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Inhibition of $CaCO_3$ scale formation in ground waters using mineral phosphates

Yasmina Boulahlib-Bendaoud[a], Samira Ghizellaoui[b,*], Mohamed Tlili[c]

[a]*Département de SM, Institut des Sciences et Technologie, Université de Tébessa, Algérie*
[b]*Département de Chimie, Université de Mentouri de Constantine, Route de Ain el Bey 25000 Algérie*
Tel./Fax: 00 213 31 818816; email: gsamira@yahoo.com
[c]*Laboratoire de Traitement des Eaux Naturelles, Centre des Recherches et Technologies des Eaux, Technopôle de Borj Cedria; BP 273 Soliman 8020, Tunisie*

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ABSTRACT

The present work examines the effect of two mineral inhibitors on the $CaCO_3$ precipitation in two Algerian ground waters. The main objective was to reduce the scaling power and then to prevent the fouling phenomenon met in the equipments supplied by these waters. It was shown that, for a large rang of temperature, Hamma water is more scale-forming water than the one of Negrine because its lower content in foreign ions to the calcocarbonic system, especially magnesium. Chronoamperometry tests show that the antiscale treatment with mineral phosphates is more efficient for the Hamma than Negrine water. Tested inhibitors affect strongly the nucleation-growth kinetics in the case of Hamma water and only the scale compactness in Negrine water. This was attributed to the difference in the chemical composition of the studied waters. Besides, it was shown that polyphosphate is more efficient as scaling inhibitor than the dihydrogenophosphate ions.

Keywords: Drinking water; Hardness; Calcium carbonate; Inhibition; Mineral phosphates; Precipitation

1. Introduction

Ground waters are generally known as scale-forming waters compared to surface one. This potentiality to form scale, mainly made of calcium carbonate, is related to the displacement of the calco-carbonic equilibrium (R1) toward the precipitation by degassing of the dissolved CO_2 after contact with air. Indeed, atmospheric air is poor in CO_2 ($pCO_2 = 3.10^{-4}$ atm.) whereas ground waters are reach in this gas [1,2].

$$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3 + CO_2\uparrow + H_2O \quad R1$$

The sources of Hamma and Negrine, subject of the present work, are one of scale forming waters. The drilling of Hamma is located at the north-east of Constantine, one of the Algerian big cities, and feeds 900,000 inhabitants in drinking water. Nevertheless, the drilling of Negrine is located at the south-east of Tebessa and feeds all the area with drinking and irrigation water. The domestic, agricultural and industrial equipments supplied with these waters are meted to a serious problem of a compact and adherent deposit on the surfaces in the contact of waters [3]. As known, these deposits have very serious consequences: reduction of the heat transfer efficiency, clogging of the pipes, seizing of the stopping devices (taps, valves) as well as the health issues like the renal diseases and diseases dermatological.

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*Corresponding author.

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Several techniques are, therefore, developed to prevent scale formation by a physical [4–9] or a chemical [10,11] process. To assess the efficiency of the water treatment, methods and techniques called "accelerated scaling methods" were developed. They were also used to compare the scaling power of waters and to estimate the effect of water composition on the scale rate formation. The main among these techniques were succinctly and well presented in the paper of Hui and Lédion [12]. The effects of temperature and concentration of five scale inhibitors have been reported also in the study of [13].

The aim of this work was to characterize the scaling power of the ground waters of Hamma (HW) and Negrine (NW) and to optimize a chemical anti-scale treatment. For this, electrochemical precipitation test, chronoamperometry, was used. The tested inhibitors were dihydrogenophosphate of potassium and polyphosphate.

2. Material and methods

Precipitation tests of calcium carbonate were induced using the electrochemical accelerated scaling method [8,9]. Thus, experiments were performed in the natural waters of Hamma and Negrine using a classical three-electrode cell. The schema of the experimental arrangement is presented in Fig. 1. The working electrode is made of Steel XC10 with 1.00 cm^2 area. The electrode surface was polished with silicon carbide paper (P #400), rinsed thoroughly with pure water and carefully dried. Potential was measured versus the reference saturated calomel electrode (SCE). A platinum electrode was used as counter electrode and a potentiostat was connected to the three electrodes. Work temperature was maintained using a double glass wall recipient. Its large volume (500 ml) allowed to avoid a significant variation of species concentration during the formation of the deposit. Electrochemical experiments were driven under potentiostatic condition at –1V/SCE, corresponding to the limiting current of the reduction reaction of the dissolved oxygen. Chronoamperometric were thereafter recorded by a computer using a serial connection.

