(RESEARCH ARTICLE)

Study of the influence of crystallisation companions on the oxidation - precipitation of Fe²⁺ applied to the synthetic water of Dan Daji -Illela (Tahoua -Niger)

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Abstract

The elimination of iron by the oxidation-precipitation technique applied to Dan Daji water requires the study of the influence of certain parameters that frequently coexist with iron in water, such as Ca^{2+}, Mg^{2+}, Na^+, K^+, SO_4^{2-}, HCO_3^-, CO_3^{2-} and NO_3^-. The use of natural water does not make this study possible. To overcome this limitation, synthetic water was adopted to study the influence of these parameters on iron precipitation. For the needs of this study, the physico-chemical characteristics of the synthetic groundwater are identical to those of the Dan Daji drilling. All the experiments were carried out in a 1000 mL beaker with stirring to allow contact with atmospheric oxygen for a precipitation time of 60 minutes. Among the ions that accompany Fe^{2+} precipitation, certain ions such as HCO_3^-, Ca^{2+}, K^+ and Mn^{2+} promote the precipitation of iron to $Fe(OH)_3$. On the contrary, other ions such as Mg^{2+}, SO_4^{2-} and NO_3^- inhibit the formation of $Fe(OH)_3$.

Keywords: Precipitation; Oxidation; Iron; Synthetic water; Dan Daji

1. Introduction

Iron is abundant in its natural state in all rocks and was found in dissolved form in most groundwater [1, 2]. In well-aerated water, its concentration is very low. On the contrary, in poorly aerated water (groundwater in particular), high levels of iron can be observed, when the conditions for solubilisation were united. The most frequent sources of iron in groundwater are natural. For example, the alteration by meteoric processes of minerals and rocks containing them (amphiboles, ferromagnesian micas, iron sulphides, magnetites, oxides, carbonates, etc.)[3, 4]. However, industrial effluents, acid mine drainage, waste water and leachate from landfill sites can also contribute to the presence of iron in groundwater [5, 6, 7]. In almost all regions of Niger, chemical analyses of groundwater samples reveal abnormally high concentrations of iron in the majority of water drillings. A study carried out by the Ministry of Hydraulics, the Environment and the Fight against Desertification (MHE/LD) in 2005 on the physico-chemical analysis of water showed that, out of a total of 148 drillings studied, 28.4% had an iron concentration well in excess of 0.3 mg/L (the value recommended by the WHO). Iron is essential in small quantities for all living organisms. However, at concentrations higher than those recommended for drinking water, iron can alter the taste, odour or colour of water. Water with high concentrations of iron can cause stains to form on plumbing fittings or clothes. Iron can also build up and block pipes or plumbing connectors, leading to rust flakes in the water. It can encourage the growth of unwanted bacteria that form a viscous layer inside pipes. In another aspect, higher ratios of iron could increase the risk of cardiovascular diseases

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and cancer [8]. Too much iron was also implicated in a number of neurodegenerative diseases [9]. Drilling water with high iron concentrations in the study area was sometimes abandoned by local people because of its bad taste or strong colouring, in favour of spring water. In view of this alarming situation, it is imperative to take steps to improve the quality of drinking water in rural areas. Several methods of iron removal were currently being developed. Among these processes we can cite physico-chemical processes, biological processes, catalytic processes and membrane processes [10, 11, 12, 13]. These treatment methods were not without their limitations, both in terms of the use of certain materials and the control of certain physico-chemical parameters, and above all in terms of the accessibility of the necessary materials and chemicals. Of all these methods, we have chosen the elimination of iron by oxidation-precipitation with atmospheric oxygen in a bicarbonate solution, in the form of oxyhydroxides, which was a less expensive and easily accessible method [14]. Natural water also frequently contain other cations such as Ca^{2+}, K^+, Mg^{2+}, and anions such as SO_4^{2-}, CO_3^{2-}, HCO_3^-, NO_3^-, etc. which coexist with Fe^{2+}. A study to understand the influence of these elements when iron was eliminated from water is necessary. However, the use of natural groundwater makes it impossible to control certain variables and to study the specific behaviour of each element. It was with this in mind that we proposed the use of synthetic water. To achieve this, the synthetic water had to behave in a similar fashion to natural water. It was with these objectives in the lead that the procedure for preparing synthetic water was developed. The objective of this research is to study the influence of crystallisation companions on Fe^{2+} precipitation applied to Dan Daji -Illéla synthetic water.

