113°$.

Figure 4. Spectrums of XRF qualitative analysis of scale deposited in water irrigation system

Quantitative chemical analysis

The quantitative results of the XRF analysis are presented in Table 3. The chemical composition of the scale sample shows that calcium oxide CaO was the most abundant component (51.64 %). The high amount of calcium oxide shows that calcium carbonate is the predominant component of the calamine deposited from irrigation water at 92.21 %. Other oxides were detected in very small quantities: magnesium oxide MgO, silica SiO_2 are found in a

percentage of 1.04 % and 1.63 % respectively. Other oxides such as alumina Al_2O_3, sulfur trioxide SO_3, iron oxide Fe_2O_3, potassium oxide K_2O, phosphorus pentoxide P_2O_5 and sodium oxide Na_2O contribute less than 0.37 % by weight of the total composition. Also, it was also observed that the ignition loss for hot water scale was 41.93 %. The inflammation has a significant loss due mainly to the decomposition of calcium carbonate with the formation of CaO and carbon dioxide (CO_2) [22].

Table 3. Chemical analysis (in% by weight) of the scale recovered in the irrigation water pipes (L. I.: loss on ignition).

SiO_2	Al_2O_3	Fe_2O_3		CaO	MgO	SO_3	K_2O	Na_2O	P_2O_5	L.I.	$CaCO_3$
1,63	0,07	0,05		51,64	1,04	0,09	0,02	0,13	0,01	41,93	92,14

X-Ray analysis

The X-ray diffraction realized on the deposit of scale collected from the water pipes of the localized irrigation of Biougra circle was carried out using a diffractometer type XPERT-PRO.

The XRD spectrum (Fig. 5) shows that the scale consists essentially of calcite ($CaCO_3$) with a percentage of 98.8 % compared to the JCPDS file number 00-005-0586. Indeed, the position of the peaks at angles 2θ of the literature coincides well with the experimental values 2θ [23], these diffraction peaks can be well indexed in Rhombohedral calcite with mesh parameters: a = 4.9890 Å, b = 4.9890 Å and c = 17.0620 Å, and the space group R-3C, with a presence of quartz (SiO_2) as a percentage of 1.2 % compared to the JCPDS card number 00-046-1045.
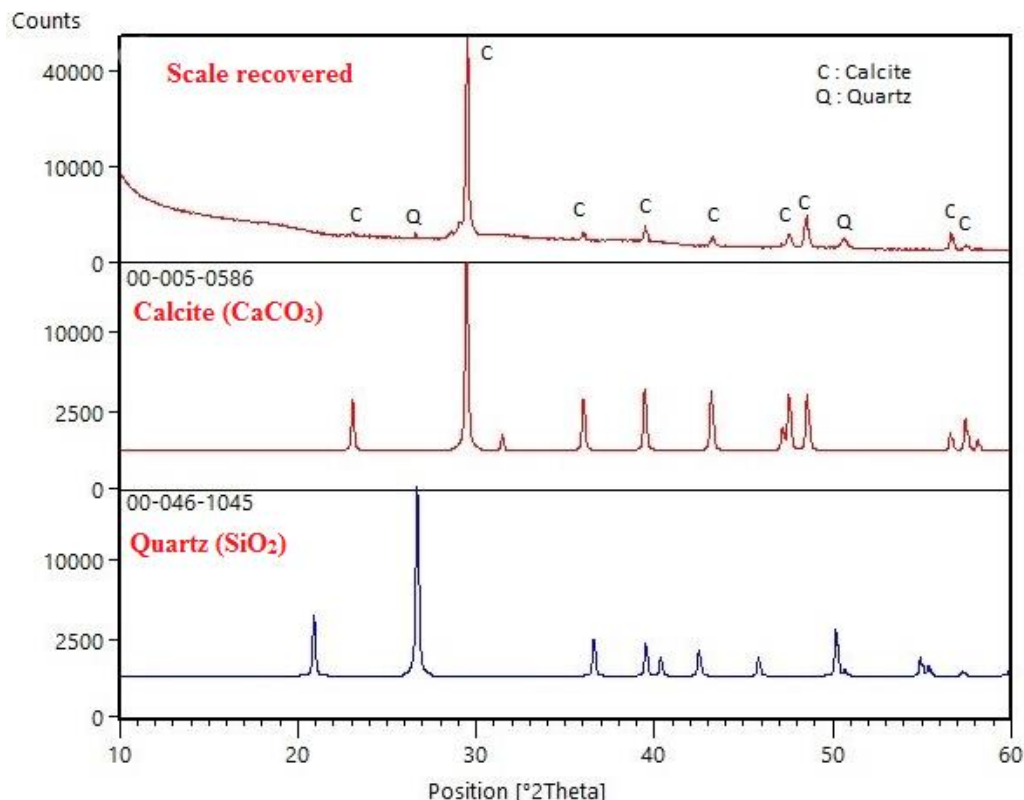
Figure 5. X-ray diffractogram of scale recovered from the water pipes of the localized irrigation of Biougra circle

