

Characterization of scale deposits formed in sanitary hot water pipelines in the northern tourist zone of Agadir city

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Abstract: The formation of scale on surfaces in contact with water is due to many reasons as the hardness of water and its temperature. Therefore, this phenomenon of scale in water pipelines is a common and inevitable problem in the regions that exploit or use groundwater with high rigidity. The circuits fed by hot water are easily reached by hard water scaling. The deposition of encrusting curst at the level of walls in touch with water is due to many technical, economic and environmental problems. It causes a reduction in water flow and a decrease in the efficiency of heating systems.

In this study, we are particularly interested in studying the phenomenon of hard water scaling caused by sanitary hot water in a tourist unit situated in the north of the seaside in the city of Agadir. First, we have evaluated the physico-chemical quality of water in use in this tourist unit. Secondly, we conducted a qualitative and quantitative analysis of the scale found in the circuits that transport sanitary hot water. Several analytical techniques were used to reach this goal namely: X-ray fluorescence (XRF) which shows that 85.50% of scale is represented by Calcium Carbonate. Whereas infrared spectrometry (IR) demonstrates the existence of the Carbonate anion CO_3^{2-} . In addition, due to thermogravimetric analysis (TGA) and differential thermal analysis (DTA) we found that the endothermic event shows the decomposition of Calcium Carbonate of CaO and CO_2 in the temperature range of 660 C° to 820 C°. For scanning electron microscopy (SEM), it indicates that the scale takes the form of needle-like aragonite crystals. At last, the X-ray diffraction (XRD) shows that the scale is composed essentially of Calcium Carbonate of the type aragonite.

The results of the different techniques of characterisation are in concordance in the scaling of the circuits of sanitary hot water in the tourist unit under study.

Keywords: Scaling; sanitary hot water; calcium carbonate; analysis; Agadir.

Introduction

The city of Agadir is considered the capital of tourism in the state of Souss Massa and has a capacity of 27200 beds with hosts about 900000 tourists annually. It is also the first seaside resort in Morocco. The regional council of tourism in Souss Massa has taken significant measures so as to make tourism a magnet to attract people all over the world. Hence, it seems essential for us to contribute to the development of tourism in this city by participating in the research for solutions to the problem of sanitary hot water pipelines in the northern tourist zone. One of the consequences of this problem is the clogging of pipes that transport sanitary hot water to these tourist units in the Agadir city.

The problem of scaling in water pipelines and facilities is a disastrous curse in Moroccan regions that exploit groundwater. In fact, hotels in the north of the tourist zone of Agadir are concerned with this

problem due to the high hardness which range between 25 and 55.63 °F (French degree), the high temperature and uncontrolled precipitation of scale. This phenomenon causes the formation of solid deposits adhering to the inner walls of pipelines and water facilities. This scale deposition is the cause of several percussions technically, economically and even environmentally. It consists a real threatening for the lifetime of boilers, partial or complete obstruction of pipes, seizing stopping devices (taps) and a reduction of heat exchange in the case of boilers and therefore a decrease in the energy an efficiency of heating systems^{1,2}.

The aim behind this study is to find a solution to the problem of hard-water scaling. The present work targets the identification and characterization of scale deposits formed in sanitary hot water pipelines in the northern tourist zone facilities of Agadir using different analytical methods as following: XRF, IR, TGA, DTA, SEM, and XRD.

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Materials and methods

Site of the study

The city of Agadir is bordered by the Atlantic Ocean in the west and the last hills of the western high Atlas in the North. The collection of scale has been made at different installations of sanitary hot water in the touristic facilities of the northern seaside zone of the city of Agadir, located in the coordinates (30.41, -9.60).

Characterization

X-Ray Fluorescence (XRF) analyses are performed on a PAN Analytical Axios. The applied voltage is 60 kV with a current of 125 mA and Power 4000W. Infrared spectroscopy (IR) analysis is held through Bruker FTIR-ATR vertex model 70, with a resolution of 4 cm^{-1} in 16 scans to gather the data in a scope ranging from 400 to 4000 cm^{-1} . The samples are placed directly on the ATR crystal (Diamond of reflection). The mode used is the "total reflectance attenuated" (ATR). X-ray diffraction analysis was conducted via the PAN Analytical appliance using a diffractometer type X-Pert-Pro with an anode material of copper and a monochromator of Cu-K α radiation ($\lambda= 1.5406\text{ \AA}$). The applied voltage is 45 kV with a current of 40 mA at 25°C. The morphology was analyzed using scanning electron microscopy (SEM) with a FEG Zeiss Supra running at an accelerating voltage of 3 kV to limit load on the sample. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on a thermal

analyser (DTG-60) with a heating rate of $10\text{ }^{\circ}\text{C}/\text{min}$, under air from $0\text{ }^{\circ}\text{C}$ to $1100\text{ }^{\circ}\text{C}$.

