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Study of Pipes Scaling of Purified Wastewater Intended for the Irrigation of Agadir Golf Grass

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Abstract**—**In Morocco's Agadir region, the reuse of treated wastewater for irrigation of green spaces has faced the problem of scaling of the pipes of these waters. This research paper aims at studying the phenomenon of scaling caused by the treated wastewater from the Mzar sewage treatment plant. These waters are used in the irrigation of golf turf for the Ocean Golf Resort. Ocean Golf, located about 10 km from the center of the city of Agadir, is one of the most important recreation centers in Morocco. The course is a Belt Collins design with 27 holes, and is quite open with deep challenging bunkers. The formation of solid deposits in the irrigation systems has led to a decrease in their lifetime and, consequently, a loss of load and performance. Thus, the sprinklers used in golf turf irrigation are plugged in the first weeks of operation. To study this phenomenon, the wastewater used for the irrigation of the golf turf was taken and analyzed at various points, and also samples of scale formed in the circuits of the passage of these waters were characterized. This characterization of the scale was performed by X-ray fluorescence spectrometry, X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and scanning electron microscopy (SEM). The results of the physicochemical analysis of the waters show that they are full of bicarbonates (653 mg/L), chloride (478 mg/L), nitrate (412 mg/L), sodium (425 mg/L) and calcium (199mg/L). Their pH is slightly alkaline. The analysis of the scale reveals that it is rich in calcium and phosphorus. It is formed of calcium carbonate ($CaCO_3$), silica (SiO_2), calcium silicate (Ca_2SiO_4), hydroxylapatite ($Ca_{10}P_6O_{26}$), calcium carbonate and phosphate ($Ca_{10}(PO_4)$ $6CO_3$) and silicate calcium and magnesium ($Ca_5MgSi_3O_{12}$).

Keywords**—**Agadir, irrigation, scaling water, wastewater.

I. Introduction

The region of Souss Massa is known for its semi-arid climate and its very limited water resources. In order to mitigate this water deficit, the development master plan for this region recommends resorting to unconventional resources. The reuse of treated water to reduce this water deficit is now inevitable. Infrastructures have been made to serve the golf ranges and green spaces of the city of Agadir by treated wastewater from Mzar station. The average flow is 30000 m^3/d [1], [2]. Nevertheless, this reuse of treated water has encountered the problem of scaling of water pipelines. This phenomenon has created technical economic and environmental problems.

This study aims, on the one hand, to examine the physical and chemical quality of the treated wastewater used for irrigation of golf turf. While on the other hand, it aims at identifying and characterizing the scale deposits assembled at the level of the pipes and sprinklers of Ocean Golf. Samples of treated water were taken from the transport pipelines of treated water at the golf entry, at the level of the tank and at the exit of the sprinklers. The samples of treated wastewater and obtained scale were studied using different techniques.

II. Materials and Methods

A. Site of the Study and Sampling

The sewage treatment plant of wastewaters Mzar is located at approximately 4 km in the south of Agadir city on the left coast of Oued Souss on the coastal dunes of Mzar. Its western limit is about 1500 m from the sea.

The Ocean Golf Resort, which opened in January 2010, is located at 11 km from the city center of Agadir in the forest of Bensergao (Fig. 1). Its total area is 100 hectares, of which, 75 hectares are grassed. It has a storage tank capacity of 15,000 m^3 with a depth of 1.5 m. The flow of daily watering rate ranges from 3000 m^3 to 4000 m^3.

Fig. 1 Location of the Mzar's sewage treatment plant and Ocean Golf

The studied scale was collected inside the Ocean Golf Resort at three different points. Fig. 2 shows a sprinkler clogged by scale while Fig. 3 shows the scale taken from a sprinkler.

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Fig. 2 Sprinkler clogged by scale

Fig. 3 Golf sprinkler scale

B. Methods of Analysis

1. Physicochemical Analyzes

Calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions were determined by atomic adsorption method, while sodium (Na^+) and potassium (K^+) ions by flame spectrophotometry, chloride (Cl^-) by Mohr method, sulfates (SO_4^{2-}) by gravimetry, nitrates (NO_3^-) by visible spectrophotometry and bicarbonate by volumetry.