DTA and GTA analysis

A substance subjected to thermal treatment can undergo modifications of its physico-chemical properties as a phase change, a structural alteration, a decomposition, a volume variation, etc...[24]. Among the techniques used, we can cite differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

Differential Thermal Analysis (DTA)

The method consists of measuring the temperature difference ΔT between the sample to be studied and an inert reference sample; both are subjected to the same heating law. This difference is related to the amount of heat released or absorbed by the material studied. Thus ΔT is recorded according to the temperature. This allows detection of endothermic and exothermic transformation peaks. The device used is type DTG-60, and it allows to work in a temperature which ranges from 10 °C to 1100 °C. The heating rate we have adopted is 10 °C/min. The reference sample is alumina.

Thermogravimetric analysis (TGA)

The principle is based on following continuously the variation of the mass of a sample according to the temperature. The sample, placed in an alumina nacelle suspended from a balance flail, is located in a temperature-controlled enclosure. The equilibrium of the balance is ensured by an electromagnetic compensation system. The variation of the mass, given by the balancing system, is recorded as a function of the temperature rise.

Fig. 6 shows the thermal analysis (DTA / TGA) of the scale recovered in the irrigation water pipes. We observed three endothermic peaks. The first around 50 °C, corresponds to the departure of the surface and lattice water. The second peak, beginning at 450 °C, is characteristic of the elimination of the constitution water. Finally, the last peak corresponds to the decomposition of calcite at 880 °C [25-29]. This decomposition corresponds to the departure of CO_2 according to the following reaction:

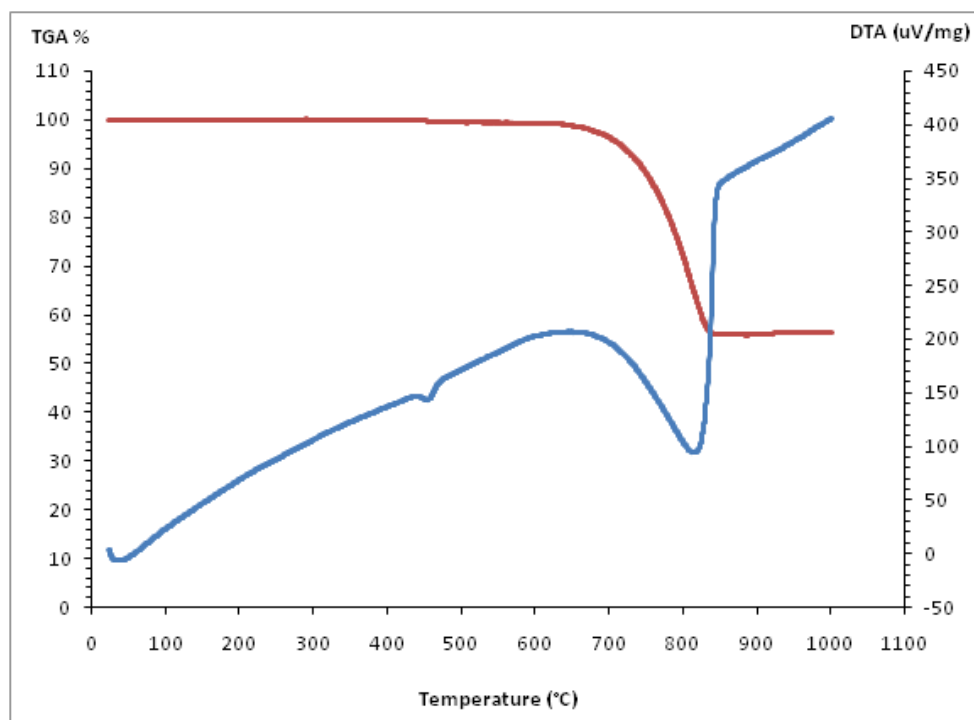$$CaCO_3 \longrightarrow CaO + \overrightarrow{CO_2}$$
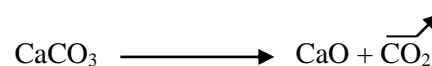
Figure 6. Thermal analysis curves (DTA / TGA) of scale recovered from the water pipes of the localized irrigation of Biougra circle