The characterization concerned 5 samples gotten from galvanized steel pipes of hot sanitary water of the northern tourist zone of Agadir. About 40 g of scale were taken from each source of sample. All samples are in the white color. The characterization targeted deposits which are in a direct contact with the support and also with the other scale layers already gotten. All the used techniques guided to similar results for the different samples. Thus, we present below results of one scale deposit.

Results and Discussion

XRF Analysis

The qualitative analysis by X-ray fluorescence (XRF) used means to spot the chemical components in the scale samples. The Fig. 1 shows spectrums of major elements found in hot water scale samples. According to the (Fig. 1b), the calcium is the major element existing. It presents an intense peak at the wavelength 0.336 nm. It is followed by the Sulfur at 0.537 nm (Fig. 1c), the Iron at 0.193 nm (Fig. 1a), the chromium at 0.229 nm (Fig. 1a) and the Silicon at 0.713 nm (Fig. 1d).

Quantitative XRF analysis results are presented in Table 1. The chemical composition of scale sample shows that calcium oxide CaO was the most abundant component (47.92 %). The high amount of calcium oxide shows that calcium carbonate is the predominant component of scale deposited from hot water 85.50 %.

Table 1. Chemical composition of the scale samples in hot water system.

| Compound | Weight % |
|---|----------|
| Calcium oxide (CaO) | 47.92 |
| Magnesium oxide (MgO) | 4.27 |
| Silica(SiO ₂) | 2.33 |
| Alumina (Al ₂ O ₃) | 0.87 |
| Sulfur trioxide (SO ₃) | 0.47 |
| Iron oxide (Fe ₂ O ₃) | 0.41 |
| Potassium oxide (K ₂ O) | 0.10 |
| Phosphorus pentoxide (P ₂ O ₅) | 0.09 |
| Sodium oxide (Na ₂ O) | 0.03 |
| Loss on ignition(LOI) | 42.92 |
| Calcium carbonate(CaCO ₃) | 85.50 |

Other oxides were detected in very low quantities: Magnesium oxide MgO, Silica SiO₂ are found in a percentage of 4.27 % and 2.33 % respectively. Other oxides like Alumina Al₂O₃, Sulfur trioxide SO₃, Iron oxide Fe₂O₃, Potassium oxide K₂O, Phosphorus pentoxide P₂O₅, and Sodium

oxide Na₂O reporting less than 2 Wt % of the total composition. In addition, it was also observed that the loss on ignition for hot water tartar was found to be 42.49 %. The ignition knows a high loss mainly due to the decomposition of the calcium carbonate with formation of CaO and carbon dioxide (CO₂)³.