2. Material and methods

2.1. Présentation of the study zone

The Tahoua region covers an area of 113,317 km². Its Northern latitude lies between 13° 40' and 19°, and Eastern longitude between 4° and 12° 40'. It is entirely locuted in the Sahelo-Sudanian climatic zone, with extreme precipitation limits of 150 mm and 600 mm. Temperatures ranging from 10° (harmattan) to 45° (hot season). This study was carried out in the village of Dan Daji in the Tahoua region, more specifically in the Illéla department (Figure 1).
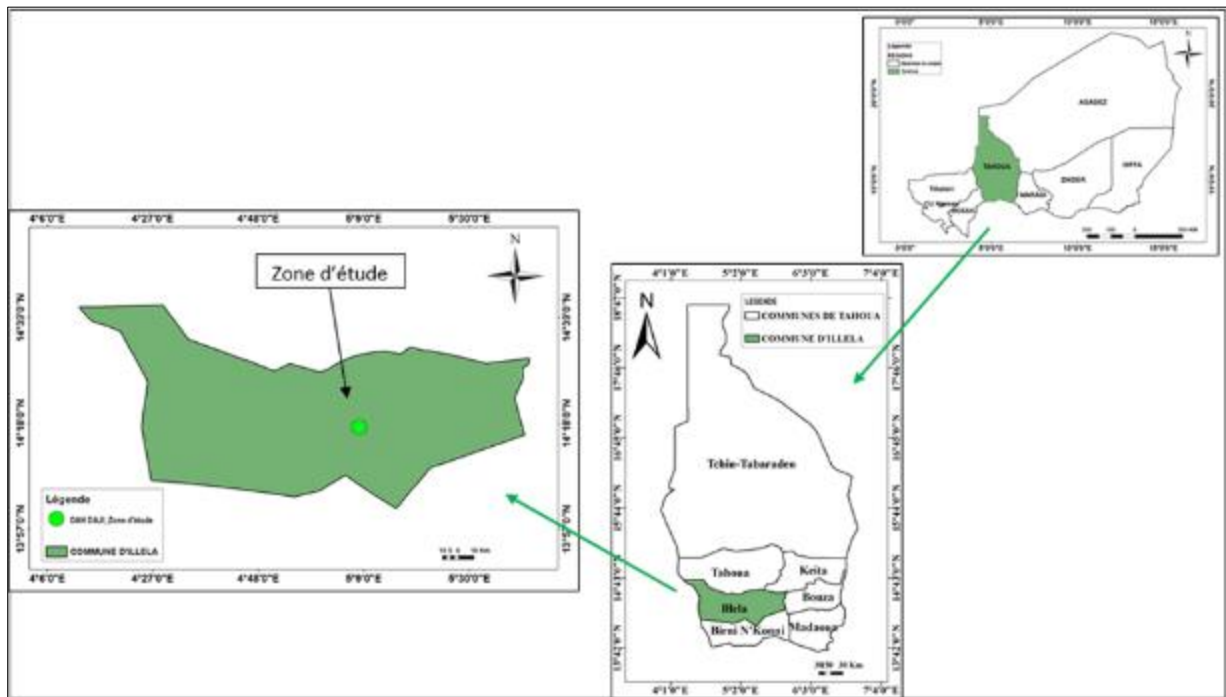
Figure 1 Geological map of the Tahoua region showing the location of the study zone

2.2. Hydrogeology of the Tahoua area

The hydrogeology of the Tahoua aera is complex. The region has a multitude of superimposed nappes in the Southern band. Their debits vary from one zone to another. As a result, we can have very productive reservoirs at shallow depths, just as we can have uncertain debits in the same nappe but with very different implantation. This is due to the deep and geological formation of the nappe. The main nappes are: Alluvial nappes, Continental Terminal(CT1) nappes,

Continental Intercalaire/ Hamadien (CIH) and Cretaceous nappes [10]. For the present study, the nappe is of the Continental Intercalaire (CI) type.

2.3. Preparation of Dan Daji synthetic water

The procedure and the different salts used in the preparation of this water are the same as those used in the study by Knock et al. 1990 [15] and those used in the study by Donald Ellis, 1998 [16]. Unlike the study by Knock et al, 1990 [15] (where the artificial water was bubbled with nitrogen alone) and that by Donald Ellis, 1998 [16] (where the artificial water was bubbled with the CO_2/N_2 mixture). In the present study we used CO_2 only. For the needs of this study, the main characteristics that will guide the manufacture of the groundwater are consistent with those of the Dan Daji drilling. The physico-chemical parameter values for the Dan Daji drilling are given in Table 1.

Table 1 Physico-chemical parameters of water in the village of Dan Daji

Physico-chemical parameters	Value of physico-chemical parameters	Units
pH	7, 35	-
Fe^{2+}	1,69	mg/L
HCO_3^-	37,5	mg/L
SO_4^{2-}	36	mg/L
NO_3^-	1,32	mg/L
Mg^{2+}	4,35	mg/L
Ca^{2+}	12	mg/L
Mn^{2+}	1,2	mg/L
K^+	15,93	mg/L

The different stages in the preparation of synthetic water before each use are as follows:

- Mix solutions of volumes with the same chemical element concentration as Dan Daji water in one litre of solution.

Table 2 Mixed volumes of different solutions for the preparation of Dan Daji synthetic water

N°	Solutions for	Volume
1.1	$MgCl_2$	50 mL
1.2	KCl	47 mL
1.3	Na_2SO_4	43 ml
1.4	$CaCl_2$	50 mL
1.5	KNO_3	50 mL
1.6	$NaHCO_3$	50 mL

- Adjustment to pH 7.35 with CO_2.
- Add 50 ml of iron sulphate heptahydrate solution ($FeSO_4 .7H_2O$) and 50 mL of manganese sulphate monohydrate solution ($MnSO_4.H_2O$) and make the mixture up to 1 L with distilled water.

2.4. Study of the influence of crystallisation companions

To study the influence of each element, three (3) concentrations were used: C_0 (concentration of synthetic water with no element), C_1 (concentration of the element in Dan Daji's water) and C_2 (concentration of the element greater than that in Dan Daji's water). These concentrations were obtained by varying the volumes V_0, V_1 and V_2 of the solution respectively, while maintaining the desired content of the element in the mixture. The concentrations of the other

elements were maintained at the values of the concentrations of these elements in the natural water of Dan Daji. Table 3 shows the volumes of solutions and corresponding concentrations of the various crystallisation additives used.