Anti-scalant behavior of a food product phosphate based

Calcium carbonate scale is a serious problem in water pipelines. The formation of scale can be alleviated or at least reduced by the use of antiscalant chemicals. Some different antiscalants are commercially available but still little is known about their mechanism of inhibiting scale formation [30].

The use of inhibitors is one of the best techniques to prevent or delay the formation of these deposits. It is therefore essential to find a novel environmentally friendly anti-scalant, characterized by the better inhibiting effectiveness of calcium carbonate, on the one hand, and their respect of health and environment norms, on the other hand. The food products have become a source of inhibitors with high added value. These types of inhibitors do not contain heavy metals or toxic compounds, and they are biodegradable.

The experimental installation is shown in Figure 7.

In the present work, we are interested in studying the effect of a food inhibitor of a trademark called "Leval®15" on the water scaling power.

Leval 15

The "LEVAL®15" is food that is compound, complex, pulverulent and soluble in the water, with a white powdery appearance. It contains 64.5 % of phosphoric anhydride (P_2O_5) and 28.5 % of Na_2O. This product is currently used as a food additive.

The study was conducted at a temperature of 25 ˚C, using the technical LCGE on the pure calco-carbonic water with 40 °F. Always beginning by increasing amounts; the quantity of designated tartrifuge (a product used to prevent the formation of scale) for each test was used before the start of the experimentation. In all cases, the presence of tartrifuge does not change the values of the CAT, and TCa measured before the start of the experiment.

1. Stripping gas
2. Thermostat baths
3. Immersion circulator-heating
4. Humidifier
5. Humidity traps
6. Work cell
7. Simple taken for the dosage of [Ca^{2+}]
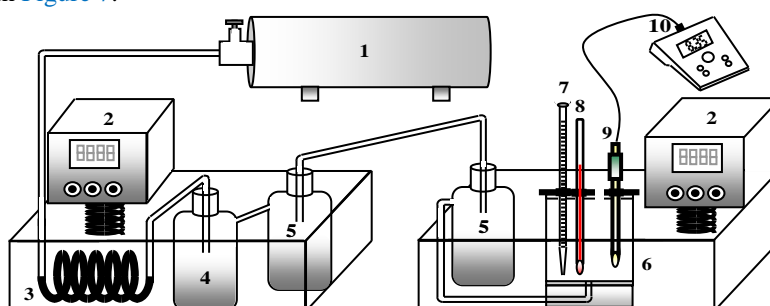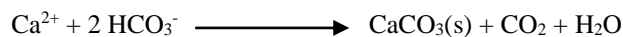8. Temperature probe
9. pH mete

Figure 7. Experimental set-up of the LCGE method

The principle of technical LCGE is based on the accelerated formation of deposits of calcium carbonate under the effect of degasification of the studied water, usually atmospheric air, according to the following reaction:

