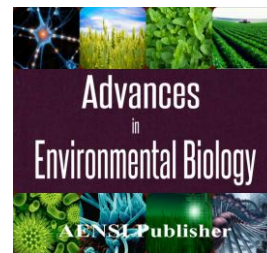




AENSI Journals

Advances in Environmental Biology

ISSN-1995-0756 EISSN-1998-1066

Journal home page: <http://www.aensiweb.com/AEB/>

Controlling the Corrosiveness of Fernana Plant's Water (Tunisia) Using a New Treatment Estimation Method

Mohamed Ali Ben Farh and Béchir Hamrouni

UR Dessalement et Traitement des Eaux, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Manar 2 Tunis, Tunisia

ARTICLE INFO

Article history:

Received 4 September 2014

Received in revised form 24 November 2014

Accepted 8 December 2014

Available online 16 December 2014

Keywords:

Drinking water; calcite; monohydrated form of calcium carbonate; treatment assessment; water corrosiveness.

ABSTRACT

Corrosion threatens water quality and can cause damages in pipelines and equipments. The drinking water produced by Fernana's plant, situated in the North Western region of Tunisia, started to be remarkably corrosive in the year 2011. In this work we tried to reach two objectives: the first is choosing a suitable method allowing water tendency prediction and the second is applying a suitable treatment preventing Fernana's water from corrosiveness. The different indices of Langelier saturation index, Ryznar stability index, Larson ratio, the modified Langelier saturation index, predicted variations of pH based on a thermodynamic model were all calculated. Considering the existence of a metastable state in which ionic product activity of calcium carbonate is above the solubility product of calcite and is under the solubility product of the monohydrated form $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$, a new calco-carbonic equilibrium graphical presentation comprising the curve of calcite and that of the monohydrated calcium carbonate form as well as an experimental method based on marble test were applied to estimate water treatment. Both diagrams of $[\text{CO}_2\text{T}]$ vs. $[\text{Ca}^{2+}]$ and pH vs. $[\text{Ca}^{2+}]$ were exploited. The drawing of these diagrams needs the determination of the entire water composition. The experimental method is destined for low equipped laboratories such Fernana's lab. Fernana's water samples collected at different months between January 2011 and April 2012 were studied. The used indices didn't predict water character change but the new diagram allowed reliable estimation to water samples studied. The new graphical treatment estimation method as the applied experimental method were efficacy in determining water character and in estimating treatments making Fernana's water slightly scaling. In the diagram of $[\text{CO}_2\text{T}]$ vs. $[\text{Ca}^{2+}]$, the monohydrated equilibrium curve position was distant from calcite curve. This removed any risk of precipitation during treatment or before water distribution. The application of the treatment estimation methods proposed in this work would allow the maintenance of the supply pipe system and a safe drinking water distribution.

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To Cite This Article: Mohamed Ali Ben Farh and Béchir Hamrouni., Controlling the Corrosiveness of Fernana Plant's Water (Tunisia) Using a New Treatment Estimation Method. *Adv. Environ. Biol.*, 8(21), 386-395, 2014

INTRODUCTION

Fernana's Water:

Fernana's plant is located in the North Western region of Tunisia and is destined to distribute drinking water to a large community. Its maximum daily production is $86,400 \text{ m}^3$. It treats the water of Beni M'Tir dam remote 10 km from it and belonging to Medjerda River Basin. The Medjerda ($23,700 \text{ km}^2$) is Tunisia's principal watercourse and constitutes, totally or partially, the water supply for more than half of the Tunisian population (5.5 million inhabitants out of 10 millions) [24]. Before reaching Fernana plant mechanical operations (Screening and sieving, grit and oil removal) are carried out. Fernana's plant comprises two major parts. The first is destined to chemical treatment and decantation. It comprises a settler having a capacity of $100,000 \text{ m}^3$. The second concerns filtration. It involves 14 open sand filters having a capacity of $80,000 \text{ m}^3$ per day. The drinking water produced by this plant started to be remarkably corrosive in the year 2011. Pipes, filters, industrial and domestic equipments were attacked and public health can be consequently affected. Corrosion causes an increase in certain metals concentrations in tap water. These metals can be toxic. Corrosion can affect also disinfectants efficiency.

Corresponding Author: Mohamed Ali Ben Farh, UR Dessalement et Traitement des Eaux, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire, 2092 Manar 2 Tunis, Tunisia
Tel./Fax +216 71871282; E-mail: mohamedalibenfarh@gmail.com

Calcium Carbonate Chemistry:

Water corrosiveness is defined by water tendency to attack metallic or concrete surfaces. The phenomena controlling both of types of corrosiveness are different. However, studies dealing with drinking water distribution associate corrosion to a deviation of the water character from calco-carbonic equilibrium. Equilibrated water does not dissolve pipeline walls or deposit scale.

Calcium carbonate is the main salt forming scale in natural water. Moreover, pipes transporting drinking water are generally protected by a thin inner coating of calcium carbonate. Once this protective layer is deteriorated water could attack concrete walls. According to Melidis et al. [19] water should be maintained slightly scaling to assure the existence of a protective layer. However, during long periods of slightly scaling water distribution, pipes would be clogged.