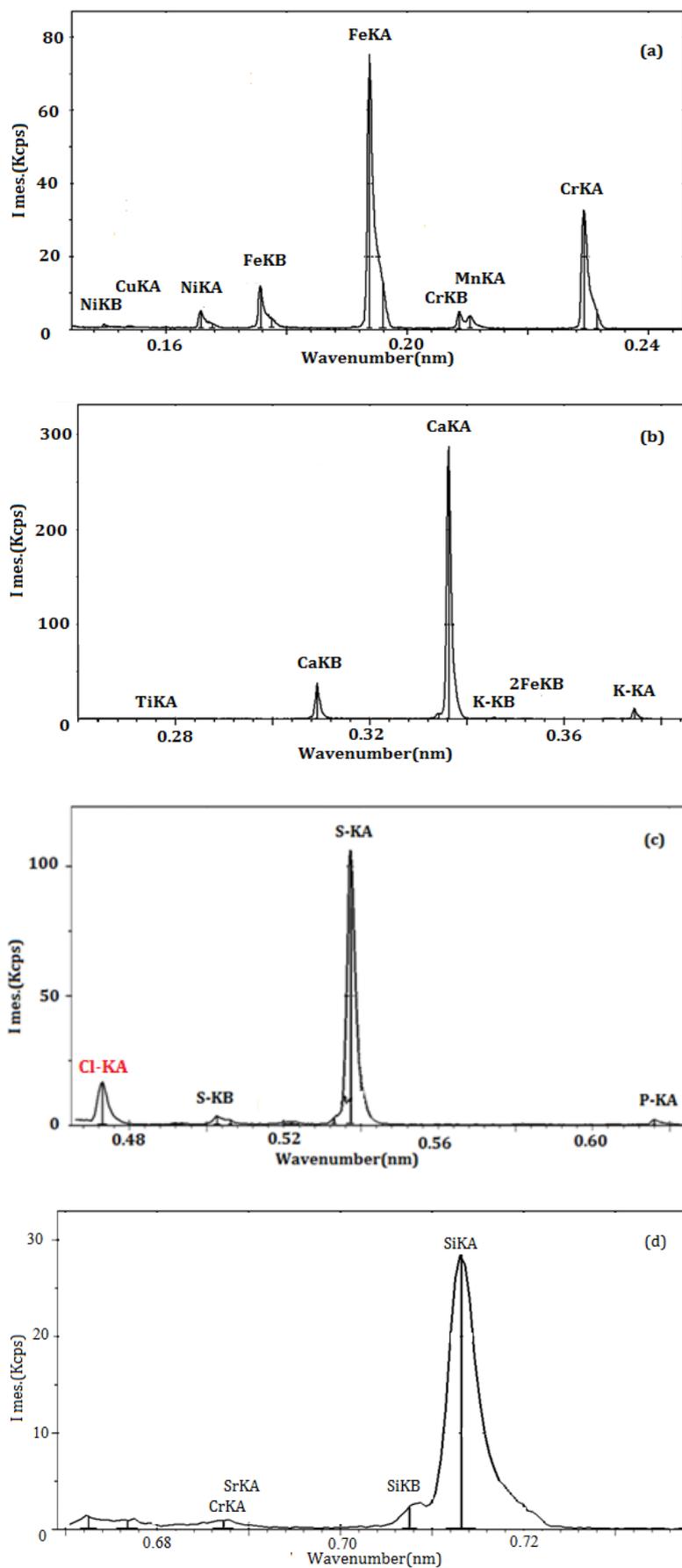


Figure 1. Spectrums of XRF qualitative analysis of scale deposited in hot water system

Infrared analysis of water scale

The analysis by IR spectroscope has given the results presented in Fig. 2. The spectrum allowed to identify the absorption bands corresponding to the different vibration characteristics bonds in the scale sample. The spectral data gained from the samples show a considerable absorption peak of CO_3^{2-} carbonate ions. FTIR spectroscopy is a vital instrument which is utilized to determine the various phases of the organic and inorganic components and more specifically, calcium carbonate phases which are due to the differences in their carbonate ions, CO_3^{2-} . Carbonate ions and similar molecules have four normal modes of vibration peaks: ν_1 , symmetric stretching; ν_2 , out-of-plane bending; ν_3 , doubly degenerate planar asymmetric stretching; and ν_4 , doubly degenerate planar bending⁴. However, the observed bands at 1084.29 cm^{-1} and 857.12 cm^{-1}

that can be attributed to the characteristic aragonite symmetric carbonate stretching (ν_1 mode) and a carbonate out-of-plane bending (ν_2 mode) vibration, respectively. Moreover, the bands at about 712 cm^{-1} can also be attributed to the in-plane bending modes (ν_4) of aragonite⁵. The band observed at 1473 cm^{-1} we have assigned to the combination $220 + 273 + 290 + \nu_4b = 1473 \text{ cm}^{-1}$, 220 , 263 and 290 cm^{-1} bands associated with lattice modes⁶. In addition, the band near 1794 cm^{-1} pointed to the presence of carboxyl (COO^-), which came from CO_3^{2-} and the surface adsorption of ambient water⁷. The resulting spectra (Fig. 2) are, in general, strongly dominated by the vibration bands of calcium carbonate aragonite, due to the vibration of carbonate ions CO_3^{2-} , which is a metastable polymorph of calcium carbonate. It is a common mineral occurrence and mechanically it is highly strong⁸.

