

## Geothermal Water Quality in Oued R'hir Valley (Southeast Algeria). Scaling Problem and Hardness Treatment

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**Abstract:** The conducts of drinking water supply in Oued R'hir valley, have been for a long time jeopardized by encrusting. Geothermal water, the only source of drinking water, has a high capacity tendency to form scale is the origin of this phenomenon. This water is highly mineralized ( $2.5 \text{ g L}^{-1}$ ) and of a very high degree of hardness ( $1120 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$ ). The maximum scaling rate ( $1.4 \text{ cm y}^{-1}$ ) is observed in the conducts located at the first kilometer of the water source, where the water temperature and pressure are very favorable. The calcareous mass produced is estimated at  $1.6 \text{ g L}^{-1}$ , or  $2243 \text{ t y}^{-1}$ . The treatment results show that hydrated lime process has very low efficiency (11.5%) facing water hardness, compared with that obtained by the sodium carbonate (61%). They, thus testify that water hardness dominated is the permanent hardness. Yet the process with  $\text{Na}_2\text{CO}_3$  added to produced water  $255 \text{ mg L}^{-1}$  of the sodium with the initial water content ( $323 \text{ mg L}^{-1}$ ) for each  $682 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$  of water hardness removed.

**Key words:** Hardness, decarbonation, hydrated lime, sodium carbonate, geothermal waters

### INTRODUCTION

The Oued R'hir valley, located in the Southeast of Algeria, is characterized by hyper arid climate. With an annual precipitation less than 67 mm, the geothermal water, called (Albian), is the only source of drinking water, irrigation and many industries. This aquifer is fossil waters (Cheverry and Robert, 1998) drawn from wells with depths reaching 1800 m. The temperature of the water withdrawn varies between 55 and  $60^\circ\text{C}$ , its hardness is around  $1120 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$ .

Chemical analysis revealed that this water had a scaling power to a hardness of  $1120 \text{ mg L}^{-1}$  as  $\text{CaCO}_3$ . The total water volume annually drawn is about 14 million cubic meters. This valley is suffering from a serious situation caused by the scaling. The conducts water supply (432 km) and localised irrigation techniques have been for a long time jeopardized chemical plugging by scale precipitation. After ten years, the diameters of water supply networks were reduced by 50%. To solve this serious problem, the municipal public water supplies had to change periodically the water conducts. This solution costs about 4 million dinars (US\$ 56,000) per annum. Scaling problems mainly result from combined temperature ( $55\text{-}65^\circ\text{C}$ ) and output pressure between 10 and 15 bars, favorable condition on fluids, which accelerate the scaling

by favoring the exhaust of  $\text{CO}_2$ . Although, the calcium ( $273 \text{ mg L}^{-1}$ ) and magnesium ( $85.3 \text{ mg L}^{-1}$ ) water contents, are moderated and acceptable compared to the OMS norms, respectively 200 and  $150 \text{ mg L}^{-1}$ . The concentration of these two elements is sufficient, under the condition (temperature and pressure), to involve the encrusting tartar deposits. It is evaluated  $2243 \text{ t y}^{-1}$  of tarter deposit in the three wells exploited in Oued R'hir valley. Since the first geothermal water exploitation in 1974, this water was directly consumed without any treatment, the cool water solution has led the local authorities to realises, in 1987, three cooling towers. Yet during the cooling of the geothermal water, the considerable scaling occurred in the inlet to the tower, which nowadays is abandoned. The non adapted dimensioning and the inadequate management of the cooling tower seem to be the principal cause of the project failure.

The extended geothermal water exploitation raised serious problems and the public water supplies agency must consider both the efficiency and the economic aspect in order to get a rational process to solve this issue. To attempt to resolve this problem, decarbonation data ( $\text{CaCO}_3$  precipitation) processing, successively with hydrated lime (temporary hardness removed) and sodium carbonate (permanent hardness treatment) has been

studied. This process has the advantage of avoiding the scaling in the cooling tower, is easily used and economically processing compared to other methods. The main objective of this study, is to reduce the water hardness to around the degree adapted from the World Health Organization (500 mg L<sup>-1</sup> as CaCO<sub>3</sub>), which is considered to provide an acceptable balance between corrosion and incrustation.