The calco-carbonic system involves species distributed on three phases: the carbon dioxide CO_2 of the air in contact with the liquid phase, CO_2 , H_2CO_3 , HCO_3^- , CO_3^{2-} , H^+ , OH^- , Ca^{2+} dissolved in water and the solid phase of calcium carbonate CaCO_3 . The calco-carbonic system can be described by the parameters: calcium concentration $[\text{Ca}^{2+}]$, bicarbonate concentration $[\text{HCO}_3^-]$, carbonate concentration $[\text{CO}_3^{2-}]$, pH value or the concentration of H^+ ions $[\text{H}^+]$ or the OH^- ions concentration $[\text{OH}^-]$, total carbon dioxide ($[\text{CO}_{2T}] = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$) and the total alkalinity TA. The formation or the dissolution of calcium carbonate depends on the concentrations of species existing in water, the temperature and the ionic strength.

Scale formation depends on complex phenomena involving crystallization and transport mechanisms. Precipitation becomes thermodynamically possible when the ionic activity product is above the calcium carbonate solubility product. In supersaturated water, scaling occurs by two crystallization pathways, surface crystallization accompanied with heterogeneous nucleation and bulk crystallization associated to homogeneous nucleation [3]. Supersaturation is necessary but is not sufficient to scaling occurring. It is shown by several studies that precipitation depends on certain allotropic forms of calcium carbonate. Elfil and Roques [7] demonstrate the existence of a metastable state in which ionic product activity of calcium carbonate is above the solubility product of calcite and is under the solubility product of the monohydrated form $\text{CaCO}_3 \cdot 2\text{H}_2\text{O}$. Spontaneous germination occurs only beyond the solubility product of the monohydrated calcium carbonate. When the ionic activity product of calcium carbonate stabilizes between solubility products of monohydrated and amorphous forms, the germination depends highly on the wall nature [7]. The monohydrated form crystallizes in a hexagonal system under spheroid shapes [14]. Without scale inhibitors, metastable phases usually transform into stable phase [25]. The instability of the calcium carbonate hydrated forms leads to their decomposition into more stable and more dehydrated forms [8]. Ihli et al. [12] give a detailed description of the mechanisms by which hydrated and amorphous intermediates transform into crystalline materials.

Methods Applied for Prevention from Corrosion and Scaling:

Calco-carbonic system has been studied with a large number of methods and tools aiming to give reliable approaches preventing from corrosion and scaling. The marble test is the most aptly manner to determine the water tendency towards calcium carbonate; however, it takes 48 hours to be realized and it is not then practical when immediate water treatment has to be done. Different indices and graphical methods exist and work is still continuing to improve the existing tools. The simplest saturation index is the ratio of the ionic activities product and the thermodynamic solubility constant of calcium carbonate. The indices which are generally used to assess water character are the Langelier Saturation Index (LSI), the Ryznar Stability Index (RSI) and the Stability Index of Stiff and Davis (S&DSI) which are based on simple assessments of the saturation pH. The calcium carbonate precipitation potential (CCPP) needs computer programming since its calculation is complicated [1]. These indices still have much interest in industry and in new researches dealing with calco-carbonic equilibrium [1,2,11,19]. The Monohydrated form of the Langelier Saturation Index (MLSI) is relatively a new index [6]. Elfil and Hannachi consider the monohydrated form of calcium carbonate instead of calcite and they replaced the total dissolved salt TDS expressed in LSI by the activity coefficients of calcium and carbonate ions.

Graphical methods are also used like the Hallopeau Dubin as well the Legrand and Poirier diagrams [21]. The graphical method of Legrand and Poirier L&P [16] has the advantage of determining graphically both the water character and panopoly of the necessary calco-carbonic treatments. Despite its advantages, the L&P method didn't take a large interest in the published works dealing with the scaling and the aggressiveness phenomena. This could be due to the large number of variables needed to draw the diagram.

Plottu-Pecheux et al. [20], based on the Hallopeau-Dubin model, proposed an automatic method allowing the control of the corrosiveness of blended waters. Hamrouni and Dhahbi gave in 2002 an improved and refined computerized representation of Legrand and Poirier by taking into account the ion pair formation, temperature effect and by performing adequate activity coefficient calculations [10]. Elfil and Hannachi established in 2006, based on the thermodynamic data of the calcium carbonate monohydrate form, a novel scaling index form of the Langelier Scaling Index [6]. Imran et al. proposed in 2005 a modified form of the Larson Ratio. This modified form takes into account the effects of temperature and hydraulic retention time [13]. Sheikholeslami [22] studied composite scales formation using the theoretical Scaling Potential Index (SPI). Ben Farh et al. [4] extended the

ionic strength range application of Legrand and Poirier model and proved experimentally the efficiency of the enhanced model in predicting water character and in assessing treatments bringing corrosive waters to equilibrium. De Moel et al. [5], considering a new German standard for calcium carbonate saturation in drinking water, calculated saturation indices using the PHREEQC chemical database. The lack of accuracy led them to conclude that there is a need to international unification of the standard for calcium carbonate saturation in drinking water.