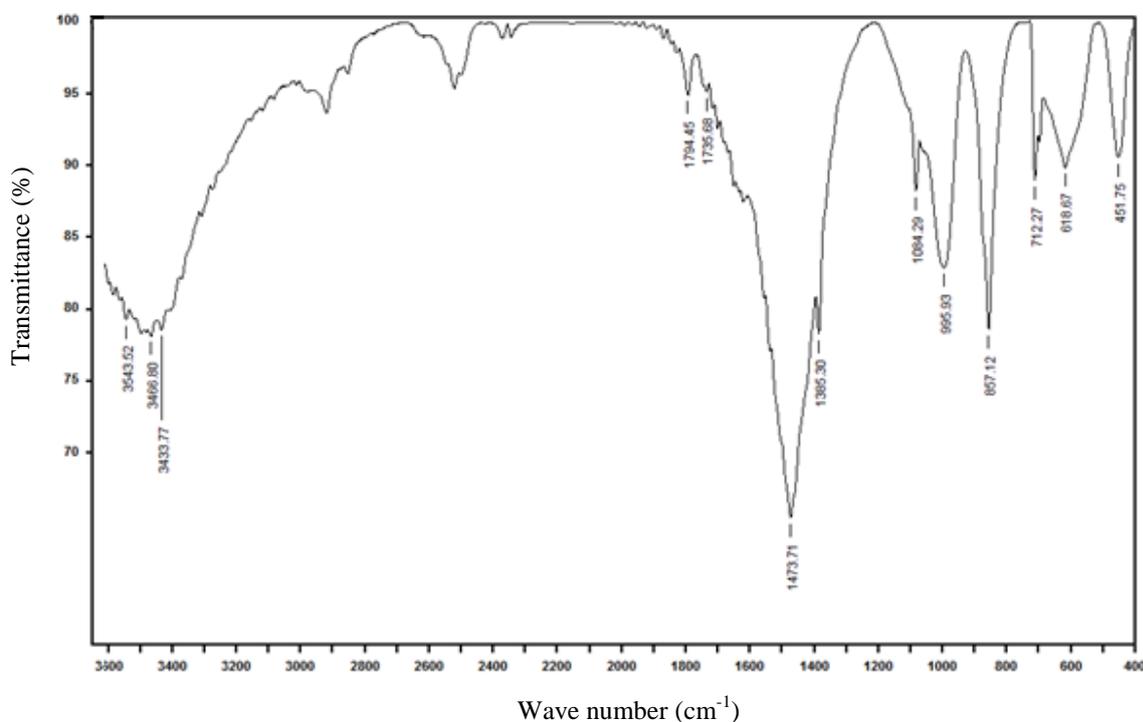
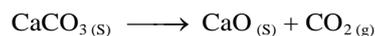


Figure 2. Infrared spectrum of scale formed in hot water system

GTA and DTA analysis of water scale

Thermogravimetric analysis was used first complement DTA because it can continuously show weight variation data relative to DTA peaks. The curves obtained are given in Fig. 3. The results show the presence of three thermal events. The first event of 60°C is endothermic, which is accompanied by mass loss of 5% in the region of 0 to 500°C associated to the elimination of the surface and lattice water. The second event of 260°C is endothermic⁹, due to decomposition of organic matter. The third event of 800°C is endothermic, which is accompanied by very important the mass loss (40%) which attributed to the decomposition of calcium carbonate of CaO and CO_2 in the temperature range of 660°C to 820°C ^{10,11}. On the

other hand, the mass loss in the temperature range $660 - 830^\circ \text{C}$ corresponds to the proportion of CO_2 evolved from the sample according to reaction:



at high temperature¹². Is maintained at 1223 K , at this temperature, the equilibrium CO_2 partial pressure is 1.9 atm ¹³. This decomposition is accompanied of a mass loss total of about 45% a hot water scale. These findings are in accordance with the ignition loss. (Table 1) XRF results above and the literature value of 44% caused the decomposition of CaCO_3 into CaO with the loss of carbon dioxide¹⁴⁻¹⁷.