2. X-Ray Fluorescence Spectrometry Analysis

X-rays are electromagnetic radiation ranging approximately between 0.1 Å and 50 Å. They are emitted by the bombardment of the surface of a solid by cathode rays. The scale was analyzed using XRF spectrometer Axios. The applied voltage is 60 kV with a current intensity of 125 mA and 4000 W power.

3. XRD

The use of XRD spectroscopy is an essential step in accurately identifying the scale structure formed during the scaling process. The diffractometer used for these measurements is a goniometer with direct optical encoding connected to computer and using a copper anticathode Kα (λ = 1.5406 Å), with an absolute angular accuracy of 0.0025 and a reproducibility lower than 0.0001 degrees. The scan is adopted with a step of 0.06682°.

4. Differential Thermal and Gravimetric Analysis

DTA is a technique that measures the temperature difference between a sample and a reference according to time and/or temperature. TGA is a technique that measures the mass variation of a sample when it is subjected to temperature variation programming, under a controlled atmosphere. The thermal and gravimetric analysis of the scale was carried out by a TGA apparatus combined with DTA of the type Shimadzu DTG- 60, under air with 10 °C/mn, from 0 °C to 1100 °C. The flow rate used is 10 mL/mn.

5. SEM Analysis

SEM is used to gain visual mastery of the objects: the morphology of the grain boundaries and the porosity. It also allows to highlight the textural state of a powder or a material. The scale samples were dehydrated, treated and then placed on the slide. The micrographs of the scale are obtained by scanning electron microscope FEI Quanta 200 equipped with an EDX probe. The surface microanalysis is carried out with a resolution of 3.5 nm and an optical magnification of 20-106 times.

III. Results and Discussion

A. Physicochemical Analysis of Treated Wastewater

To determine the physicochemical parameters of the wastewater related to the scaling phenomenon, water samples were taken at three points: the transport pipeline of water at the golf course entry, the tank and from the sprinklers [3]. The obtained results are given in Table I.

TABLE I
PHYSICOCHEMICAL PARAMETERS OF TREATEDABO

Symbol	Golf entrance	Tarpaulin	Sprinkler	Moroccan norms
T(°C)	27.9	27.9	27.5	35
pH	7.8	7.8	8.3	6.5-8.5
EC (mS/cm)	2.82	2.86	2.9	12
Ca^+ (mg/l)	199	196	201	-
Mg^{2+} (mg/l)	55.1	49.3	51	-
K^+ (mg/l)	36	38	37	-
Na^+ (mg/l)	414	431	430	69
HCO_3^- (mg/l)	635	659	665	518
PO_3^- (mg/l)	5.7	6.1	4.6	
SO_4^{2-} (mg/l)	216	235	220	250
NO_3^- (mg/l)	428	402	405	30
Cl^- (mg/l)	458	484	493	105

According to these results, treated wastewaters are slightly rich in alkaline pH of 8.3 at the level of sprinkler. These waters have high contents of bicarbonate ions HCO_3^-, sodium Na^+, nitrate NO_3^-, chloride Cl^- and sulphate SO_4^{2-}. These contents widely exceed the values fixed by the Moroccan norms relating to the reuse of wastewaters for the irrigation of the public green spaces [4]-[6].

The water used to irrigate golf turf at Ocean Golf has a slight amount of alkaline pH which has the effect of promoting the formation of scale [7]-[9]. The medium value of the electrical conductivity highlights a strong mineralization of these waters. Similar results were obtained on the treated waters of Mzar station by Touyer (1997) and Eddabra (2011) [10], [11]. For the waters of the Ocean Golf tank, a slight variation of the pH and the contents of calcium, bicarbonate, sulphate and chloride were noticed.

The treated water thus presents favorable conditions for the formation of chemical deposits in their passageways. All the sprinklers of the Ocean Golf Resort are thus clogged up in the first weeks of the beginning of their operation. To overcome this problem, filters were installed upstream and downstream of the pipes. However, within a few hours of operation, these filters become clogged and must be disassembled for cleaning.