Aims of the Study:

Aiming at concluding about the most suitable method to predict Fernana's water character, we applied Langelier saturation index LSI, Larson ration LR, Ryznar stability index RSI, the modified Langelier saturation index MLSI. Besides, both diagrams of $[\text{CO}_{2\text{T}}]$ vs. $[\text{Ca}^{2+}]$ and pH vs. $[\text{Ca}^{2+}]$ proposed in this study were exploited to estimate the pH of saturation regarding calcite and regarding the monohydrated form of calcium carbonate. Further, intending to estimate a suitable treatment allowing water to be slightly scaling, we applied a new method based on the proposed diagram of $[\text{CO}_{2\text{T}}]$ vs. $[\text{Ca}^{2+}]$ and also an experimental method that we call rapid marble tests method. Since treatments applied in this work aim to give water the tendency of forming a thin protective layer, we use the equilibrium curve of the monohydrated form of calcium carbonate to insure that spontaneous precipitation is avoided after treatment. The rapid marble tests method is proposed as an alternative solution for low equipped laboratories such as Fernana's. Since the protective layer is formed from calcium carbonate, aggressiveness and scaling were defined regarding this salt. As Fernana's water is aggressive, the treatment applied aimed at bringing the water to be slightly calcium carbonate forming.

MATERIALS AND METHODS

Water Sampling and Analysis:

Water samples were collected from the reservoir just before Fernana's plant outlet. pH was measured at the sampling point. The total alkalinity is determined by a titration with a solution of hydrochloric acid (0.02 mol L^{-1}) until reaching the pH value of 4.30. The TDS (total dissolved salts) is estimated from the conductivity by the method of Richard and Van Cu [21]. Calcium, magnesium, potassium, sodium, chlorides, sulfates and nitrates were analyzed by ion chromatography. The concentration of fluoride was determined with an ion-specific electrode. Iron and zinc were determined by atomic absorption spectroscopy. Analysis of the water produced by Fernana's plant was carried out under the periodic quality control held by the National Water Distribution Utility of Tunisia (abbreviated and known as SONEDE). Samples were artificially reconstructed in laboratory and then treated. After determining an appropriate chemicals composition, pure salts were dissolved in deionized water. pH was adjusted with an aqueous solution of hydrochloric acid (HCl 3.7% of weight).

Prediction of Water Tendency:

The marble test is the most aptly manner to determine the water tendency towards calcium carbonate. Marble test was carried out at the sampling point. The pH and the total alkalinity TA, obtained after 24 hours of calcium carbonate contact to water, are compared respectively to the pH and TA determined at sampling point. ΔpH and ΔTA are hence calculated (ΔpH and $\Delta\text{TA} > 0$: water is corrosive, ΔpH and $\Delta\text{TA} < 0$: water is scaling, ΔpH and $\Delta\text{TA} = 0$: water is in equilibrium). For each water sample, we calculated the percentage of alkalinity variation $\% \Delta\text{TA}$ ($= \Delta\text{TA} \times 100 / \text{TA}_{\text{saturation}}$).

The equations used to calculate Langelier saturation index and Ryznar saturation index are given:

$$\text{LSI} = \text{pH} - \text{pH}_s \quad (1)$$

$$\text{RSI} = 2\text{pH}_s - \text{pH} \quad (2)$$

The saturation pH is calculated according to the following equation (Kucera, 2010):

$$\text{pH}_s = (9.30 + A + B) - (C + D) \quad (3)$$

$$A = \frac{(\log_{10} \text{TDS} - 1)}{10} \quad (4)$$

$$B = -13.2 \times \log_{10}(\theta + 273.15) + 34.55 \quad (5)$$

$$C = \log_{10} [\text{Ca}^{2+}] - 0.4 \quad (6)$$

$$D = \log_{10} \text{TA} \quad (7)$$

TDS is in mg L^{-1} , θ is temperature in $^{\circ}\text{C}$, $[\text{Ca}^{2+}]$ is in ppm CaCO_3 and TA is in ppm CaCO_3 .

LSI < 0 means corrosiveness. LSI > 0 signifies scaling. RSI > 8.7 indicates that the water is very corrosive. $5.8 < \text{RSI} < 6.9$ means water is equilibrated and RSI < 5.8 indicates scaling.

The modified Langelier saturation index MLSI is calculated by using the following equation [6]:

$$\text{MLSI} = \text{pH} - \text{pH}_{s/\text{Monohydrate}} \quad (8)$$

$$pH_{s/\text{Monohydrate}} = pK_2 - pK_{s/\text{Monohydrate}} - \log \gamma_{\text{HCO}_3^-} - \log \gamma_{\text{Ca}^{2+}} - \log [\text{Ca}^{2+}] - \log \text{TA} \quad (9)$$

K_s is the solubility constant for CaCO_3 and K_2 is the acidity constant for dissociation of bicarbonate.