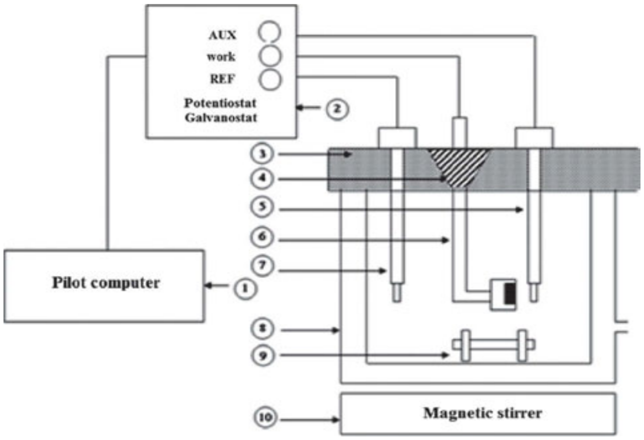

Fig. 1. Experimental arrangement (1-Pilot computer equipped with software; 2-Potentiostat-galvanostat; 3-Cover electrode holder; 4-Door plug-sample; 5-Platinum electrode; 6-Working electrode: pellet steel XC10 (11.3 mm diameter) embedded in a resin chemically inert; 7-Reference electrode saturated in KCl; 8-Cell thermostatted with a capacity of 500ml; 9-Bar magnet; 10-Magnetic stirrer).

On the metallic surface of the work electrode, cathodically polarized, the electrochemical reduction of the oxygen molecules occurs according to [2,6]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad \text{R2}$$

The hydroxyl groups, which are generated by this reaction, induce a strong increase of the pH in the immediate vicinity of the metal surface. The resulting displacement of the carbonic equilibriums following the reaction (R3) promotes the nucleation and the growth of calcium carbonate crystals onto the metal surface according (R4).

$$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O \quad \text{R3}$$

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)} \quad \text{R4}$$

The progressive occupancy of the metal surface by the insulating layer reduces the current intensity down to zero for a fully compact layer or to a small value for a porous layer. Therefore, the time variations of the current intensity (chronoamperometric method) can be used empirically as an indicator of the scaling rate [14,15]. In particular, it could be possible to detect the nucleation time corresponding to the formation of the first nuclei and to estimate the "scaling time" related to the full occupancy of the surface.

3. Results and discussion

3.1. Characterization of ground waters

3.1.1. Waters analysis

The results of physico-chemical water analysis of Hamma and Negrine are given in Table 1.

From these analyses it is difficult to predict if the HW is more or less scale forming than the one of NW. Indeed,

- HW can be more scale forming because: (i) its content in $CaCO_3$, calculated basing on (R1) and by neglecting the solubility, which was about 400 mg/l is more important than the one of NW (168 mg/l); (ii) its salinity is less important and then it reduces slightly the

Table 1
Analysis of Hamma and Negrine waters

The parameters	Water of Hamma (HW)	Water of Negrine (NW)
T, °C	32	30
pH	6.95	7.70
CE, ms/cm	0.9	3.3
HCO_3^-, mg/l	517	206
Cl^-, mg/l	170	390
Ca^{2+}, mg/l	160	326
Mg^{2+}, mg/l	46	150

calcium and the carbonate activities regarding to the case of NW.

- From pH values, NW can also be the most scale forming. Indeed, the pH, main driving force of the precipitation, influences the bicarbonate ion activity:

$$(CO_3^{2-}) = (HCO_3^-) \times 10^{pH-pk} \quad (1)$$

where k is the constant of the second carbonic acid dissociation equilibrium.