$$Ca^{2+} + 2\ HCO_3^- \longrightarrow CaCO_3(s) + CO_2 + H_2O$$

The statement of the pH values and the concentration of a Ca^{2+} ion over time allow making a description of the precipitation kinetics of calcium carbonate [8].
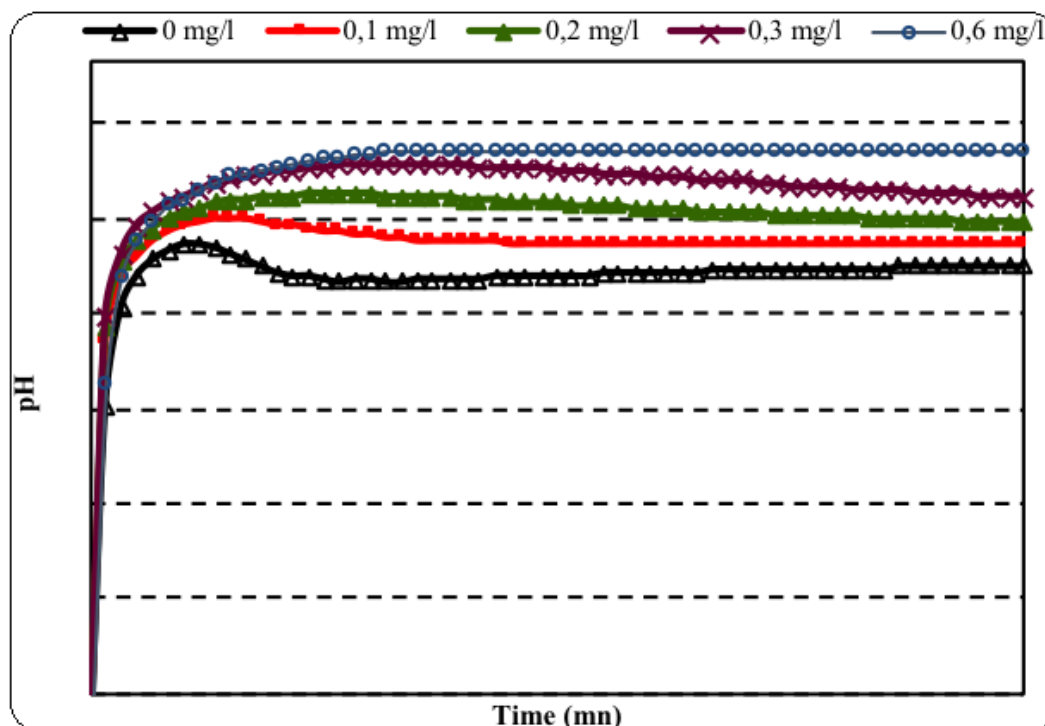
Application for pure water at 40 °F

Figure 8. Variation of pH according to the time of the tests with inhibitor LEVAL®15
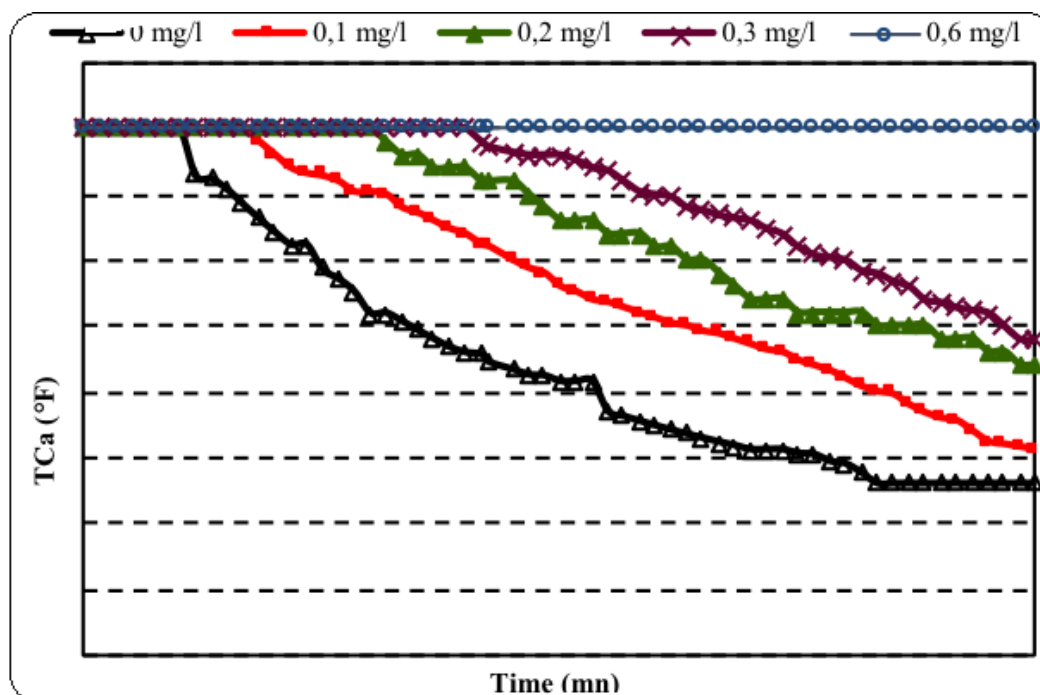

