DILUTION OF SULFURIC ACID BY USING FILTERED WATER: IMPACT ON THE CONSTRUCTION MATERIAL OF THE ACID COOLER

H. Hassoune[1,*], K. Morsli[1], N. Semlal[1], Y. Lahmiti[2], A. Bourras[2], A. Hanine[2], R. Boulif[1], and A. Kossir[1]

[1] R&D Direction, OCP Group, Jorf Lasfar, El Jadida. Morocco
[*] Corresponding author (email: h.hassoune@ocpgroup.ma)
[2] Maroc Phosphore, OCP Group, Jorf Lasfar, El Jadida. Morocco

ABSTRACT

The importance accorded to the role of water in the chemical industry leads to the interest of adopting a better management of this resource. In this context, the aim of this work is to replace the demineralized water by filtered water for production of sulfuric acid at lower cost. The samples of filtered water were collected and analyzed to determine the concentrations of elements that can be responsible for different impacts (corrosion, fouling) on the equipment of the sulfuric acid production unit. Our attention is particularly focused on the construction material of the acid cooler. The concentrations of chloride, calcium, magnesium and silica have been determined. The results obtained for these elements showed that the experimental values are below the maximum admissible values. These results were confirmed by those of corrosion studies that suggest the possible use of filtered water in the dilution step of sulfuric acid.

Keywords: Filtered water; Dilution; Sulfuric acid; Corrosion; Acid Cooler.

1. INTRODUCTION

The concept of water being a never-ending resource with a limitless renewable capacity belongs to the past (Casani et al. [1], Beekman [2]). Indeed, it is known that water has not been considered as a non-renewable resource until the end of the 1960s or the beginning of 1970s (Sans et al. [3], Alvarez et al. [4]). Moreover, it was believed that the resources in the natural environment were limitless. That is the reason why the economic cost of water was not important in relation to the total cost of the industrial activities (Alvarez et al. [4]). Compared to other industrial sectors, the chemical industry uses much greater amount of water for each ton of product (Issar and Oron [5]). Indeed, water is involved in many chemical processing methods and unit operations (Demadis et al. [6]), e.g., washing, rinsing, fluming, heating, cooling, steaming, and for general cleaning and sanitation. For the case of the Jorf Lasfar industrial complex of OCP Group, three main water qualities are produced: filtered water, demineralized water and drinking water. Fig. 1 shows a simplified flow diagram indicating the process water treatment to produce these three water qualities. These

qualities are used as process water (for the production units of sulfuric and phosphoric acids), vapor production, but also for sanitation installations and other industrial units of the Jorf Lasfar complex.
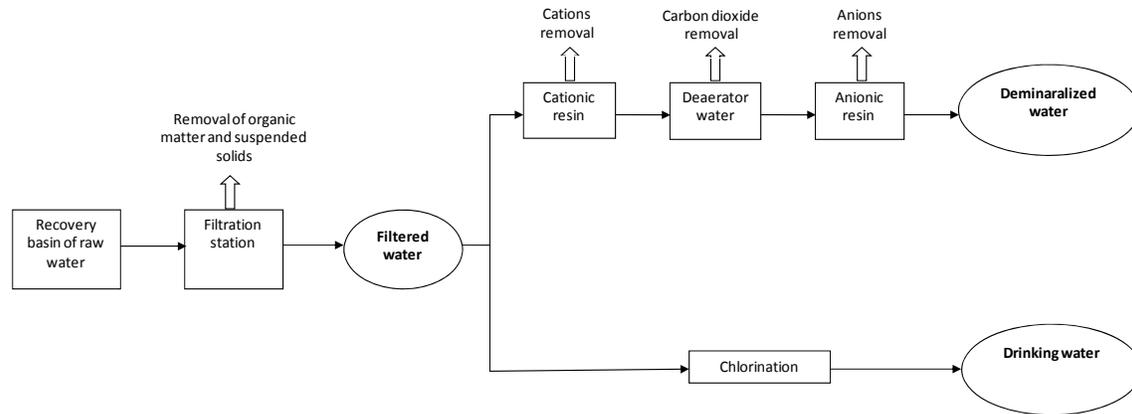

Fig. 1 Simplified flow diagram of production of different water qualities at the Jorf Lasfar industrial complex