## MATERIALS AND METHODS

**Geothermal water characteristic:** Table 1 shows the characteristics physicochemical of geothermal waters from the Oued R'hir valley. These waters have relatively laden chloride concentrations, sodium and sulfate. However, the calcium and magnesium water content, are acceptable and moderate concentration compared to the OMS norms, respectively 200 and 150 mg L<sup>-1</sup>. This water is characterized by hot temperature at emergence (55-60°C) and relatively high pressure (10-15 bars) favouring the exhaust of CO<sub>2</sub>. We examined water characteristics having a high permanent calcic hardness (1120 mg L<sup>-1</sup> as CaCO<sub>3</sub>) accelerating the scaling and salinity higher than 2.5 g L<sup>-1</sup>.

**Scaling problems in Oued R'hir valley:** The conducts water supply situation analysis shows, the geothermal water it's highly alkaline character. Scaling problems results mainly from temperature (55-65°C) and pressure (10 bars) favorable condition. One realises that it is the combined high temperature and pressure on fluids that accelerates the scaling by favoring the exhaust of CO<sub>2</sub>. The maximum quantity of settling, with scaling rate of 1.4 cm y<sup>-1</sup> is observed in the conducts located at the first kilometer of the water source (Fig. 1), where the temperature and pressure are favorable. Numerous studies were carried out on the influence of temperature (Lédion *et al.*, 1997; Nefzi *et al.*, 2004) that accelerated the calcium carbonate precipitation. The further from the well water source, as temperature decreases, the more water tends towards equilibrium. From this water we can precipitate 1.6 g L<sup>-1</sup> of salts alkaline-earth. For 14.10<sup>6</sup> m<sup>3</sup> of water annually used, it is estimated 2 243 t y<sup>-1</sup> of tarter deposit in the 3 wells exploited. The precipitate analysis by X-ray diffraction shows that it is constituted of 97% of salts alkaline-earth (CaCO<sub>3</sub> and Mg(OH)<sub>2</sub>).

**Experimental procedure:** Decarbonation (CaCO<sub>3</sub> precipitation) with hydrated lime and sodium carbonate is a common water treatment to remove carbonate and non-carbonate hardness, respectively. The advantages of the process are: It is readily available, easily used and economical compared to the other processes such as

Table 1: Chemical composition and physical properties of geothermal waters

Ionic	mg L <sup>-1</sup>	meq L <sup>-1</sup>	mg L <sup>-1</sup> as CaCO <sub>3</sub>
Calcium	273.2	13.7	683.0
Magnesium	85.3	7.0	350.9
Sodium	323.3	14.1	702.6
Potassium	43.1	1.1	55.1
Total cations		35.9	
Chlorides	532.5	15.0	751.1
Bicarbonates	160.2	2.6	131.3
Sulphate	837.0	17.4	871.9
Total anions		35.0	
Temperature (°C)			55-60
pH			7.5
EC (mS cm <sup>-1</sup> )			2.44
Salinity (g L <sup>-1</sup> )			>2.5
Hardness (mg L <sup>-1</sup> as CaCO <sub>3</sub> )			1120



Fig. 1: Conducts water supply state in Oued R'hir valley

(electrodialysis, distillation, freezing, inhibitor, resin ion exchanger and reverse osmosis), which are complex and expensive. Another important aspect of lime precipitation is the appreciable degree of disinfection occurring in the process (Semerjian and Ayoub, 2003). Hydrated lime and sodium carbonate use, however, are the only inconveniences are that it generates much large volume of sludge (Delire *et al.*, 1999; El Fil *et al.*, 2003). Resin ion exchanger regeneration, is a large chemicals matter consumer. Reverse osmosis, competitor of the nano-filtration, accompanied as electrodialysis, with a high consumption of the electrical energy. In agriculture, the addition of chemical inhibitors has produced good results (Rosset *et al.*, 1999).

The water used in this research is a groundwater of the Oued R'hir valley. Its hardness is around 1120 mg L<sup>-1</sup> as CaCO<sub>3</sub>. The precipitation of CaCO<sub>3</sub> was carried out in glass beaker at room temperature (20-25°C). Aqueous solution of Ca(OH)<sub>2</sub> (97% pure Ca(OH)<sub>2</sub>) and sodium carbonate (99% pure Na<sub>2</sub>CO<sub>3</sub>) were first prepared. In a

hard water sample (250 mL), a solution of  $\text{Ca(OH)}_2$  and  $\text{Na}_2\text{CO}_3$ , with variable concentration, was mixed sparingly into the sample. The time and the optimal concentration, in  $\text{Ca(OH)}_2$  and  $\text{Na}_2\text{CO}_3$ , corresponding to the precipitation onset were identified.