Figure 9. Variation of TCa according to the time of the tests with inhibitor LEVAL® 15

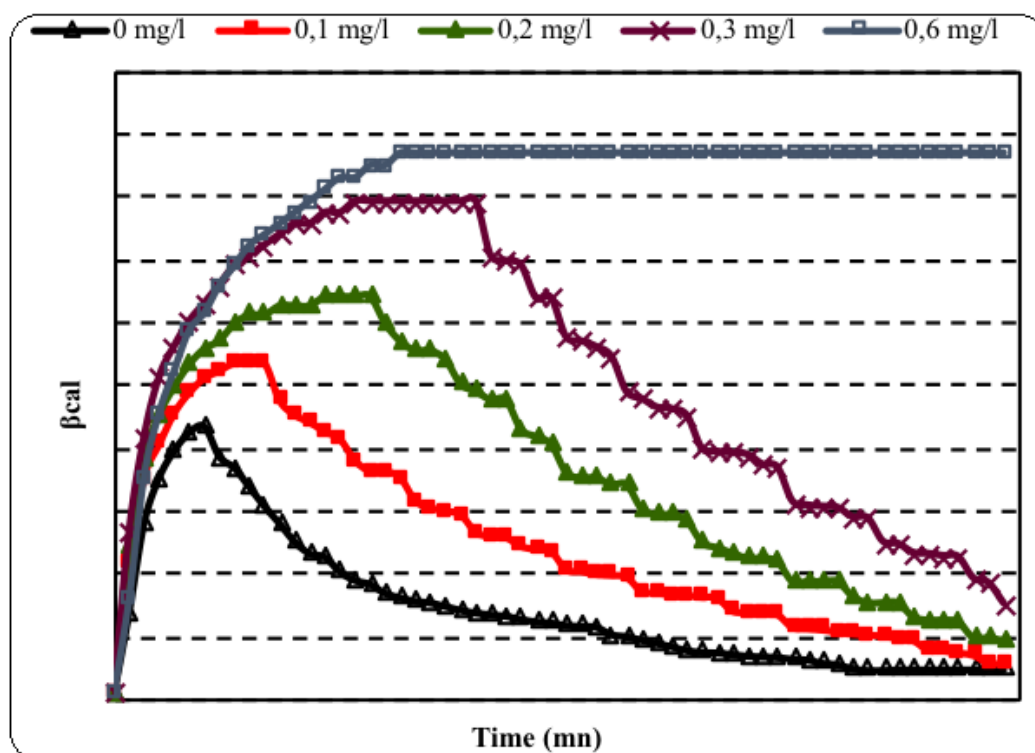**Figure 10.** Variation of the rate of supersaturation βcal according to the time of the tests with inhibitor LEVAL®15.

The analysis of these curves and the kinetic modelling lead to the values presented in Table 4.

Table 4. Germination time (T_g), pH of germination (pH_g) supersaturation coefficient overlooked to the calcite ($β_{calcite}$) and precipitation speed of calco-carbonic solution at 40˚F added increasing quantities of a food product phosphate based.

Concentration (mg/L)	Time of germination (mn)	pH_g	$β_{calcite}$	Diffusional calcite		Reddy calcite	
				K_D (mn^{-1})	R²	K_R (˚F^{-1}·mn^{-1})	R²
0	16	8,42	77,65	1,53E-02	0,994	6,58E-04	0,983
0,1	22	8,5	107,23	9,64E-03	0,978	3,45E-04	0,990
0,2	36	8,58	120,32	8,31E-03	0,959	2,88E-04	0,976
0,3	50	8,67	158,6	1,49E-02	0,957	2,30E-04	0,989
0,6	-	-	-	-	-	-	-

The analysis of these results proved the following observations:

- The germination time increases with the concentration of the scaling inhibitor. From concentrations that are more than or equal to 0.6 mg/L (effective concentration), the inhibition becomes total, and precipitation is not observed during the test.