Annual consumption levels of these qualities are presented in Table 1. It's showed that, the filtered water is only used for producing demineralized water that requires further treatments. The consequences of the use of filtered water as process water are a decreasing cost factor due to treatment. In this context, particular attention was given to the water used in the sulfuric acid production unit, especially for dilution, which is currently carried out with demineralized water. This water quality is necessary to dilute the sulfuric acid (from 99.5% to 98-98.5%), which is directed towards its commercialization and the production of phosphoric acid. The aim of this work is to study the feasibility of using filtered water to dilute sulfuric acid instead of the demineralized water. However, we suspect that this substitution could be responsible of adverse effects on equipments, especially on the acid coolers (Fig. 2). Indeed, mineral scale deposits could become major operational problems for poorly treated waters (Demadis et al. [6], Demadis [7]). These sparingly soluble electrolytes include calcium carbonate and phosphate, calcium oxalate, barium and strontium sulfate, and others which are largely dependent on a plethora of variables, such as water chemistry, temperature, pH, etc. Silica and magnesium silicate are especially troublesome because they can cause some operational failures in process water systems due to deposit formation. Deposits cause a drastic reduction in heat transfer rates in equipment such as boilers, steam generators, evaporators, distillation units, heat exchangers, cooling tower fill, engine jackets, etc. (Amjad [8]). Boiler tube failures caused by overheating, increased fuel consumption, and reduced efficiency of equipment (Michaud [9,10]). Equipment failure from corrosion as a result of under deposit corrosion can significantly add to this cost. Biofouling can directly contribute to corrosion in addition to constituting a complex matrix for sparingly soluble salt deposition (Lee et al. [11]). Therefore, the concentrations of these elements (calcium,

magnesium, silica and chloride) and the parameters that can promote these deposits must be controlled and compared to the maximum admissible values.

Table 1 Annual water consumption (m³) at the sulfuric acid production units of the Jorf Lasfar industrial complex

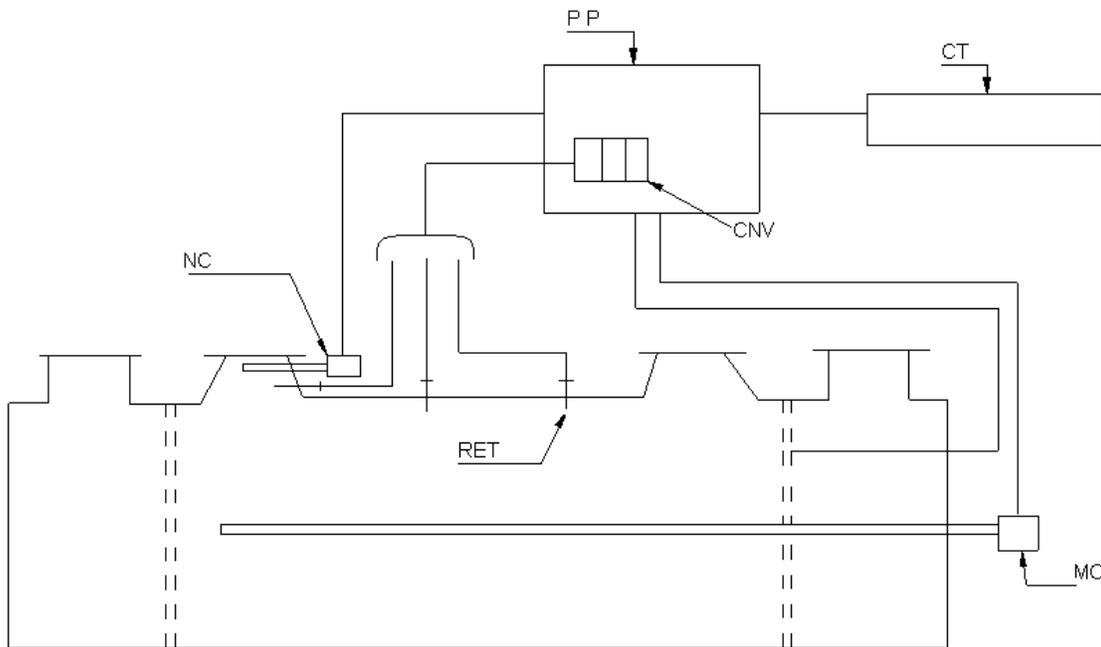| Water quality	Sulfuric acid production units
Filtered water	0
Demineralized water	700000
Drinking Water	20000

Fig. 2 Scheme of the acid cooler: PP is power pac, CNV is converters, CT is controller, MC is main cathode, RET is reference electrode typ, NC is nozzle cathode