Table 3 Volumes of solutions and concentrations of crystallisation companions used

	V_0 (mL)	V_1 (mL)	V_2 (mL)	C_0 (mg/L)	C_1 (mg/L)	C_2 (mg/L)	pH
HCO_3^- $NaHCO_3^-$	0	50	325	0	37, 5	244	7, 35
Mg^{2+} ($MgCl_2$)	0	50	280	0	4, 35	24, 3	7, 35
Ca^{2+} ($CaCl_2$)	0	50	417	0	12	10	7, 35
SO_4^{2-} (Na_2SO_4)	0	43	358	0	36	300	7, 35
$Mn^{2+}MnSO_4.H_2O$	0	50	100	0	1, 2	2,4	7, 35
NO_3^- (KNO_3)	0	50	500	0	1, 32	13, 2	7, 35
K^+	0	47	236	0	15, 93	80	7, 35

2.5. Practical conduct of the test

The experiments were carried out in a 1000 mL bath on a magnetic agitator. At each manipulation, the pH of the water in the bath was brought back to pH =7.35 (pH of Dan Daji water in its natural environment) by bubbling in CO_2. The agitator and chronometer were then started at the same time for a period of 60 minutes. The agitation introduced atmospheric oxygen into the water in the bath. Contact between the water and the atmospheric air causes the dissolved CO_2 to be released, resulting in alkalinisation of the environment and an increase in pH. This increase in pH favours the oxidation of Fe^{2+} to Fe^{3+} and the formation of a red-orange precipitate of ferric hydroxide, $(Fe(OH)_3(s))$ as shown in Figure 2. This results in the following reactions:

$$4 Fe^{2+} + O_2 + 2H_2O \rightarrow 4 Fe^{3+} + 4OH^- (R_1)$$

$$4 Fe^{3+} + 4OH^- + 8H_2O \rightarrow 4 Fe (OH)_3 + 8H^+ (R_2)$$
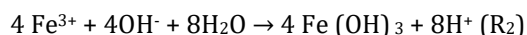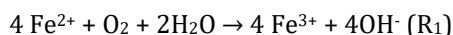
For all the tests, three (3) concentrations C_0, C_1 and C_2 of the element which influence is to be studied were studied. Where C_0 is equal to 0 mg/L for any element which effect was being studied, C_1 is the concentration of the element in its natural environment (in the water from the Dan Daji drilling). C_1 was obtained by adding to the mixture a volume of solution capable of bringing about the same concentration of the element as in Dan Daji water. C_2 was obtained by adding a volume capable of bringing a concentration higher than the concentration of the element in Dan Daji water. After each 10 minutes, a 1mL dose of water was taken from the bath and placed in a 50 mL calibrated flask to determine the residual Fe^{2+} concentration. The 1 mL was taken by syringe equipped with a 0.45 μm membrane microfilter. A pH value was noted for each sample to monitor the evolution of the pH during the reaction. Figure 2 shows a photograph of the installation used for the precipitation experiments.

Figure 2 Photograph of the experimental montage of iron precipitation

2.6. Dosage

To 1 mL of solution taken, we successively added 1 mL of hydroxylamine, 2 mL of ammonium acetate and 2 mL of orthophenanthroline. After introducing these reactants, the mixture was made up to 50 mL with distilled water. The optical density was read at a wavelength of 510 nm.

2.7. Determination of precipitation ratio

The iron hydroxide precipitation ratio, τp(Fe), is calculated from the following equation:

$$\tau_{p(Fe)} = \frac{[Fe]_0 - [Fe]_t}{[Fe]_0} \times 100$$

With:

$[Fe]_0$ = The initial ionic iron concentration in mg/L

$[Fe]_t$ = The total concentration of iron at time t in mg/L

3. Results

3.1. Iron precipitation ratios

The precipitation rates of (τp(Fe)) as well as the precipitation pH (pHp) at the different concentrations of crystallization companions for a precipitation time (Pt) of 2 minutes, are consigned in the following table:

Table 4 Influence of $[HCO_3^-]$ on precipitation pH pHp, precipitation rate τp(Fe)

Concentration in mg/L	Pt (min)	pHp	τp (Fe) in %
$[HCO_3^-]$ = 0	2	5,576	-
$[HCO_3^-]$ = 37,5	2	7,030	-
$[HCO_3^-]$ = 244	2	7, 294	71,60
$[SO_4^{2-}]$ = 0	2	7,022	71,60
$[SO_4^{2-}]$ = 36	2	6,75	-
$[SO_4^{2-}]$ = 300	2	6,029	-
$[NO_3^-]$ = 0	2	7, 013	57, 39
$[NO_3^-]$ = 1,32	2	6,75	-
$[NO_3^-]$ = 13,2	2	6, 613	-
$[Mg^{2+}]$ = 0	2	6,961	14,20
$[Mg^{2+}]$ = 4,35	2	6,75	-
$[Mg^{2+}]$ = 24,3	2	6,527	-
$[Ca^{2+}]$ = 0	2	6, 743	-
$[Ca^{2+}]$ = 12	2	6,75	-
$[Ca^{2+}]$ = 100	2	7, 596	100
$[Mn^{2+}]$ = 0	2	6, 86	-
$[Mn^{2+}]$ = 1,2	2	6,75	-
$[Mn^{2+}]$ = 2,4	2	6,933	28,40