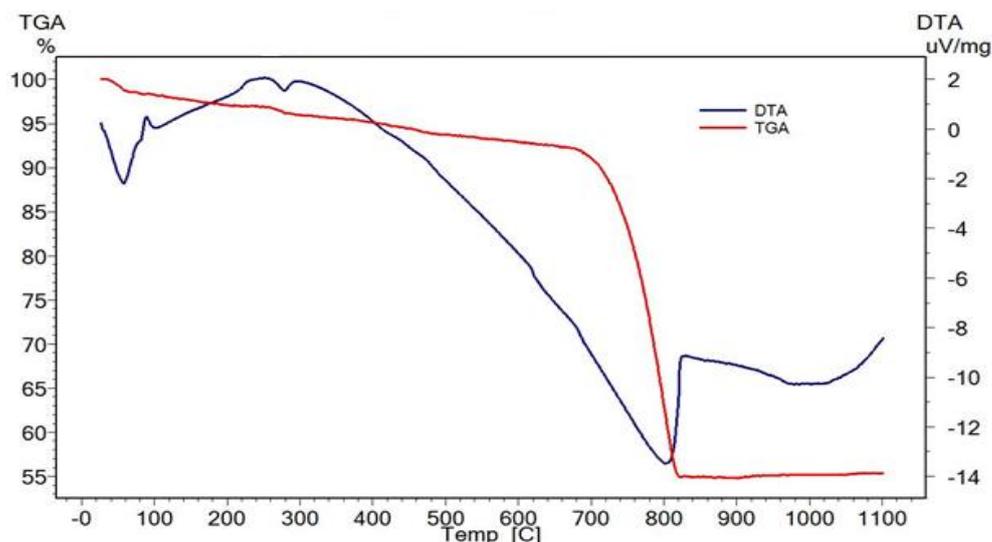


Figure 3. Thermogravimetric and differential thermal analysis curves of scale samples in hot water

SEM analysis of water scale

The adsorption of Ca^{2+} on the surface promotes the adsorption of CO_3^{2-} and can possibly also promote nucleation of calcium carbonate CaCO_3 particles. The SEM micrographics in Fig. 4 show CaCO_3 crystallization in the scale sample deposit obtained from hot water. Micrographs obtained show that the scale structure is in the form of needle-like

aragonite crystals, which is in accordance with the results obtained by literature^{3,18,19}. Due to the crystal morphology we assume that the needle like crystals refer to aragonite and the rhombohedral to calcite. Mantilaka et al. stated that calcium carbonates can bring about three kinds of crystal structures²⁰: aragonite, calcite and vaterite. These structures are reversible under some conditions²¹.

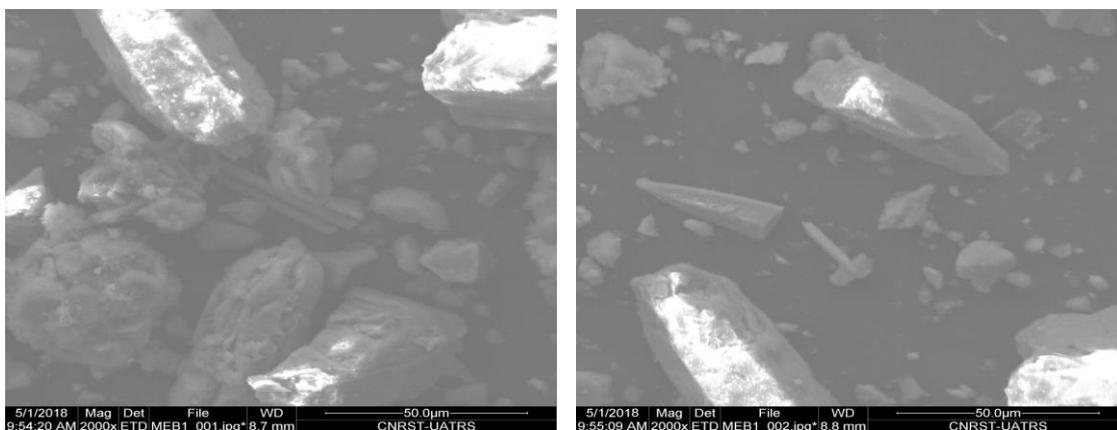


Figure 4. Scanning electron micrographs (SEM) of Scale samples in hot water

X-ray diffraction analysis of water scale

X-ray diffraction (XRD) is an effective method for determination of the crystalline phases. In Fig. 5, the peaks at $2\theta = 26.25^\circ$; 27.25° ; 38.47° and 45.95° with higher intensity, followed by peaks at 48.39° ; 33.17° ; 37.32° and several lesser peaks corresponding to the aragonite²², while the diffraction angle, $2\theta = 29.7^\circ$ is associated to Mg-calcite with low intensity, because the diffraction angle for pure calcite is $2\theta = 29.3^\circ$ ²³.