B. Chemical Analysis of Scale

The results of the chemical analysis of the scale taken at the entrance of the golf course, in the storage tank and at the level of the sprinklers are collected and presented in Table II.

TABLE II
CHEMICAL PROPERTIES OF SCALE TAKEN AT DIFFERENT POINTS OF THE OCEAN GOLF COURSE

Symbol	Golf course entrance	Inside storage tank	Sprinklers
Dry matter (%)	78	78.32	76
Humidity (%)	22	21.68	24
Organic matter (%)	3.75	3.2	3.15
EC (µS/cm)	7.95	7.52	8.20
pH	9.32	9.29	9.4
N (%)	0.47	0.56	0.5
P_2O_5 (%)	17.92	19.27	16.95
Cl^- (%)	0.34	0.31	0.37
K_2O (%)	0.02	0.019	0.017
MgO (%)	1.1	1.03	0.93
CaO (%)	31.83	34.07	38.92
Na_2O (%)	0.27	0.23	0.32
Fe (%)	0.26	0.24	0.038
Cu (mg/Kg)	206	44	31
Mn (mg/Kg)	470	395	278.16
Zn (mg/Kg)	280	88	76.38

The chemical analysis of the studied scale reveals that the rates of dry matter and organic matter vary slightly from one point to another. They range from 76% to 78% and from 3.15% to 3.75%, respectively. At the three sampling points, the pH is alkaline and the electrical conductivity have higher values.

The chemical compositions of scales collected at the entrance to the golf course, inside the storage tank and at the watering sprinklers are relatively similar. The major oxides in these scales are CaO (35%) and P_2O_5 (18%). These samples are completely and rapidly dissolved in the acid. Other elements and other oxides are present but with very low contents compared to the content of CaO and P_2O_5. They have iron contents of 0.26%, 0.24% and 0.038%, respectively.

IV. X-RAY FLUORESCENCE ANALYSIS

The product collected at the sprinkler is moist and reddish. It was dried in an oven at 105°C for 24 hours and then ground to obtain a fine and homogeneous powder. This drying gave a mass loss of 24%. The product color changed and became light brown.

The qualitative analysis by X-ray fluorescence spectrometry made it possible to identify the chemical elements in the scale sample. Calcium and phosphorus are the major elements in the scale. They have two intense peaks (see Fig. 4).

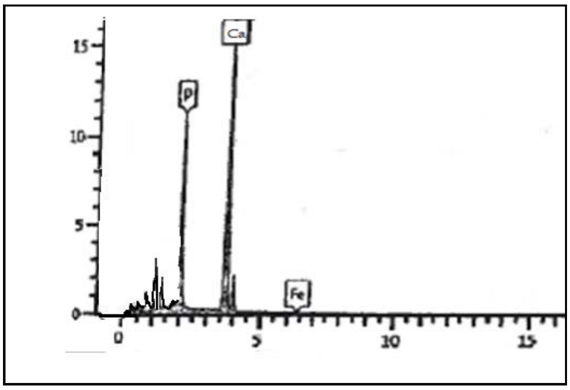

Fig. 4 X-ray fluorescence spectrum of deposited scale

They are followed by the magnesium and silicon elements. Other elements such as oxygen, carbon, sulfur, iron and sodium are also present with peaks of very low intensities. The quantitative analysis (XRF) of scale is shown in Table III.

TABLE III
ELEMENTAL COMPOSITION OF DEPOSITED SCALE

%	Ca	P	Mg	Si	Na	Fe
Mass	71.92	25.85	0.89	0.73	0.24	0.38
Atomic	66.25	30.82	1.35	0.96	0.38	0.25

The scale contains 72% of calcium and 26% of phosphorus in complete weight. The other elements Mg, Si, Na and Fe are present with mass percentages lower than 1. In the calcined product, calcium oxide (CaO) is the major compound with a level of 38.92%, followed by phosphorus pentoxide (P_2O_5) with a percentage of 16.95% in weight. Other trace oxides have been detected such as magnesium oxide MgO (0.93%), sulfuric oxide SO_3 (0.39%), sodium oxide Na_2O (0.32%) and iron oxide Fe_2O_3 (0.038%).

