

Study of Inhibiting and Temperature Effect of Phosphonate on Hard Growth Water

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Hard growth water forms compact and adherent deposits to the walls of pipes and industrial or domestic installations causing enormous technical and economic consequences. Therefore, it is very important to applied chemical treatment to hard ground waters at low concentration of inhibitor in order to reduce their hardness, the negative consequences and exploit them.

In this work we used the electrochemical technique of chronoamperometry at imposed potential that determines the evolution of the reduction current of oxygen through the electrode as a function of time in the absence and presence of organic phosphate (HEDP) in water of Negrine. According to the chronoamperometric study at the source temperature of 30°C, Negrine raw water is characterized by time of scaling (t_E) of 13.5min and with a scaling index ($I_E = 74 \text{ min}^{-1}$). Thus, we can classify water of Negrine as a very scale forming. In the presence of phosphonate inhibitor, the risk of scaling is reduced. The scaling time and the residual current increase with the addition of inhibitor and the effective concentration for the inhibition of scaling of water of Negrine is 0.1mg/L. The increase of temperature of Negrine water increases the inhibitor concentration because in the high temperature the Negrine water become more hardness.

Key words: Scaling, calcium carbonate, inhibition, HEDP, electrochemical process.

1. Introduction

The pumping of the underground water is very necessary to cover most of the enormous requirements out of water, but unfortunately most these ground waters are of important hardness.

Hard water forms compact and adherent deposits to the walls of pipes and industrial or domestic installations (Ghizellaoui, 2006) causing enormous technical and economic problems, such as total or partial obstruction of pipes, leading to a decrease in flow rate, reduced heat transfer, seizure of valves and clogging of filters. In nuclear power plants, the scaling phenomena can reduce efficiency and limit the power production (Gauthier et al. 2012). Therefore, it is very important to establish a treatment of hard ground water in order to reduce their hardness and exploit them.

The chemical treatment based on the chemical addition have the property remarkable to be adsorbed on the calcium carbonate germs and to modify their growth and their morphology in order to prevents they adherent between them on the solids surfaces of the solids, they are the inhibitors of scaling, their effective concentration is very weak (Lin and Singer, 2005; Ghizellaoui et al. 2007). Electrochemical methods (Khalil et al. 1993; Rosset et al. 1999), based on formation of deposit of a carbonate of calcium provoked on metallic electrode by the reduction of dissolved oxygen. For a content of 56 French degrees, water of Negrine is known as a very hard and must undergo a treatment of scaling before use, because they deposit significant quantities of calcium carbonate during their circulation in the network of distribution (Ghizellaoui^a and Ghizellaoui^b, 2015).

In this study, firstly we present the results of physicochemical analysis of Negrine water, and secondary using chronoamperometric method, we determined the scaling power of ground water of Negrine and studied the effect of the temperature and the concentration of the inhibitor HEDP on the scaling capacity of this water.

2. Materials and methods

Precipitation tests of calcium carbonate were induced using the electrochemical accelerated scaling method (Rosset, 1993; Bannoud, 1993). Thus, experiments were performed in the natural water of 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 cm² 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 avoiding a significant variation of species concentration during the formation of the deposit. Electrochemical experiments were realized under potentiostatic condition at -1V/SCE , corresponding to the limiting current of the reaction of reduction of the dissolved oxygen. The chronoamperometric tests were thereafter recorded by a computer using a serial connection. On the metallic surface of the work electrode, cathodically polarized, the electrochemical reduction of the oxygen molecules occurs according to (Rosset, 1999; Bannoud et al. 1993):



The hydroxyl group, which is generated by this reaction, induces a strong increase of the pH in the immediate vicinity of the metal surface. The resulting displacement of the carbonic equilibriums following the reaction (R2) promotes the nucleation and the growth of calcium carbonate crystals onto the metal surface according (R3).



The progressive occupancy of the metal surface by the insulating layer reduces the current intensity down to zero for a fully compact and complet 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 (Ledionet al. 1985; Lin et al.1990. 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.