Finally, the XR diffractogram of studied scale shows that the scale essentially consists of aragonite CaCO_3 with a percentage of 88 % compared with the JCPDS file of N°. 00-005-0453, these diffractions

peaks can be well indexed to orthorhombic aragonite with lattice parameters of $a_0 = 4.959 \text{ \AA}$, $b_0 = 7.968 \text{ \AA}$, $c_0 = 5.741 \text{ \AA}$, and space group Pmcn ²⁴, with a presence of the Mg-calcite $\text{Mg}_{0.06}\text{Ca}_{0.94}(\text{CO}_3)$ with a percentage of 12 % compared with JCPDS card N°.01-089-1306²⁵. The temperature increases in pipes that transport hot water contribute in the formation of aragonite which is metastable at normal ambient temperature¹⁸. Wray and Daniels, who studied the calcium carbonate polymorphs made from highly supersaturated solutions of calcium carbonate, said that aragonite was the predominant component that can precipitate at high temperature near 70°C ²⁶.

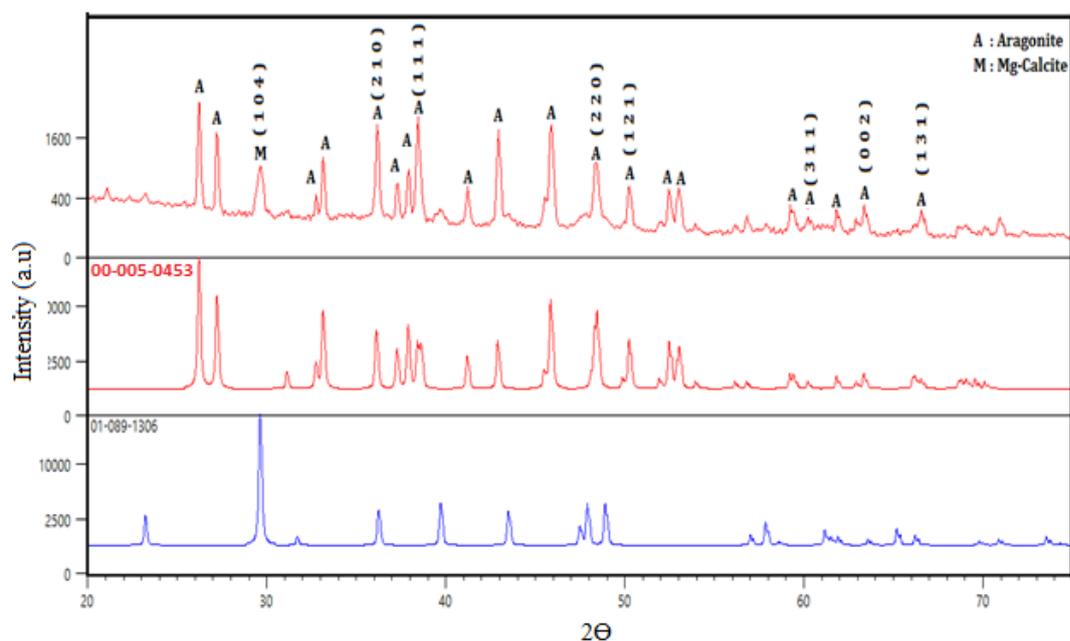


Figure 5. X-ray diffraction Spectrum of hot water scale

Indeed, the high temperature of the hot water in the pipes leads to the formation of aragonite. At higher temperatures, the latter was attributed to a decrease in supersaturation conditions. Higher temperatures were also reported to increase the aspect ratio of the precipitated crystals. This result was also confirmed by Hu and Deng²⁷.

Conclusion

The combination of various analytical techniques XRF qualitative analysis, XRF quantitative analysis, IR, SEM, GTA, DTA and XRD has been very useful for identifying and characterizing the scale deposits in hot water pipelines in the North of the touristic area of Agadir city.

The founded results of all the analytical techniques are as following: The Scale sample studied is chemically constituted basically by calcium oxide CaO (47.92 %). The carbonates anion has been well identified in the infra-red spectrum. Quantitative analysis results showed that calcium carbonates amount goes beyond 85.50 wt %. Results of X-ray diffraction showed that the crystalline phase present in the Scale sample is essentially calcium carbonate in the form of aragonite (CaCO₃), which is confirmed by SEM images which approves that the scale structure is in the form of needle-like aragonite crystals. GTA measurement indicated high total mass loss (45 %), which was caused mainly by evolved CO₂ and organic matter decomposition which is in accordance agreement with the loss on ignition in XRF analysis results (Table 1).

We can conclude that water scale samples deposited in pipes are calcium carbonate, believed that aragonite was the principle precipitate at high temperature which are confirmed by all the

analytical techniques. These findings will let us make our research more channelled towards finding out more suitable inhibitors of scaling so as to prevent the deposit of scale in the hot water system in the touristic area of Agadir city.

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