Water is very scaling if $\text{MLSI} > \Delta pK_s = pK_{s/\text{Monohydrate}} - pK_{s/\text{Amorphe}}$. Water is scaling if $0 < \text{MLSI} < \Delta pK_s$. Water is in calco-carbonic equilibrium: $\text{MLSI} < 0$ and $\text{LSI} > 0$. Water is aggressive if $\text{MLSI} < \Delta pK_s$ or $\text{LSI} < 0$.

$$pK_{s/\text{Monohydrate}} = 7.05 + 0.00159 \times \theta^2 \quad (10)$$

$$pK_{s/\text{Amorphe}} = 6.1987 + 0.0053369 \times \theta + 0.0001096 \times \theta^2 \quad (11)$$

Larson ratio LR should be low. High Larson ratio indicates water aggressiveness regarding iron.

$$\text{LR} = \frac{[\text{Cl}^-] + 2 \times [\text{SO}_4^{2-}]}{[\text{HCO}_3^-]} \quad (12)$$

Using the model elaborated by Ben Farh et al. [4] (considering the ionic concentrations, the formation of ionic associations, the ionic strength, the temperature and the total inorganic carbon concentration and calculating the activity coefficients based on the generalized model of Debye-Hückel), two diagrams were drawn for each water sample (Figure 1). The first gives the variation of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$ and the second presents the variation of pH vs. $[\text{Ca}^{2+}]$. Each diagram comprises two equilibrium curves; the first curve corresponds to calcite and the second corresponds to the monohydrate form of calcium carbonate. Using these two diagrams, saturation pH values were predicted regarding both allotropic forms. We started by drawing the line of slope one passing through the figurative point of the water sample. As the reaction of calcium carbonate dissolution consumes one mole of CaCO_3 to give one mole for both $[\text{CO}_{2T}]$ and $[\text{Ca}^{2+}]$, during this reaction the water figurative point follows the line of slope one to reach the equilibrium curves of calcite and of the monohydrated form of calcium carbonate. The saturation points S_{Calcite} and $S_{\text{Monohydrate}}$ are the intersections of the equilibrium curves of the diagram of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$ with the drawn line of the slope 1. The x-coordinate of each saturation point is then figured out. Using the diagram of pH vs. $[\text{Ca}^{2+}]$, y-coordinate of the equilibrium points associated to the saturation points are determined. The y-coordinates find out correspond to $pH_{s/\text{Calcite}}$ and $pH_{s/\text{Monohydrate}}$. $\Delta pH_{\text{predicted}/\text{Calcite}}$ and $\Delta pH_{\text{predicted}/\text{Monohydrate}}$ are then calculated.

$$\Delta pH_{\text{predicted}/\text{Calcite}} = pH_{s/\text{Calcite}} - pH_0 \quad (13)$$

$$\Delta pH_{\text{predicted}/\text{Monohydrate}} = pH_{s/\text{Monohydrate}} - pH_0 \quad (14)$$

On the other hand, using the diagram of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$ the horizontal distances between the figurative water sample point and the equilibrium curves are graphically determined. $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$ and $\Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}$ are then obtained.

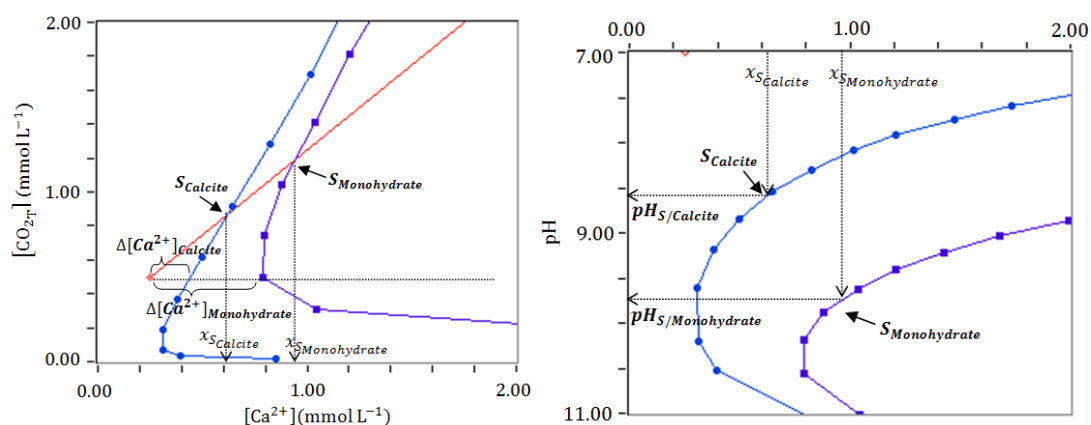


Fig. 1: New diagrams of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$ and of pH vs. $[\text{Ca}^{2+}]$ and graphical determination of $pH_{s/\text{Calcite}}$, $pH_{s/\text{Monohydrate}}$, $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$ and $\Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}$ (♦: water figurative point, ●: calcite equilibrium point and ■: monohydrate equilibrium point).

*Treatment Estimation:**Treatment estimation method based on the new diagram of $[CO_{2T}]$ vs. $[Ca^{2+}]$.*

The variation of calcium concentration, the total carbonic dioxide concentration or any other ionic concentration yields to a displacement of either water sample point or the equilibrium curve on the diagram of $[CO_{2T}]$ vs. $[Ca^{2+}]$. Based on these possible displacements, it is possible to determinate the necessary variations of ions concentrations allowing reaching water calco-carbonic equilibrium (water sample point merged to the equilibrium curve). On the diagram two equilibrium curves are considered. The amount of the reagent allowing bringing water into equilibrium is determined regarding calcite equilibrium curve. The second curve of the monohydrated form presents the threshold of calcium carbonate spontaneous precipitation.