3.1.2. Scaling power

Fig. 2 shows the chronoamperometric curves plotted for Hamma and Negrine waters. It can be concluded that HW is more scale forming than the one of Negrine. Indeed, the scaling time t_E, obtained for the same residual current (I_R = 42 µA), is about 9.7 and 13.5 min for Hamma and Negrine waters, respectively. This can be explained by the inhibitory effect of the magnesium ions [16–18], three times more important in Negrine water. Also, the content in salts, with the exception of $CaCO_3$, is more important in Negrine water (Table 1) which reduce the ionic activities and then the supersaturation coefficient defined as

$$\delta = \frac{(Ca^{2+})(CO_3^{2-})}{k_{sp}} \quad (2)$$

where (i) are the ionic activities of the ions i and k_{sp} is the solubility product of calcite, most stable variety of calcium carbonate. From Eqs. (1) and (2), the carbonate and the calcium ions concentrations, the supersaturations coefficients for HW and NW were determined:

$$\delta_{HW} = 5\gamma_{Ca^{2+}} + \gamma_{HCO_3^-}$$

and

$$\delta_{HW} = 23\gamma'_{Ca^{2+}} + \gamma'_{HCO_3^-}$$

where γ_i and γ_i' are the activities coefficients of the ion i in Hamma and Negrine waters, respectively. Considering that the precipitation rate increases with δ, it can be concluded that $\delta_{HW} > \delta_{NW}$. This shows clearly the effect of the water salinity. Indeed, the activity coefficient depends of the ionic strength.

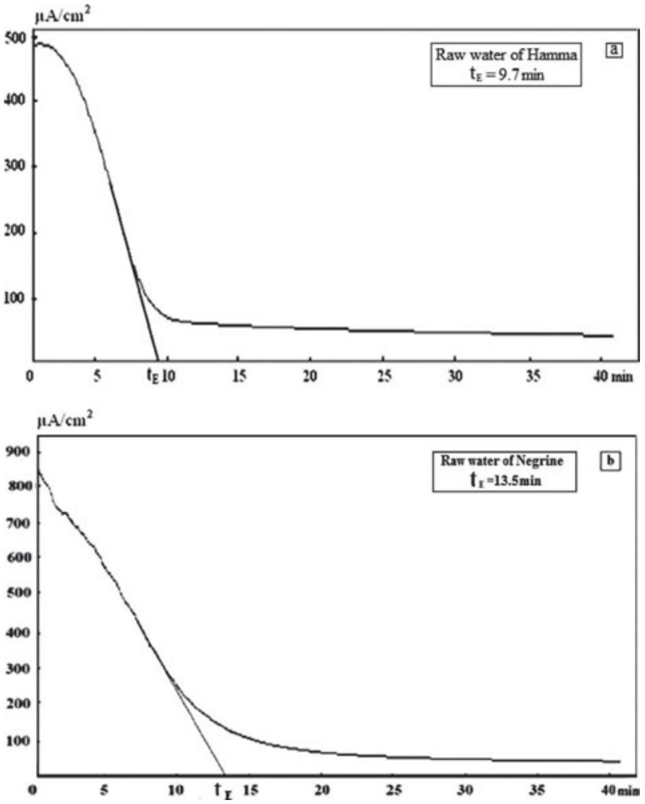

Fig. 2. Chronoamperometric curves of (a) Hamma and (b) Negrine raw waters at 30°C.

On the other hand, it is possible to classify the potentiality of waters to form scale basing on the scaling index I_E defined by [14]:

$$I_E(\text{min}^{-1}) = \frac{1000}{t_E}$$

- $100 < I_E < 1000$: extremely scale-forming water.
- $15 < I_E < 100$: very scale-forming water.
- $5 < I_E < 15$: medium scale-forming water.
- $0.5 < I_E < 5$: slightly scale-forming water.

Basing on this classification, Hamma waters is an extremely scale-forming water with $I_E = 103$ min^{-1} whereas Negrine water is a very scale-forming water ($I_E = 74$ min^{-1}).

3.2. Effect of temperature on the scaling power

The accelerated scaling tests using the water of Hamma at various temperatures (20°C, 30°C, 40°C and 50°C), gave the chronoamperometric curves of the (Fig. 3).