2. THEORETICAL APPROACH

Determination of corrosion rate

The plot of the polarization curve is an important electrochemical technique for corrosion studies. Indeed, this curve represents the evolution of the current density versus potential. It predicts the behavior of a metal in an electrolyte (current density, corrosion potential...), and provides much information about the electrochemical behavior of a metal immersed in any reagent. When corrosion is uniform, the curve plotting log (I) = f(E) determines the value of the corrosion current density of I_{cor} by

the Tafel linear plotting. The corrosion rate V_{corr} can be calculated from the corrosion current intensity I_{corr} as follows:

$$V_{cor} = \frac{M \; I_{cor} \; 24.365}{n \; F \; \rho \; S \; 100} \tag{1}$$

Where:

V_{cor}: Corrosion rate.
M: Atomic mass of metal.
n: Valence of metal ion.
I_{cor}: Corrosion current density/surface unit.
F: Faraday constant.
ρ: Volumic mass of metal.
S: Steel surface in contact with electrolyte.

3. EXPERIMENTAL

3.1. Reagents

All chemicals and reagents used for analyses of the water samples and for corrosion assays were of the highest analytical grade. Perchloric acid and nitric acid were provided by Technilab and were used as received without further purification.

3.2. Samples

The filtered water samples were collected at the water treatment station of the Jorf Lasfar industrial complex. We ensured the homogeneity of these water samples.
The construction material samples were collected from the acid cooler at the sulfuric acid production unit.

3.3. Apparatus

Elemental analysis of the filtered water samples was performed with an inductively coupled plasma spectrometer (HORIBA Jobin Yvon/ACTIVA-S). The spectrometer was equipped with a Fassel torch and a Meinhard coaxial flow nebulizer (gas pressure at 32 psi). The flow rate of the pump was 1.2 mL min^{-1}. Data acquisition was made using the Activa Analysis software. The correction for signal instability was made using standard solutions provided by HORIBA Jobin Yvon. Corrosion assays were performed using a VoltaLab PGZ 301 potentiostat. A saturated sulfate electrode (SSE) was used as reference electrode. A stainless steel 904L (the exposed area was 0.59 cm[2]) was used as the working electrode and a platinum wire was used as counter-electrode. Data are acquired by means of VoltaMaster 4 software.

4. RESULTS AND DISCUSSION

4.1. Chemical analysis of filtered water samples

The filtered water samples were collected at the water treatment station and were analyzed for controlling the concentrations of elements that could be responsible of deposits. The mean values obtained for these parameters are shown in Table 2.

Table 2 Results of chemical analysis of filtered water samples

Parameter	*Mean* value	Unit
σ	869±ND	µs cm^{-1}
pH	7.19±ND	---
Ca	55±0.58	mg L^{-1}
K	4±0.04	mg L^{-1}
Mg	26±ND	mg L^{-1}
Na	101±0.82	mg L^{-1}
Free Cl	0.16±ND	ppm
Total Cl	0.24±ND	ppm
SiO$_2$	5.07±0.05	mg L^{-1}
F	0.16±ND	ppm
N$_2$H$_4$	4.8 10^{-3}±10^{-3}	ppm
TH	22.40±ND	°f

ND: not determined

For the parameters that can be responsible of corrosion or of various deposits (tartar, sulfate, silica, etc.), the experimental values were compared to the maximum admissible values (Table 3).

Table 3 Comparison of experimental values with the maximum admissible values

Parameter	Experimental value	Unit	Maximum admissible value[*]	Unit
pH	7.19	---	6.5 to 7.5	---
Free Cl	0.16	ppm	300	ppm
SiO$_2$	5.07	mg L^{-1}	125	mg L^{-1}
Ca	55	mg L^{-1}	90	mg L^{-1}
Mg	26	mg L^{-1}	90	mg L^{-1}
N$_2$H$_4$	4.8 10^{-3}	ppm	0.3	mg L^{-1}

[*] Recommended by Engineering Service/MECS, leading provider of technology, products and services to the global sulphuric acid industry

Table 3 shows that all experimental values are significantly below the maximum admissible values. This observation suggests the possible replacement of demineralized water by filtered water to dilute the sulfuric acid. This result was

complemented by corrosion assays to test the corrosion resistance of the construction material of the acid cooler.