Lime is chosen as reagent and it was added to water samples as saturated aqueous solution of calcium hydroxide $Ca(OH)_2$. The amount of calcium hydroxide necessary to bring water into equilibrium is equivalent to the amount of calcium necessary to merge the water sample point with the equilibrium curve. The aim of the treatment, proposed in this work, was to make water slightly scaling intending to give water the character of forming protective layer inside pipes. Firstly we calculated the necessary amount of calcium ($\Delta[Ca^{2+}]_{Calcite}$) to bring the water sample point into calcite equilibrium curve. Then we summed $\Delta[Ca^{2+}]_{Calcite}$ and the calcium concentration of the water sample $[Ca^{2+}]$. To this sum we added its 2%. We obtained hence the amounts of calcium added in the treatment. The equivalent amount of lime is then calculated and added to water as a saturated aqueous solution. The choice of lime solution aimed at avoiding a possible precipitation induced by lime powder adding. During preliminary experiments, precipitation generally occurred when lime was added as powder. It is important to note that the figurative point must not in any case exceed the equilibrium curve of the monohydrated form. The new proposed graphical treatment estimation method is not hence destined for waters with very close metastability domain.

Treatment estimation based on the rapid marble tests method:

The principle of the rapid marble tests method, proposed in this study, is based on the stability of the total alkalinity TA for equilibrated water during the 48 hours of a marble test. During just two hours from a marble test starting, the calco-carbonic characteristics of equilibrated water remain stable. The method applied is described by the following steps:

- Three volumes of 500 mL were sampled from the studied water and then treated with different doses of calcium hydroxide $Ca(OH)_2$. Calcium hydroxide was applied as an aqueous saturated solution.
- pH was measured (pH_i) and total alkalinity (TA_i) was determined for each treated water,
- To conic flasks of 250 mL pure marble powder was added. Treated water samples were then poured in until the overfilled of the flask. A magnetic bar was put in each flask. Flasks were covered thoroughly to avoid air presence.
- During 2 hours continuous shaking was carried out,
- Each water sample was then filtered using filter paper. pH of the filtrate was measured (pH_f) and total alkalinity (TA_f) was determined,
- Alkalinity variations $\Delta TA (= TA_f - TA_i)$ were calculated. At least one of the variations had to be negative meaning that the water became scaling after treatment with calcium hydroxide. Otherwise, the steps below were applied to a new treated water sample with a higher dose of calcium hydroxide than those used.
- The curve giving the linear variation of ΔTA vs. the lime dose was drawn (Figure 2). The equation relating the two variables of the curve was then figured out. The optimum dose bringing water to equilibrium corresponds to $\Delta TA=0$.

Since we aimed through the treatments to give the water a slight scaling tendency, the optimum dose of lime (corresponding to $\Delta TA=0$) was incremented identically to the manner described below for the treatment based on the new diagram.

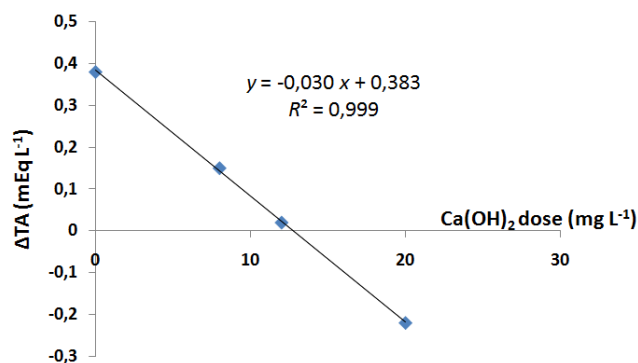


Fig. 2: Example of the variation of ΔTA vs. calcium hydroxide dose.

*Evaluation of the Treatment Efficiency:**Stability regarding calcium carbonate presence:*

The standard marble test (during 48 hours) was applied, for each treated water sample, to prove the efficiency of the treatments applied. This test is the most reliable manner to determine if the water is in calco-carbonic equilibrium or not. On the other hand, pipelines transporting the drinking water produced by Fernana's plant are generally formed of concrete. The marble test allows in this case the evaluation of the stability of the calco-carbonic variables during water distribution.

Stability regarding temperature variation:

Each Fernana's water sample was treated based on analysis realized at a definite temperature θ . The treatment estimated is hence destined to be applied at a fixed temperature. However, in practice, temperature varies during water transportation and consequently water character can change as a reply to this variation. It was then required to check water character response at the limit temperatures reached during water distribution. Marble test was therefore applied for the treated water samples at $\theta + 5^\circ\text{C}$ and at $\theta - 5^\circ\text{C}$. Temperature was fixed with a temperature-controlled bath.

*Results:**Fernana's Water Characteristics:*

Water samples had been collected and analysed between January 2011 and April 2012. The sampling point is the tank of the water destined to distribution. Table 1 shows the obtained analysis results. Depending on season change, water temperature varied between 16 and 25°C . Fernana's water composition depends on the properties of Beni Mtir's dam water and from the treatments applied before distribution within Fernana's plant. Concentrations of Fernana's water species maintained in general the same magnitude during the study. Total dissolved salts TDS varied randomly between 130 and 245 mg L^{-1} . Calcium, pH and the total alkalinity varied respectively between 7.80 and 31.00 mg L^{-1} , 6.60 and 7.64 and 0.31 and 0.82 mEq L^{-1} . Iron, zinc and ions concentrations (Table 1) determined were under limit concentrations fixed by Tunisian standards for drinking water (NT09.14).