**Analysis methods:** After the end of the mixing waters and hydrated lime or the sodium carbonate, precipitates were separated by filtering out the solution using 0.45  $\mu\text{m}$  Millipore filters. The residual hardness ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ) and other elements ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ) are analyzed. The calcium and the magnesium are determined by titrating it with a standard solution of Ethylene Diamine Tetra-acetic Acid (EDTA). The carbonate concentrations were measured by acid titration. The chloride concentration is dosed according to Mohr method. Whereas, the sulfate, using colorimetric method. Sodium and potassium concentrations are dosed by an atomic absorption system "Perkins-Elmer 1100B". The water pH and the Electrical Conductivity (EC) are measured, respectively by pH-meter "Hannas-212" and a conduct-meter "WTW LF-315".

### RESULTS AND DISCUSSION

The experimental results are tabulated in Table 2 and presented graphically in Fig. 2 and 3. Figure 2 shows that the temporary hardness removed occurring in the presence of various hydrated lime concentration. It is also observed that increasing dosage of lime from 0 to 33  $\text{mg L}^{-1}$ , results in increasing levels of initial hardness from 1120 to 991  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ . The results show that hydrated lime process has a low efficiency treatment (11.5%). Thus this, testifies that water hardness dominated is non-carbonate.

Whereas, softening water with the sodium carbonate shows a better efficiency. Process efficiencies up to 61% are obtained for a dose of 180  $\text{mg L}^{-1}$  in  $\text{Na}_2\text{CO}_3$ . It is observed (Fig. 3), that varying levels of initial hardness from 1120 to 438  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$ , increases dosage of sodium carbonate from 0 to 450  $\text{mg L}^{-1}$ . Whereas, the

Table 2: Qualities of groundwaters treatment

Parameters	Raw waters	Single-stage lime	Sodium carbonate
pH	7.24	8.86	10.1
EC ( $\text{mS cm}^{-1}$ )	2.44	2.4	3.84
Hardness ( $\text{mg L}^{-1}$ as $\text{CaCO}_3$ )	1120	991	438
$\text{Ca}^{2+}$ ( $\text{mg L}^{-1}$ )	273.2	257.8	62.5
$\text{Mg}^{2+}$ ( $\text{mg L}^{-1}$ )	85.3	75.9	102.1
$\text{Na}^+$ ( $\text{mg L}^{-1}$ )	323.3	290	578.7
$\text{K}^+$ ( $\text{mg L}^{-1}$ )	43.1	--	--
$\text{HCO}_3^-$ ( $\text{mg L}^{-1}$ )	160.2	19.8	25.6
$\text{SO}_4^{2-}$ ( $\text{mg L}^{-1}$ )	837	--	--
$\text{Cl}^-$ ( $\text{mg L}^{-1}$ )	532.5	--	--

sodium carbonate process adds 255  $\text{mg L}^{-1}$  of sodium to initial water content (323  $\text{mg L}^{-1}$ ), for each 682  $\text{mg L}^{-1}$  as  $\text{CaCO}_3$  of hardness removed. The amount of sodium added depends on the hardness of the water supply. The sodium content increases approximately by 40  $\text{mg L}^{-1}$  for every 100  $\text{mg L}^{-1}$  of hardness removed.

Calcium carbonate was precipitated by rapidly mixing the waters, hydrated lime or/and sodium carbonate aqueous solution. Immediately after mixing, the electrical conductivity and water pH increase. The evolution of pH (Fig. 4) and electrical conductivity (Fig. 5) is monitored throughout the experiment. The maximum in the pH-time curves corresponds to the precipitation threshold in the water concerned. The start of precipitation is also indicated by a change in slope of the electrical conductivity-time curves, while the slope beyond the inflection characterises the kinetics of the  $\text{CaCO}_3$  precipitation. At these experimental conditions, the precipitation occurs spontaneously after 5 min and about 10 to 15 min the equilibrium is obtained.