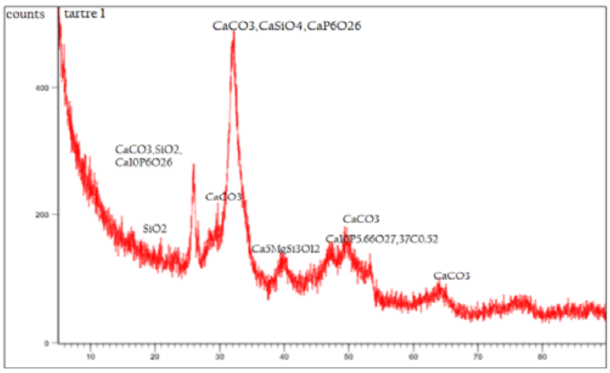

Fig. 5 X-ray diffractogram of the scale taken from the sprinklers

V. XRD ANALYSIS

To identify and analyze the scale structure formed at the sprinklers, XRD analysis allowed obtaining the results shown in Figs. 5 and 6.

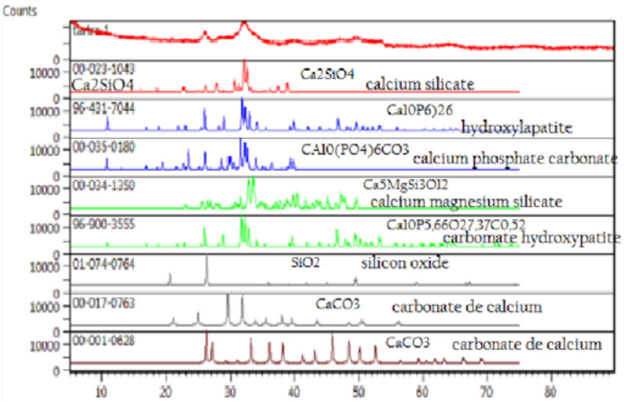

Fig. 6 X-ray diffractograms of the compounds present in scale

The wide peaks observed in Fig. 5 indicate low crystallinity of the scale samples. It is seen that samples scale contain different minerals. The highest intensity peak refers to calcium carbonate, calcium silicate and hydroxylapatite. Many other chemical compounds are presents at low percentage. Fig. 6 shows X-ray diffractograms of some of those compounds.

VI. TGA and DTA

The thermal behavior of the scale collected on watering sprinklers of turf is followed by DTA and TGA techniques, the result of which are shown in Fig. 7.

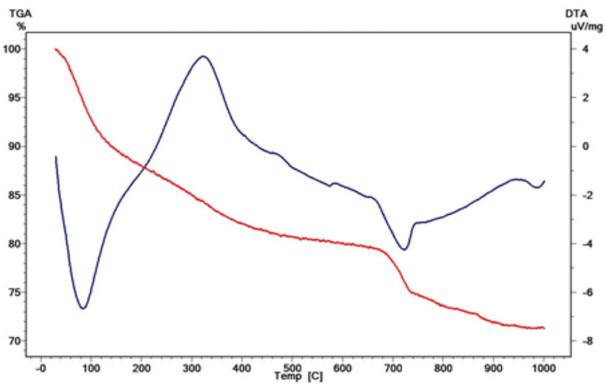

Fig. 7 TGA/DTA thermograms of deposited scale in the sprinklers

The DTA curve shows two endothermic and two exothermic peaks. The TGA curve shows four mass losses. The most important is recorded before 450°C. Between 0°C and 200 °C, the mass loss is of the order of 12% and it is due to the evaporation of water adsorbed on the crystals of scale. This is illustrated on the DTA curve by an endothermic peak centered at 95 °C. Between 200 °C and 440°C, the ATG curve recorded a mass loss of about 8% which can be attributed to the departure of strongly bound intercrystalline water. In the temperature that ranges from 440 °C to 740 °C, the DTA curve presents a marked endothermic peak at a temperature of about 725 °C which illustrates the process of carbonate decomposition and departure of CO_2 [12]-[15]. This decomposition corresponds to a mass loss of about 6%. A fourth mass loss was measured between 740°C and 1000°C. It is weak in the order of 3% and may be due to decomposition of another carbonate or a morphological transformation of the compounds present in the scale [16]. This transformation is illustrated by an exothermic peak around 950 °C [17], [18].