4.2. Corrosion assays

For these corrosion assays, a sample was taken from a tube of the acid cooler. The construction material of the tubes of coolers is 904L stainless steel. This is a super austenitic stainless steel (SASS) (Sathiya et al. [12]). Since the steel retains its corrosion resistance at moderate and high temperature, it is utilized extensively in the chemical, pulp paper and pollution-control industries. SASS is the preferable material for high-corrosion resistance requirements (Sathiya et al. [12]). Its chemical composition is given in Table 4.

Table 4 Chemical compositions of 904L stainless steel (wt. %)

C	Cr	Ni	Mo	Cu	Fe
0.01	20	25	4.3	1.5	Balance

The sample was tested in two mediums:
- Sulfuric acid diluted to 95% with filtered water.
- Sulfuric acid diluted to 95% with demineralized water.

The corrosion assays were carried out at ambient temperature and at 80 °C. The characterization of resistance to corrosion in different mediums will be made by using electrochemical techniques, namely, the plot of polarization curve. The values of the corrosion current density and the corrosion rate determined from the polarization curves are given in Table 5.

Table 5 Corrosion parameters derived from polarization curves

	I_{cor} (mA cm^{-2})		V_{cor} (mm y^{-1})	
	Ambient temperature	$T = 80$ °C	Ambient temperature	$T = 80$ °C
95% H$_2$SO$_4$ diluted with filtered water	0.060	0.114	0.700	1.330
95% H$_2$SO$_4$ diluted with demineralized water	0.082	0.119	0.960	1.380

The polarization curves of 904L alloy obtained in different mediums are given in Figs. 3 and 4.
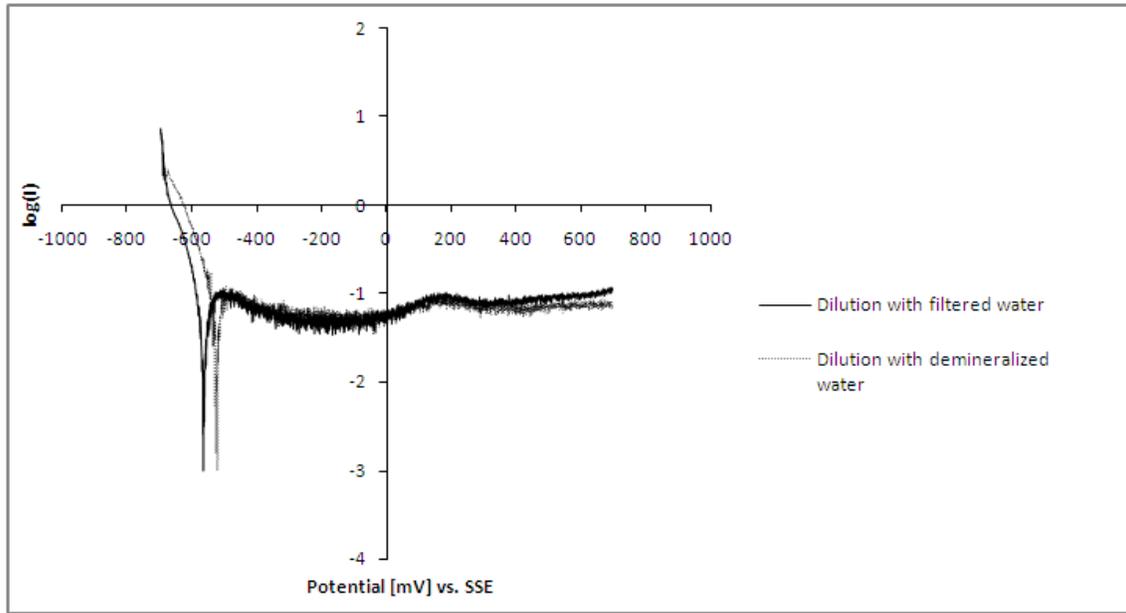
Fig. 3 Polarization curves in 95% sulfuric acid diluted with filtered water and with demineralized water at ambient temperature
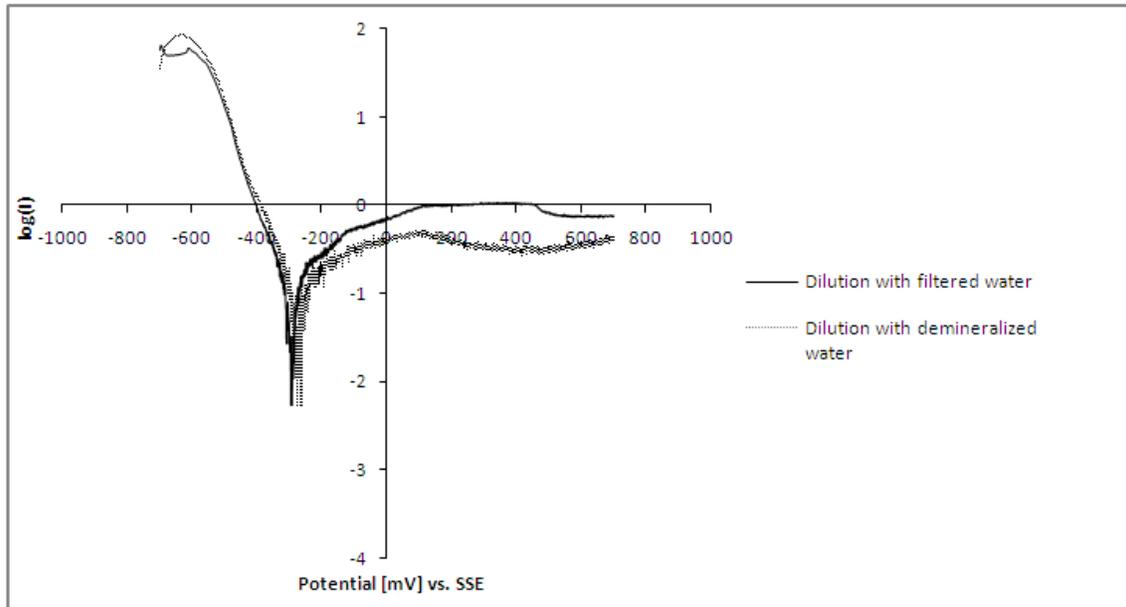