[K$^+$] = 0	2	6, 68	-
[K$^+$] = 15,93	2	6,75	-
[K$^+$] = 80	2	7, 005	42,60

3.2. Effect of bicarbonate ions

Figures 3-a and 3-b show, respectively, the graphs showing the variation in iron concentration and pH at different bicarbonate concentrations in function of time.
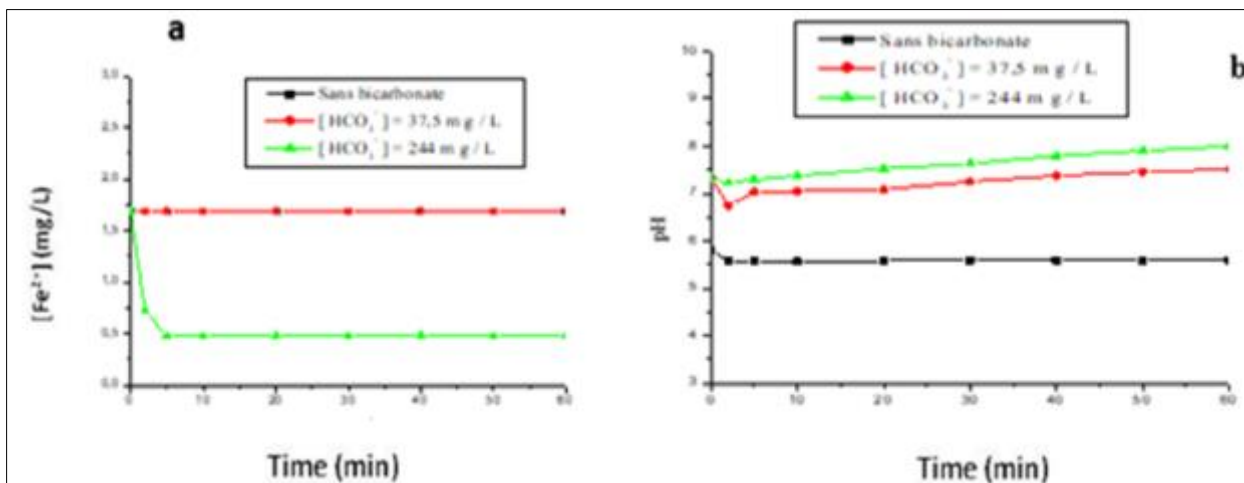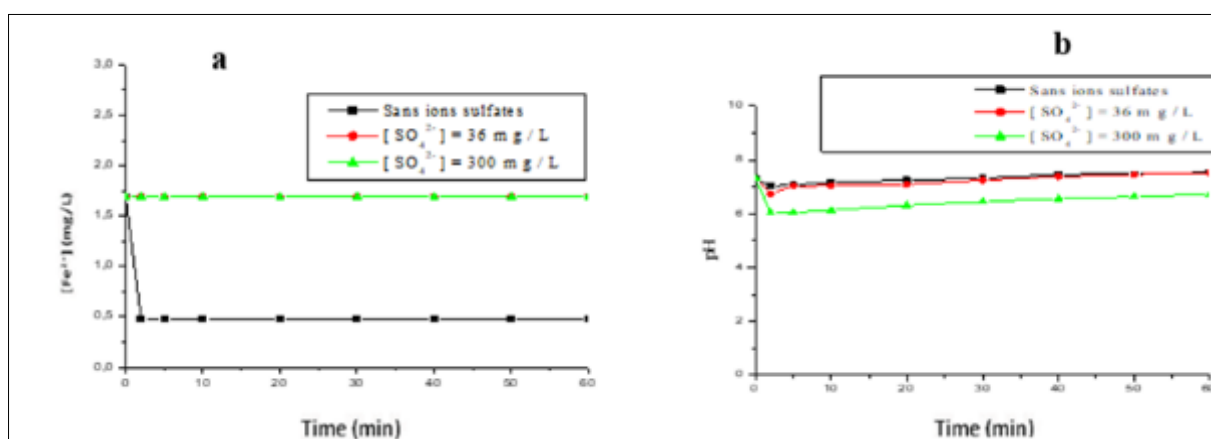

Figure 3 Changes in dissolved iron content (a) and pH (b) at different [HCO$_3^-$] values

Figure 3-a shows that the iron(II) concentration stays practically constant in the absence of bicarbonate and at the bicarbonate concentration in Dan Daji water ([HCO$_3^-$] = 37.5 mg/L). However, at a concentration of 244 mg/L, a drop in Fe(II) concentration was observed. This drop in Fe^{2+} concentration corresponds to a precipitation rate of 71.60% (Table 3). This result confirms that bicarbonate favours Fe^{2+} precipitation from a concentration of 244 mg/L, even in the presence of iron crystallisation companions. Bicarbonate leads to an increase in pH (Figure 3-b). In the absence of bicarbonate, the pH remained practically acidic (pH below 6) for the duration of the experiment.

3.3. Effect of sulphate ions SO$_4^{2-}$

Figures 4-a and 4-b show, respectively, the graphs showing the variation in iron concentration and pH in function of time at different sulphate ion concentrations.
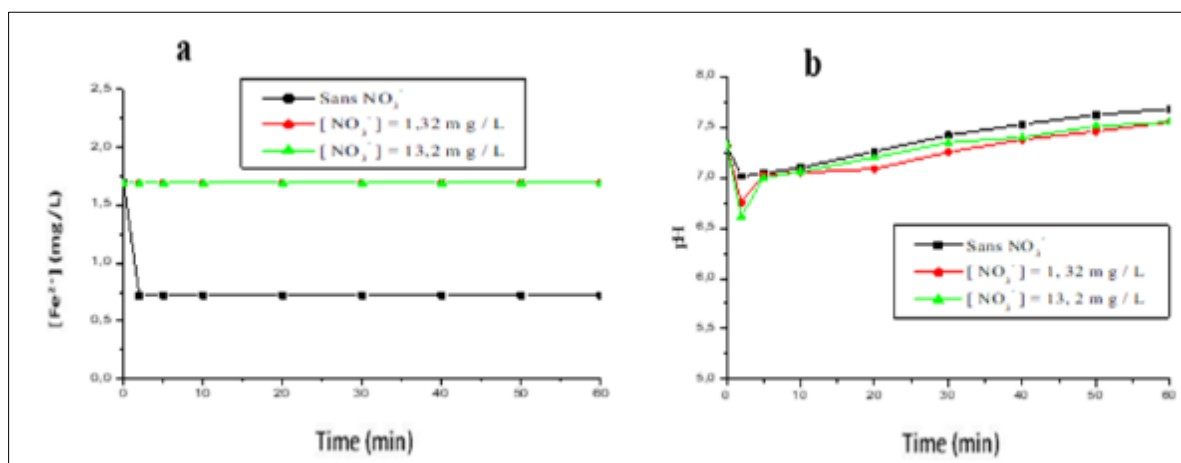