VII. SEM Analysis

The SEM analysis of the scale sample deposited in the sprinklers is given in Fig. 8. It shows that the scale collected consists of crystals of various forms, corresponding to the different compounds present in the scale and confirming the results obtained by the previous analysis techniques.

It includes rhombohedral crystals of calcium carbonate of calcite-type, irregular forms of calcium silicate polymorphs and hydroxyapatite [19].

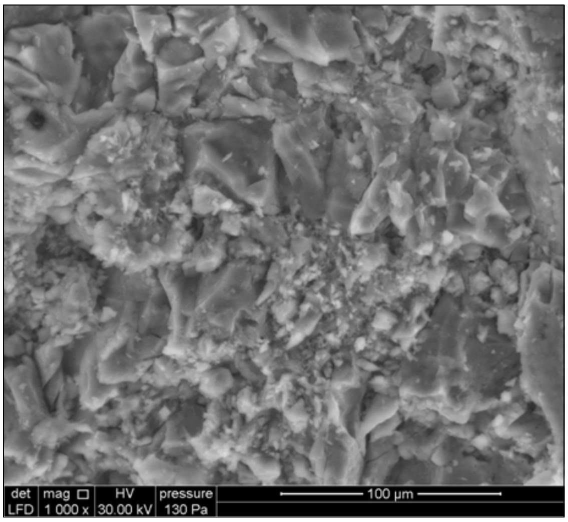

Fig. 8 SEM microphoto of scale in the sprinklers

VIII. Conclusion

The results of the physicochemical analysis of the treated wastewater of the Mzar treatment plant, intended for the irrigation of the turf of the Ocean Golf Resort, show that all factors are favorable for the formation of scale in the passageways of these waters. Thus, the formation of scale has caused difficulties in the irrigation system. The scale analysis, collected at the level of the sprinklers, by X-ray fluorescence shows that it is rich in calcium Ca (72%) and phosphorus P (26%). Other elements such as O, Mg, Fe, S and Si are present with percentages lower than 1. In the calcined product, calcium oxide (CaO) is the major compound with a level of 38.92%, followed by phosphorus pentoxide (P_2O_5) with a percentage of 16.95% in weight. Other trace oxides have been detected.

XRD scale analysis shows the presence of calcium carbonate, silica, calcium silicate, hydroxyapatite, calcium and phosphate carbonate, calcium silicate and magnesium. The various analysis techniques used in this study allowed to characterize the scale deposited by the treated wastewater and show that it is a mixture of chemical compounds. Indeed, the scale deposits are the result of various actions of chemical, physical or mechanical origin. This explains how hard it is to find adequate protection for this types of encrustation deposited by liquid effluents charged with various substances. However, this physicochemical characterization will undoubtedly make it possible to decide on the appropriate and effective treatment to put an end to scaling of the irrigation circuits by using purified water.

References

[1] E. Ibariouen, La réutilisation des eaux usées épurées dans le Grand-Agadir, Régie Autonome Multi-Services d’Agadir, Les cahiers d’échange Med N°8, XIVème Rencontre Internationale d’Echanges Méditerranéens au Maroc, 25/11 au 02/12/2015.

[2] B. Boudinar, H. Mouhanni, M. Houari, A. Bendou, Analyses physico-chimiques du gazon irrigué par les eaux usées épurées de la station Mzar du grand Agadir- Maroc, revue internationale d'héliotechnique n° 46 (2015) 1-7.