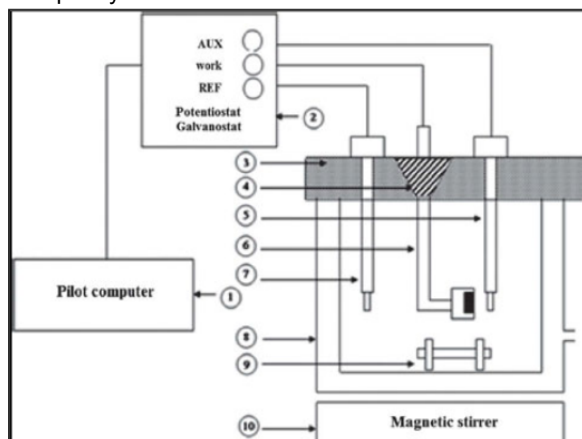


Figure 1: Experimental arrangement (1-Pilot computer equipped with software; 2-Potentiostat galvanostat; 3-Cover electrode holder; 4-Door plug-sample; 5-Platinum electrode; 6-Working electrode: pellet steel XC10 (11.3 mm diameter) embedded in a resin chemically inert; 7-Reference electrode saturated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

3. Results and discussion

3.1. Physico-chemical characterization of water of Negrine

The composition of the water of source of Negrine is given in the Table 1. It shows that the considered water of Negrine is mineral-bearing (EC = 3.3 mS/cm) and present an important hardness (Hydrometric title is 560mg/L).

Table 1: Qualities of raw water of Negrine

Parameters	Negrine Water (NW)
pH	7.7
T (C°)	30
Conductivity (mS/cm)	3.3
HCO ₃ ⁻ (mg/L)	206
TH (mg/L CaCO ₃)	560
Ca ²⁺ (mg/L)	326
Mg ²⁺ (mg/L)	150

3.2. Tests of accelerated scaling

3.2.1. Raw Water of Negrine

Figure (2) shows the shape of the Chronoamperometric curve of raw water of Negrine at source temperature. From this curve, we can determine: the scaling time (t_E) of raw water of Negrine which is 13.5min and the residual current (I_R) of raw water of Negrine which is 0.044mA.

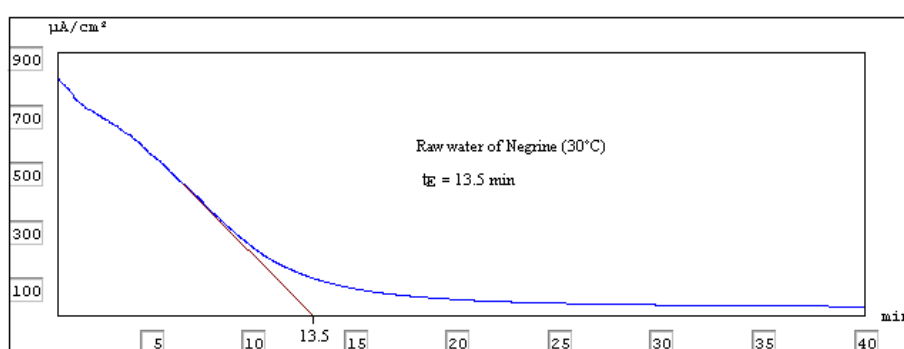


Figure 2: Chronoamperometric curve of Negrine raw water at 30°C.

According to Ledion (Ledion et al.1985), we can classify the scaling power of water of Negrine by scaling time and the scaling index of raw water of this source. The index of scaling is defined by:

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

- $100 < I_E < 1000$: 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 and at the temperature of source (30°C), Negrine water is classified as a very scale-forming water ($I_E=74\text{min}^{-1}$).

3.2. Effect of temperature on the scaling power

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

According to the pace of accelerated scaling curves registered at different temperatures of the raw water of Negrine, time scaling decreased by increasing of the temperature (Table 2); it results of both the increase of the oxygen reduction rate (Rosset, 1993) and the decrease of the deposit of CaCO₃. 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 22.3 to 7.4 min and increase of the scaling index from 44 to 74 min⁻¹ were founded (Table 2). Raising the temperature increases the speed of oxygen reduction reaction and the chemical precipitation of tartar.