From the slope of the linear part of the curves, it can be concluded that the scaling rate increases with

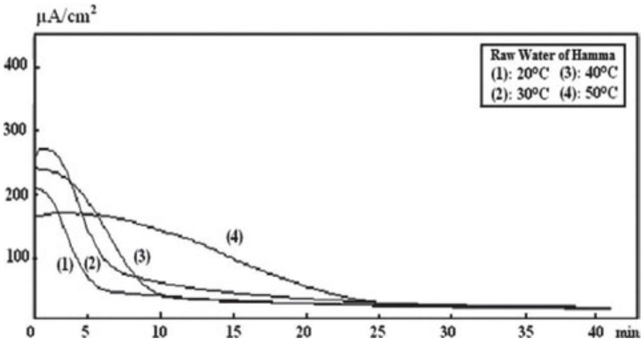

Fig. 3. Chronoamperometric curves plotted for different temperatures in the water of Hamma.

Table 2
Effect of temperature on the scaling time, residual current and the scaling index: case of the Hamma water

Work temperature (°C)	t_E (min)	I_R (μA)	I_E (min^{-1})
20	26.20	40	38
30	09.70	44	103
40	07.40	46	135
50	06.30	49	159

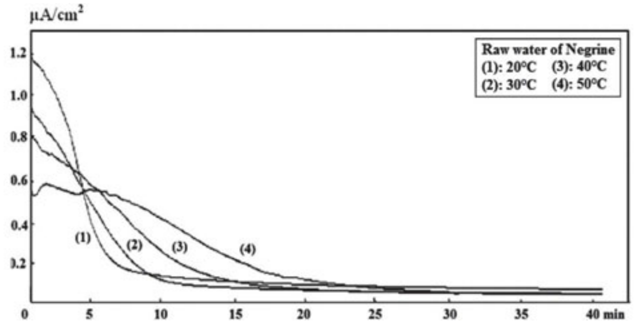

Fig. 4. Chronoamperometric curves plotted for different temperatures in the water of Negrine.

Table 3
Effect of temperature on the scaling time, residual current and the scaling index: case of the Negrine water

Work temperature (°C)	t_E (min)	I_R (μA)	I_E (min^{-1})
20	22.30	38	44
30	13.50	42	74
40	09.90	45	101
50	07.40	68	137

temperature; it results of both the increase of the oxygen reduction rate [8] and the decrease of the $CaCO_3$ solubility. For this, the scaling time decreases from 26.2 to 6.3 min when the work temperature increases from 20 to 50°C (Table 2). Here, it could be noted that the more significant effect of temperature was registered between 20°C and 30°C. Indeed, a sharply decrease of the scaling time from 26.2 to 9.7 min and increase of the scaling index from 38 to 103 min^{-1} were founded (Table 2).

As for the HW, scaling tests were performed to study the effect of temperature on the NW (Fig. 4) and (Table 3).

Overall, the same effect of temperature on the scaling kinetics, as for the case of Hamma water, has been found: the scaling time decreases from 22.3 to 7.4 min and the scaling index increases from 44 to 137 min^{-1} if work temperature passes from 20 to 50°C. However, some differences can be evoking:

- Firstly, the effect of temperature is less important on the scaling time and index for the NW; t_E and I_E varied by about 39 and 68% for NW whereas they were about 63 and 170% in the case of HW when temperature varied from 20 to 30°C.
- Secondly, the temperature does not affect the compactness of the formed scale layer on the metallic surface when precipitation tests were done using HW ($I_R = 44 \pm 4$ μA) (Table 2). This was not the case for NW where the I_R (Table 3) increases from 38 (20°C) to 68 μA (50°C) showing that the formed layer is more porous than the temperature increases.

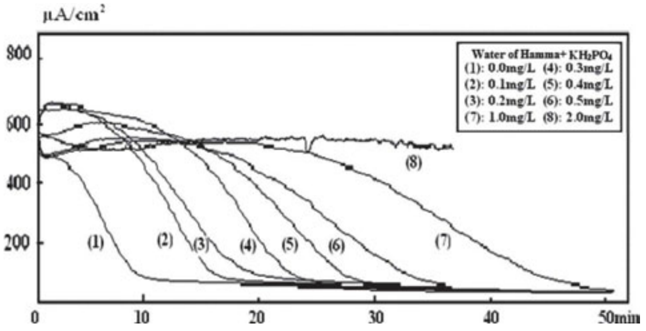

Fig. 5. Chronoamperometric curves plotted for the Hamma treated water with KH_2PO_4 at 30°C.