Figure 4 Changes in dissolved iron concentration (a) and pH (b) at different [SO$_4^{2-}$] values

According to Figure 4-a, a drop in iron concentration is observed after 2 minutes of the experiment in the absence of SO$_4^{2-}$ ions. This drop in Fe^{2+} concentration gives a Fe^{2+} precipitation ratio of 71.60% (Table 4). However, in the presence

of SO_4^{2-} ions, the iron concentration stayed practically constant throughout the experiment. These results suggest that sulphate ions inhibit Fe^{2+} precipitation. Figure 4- b shows the same graphs in the absence and presence of sulphate ions. However, it was found that the drop in pH, which appears in the first minutes of the reaction, was greater when the concentration of sulphate ions was increased and that the pH changes more rapidly when the concentration of sulphate ions decreases. This variation in pH confirms that the presence of sulphate ions acidifies the environment. This is why the formation of Fe^{2+} was inhibited in the presence of SO_4^{2-} ions.

3.4. Effect of nitrate ions NO_3^-

Figures 5-a and 5-b show, respectively, the graphs of variation in iron concentration and pH in function of time at different nitrate ion concentrations.

Figure 5 Evolution of dissolved iron concentration (a) and pH (b) at different $[NO_3^-]$ values

Figure 5-a shows that, in the absence of NO_3^-, a decrease of iron concentration is observed after 2 minutes of the experiment. This drop in Fe^{2+} concentration corresponds to a precipitation rate of 57.39%. However, in the presence of NO_3^- ions, the concentration of iron remained virtually constant for the duration of the test. These results indicate that the presence of nitrate ions inhibits the precipitation of Fe^{2+}. Figure 5-b shows the same graphs in the absence and presence of nitrate ions. However, we did notice a significant drop in pH, which appeared in the first minutes of the reaction when the concentration of nitrate ions was increased. On the other hand, we observed that the pH evolution was faster when the concentration of nitrate ions decreases. We can conclude from this result that the presence of nitrate ions acidifies the environment, which inhibits the precipitation of Fe^{2+}.

3.5. Effect of magnesium ions
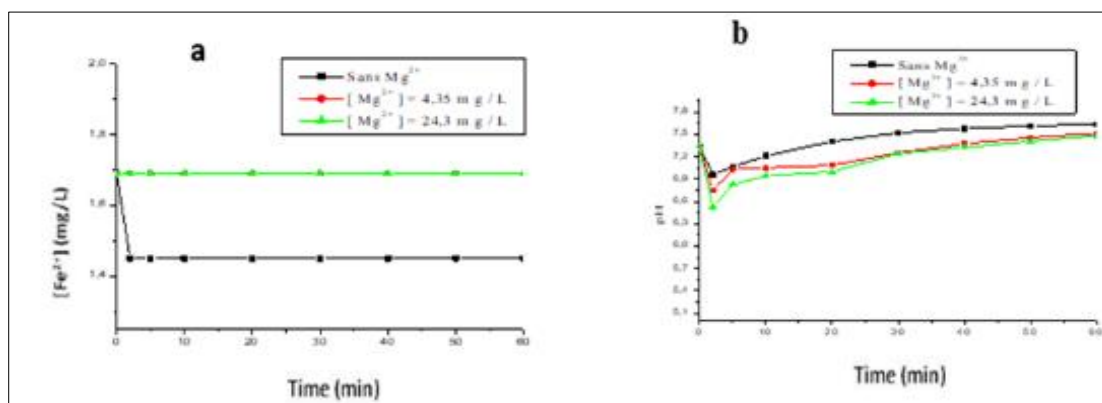
Figure 6 Evolution of dissolved iron concentration (a) and pH (b) with different $[Mg^{2+}]$ values

Figures 6- a and 6 -b indicate the variation in Fe^{2+} concentration and pH in function of time, respectively. The tests were conducted at different Mg^{2+} concentrations. Figure 6-a shows that in the presence of magnesium, the iron concentration stayed constant for the duration of the test, so no precipitation occurred. However, in the absence of magnesium, a drop

in iron concentration was registered, corresponding to a precipitation ratio of 14.20% (Table 4), after approximately 2 minutes of the experiment. This result means that the presence of magnesium inhibits Fe^{2+} precipitation. Figure 6-b shows a drop in pH in the presence and absence of magnesium from the beginning of the experiments. Figure 6-b reveals that the pH resumes its ascension a few minutes after the fall.
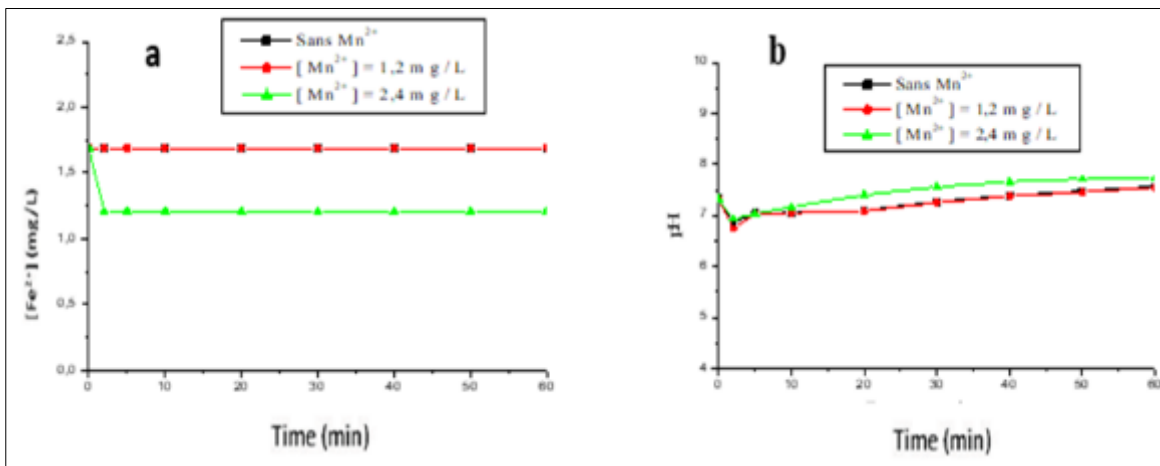
3.6. Effect of calcium ions Ca^{2+}