- The pH at the germination point increases with inhibitor concentration from 8.42 for 0 mg/L to 8.67 for 0.3 mg/L. The fall in pH is evident for the test without inhibitor, whereas for increasing concentrations this fall becomes less remarkable. A stage is obtained before precipitation, which proves that the duration of the germination phase exceeds that of degassing.

- The precipitation follows a diffusion model for the test without inhibitor. It is modelled by the Reddy model for tests with the inhibitor.

The experimental results (Fig. 8 to 10) obtained make it possible to conclude that the germination time in the case of the calco-carbonic solution at 40 °F is 16 minutes without inhibitor. The addition of 0.6 mg/L of "LEVAL®15" to the solution prevents the precipitation of calcium carbonate under the conditions of the experiment, i.e. total inhibition of scaling.

The mechanism suggested for this inhibition is the adsorption of pyrophosphate (P_2O_7)$^{4-}$ on the calcite surface, which blocks the active crystal growth sites.

The inhibition of calcite crystal growth by pyrophosphate can be explained by blockage of

surface crystal growth sites by adsorbed pyrophosphate ions. The adsorption of pyrophosphate can be described by a simple Langmuir adsorption model [31], giving rise to preventing any precipitation of calcium carbonate under the conditions of the experiment.

Application to water of irrigation

This study was conducted using the LCGE technique at a temperature of 25 °C. Fig. 11 to 13 show the LCGE curves for irrigation water after adding increasing amounts of the phosphate-based food inhibitor
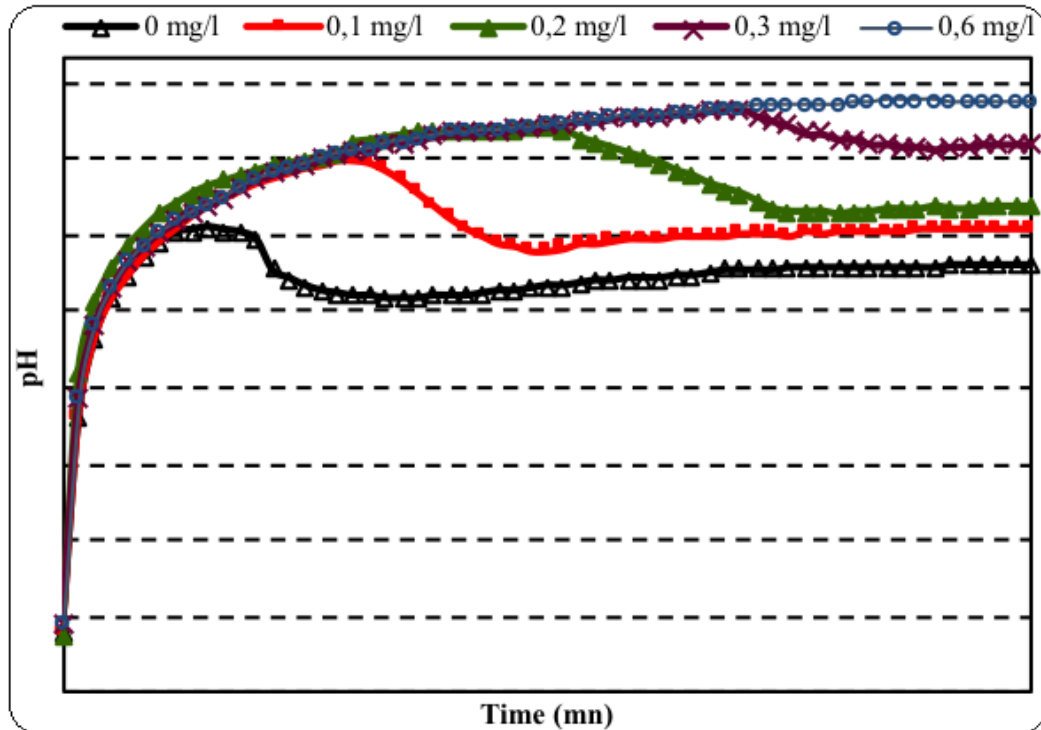