Table 1: Fernana's water characteristics (January 2011-April 2012)

Date		25/01/11	31/05/11	28/06/11	26/07/11	23/08/11	29/11/11	30/01/12	16/04/12
θ	$^\circ\text{C}$	16	24	24	24	25	19	19	20
pH		7.29	7.50	7.54	6.81	6.60	7.64	7.38	7.52
Ca^{2+}	mg/L	31.00	29.00	28.00	21.00	22.00	26.00	7.80	10.12
Mg^{2+}		7.00	7.00	6.00	5.00	6.00	6.00	6.00	5.21
Na^+		10.60	8.12	14.96	15.01	40.10	22.20	48.30	41.53
K^+		2.11	1.54	1.66	1.48	1.73	1.72	1.32	1.66
Cl^-		24.00	21.00	24.00	21.00	20.00	21.00	23.00	24.26
SO_4^{2-}		42.00	55.00	49.00	53.00	115.00	66.00	67.00	71.84
NO_3^-		18.90	7.80	8.30	9.20	5.50	6.80	14.50	7.46
F		0.15	0.25	0.36	0.38	0.35	0.36	0.25	0.31
TDS		235	130	170	230	194	245	200	202
Fe		0.09	0.08						0.11
Zn	0.57	0.32						0.63	
TA	mEq/L	0.82	0.57	0.77	0.31	0.41	0.57	0.75	0.59

Prediction of Water Tendency:

Results of water character prediction are assembled in Table 2. Marble tests results show that Fernana's water tendency was variable. Water character is deduced on the basis of the percentage of alkalinity variation during marble tests ($\%\Delta\text{TA}$). In 31/05/2011 water was in calco-carbonic equilibrium ($\%\Delta\text{TA}=0.0\%$). Water samples collected in June and November 2011 were practically in equilibrium (respectively $\%\Delta\text{TA}= -2.6$ and $+1.7\%$). Water sample of 28/06/11 was slightly scaling. The four samples of 25/01/11, 26/07/11, 23/08/11, 30/01/12 and 16/04/12 were corrosive based on $\%\Delta\text{TA}$ which varied between $+6.1$ and 10.2% . It should be noted that only 8 sampling were realized during 16 months and hence the realized analysis does not give the whole variation of water character during this period. However the corrosive tendency evaluated with marble test for water sampled in 2012 are in accordance with our observations showing the deterioration of pipelines and equipments.

The results obtained with marble tests were generally in accordance with $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$ variation. $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$ varied between 0.00 and $+0.04\text{ mmol L}^{-1}$. The diagram of $[\text{CO}_2\text{T}]$ vs. $[\text{Ca}^{2+}]$ gives only the position of the water figurative point relative to the equilibrium curve to predict water's tendency. The stability of the equilibrated or practically equilibrated water samples of 31/05/11, 28/06/11 and 29/11/11 were expected focusing on the nil value of $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$. The new diagram allowed also to predict the corrosive character of the water sampled in 25/01/11, 26/07/11, 23/08/11, 30/01/12 and 16/04/12 since $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$ varied between $+0.01$ and 0.04 mmol L^{-1} for these samples.

Table 2: Saturation index and parameters of Fernana's water samples

Date	LR	LSI	$\Delta\text{pH}_{\text{Calcite}}$	RSI	ΔpK_s	MLSI	$\Delta\text{pH}_{\text{Mono}}$	Δ_{Calcite} (mmol L ⁻¹)	Δ_{Mono} (mmol L ⁻¹)	ΔTA (mEq L ⁻¹)	% ΔTA
25/01/11	1.89	-1.30	-1.24	9.89	1.16	-2.74	-2.49	+0.02	+0.21	+0.05	+6.1%
31/05/11	3.05	-1.11	-1.19	9.72	1.55	-2.65	-2.35	0.00	+0.26	0.00	0.0%
28/06/11	2.21	-0.96	-1.05	9.47	1.56	-2.51	-2.27	0.00	+0.20	-0.02	-2.6%
26/07/11	5.47	-2.22	-2.22	11.26	1.58	-3.72	-3.27	+0.02	+0.68	+0.02	+6.4%
23/08/11	7.22	-2.26	-2.40	11.12	1.67	-3.82	-3.43	+0.01	+0.53	+0.03	+7.3%
29/11/11	3.69	-1.13	-1.16	9.90	1.29	-2.60	-2.31	0.00	+0.27	+0.01	+1.7%
30/01/12	2.72	-1.80	-1.73	10.98	1.26	-3.26	-2.64	+0.04	+0.42	+0.06	+8.0%
16/04/12	3.69	-1.62	-1.58	10.77	1.34	-3.10	-2.55	+0.03	+0.44	+0.06	+10.2%

$$\Delta_{\text{Calcite}} = \Delta[\text{Ca}^{2+}]_{\text{Calcite}}, \Delta_{\text{Mono}} = \Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}, \Delta\text{pH}_{\text{Calcite}} = \Delta\text{pH}_{\text{predicted/Calcite}}, \Delta\text{pH}_{\text{Mono}} = \Delta\text{pH}_{\text{predicted/Monohydrate}}$$