Figures 7-a and 7-b present, respectively, the graphs showing the variation in iron concentration and pH in function of time at different calcium concentrations.
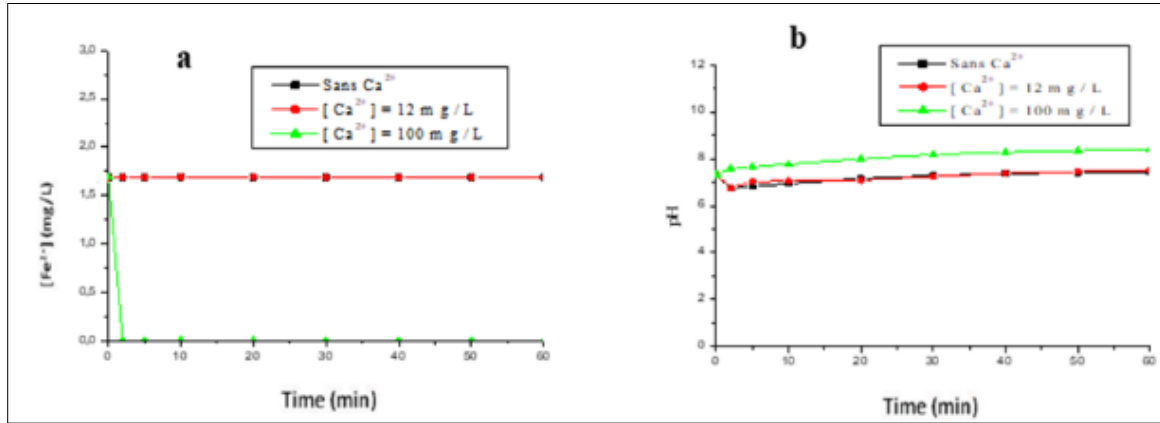
Figure 7 Evolution of dissolved iron concentrations (a) and pH (b) at different $[Ca^{2+}]$

Figure 7-a shows that in the absence of Ca^{2+} and in the presence of Ca^{2+} at the Dan Daji drilling water concentration (12 mg/L), the iron concentration is practically constant during the experiment. However, at a concentration of 100 mg/L, the Fe(II) concentration is practically null. From this result, we can conclude that the presence of calcium ions at concentrations above 12 mg/L favours the precipitation of $Fe(OH)_3$. Figure 7 -b shows the same graphs in the absence and presence of calcium ions. However, the drop in pH is only observed in the absence of Ca^{2+} and at a concentration of 12 mg/L after the first two minutes of reaction. Figure 7-b shows that the evolution of pH is more important at a concentration of 100 mg/L. From these observations, we can say that the existence of Ca^{2+} ions in the environment increases the pH, rendering the environment favourable to the precipitation of ferric hydroxide.

3.7. Effet des ions manganèse Mn^{2+}

Figure 8 Evolution of dissolved iron content (a) and pH (b) at different $[Mn^{2+}]$

Figures 8-a and 8-b show, respectively, the graphs of variation in iron concentration and pH in function of time at different manganese concentrations.

From Figure 8-a, we can see that in the absence of Mn^{2+} or in its presence at a concentration equal to that of Dan Daji's natural water ($[Mn^{2+}]$ = 1.2mg/L), the concentration of iron is practically constant during the experiment. However, at a concentration of 2.4 mg/L, the Fe(II) concentration decreased, giving a precipitation ratio of 28.40% (Table 4). Figure 8-b shows the same graphs in the absence and presence of manganese ions with a high increase in pH at a concentration of 2.4 mg/L.

3.8. Effect of potassium ions K^+

Figures 9-a and 9-b show, respectively, the graphs of variation in iron concentration and pH in function of time at different potassium ion concentrations.
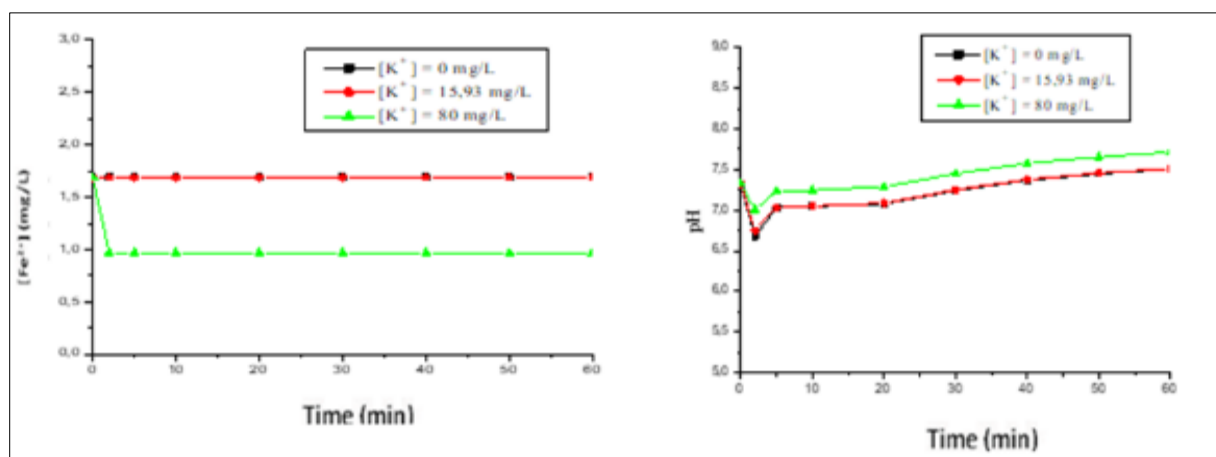