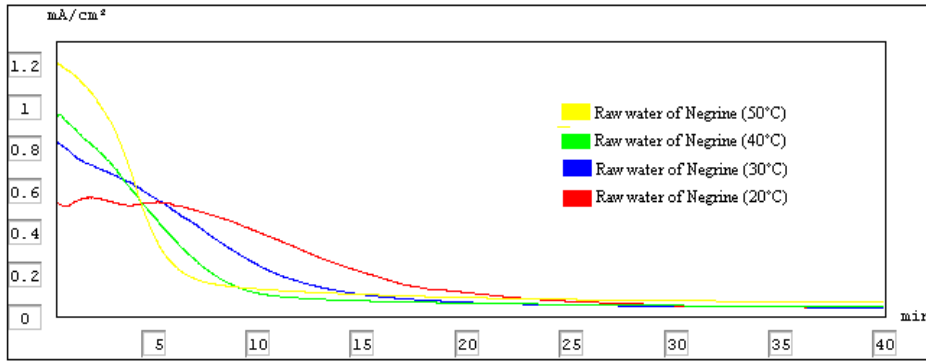


Figure 3: Chronoamperometric curves plotted for different temperatures in the water of Negrine.

Table 2: 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	22.3	38	44
30	13.5	42	74
40	9.9	45	101
50	7.4	68	137

3.3. Scale inhibition by HEDP at 30°C and 50°C.

The study of these chronoamperometric curves (Figures. 4 and 5), shows that an addition of 10^{-5} mg/L of HEDP to the water of Negrine at 30°C and 10^{-3} mg/L of HEDP at the temperature of 50°C, increases the value of the scaling time of the water of this source compared to the scaling time of raw water. Contrarily, the treatment is more efficient when it is applied at low temperature because the effective concentration of HEDP to establish total inhibition is reduced from 1mg/L at 50°C to a value of 0.01mg/L at the temperature of 30°C. This is also proved by the increase in values of index scaling according to the increase of temperature (Table 3). The effect of the HEDP inhibitor that is can form complex with calcium and magnesium ions; therefore, their concentrations, as free ions, decrease in the solution and consequently inhibition of scaling.

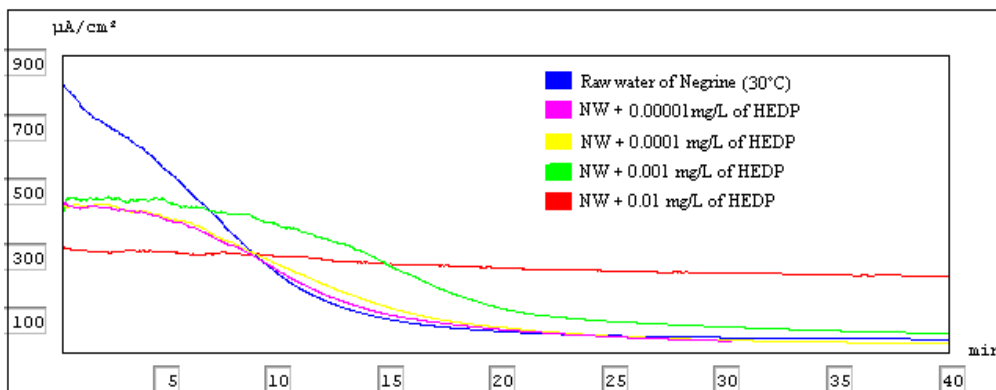


Figure 4: Chronoamperometric curves plotted for the Negrine treated water with HEDP at 30°C.

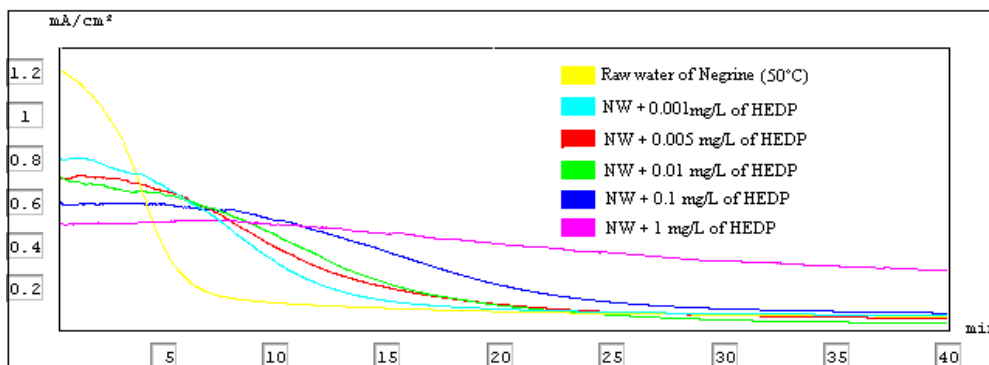


Figure 5: Chronoamperometric curves plotted for the Negrine treated water with HEDP at 50°C.