[3] Programme mixte FAO/UNW-DPC/UNU-INWEH, Montage Institutionnel et analyse environnementale et socioéconomique et concernant le projet de réutilisation des eaux usées épurées, Rapport global de synthèse, Mars 2012.

[4] Direction des affaires intérieures, Compétitivité économique du Maroc ébauche de révision des normes de qualité des eaux usées traitées destinées à l’irrigation des cultures et a l’arrosage des espaces verts USAID, Mars 2013.

[5] USAID, Réutilisation des Eaux Usées en Irrigation, United States Agency for International Development, projet de « Pérennité des Ressources en Eau du Maroc –PREM »

[6] A. Kerfati, Réutilisation en irrigation des eaux usées au Maroc, DIAEA / Ministère de l’Agriculture, Agadir, 7-11 décembre 2009.

[7] M. Aljandra - Dominguez; Contribution à l'étude des mécanismes d'entartrage: Influence de la matière humique dans l'inhibition de la croissance cristalline du carbonate de calcium, INSA Toulouse (1994).

[8] A. Hadfi, S. Ben Aazza, M. Belattar, S. Mohareb and A. Driouiche. “Evaluation of the irrigation water quality in Biougra circle along with highlighting the effectiveness of a scaling inhibitor”. Mediterranean Journal of Chemistry 2018, 7(4), 272-285.

[9] A. Kamari, F. Gharagheizi, A. Bahadori and A.H. Mohammadi, Determination of the Equilibrated Calcium Carbonate (Calcite) Scaling in Aqueous Phase Using a Reliable Approach. Journal of the Taiwan Institute of Chemical Engineers, (2014) 45, 1307-1313.

[10] O. Touyer, Eaux usées dans le Grand Agadir, Ibn Zohr University, Agadir, Morocco, 183p.

[11] R. Eddabra, (2011), Evaluation de la contamination bactériologique des eaux usées des stations d’épuration du Grand Agadir, Ibn Zohr University, Agadir, Morocco, (1997) NO 1236, 146p.

[12] J. Yin, X. Kang, C. Qin, B. Feng, A. Veeraragavan and D. Saulov, Modeling of CaCO3 Decomposition under CO2/H2O Atmosphere in Calcium Looping Processes.Fuel Processing Technology, (2014), 125, 125-138.

[13] N. Hafid, M. Belaatar, S. Ben-Aazza, A. Hadfi, M. Ezahri, A. Driouiche, Characterization of Scale Formed in Drinking Water and Hot Water Pipes in the Taliouine Downtown—Morocco, American Journal of Analytical Chemistry, (2015), 6, 677-686.

[14] M. N.Freire, J. N. F.Holanda, Characterization of avian eggshell waste aimingits use in aceramic wall tile paste. Cerâmica , (2006), 52 , no.324, 240-244.

[15] A. Hadfi, Evaluation du pouvoir entartrant des eaux du secteur agricole du grand Agadir et Mise en évidence de l’effet inhibiteur de quelques engrais phosphatés (2012) N°102. Ibn Zohr University, Agadir, Morocco, 147p.

[16] S. Serena, M.A. Sainz, A. Caballero., Single-phase silicocarnotite synthesis in the subsystem Ca3(PO4)2–Ca2SiO4, Ceramics International, (2014), 40, 8245–8252.

[17] N. Yamaguchi, Y. Masuda, Y. Yamada, H. Narusawa, C. Han-Cheol, Y. Tamaki, and T. Miyazaki, Synthesis of CaO-SiO2 Compounds Using Materials Extracted from Industrial Wastes, Open Journal of Inorganic Non-Metallic Materials, (2015), 5, 1-10.

[18] C. Remy, B. Reynard, M. Madon, Raman spectroscopic investigations of dicalcium silicate: Polymorphs and high-temperature phase transformations, Journal of the American Ceramic Society Volume 80, Issue 2, February 1997, Pages 413-423.

[19] Z. Gou and J. Chang, Synthesis and in vitro bioactivity of dicalcium silicate powders, Journal of the European Ceramic Society 24 (2004) 93–99.