Figure 9 Evolution of dissolved iron content (a) and pH (b) at different $[K^+]$

Figure 9-a shows that without K^+ and at $[K^+]$ = 15.93 mg/L, the iron content is practically null after 2 minutes of the experiment. A drop in iron concentration is observed when the potassium ion content is 80 mg/L. This drop in Fe^{2+} concentration was equivalent to a precipitation ratio of Fe^{2+}. These results show that the presence of potassium ions favours the precipitation of $Fe(OH)_3$. When their concentration in the environment was superior than 80 mg/L. Figure 9-b gives the same graphs in the absence and presence of potassium ions. However, we can see that the decrease in pH during the first minutes of the reaction is greater when the concentration of K^+ ions was decreased. In another aspect, we observe that the increase of pH is more rapid when the concentration of potassium ions increases. We can conclude from this result that the presence of K^+ ions favours the precipitation of Fe^{3+}. Figure 9-b also shows that the increase of pH during the experiments is greater in the presence of potassium ions.

4. Discussion

4.1. Effect of bicarbonate ions

In the milieu without bicarbonate ($[HCO_3^-]$ = 0 mg/L), iron(II) precipitation was not observed, but at a bicarbonate concentration of 244 mg/L, iron precipitation was massive, with a precipitation rate of 71.60%. The pH remained practically acidic during the experiment. These results could be explained by the oxidation-precipitation process. This process is expressed by the following equations:

$$4\ Fe^{2+} + O_2 + 10H_2O \rightarrow 4\ Fe\ (OH)_3 + 8H^+ \ (R_3)$$
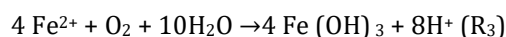
The H^+ protons released during reaction R_3 acidify the environment, rendering $Fe(OH)_3$ unstable, that is why precipitation did not occur. In the presence of bicarbonate, these protons react with HCO_3^- ions, according to the following reaction:

$$H^+ + HCO_3^- \leftrightarrow CO_2 + 2H_2O \ (R_4)$$
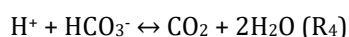
This reaction confers on the milieu an alkaline pH that is very favourable to the precipitation of iron hydroxides ($Fe(OH)_3$). This explains the obtained precipitation ratio of 71.60%. Similar results were obtained by Wided. M, 2017 [17]. At the bicarbonate concentration of 37.5 mg/L, precipitation is practically absent despite the presence of

bicarbonate ions and the pHp, which stays higher than 6, so very favourable to Fe^{2+} precipitation. Thus, the absence of precipitation at this concentration could be attributed to the presence of other ions, which could inhibit iron precipitation.

4.2. Effect of sulphate ions SO_4^{2-}

At concentrations of 36 mg/L and 300 mg/L, the precipitation ratio ($\tau p(Fe)$) is null. However, in the absence of sulphate, $\tau p(Fe)$ is 71.60%. This can be explained by the oxidation mechanism given by reactions R_3, during which H^+ protons are released. The H^+ protons react with the Fe-OH group to form $Fe\text{-}OH_2^+$. This complex adsorbs sulphate ions via coulombic attractions, to obtain a $FeSO_4^+$ complex that is stable at acidic pH. This complex inhibits the crystal development of $Fe(OH)_3$[18]. During the tests in the presence of SO_4^{2-} ions, the pH stayed practically under 7. This confirms the absence of $Fe(OH)_3$ formation, because this compound generally forms in environments with a pH superior to 7 [17].

4.3. Effect of sulphate ions NO_3^-

At concentrations of 36 mg/L and 300 mg/L, $\tau p(Fe)$ is null. However, in the absence of nitrate, $\tau p(Fe)$ is up to 57.39%. This is not similar to the results presented by certain authors such as Straub et al. 1996 [19] who showed that in an anaerobic environment, the mechanism of Fe^{2+} precipitation is ensured by the reduction of nitrate NO_3^- to nitrogen N_2 according to the following equation :

$$10Fe^{2+} + 2NO_3^- + 24H_2O \rightarrow 10\ Fe\ (OH)_3 + N_2 + 8H^+\ (R_5)$$
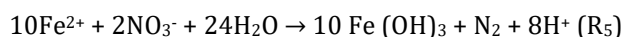
For this reason, nitrate ions can be considered as electron acceptors. Their presence in the oxygen-free environment favours oxidation of Fe^{2+} to Fe^{3+} and precipitation of $Fe(OH)_3$. Contrary to our study, the tests were realized in aerobic environment, so the oxidation of ferrous iron to ferric iron is certainly ensured by the oxygen of the air proved to be the best oxidizer of Fe^{2+} by several authors, Donald E, 1998 ; Wided M, 2017 ; Ruiti M et al, 2015[16, 17, 20]. This means that, in the presence of oxygen, nitrate ions do not constitute an oxidant of Fe^{2+}. According to this result, nitrate ions interfere with the oxidation of Fe(II) by oxygen. This is why iron precipitation is not observed in the presence of NO_3^- ions. The pH evolution is more fast when the concentration of nitrate ions decreases. This result confirms that the presence of nitrate ions acidifies the environment, inhibiting the oxidation of Fe^{2+} to Fe^{3+} and precipitating $Fe(OH)_3$.