Despite the application of the same thermodynamic model of Ben Farh et al. to predict $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$, $\Delta\text{pH}_{\text{predicted/Calcite}}$ and $\Delta\text{pH}_{\text{predicted/Monohydrate}}$ estimated pH variation indicated a permanent corrosive water character and didn't predict water tendency change. LSI kept a value less than -0.96 indicating corrosiveness of the studied samples. MLSI stayed below ΔpK_s and indicated also that Fernana's water was corrosive. LSI and MLSI values were remarkably similar respecting to $\Delta\text{pH}_{\text{predicted/Calcite}}$ and $\Delta\text{pH}_{\text{predicted/Monohydrate}}$. As an example, in 26/07/11, LSI and $\Delta\text{pH}_{\text{predicted/Calcite}}$ were both equal to -2.22. MLSI and $\Delta\text{pH}_{\text{predicted/Monohydrate}}$ showed less closeness. RSI was higher than 8.7 for all the water samples signifying that studied samples were very corrosive. Larson ratio LR varied between 9.47 and 11.26 indicating high metallic corrosive tendency of Fernana's water.

Treatment Optimisation:

Three synthetic water samples were treated. They had the same composition of the water samples collected in 23/08/11, 30/01/12 and 16/04/12. Lime doses added and alkalinity variations during standard marble test of the treated water samples are given in Table 3. Lime doses (Table 3) were determined on the basis of the new graphical estimation method and of the rapid marble tests method. Aiming to check that spontaneous precipitation would not occur just after treatments, $\Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}$ was determined. $\Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}$ of 23/08/11, 30/01/12 and 16/04/12 were respectively +0.53, +0.42 and +0.44 mmol L⁻¹. $\Delta[\text{Ca}^{2+}]_{\text{Monohydrate}}$ was noticeably higher than $\Delta[\text{Ca}^{2+}]_{\text{Calcite}}$. The large domain of metastability between the two equilibrium curves excludes the possibility of spontaneous precipitation occurring after a treatment making water slightly scaling regarding calcite. The lime doses of every water samples treated basing on the new graphical estimation method and basing on the rapid marble tests method were close and we found practically the same variations of total alkalinity ΔTA (-0.01 or -0.02 mEq L⁻¹). Calculated alkalinity variations were small and negative signifying that water samples treated were slightly scaling.

Treatments applied were carried out on laboratory. Considering the scale of Fernana's plant where thousands of cubic meters are treated, the small doses of 0.1 or 0.2 mg L⁻¹ (difference between the doses determined using the graphical estimation method and the rapid marble tests method) would be 100 or 200 g by 1000 m³ of treated water. The doses which are considered optimal are hence those determined using the new graphical estimation method.

Table 3: Lime doses based on the new graphical estimation method and on the rapid marble tests method and alkalinity variations of the marble tests applied to the water samples reconstructed based on samples compositions of 23/08/11, 30/01/12 and 16/04/12

Sample date	Based on the new graphical estimation method		Based on Rapid marble tests method	
	Lime dose* (mg L ⁻¹)	ΔTA (mEq L ⁻¹)	Lime dose* (mg L ⁻¹)	ΔTA (mEq L ⁻¹)
23/08/11	1.2	- 0.01	1.3	- 0.02
30/01/12	3.2	- 0.01	3.4	- 0.01
16/04/12	2.5	- 0.02	2.7	- 0.02

* Lime is added as a saturated solution of Ca(OH)₂

Effect of Temperature Variation on Treated Water:

For each treated water sample, we applied the standard marble test aiming at evaluating the effect of temperature variation on water calco-carbonic system stability (Table 4). Water samples treated associated to 23/08/11 gave a constant alkalinity variation equal to -0.01 at 20 and 30°C. For the treated water sample of 30/01/12, a negligible difference of 0.01 mEq L⁻¹ was noted between ΔTA obtained at 14 and 24°C indicating that the treated water remained not corrosive following temperature variation. Focusing on marble test the treated water sample of 30/01/12 became equilibrated at 24°C. The treated water of 16/04/12 became slightly more scaling when temperature was 25°C (ΔTA reached -0.02 mmol L⁻¹). Nevertheless treated water at this temperature doesn't present any risk to concrete pipes after water distribution if temperature changes.

Table 4: Response of ΔTA to temperature variation of water samples treated basing on the new graphical estimation method

Treated samples Date	Water	Treatment temperature (°C)	Marble test temperature (°C)	ΔTA (mEq L ⁻¹)	ΔTA at treatment temperature (mEq L ⁻¹)
23/08/11		25	20	-0.01	- 0.01
			30	-0.01	
30/01/12		19	14	-0.01	- 0.01
			24	0.00	
16/04/12		20	15	-0.01	- 0.02
			25	-0.02	

Discussion:

The aim of this work is to predict Fernana's water character and to apply a reliable treatment protecting the distribution system. Based on the marble test results, Fernana's water was generally corrosive except two samples were water was once equilibrated and in another scaling. The new diagram gives results matching with the marble test. However the indices applied (LSI, RSI, LR and MLSI) as well as the pH variations ($\Delta pH_{\text{predicted/Calcite}}$ and $\Delta pH_{\text{predicted/Monohydrate}}$) obtained by the model of Ben Farh et al. indicated permanent water corrosiveness. Similar results of accordance between LR and LSI with marble test results had been found by Melidis et al. [19]. Nevertheless, Haritash et al [11] and Alsaqqar et al. [2] applied recently the indices of LSI and RSI without checking their results with marble test or another experimental test. For many researchers, these indices continue to be references for water character prediction.