3.3. Scale inhibition by KH_2PO_4

With the aim to reduce the scaling tendency of the studied waters, by the increasing of the scaling time, KH_2PO_4 was added at very low amounts to the raw waters. All experiments were performed at 30°C. The found precipitation curves are given in (Figs. 5 and 6).

From these figures it can be concluded that the tested additive has a more important effect on the scaling kinetics in the HW compared to the one of Negrine. Table 4 shows that for the HW, the scaling time in presence of 0.1 mg/l is two times the one registered in the reference water (RW) whereas, even for 0.5 mg/l, any effect was found on the t_E in the case of the Negrine water. In addition, if for the water of Hamma the nucleation of calcium carbonate was delayed beyond 50 min (Fig. 5) in presence of 2 mg/l of additive, it is quasi instantaneous for the same amount added to the NW (Fig. 6). The calculated scaling index (Table 4) resumes the effect of the dihydrogenophosphate of potassium on the scaling kinetics. A sharply decrease of I_E from 103 (RW) to 22 min^{-1} (RW+1 mg/l KH_2PO_4) was registered for the HW. This scaling index decrease is slight for the case of Negrine water. On the other hand, it is important to notify that the tested inhibitor affect the compactness of the formed scale especially in the NW. Indeed, as shown in the Table 4, the residual current varied from 40 (Negrine RW) to 180 µA in the presence of 1 mg/l of inhibitor indicating the formation of a porous scale.

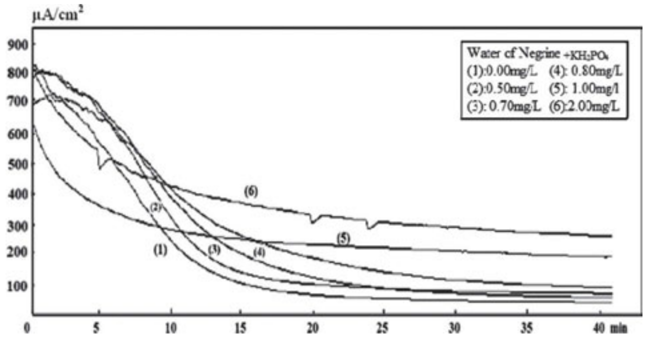

Fig. 6. Chronoamperometric curves plotted for the Negrine treated water with KH_2PO_4 at 30°C.

Contrarily at it was waited, the treatment is more efficient when it was applied to the Negrine water which almost present the lower scaling index at a wide range of temperature. This can be attributed to its higher content in calcium and magnesium ions (Table 1). Indeed, $H_2PO_4^-$, HPO_4^-, PO_4^{3-} can form complex with calcium and magnesium ions; therefore, their concentrations, as free ions, decrease in the solution.

3.4. Scale inhibition by polyphosphate

As for the KH_2PO_4, the inhibiting effect of polyphosphates on the electrochemical precipitation of calcium carbonate was performed by adding different amount of this inhibitor in the Hamma or Negrine water. Precipitation curves are shown in (Figs. 7 and 8) and results are summarized in Table 5.

From these results, it can be firstly noted that the used polyphosphate is more efficient as scaling inhibitor than the dihydrogenophosphate ions. For example, to reach a scaling time of about approx. 30 min (I_E = 33 min^{-1}) in the Hamma water, 0.4 mg/l of KH_2PO_4 must be added whereas only 0.1 mg/l of polyphosphate are sufficient. In the case of Negrine water, 0.8 mg/l of the first inhibitor against 0.4 mg/l of polyphosphate must be added to attain t_E = 23 ± 1 min (I_E = 44 min^{-1}) (Tables 4 and 5). Here, it can be concluded that the polyphosphate

Table 4
Scaling time, residual current and the scaling index variation in the presence of KH_2PO_4 additive in Hamma and Negrine waters