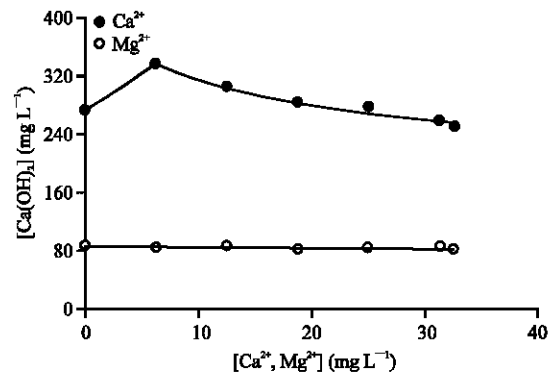


Fig. 2: Relationship between calcium and magnesium residuals and hydrated lime added

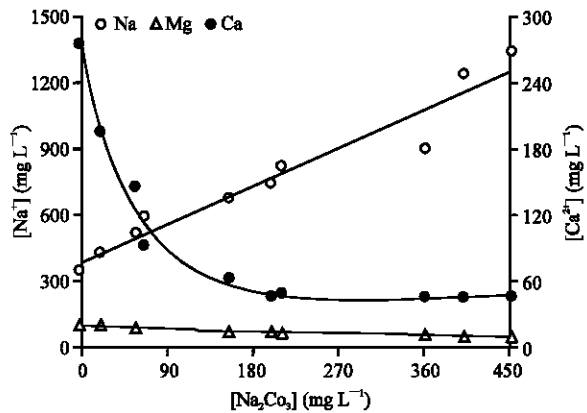


Fig. 3: Relationship between sodium carbonate dose, calcium and sodium water solution

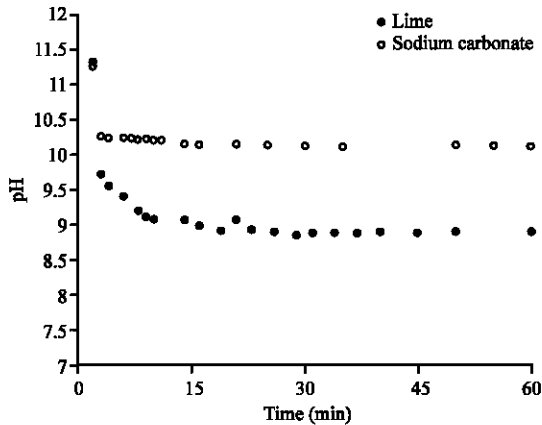


Fig. 4: Relationship between electrical conductivity, water pH and time

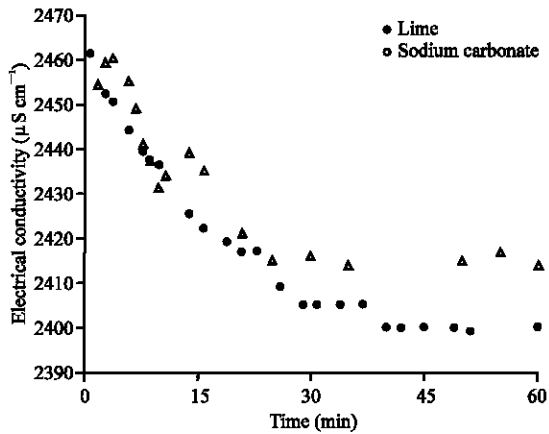


Fig. 5: Relationship between electrical conductivity, water pH and time

### CONCLUSION

The encrusting observed in the conducts water supply is due essentially to the favorable conditions of water temperature and pressure and not to the calcium and magnesium content in the water. In situ, calcium carbonate precipitation is much accelerated at high temperatures (55-60°C) and decreases the further from the well water source. The calcareous mass annually produced, for the three wells of water source, is estimated

at 2243 tons. The water decarbonation with sodium carbonate process is very effective (61%) for the geothermal water softening compared to hydrated lime process treatment (11.5%). The initial hardness varies from 1120 to 438 mg L<sup>-1</sup> as CaCO<sub>3</sub>. This result testifies that water hardness dominated is the permanent. Whereas, the sodium carbonate process adds 255 mg L<sup>-1</sup> of sodium to initial water content (323 mg L<sup>-1</sup>). Geothermal water from Oued R'hir valley seems dispenses completely from the decarbonation with hydrated lime.

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