Treatments focusing on the new treatment estimation method and the method of rapid marble tests made Fernana's water slightly scaling. Both of methods were reliable. Despite its simplicity, the rapid marble tests method was efficient in estimating lime doses. However the long time spent (at least two hours for each sample) is a drawback for this method. On the other hand, the estimation method based on the new diagram (embodied in a program) gives immediate results but it requires a previous determination of the water's composition which is not affordable to low equipped laboratories. The new method was applied at temperatures ranging between 19 and 25°C. The treated water samples remained almost slightly scaling when the sample temperature θ was varied on the range of $\theta + 5^\circ\text{C}$ and $\theta - 5^\circ\text{C}$. In the series of temperature between 14 and 30°C, the treated water samples didn't present any tendency to consume the calcium carbonate inner side of concrete pipes.

As treatments leading water into scaling tendency presents a risk of precipitation and clogging during or just after treatments, we thought that it is necessary to consider the equilibrium curve of monohydrated form to assure that treated water belongs to the metastable domain. In the diagram of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$, the monohydrated equilibrium curve position was distant from calcite curve. This removed any risk of precipitation during treatment or before water distribution. For water samples presenting a narrow metastability domain, bringing water to be slightly corrosive would present a real risk to plant equipments and for water quality. The new diagram of $[\text{CO}_{2T}]$ vs. $[\text{Ca}^{2+}]$ may be a useful tool to avoid such results.

Treatments were applied on laboratory. Applying the treatment on Fernana's plant scale needs to determine how technically lime will be added. In the actual process in Fernana's plant, lime is added as powder through the coagulation/flocculation step. It is hence necessary to decide about the technical possibility of adding lime after this step or to optimise the flocculation/coagulation process treatment to make the water slightly corrosive. Further studies could answer this question. On the other hand, keeping water slightly scaling would yield to a pipes plugging after certain time. It may be more appropriate to allow, with a carefully determined period of time, corrosive water distribution with purpose of consuming a part of the protective pipelines layer. Other alternatives may be possible by considering the kinetic aspect of scaling [17,9,23].

In this study, the water corrosiveness was determined regarding the protective pipes coating of calcium carbonate. However, metallic corrosion evaluation should not be neglected since the water is used by different industrial and domestic equipments. On the other hand, microbiologic tests have also to be performed to decide about the impact of the produced water on people health [18]. A precise evaluation of metallic corrosion and microbiologic quality has to be carried out to establish a complete judgement about the quality of the drinking water produced by Fernana plant.

Conclusion:

Studied Fernana's water was generally corrosive during the period from January 2011 to April 2012. The method adopted focusing on the new diagram proposed in this study was efficacy in determining water tendency and in making water slightly corrosive by an aqueous saturated lime solution adding. Similar results were found when the called rapid marble tests method was applied. However more studies on Fernana's water are needed to conclude on how the treatment method proposed in this study could be carried out on plant scale. The different indices of LSI, RSI, LR, MLSI, the predicted variations of pH regarding calcite and monohydrated calcium carbonate didn't allow prediction of water tendency variation.

The results of this study show that a precise prediction of water character and efficient treatment estimation could not be determined using empirical indices. These indices largely applied in water treatment field are not

destined to precise applications. It is necessary to apply computed models or experimental methods. The study showed also the importance of considering the allotropic forms in a concise aims for characterization and treatment estimation. We showed also that treatment estimation based on the variation of Ca^{2+} and $\text{CO}_{2\text{T}}$ concentrations is sufficient to reach metastability. It is not necessary to estimate pH variation to accomplish the treatment. The panoply of the possible treatments based on the proposed diagram of $[\text{CO}_{2\text{T}}]$ vs. $[\text{Ca}^{2+}]$ would allow researchers and engineers to simulate a large number of experiments.

Considering the nature of the water distribution system, marble test was adopted as reference for tendency determination and for treatments evaluation. The efficiency of the indices and methods, used in this work, may differ based on pipes material. In this study, the pipes inner side is formed from calcium carbonate. In other cases where the pipe surface interacting with water is formed from other salts or materials, it would be necessary to apply other tools. The model applied to draw the used graphics could be also applied to calculate prediction tools regarding other salts.

It was more convenient to apply the thermodynamic model of Ben Farh et al. rather than to apply the rapid marble tests method. The application of a model embodied in a program, considering water composition and temperature, allowed rapid decision making about water treatment. The new diagram of $[\text{CO}_{2\text{T}}]$ vs. $[\text{Ca}^{2+}]$, resulting from this model and comprising both equilibrium curves of calcite and monohydrated calcium carbonate gives panoply of possible treatments which can be adjusted to different cases. However the determination of the whole water composition is not affordable for low equipped laboratories. Development efforts should take care of water's laboratories especially in developing countries and assure that they are sufficiently equipped to guarantee distributed water quality preserving human health and avoiding domestic and industrial equipments deterioration.

ACKNOWLEDGEMENT

Authors thank the National Water Distribution Utility of Tunisia (SONEDE) especially Mohsen Kaabi for their assistance in water sampling and analysis.

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