The sources	Concentration of KH_2PO_4 (mg/l)	t_E (min)	I_R µ(A)	I_E (min^{-1})
Hamma water	0	09.70	44	103
	0.1	17.00	38	59
	0.2	19.40	38	51
	0.3	23.33	23	43
	0.4	29.33	33	34
	0.5	35.00	31	28
	1	45.00	–	22
	2	∞	–	–
Negrine water	0	13.50	40.00	74.07
	0.5	14.20	65.50	70.42
	0.7	19.50	85.50	51.28
	0.8	22.50	160.00	44.44
	1	∞	180.00	–
	2	∞	–	–

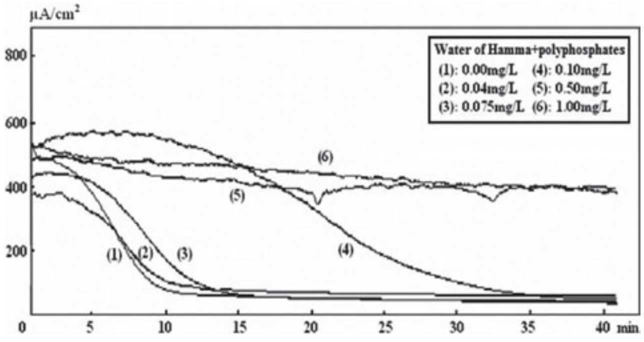

Fig. 7. Chronoamperometric curves plotted for the Hamma treated water with polyphosphate at 30°C.

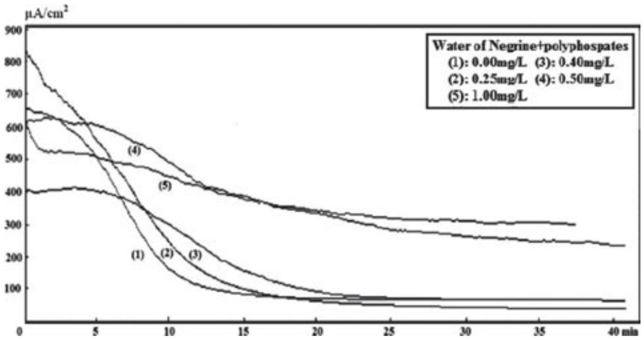

Fig. 8. Chronoamperometric curves plotted for the Negrine treated water with polyphosphate at 30°C.

additive is four times more efficient when added to the HW versus two times in the case of NW. Secondly, the presence of the polyphosphate does not inhibits the nucleation of calcium carbonate but it affects the compactness of the scale formed from the treated Negrine water (i.e., I_R = 230 μA for 0.5 mg/l of polyphosphate; Table 5), as it was the case of dihydrogenophosphate ions.

4. Conclusion

Based on the experimental data, the following conclusions can be made:

- Accelerated scaling tests show that Hamma water is more scale-forming water than the one of Negrine for a large rang of temperature. This was attributed to (i) the higher ionic strength which reduces considerably the ions activities, and (ii) the higher content in magnesium ions known by their inhibitory effect. Basing on the calculated scaling index values, Hamma and Negrine waters can be considered as extremely scale-forming waters from 30°C and 40°C, respectively.
- The antiscale treatment with mineral phosphates is more efficient for the Hamma than Negrine water. In addition, tested inhibitors affect the compactness of the formed scale especially the one formed from treated Negrine water. These results were attributed to the higher content of Negrine water in calcium and magnesium ions which can reduce the free phosphate ions by forming complex.

Table 5
Scaling time, residual current and the scaling index variation in the presence of polyphosphate additive in Hamma and Negrine waters

The sources	Concentration of of polyphosphate (mg/l)	t_E (min)	I_R μ(A)	$I_E = 1000/t_E$ (min)
Hamma water	0	09.70	50.00	103.09
	0.04	11.40	60.00	87.71
	0.075	12.00	36.00	83.33
	0.1	30.00	53.00	33.33
	0.5	∞	–	–
	1	∞	–	–
Negrine water	0	13.50	40.00	74.07
	0.25	15.40	65.50	64.93
	0.4	24.30	63.50	41.15
	0.5	27.20	230.00	36.76
	1	∞	–	–
	2	∞	–	–

- The used polyphosphate is more efficient as scaling inhibitor than the dihydrogenophosphate ions. Indeed, the polyphosphate additive is four times more efficient when added to the Hamma water versus two times in the case of Negrine water.

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