Figure 11. Curves pH according to the time of the tests with irrigation water added with the increasing concentrations in food product phosphate based.
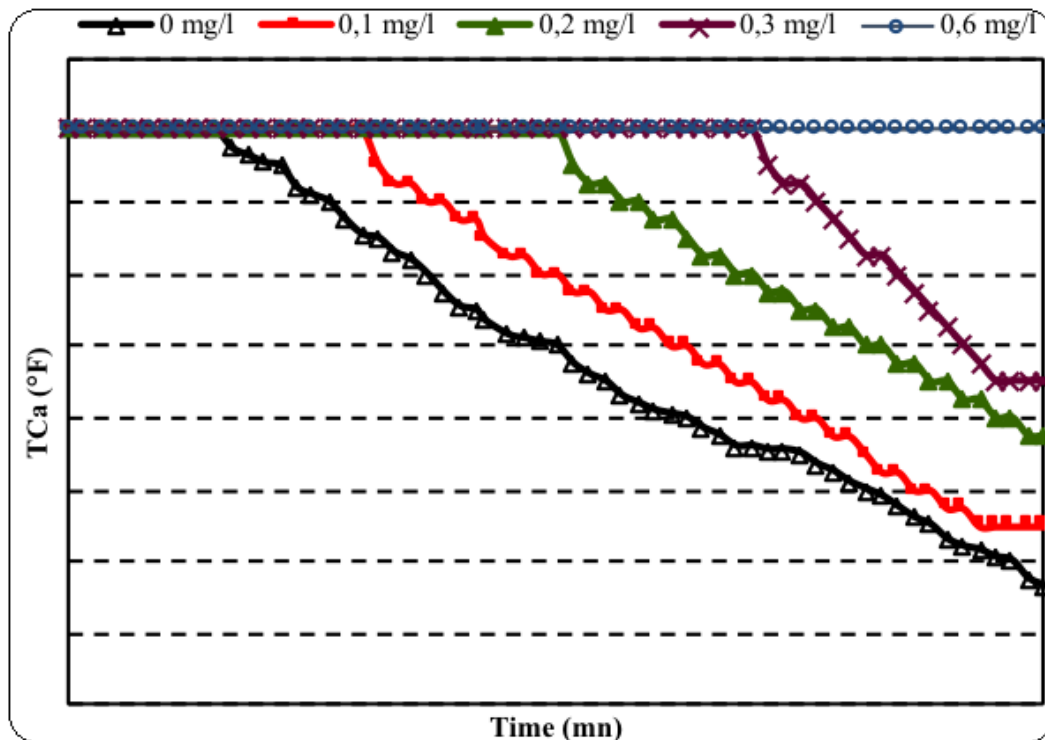

Figure 12. TH curves according to the time of the tests with irrigation water added with the increasing concentrations in food product phosphate based.
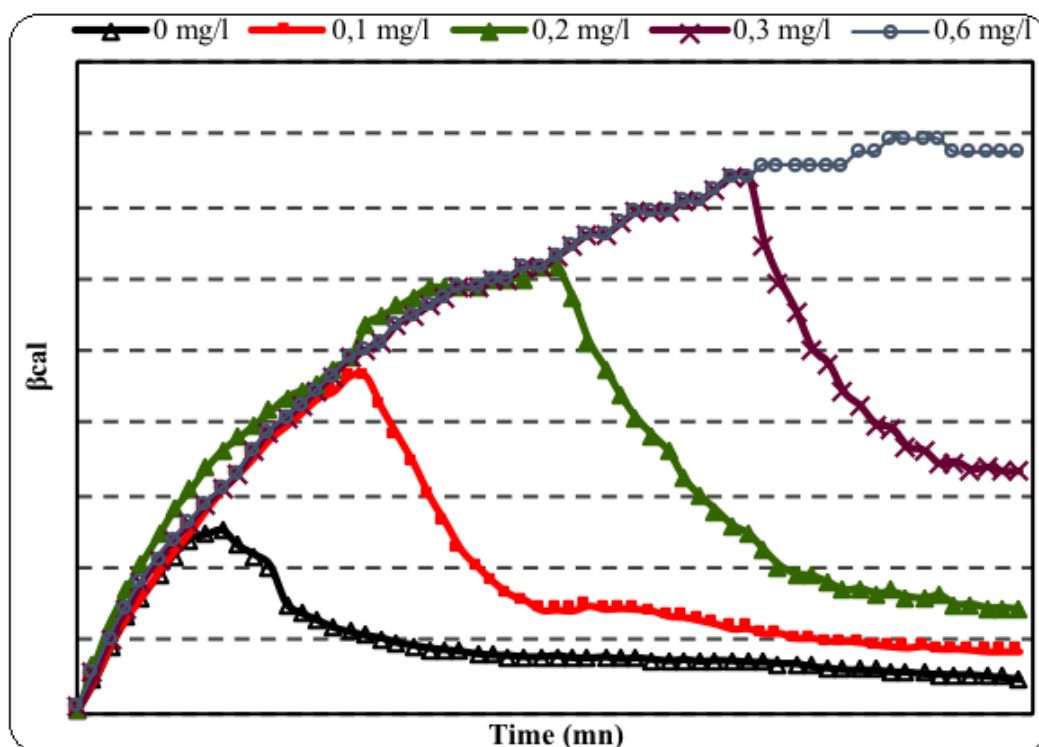
Figure 13. Variation of the coefficient of supersaturation according to the time of the tests with irrigation water added with the increasing concentrations in food product phosphate based
The analysis of these curves and the kinetic modelling lead to the values presented in Table 5.