The values of the time of scaling, the residual current and the index of scaling of each test of scaling accelerated of the water of Negrine treated by inhibitor HEDP, are summarized in Table 3.

Table 3: Time of scaling, residual current and the index of scaling of the chronoamperometric curves of the water of Negrine treated with HEDP with various concentrations.

	Concentration (mg/L)	t_E (min)	I_R (μA)	I_E (min^{-1})
Water of Negrine at 30°C	0	13.5	42	74
	10^{-5}	16.40	30	60.97
	10^{-4}	19.80	20	50.50
	10^{-3}	25	52	40
	10^{-2}	∞	-	-
	Concentration (mg/L)	t_E (min)	I_R (μA)	I_E (min^{-1})
Water of Negrine at 50°C	0	7.4	68	137
	10^{-3}	13.8	27	72.46
	$5 \cdot 10^{-3}$	18.5	20.8	54.05
	10^{-2}	25.4	25.4	39.37
	10^{-1}	35.2	44	28.40
	1	∞	-	-

According to the values of the time of scaling and residual current withdrawn from the curves of accelerated scaling carried out on water of Negrine treated with HEDP inhibitor, we noted that:

The time of scaling increases with the increase in the concentration of inhibitor until total inhibition (the deposit of calcium carbonate does not adhere on the steel electrode surface).

The residual current varies with the growth of the time of scaling and this variation depends on the quantity of the tartar deposited on the electrode of work.

Therefore, one can say that the addition of inhibitor HEDP at very low concentrations of additions decreases the scaling capacity of the water of Negrine even in high temperatures.

This compound which is adsorbed on the surface of the calcium carbonate particles which can be formed, thus cause the slow down or total blockage of the precipitation of calcium carbonate.

The mode of action of HEDP proposed by TLILI (2002) and several authors is: the molecules of the inhibitor of HEDP will be adsorbed selectively on the first nuclei of calcium carbonate. This adsorption alters the growth mechanism so that the crystals is deformed and develop more slowly and consequently, delay the growth of crystals of calcium carbonate and the deposit formation decreases.

4. Conclusion

According to the results obtained in this study:

- The use of the method of chronoamperometry makes it possible to characterize the scaling power of water of Negrine by implementing the formation controlled of calcium carbonate by the reduction of the oxygen dissolved in water at a imposed negatively potential.

The scaling accelerated at the temperature 30°C of raw water of Negrine, determine the scaling power of this water at source temperature (30°C) as 13.5min. What translates the scaling power of water.

While varying the temperature of raw water of Negrine, chronoamperometric study shows that: the increase in the temperature of raw water of Negrine decreases the time of scaling up to 7.8min at the temperature of 50°C by the activation of the formation of calcium carbonate. On the other hand, the reduction in the temperature of the water of Negrine involves a reduction in the scaling power of this water.

The anti scale treatment of the water of Negrine by chemical inhibitor HEDP at the temperature of 30°C and 50°C, increases considerably the time of scaling compared to the time of scaling of raw water. It is the effect of the inhibitor which delayed the formation of deposit. The increase in the concentrations of the HEDP in the water of Negrine makes decrease the scaling power until total inhibition.

The inhibiting effect of the HEDP on the water of Negrine at the temperature of 30°C starts starting from the concentration of 10⁻⁵ mg/L, and one reaches total inhibition with the concentration of 0.01 mg/L.

The water treatment of Negrine water at 50°C by same inhibitor HEDP shows that the variation of the time of scaling is starting from the concentration of 10⁻³ mg/L, and total inhibition is reached for an addition of 1mg/L.

Therefore, the HEDP is an effective inhibitor for the scaling water softening of Negrine. The inhibiting effect of the HEDP is pronounced more on water of Negrine at low temperature because it acts with a concentration even weaker.

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