4.4. Effect of Mg^{2+} ions

For concentrations of 4.35 mg/L and 24.3 mg/L, the precipitation ratio was practically null during the experiment. However, in the absence of magnesium, the iron elimination ratio was 14.20%. This may be attributed to the formation of $MgHCO_3^+$, obtaining this complex requires the presence of HCO_3^- ions in the environment [21, 22], which reduces the chance of $Fe(OH)_3$ formation. The pH decreases with the concentration of magnesium. This result means that the presence of magnesium acidifies the environment, rendering it unfavourable for the precipitation of $Fe(OH)_3$.

4.5. Effect of Ca^{2+} ions

Contrary, in the absence of calcium and at a concentration of 12 mg/L, the precipitation ratio is quasi null. These results are similar to those reported in the literature [23, 24]. Meyer [23] has discovered that for a solution with a calcium ion concentration of $0.982.\ 10^{-3}$ M, a small iron concentration of the order of $5.5.10^{-4}$ mg/L is sufficient to completely inhibit the crystal growth of $CaCO_3$. Gutjahr et al 1966[24] in turn showed that Fe^{2+} is the strongest inhibitor of $CaCO_3$ precipitation among the divalent cations studied such as Cu^{2+}, Zn^{2+}, Mg^{2+}, Sr^{2+}, and Ba^{2+}. With a concentration inferior or equal to $1.78.10^{-4}$ mg/L, iron totally inhibits the growth of calcite. In the light of all these observations, we can confirm that the presence of iron in the environment hinders the formation of calcium carbonate, which favours important precipitation of iron hydroxide even in the presence of calcium ions. This was quite contradictory to the results obtained in the study by Wided M, 2017 [17]. In effect, Wided M, 2017 showed that the $CaCO_3$ precipitation ratio increases from 70 to 75.5% when the iron concentration increases from 0 to 0.5 mg/L respectively. The pH increases as the calcium concentration increases. This corroborates the obtention of the important ratio of iron precipitation.

4.6. Effect of manganese ions Mn^{2+}

From a concentration of 2.4 mg/L, the precipitation ratio is 28.40%. These results are related to the method used, which necessitated an aeration system based on agitation. Aeration results a slow degassing of the CO_2, which at the same time introduces oxygen into the solution. In effect, manganese oxidises in the presence of O_2 to form manganese oxide, according to the following reaction:

$$M_n^{2+} + O_2 \rightarrow M_nO_2(s)\ (R_6)$$
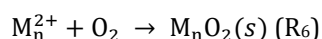
The manganese oxide particles formed at the beginning of the reaction serve as a catalyst for the oxidation reaction. Several studies have shown, on the other side, that it is very difficult to oxidise manganese by simple aeration with oxygen from atmospheric air [23, 24], because manganese oxidation was very dependent on the pH of the environment [25, 26]. Catherine Lessard; 1999; Ahmed B. J et al, 2005 [27, 28] have shown that manganese ions oxidise only at pH > 9. But Goné Droh Lanciné et al, 2008 [29] have succeeded in oxidising 20% of manganese by aeration in air at pH 7.8. This is similar to the present study, which shows that the presence of manganese has not inhibited the precipitation of Fe^{2+} to $Fe(OH)_3$. No precipitation of Fe(II) was observed in the absence of Mn^{2+} ions and at a concentration of 1.2 mg/L. This is attributable to the pHp, which stayed consistently acidic during the tests. The acidic environment is not favourable to the oxidation and precipitation of iron. This observation is made by many authors in the literature.

4.7. Effect of potassium ions K^+

At a concentration of 15.93 mg/L, the $\tau E(Fe)$ is null, but when the concentration is increased to 80 mg/L, the $\tau E(Fe)$ attains 42.60%. For the 80 mg/L concentration, the result can be explained by the pHp, which quickly takes a pH value superior to 7 (pH = 7.005) just after 2 minutes of reaction. This pH value indicates good oxidation of Fe^{2+} followed by precipitation as $Fe(OH)_3$ [17, 27]. The concentration of 15.93 mg/L can also be explained by the precipitation pHp, which is an acid pH (pH < 7). In fact, in environments with a pH inferior of 7, the precipitation of iron is not effective or inexistent. This hypothesis was also confirmed by several other authors such as Catherine L, 1999; Ruiti M et al, 2015, Wided M, 2017 [17, 20, 27]. The increase in pH was related to the continuous agitation that permits the contact between the air and the solution. This results the introduction of oxygen into the solution and the liberation of CO_2, which causes the pH to increase during the experiment [17]. From Table 3 the pHp increases as the potassium ion concentration increases. This result confirms that the presence of potassium ions makes the medium favourable to the precipitation of $Fe(OH)_3$.

5. Conclusion

The study of the synthetic solution equivalent to the natural Dan Daji water made it possible to study the influence of the ions that coexist with iron in the Dan Daji drilling water on the precipitation of Fe^{2+} to $Fe(OH)_3$. In fact, the presence of HCO_3^-, Ca^{2+}, K^+ and Mn^{2+} ions at certain concentrations favours the formation of $Fe(OH)_3$. However, the presence of Mg^{2+}, SO_4^{2-} and NO_3^- ions inhibits the precipitation of Fe^{2+} to form $Fe(OH)_3$.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they have no competing interests

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