Table 5. Germination time (T_g), pH of germination (pH_g) supersaturation coefficient overlooked to the calcite ($\beta_{calcite}$) and precipitation speed of irrigation water added increasing quantities of a food product phosphate based.

Concentration (mg/L)	Time of germination (mn)	pH_g	$\beta_{calcite}$	Diffusional calcite		Reddy calcite	
				K_D (mn^{-1})	R^2	K_R (°F^{-1}·mn^{-1})	R^2
0	20	8,83	250,64	1,53E-02	0,993	6,56E-04	0,983
0,1	38	9,1	466,71	9,63E-03	0,977	3,45E-04	0,989
0,2	62	9,22	615,24	8,32E-03	0,958	2,88E-04	0,975
0,3	86	9,3	739,69	7,11E-03	0,972	2,40E-04	0,982
0,6	-	-	-	-	-	-	-

Indeed, we notice that in the presence of the inhibitor, the precipitation curves of calcium carbonate change:

- The germination time is increased compared to the control test. The precipitation of calcium carbonate is completely inhibited at a concentration of 0.6 mg/L, under the conditions of the experiment.

- The pH at the germination point of treated water increases with inhibitor concentrations from 8.83 per 0 mg/L to 9.3 per 0.3 mg/L. The fall in pH appears clearly in the test without the inhibitor, while when concentrations increase, the fall becomes less noticeable.

- The precipitation follows a diffusion model for the test without inhibitor. It is modelled by the Reddy model for tests with the inhibitor.

Conclusion

In this study, we have analyzed the physico-chemical parameters of Biougra circle waters. The classification of these waters according to Piper revealed that the analyzed waters are characterized by calcium and magnesium bicarbonate facies with a slight tendency of migration towards calcium and magnesium chloride and sulfate facies. Thus, the chemical composition of water from the natural environment depends on the geological nature of the soil from which it comes and the reactive substances it encountered during its flow.

We also identified the scale collected in the irrigation water pipes of Biougra circle. Qualitative and quantitative, X-ray diffraction and thermal analyses have shown that the scale is mainly formed of calcium carbonate of calcite variety.

The chemical inhibition of calcium carbonate precipitation can be considered as the most evident method to prevent scaling observed in the agricultural sector in Biougra region. Pure calco-carbonic water at 40 °F and irrigation water whose hardness is around 40 °F were used to test the inhibitory efficacy of a food inhibitor: LEVALL®15, using the LCGE technique.

The experimental results gained show that in the case of the 40 °F calco-carbonic solution, a concentration of 0.6 mg/L in "LEVALL®15" totally prevents the precipitation of calcium carbonate.

The application of this inhibitor to irrigation water has also shown that a concentration of 0.6 mg/L totally prevents precipitation of calcium carbonate under the conditions of the experiment.

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