Fig. 4 Polarization curves in 95% sulfuric acid diluted with filtered water and with demineralized water at 80 °C

The polarization curves show that the corrosion rate increases with temperature in both mediums. This proportionality is coherent since the temperature activates the corrosion kinetics. However, dilution does not seem to have any significant effect on corrosion especially at 80 °C. Indeed, the values of corrosion rates obtained for sulfuric acid diluted to 95% with filtered water and demineralized water are relatively identical

(1.33 and 1.38 mm y^{-1}, respectively). Moreover, no trace of pitting corrosion was found on the sample tested in both mediums studied. Certainly, the values of the corrosion rate obtained are relatively high. However, the acid coolers are equipped with a cathodic protection system to prevent corrosion of surfaces which are in contact with hot sulfuric acid. Indeed, cathodic protection is reliable, effective method for protection against corrosion (Gurrappa [13], Gräfen and Paulekat [14]). Cathodic protection works primarily by depressing the natural corrosion potential of the structure to be protected to a value where it does not corrode (Gurrappa [13], Gräfen and Paulekat [14]). The similarity of the corrosion resistance of 904L stainless steel in both mediums studied, suggests the substitution of demineralized water by filtered water without significant risks on the corrosion resistance of the construction material of the acid coolers.

5. CONCLUSIONS

The analysis of the filtered water samples showed that the experimental values obtained for the parameters that could be responsible for corrosion or deposits are significantly below the maximum admissible values. The comparison of electrochemical parameters obtained in different tests allowed determining the effect of dilution of sulfuric acid by using filtered water on the corrosion resistance of the construction material of the acid coolers. Indeed, the values of corrosion rates obtained for sulfuric acid diluted to 95% with filtered water and demineralized water are relatively identical. Moreover, no trace of pitting corrosion was found on the sample tested in both mediums studied. These results are very satisfactory and allow concluding about the possible replacement of demineralized water by filtered water to dilute sulfuric acid, without significant risks on the construction material of the acid cooler.

AKNOWLEDGMENTS

NOMENCLATURE

c_i	Analyte concentration (mg L^{-1}, µg L^{-1} or ppm)
E_{cor}	Corrosion potential (V)
F	Faraday constant (A h mol^{-1})
i	Analyte
I_{cor}	Corrosion current Intensity (A mm^{2})
M	Atomic mass of metal (g mol^{-1})

n	Valence of metal ion
S	Steel surface in contact with electrolyte (cm^2)
T	Temperature (°C)
TH	Total hardness (°f)
V_{cor}	Corrosion rate ($mm\ y^{-1}$)
σ	Conductivity ($\mu s\ cm^{-1}$)
ρ	Volumic mass of metal ($g\ mm^{-3}$)
λ	Wavelength (nm)

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