

*Full Paper*

## **The Corrosion of White Cast Iron in Polluted Phosphoric Acid Medium Contains Fluoride Ions**

**Younes Kerroum,<sup>1</sup> Abdellah Guenbour,<sup>1</sup> Abdelkbir Bellaouchou,<sup>1</sup> Hassane Idrissi,<sup>2</sup> José García-Antón<sup>3</sup> and Abdelkader Zarrouk<sup>1</sup>**

<sup>1</sup>*Laboratory of Materials, Nanotechnology and Environment, Faculty of Sciences, Mohammed V University, Av. Ibn Battouta, P.O. Box 1014 Agdal-Rabat, Morocco*

<sup>2</sup>*Laboratoire MATEIS Equipe RI2S, bât L. de Vinci, 21 rue J. Capelle, INSA-Lyon, 69621 Villeurbanne cedex, France*

<sup>3</sup>*Ingeniería Electroquímica y Corrosión (IEC). Departamento de Ingeniería Química y Nuclear. ETSI Industriales. Universitat Politècnica de Valencia. 46022 Valencia, Spain*

\*Corresponding Author, Tel.: +212 665 201 397; Fax: +212 537 774 261

E-Mail: [azarrouk@gmail.com](mailto:azarrouk@gmail.com)

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**Abstract-** The global demand for phosphoric fertilizers will increase in the coming years, which should boost phosphoric acid production. And to ensure this production, the choice of the right materials and the search for solutions for the costs of corrosion becomes the challenge of the specialists. This is why this research focused on the corrosion resistance of white cast iron in the similar medium of the phosphoric acid production plants containing fluoride ions at 80 °C. And the techniques used are the electrochemical measurements and UV-Vis-NIR spectroscopy, Scanning electron microscopy and energy dispersive spectroscopy analysis, X-ray diffraction analysis (XRD). The results showed that fluorine influences the electrochemical parameters of the system and favors the dissolution of the alloy, in particular at the ferrite matrix. The increases current density value in the passive region and reduces the passive domain, while causing the partial chemical degradation of the passive film at the potential close to 0.5 V/SCE. And that was explained by that fluoride increases the inter-phase corrosion between the ferrite and carbide phases, and increases the dissolution of iron more than Chromium in the solution, which weakens the resistance to corrosion of the alloy.

**Keywords-** Cast iron, Corrosion, Phosphoric acid, Fluoride ions, UV-Vis-NIR spectroscopy

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## 1. INTRODUCTION

The cast irons have been used in various industries and chemical processes, mainly for their lower costs and due to the availability of raw materials. For that, the research and development of this alloy in the corrosion field known as an important reflection and challenging for the specialists, through the engineered solutions providing quality design services. The important factor that needs to be held into account for selecting cost-effective materials is the percent of additive elements. And it is necessary to know that the corrosion resistance of each material depends on the chemical environment, the concentration, and temperature [1-4]. The phosphoric acid environment in the wet process can have a wide variety of chemical species [5,6], and the corrosion of components is dominated by the presence of impurities. However, for example, the pumps and pipelines those handle and maintain the phosphoric acid moving, while being beneficial to utilize cast iron to reduce costs, but the corrosion rate of cast iron rises significantly at low pH if there are offensive species present. For that the high addition of chromium have been hardly used for give the materials special properties against the corrosion phenomenon. The white cast iron is consider as special alloy that has a high percent normally contain 25–35% chromium and have been used to fabricate the pumps, tubes, agitators, etc. in the phosphoric acid production industry, specially at wet process. This type of cast iron usually has structures containing a homogeneous distribution of carbides in a matrix of ferrite [7-10].

And its corrosion resistant properties consisting of chromium and iron oxides develop on the surface of the alloy, for that is useful in the phosphoric plants. The results published in the literature [11], suggested that high-chromium cast irons are suitable in most cases solutions of phosphoric acid, but noted that the problem with high chromium cast irons are that crude phosphoric acid if contains significant amounts of fluoride can lead to excessive corrosion rates, which need profound study especially at temperature of 80°C that characterizes the phosphoric acid production plants.

In this article we will discuss the effect of fluoride on the corrosion resistance properties of high white cast iron at a temperature of 80 °C, for more interpretation and comprehension of the degradation mechanism. By using the electrochemical techniques and UV-Vis-NIR spectroscopy, Scanning electron microscopy and energy dispersive spectroscopy analysis, and X-ray diffraction (XRD) analysis.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials and test solution

The surface of the white cast iron specimen is as follows: diameter, 89 mm. The compositions of the specimen are presented in Table 1. For preparing the specimen surface, it was abraded by the abrasive papers to 1500 grit and cleaned with deionized water prior to testing. To create the reference solution (Blank Solution), the 40% phosphoric acid aqueous

solution was mixed with 4% S<sub>2</sub>O<sub>4</sub>, 0.42% KCl) and the amount of 2% HF was added to simulate a corrosive environment and to reproduce environmental conditions similar to that of a phosphoric acid plant.

**Table 1.** The chemical compositions of white cast iron

Elements	Fe	Cr	C	Mn	Mo	Ni	Cu	V	W	Sn
Wt. %	62.290	32.470	3.300	1.060	0.420	0.210	0.170	0.047	0.023	0.010

## 2.2. Electrochemical measurements

The test equipment was composed of Volta Lab PGZ 301 Potentiostat connected to a three-electrode cell for recording and analyzing the electrochemical measurements under aerated conditions. The data were sent to the computer and then treated immediately by software. The reference electrode was a saturated calomel electrode (SCE) and auxiliary electrode was a Pt plate. Potentiodynamic polarization curves were started from the potential of  $-0.6$  V/SCE to  $1.2$  V/SCE at a scan rate of  $0.5$  mV s<sup>-1</sup>, and after the steady state condition was formed at open-circuit potential (OCP) for 1800 s. Electrochemical impedance spectroscopy (EIS) was used at OCP with the amplitude of 10 mV and frequency range of 100 kHz to 100 mHz.

## 2.3. X-ray diffraction (XRD) analysis

XRD analysis was performed directly on the white cast iron surface at room temperature a Shimadzu 6100 diffractometer equipped with a copper anticathode ( $\lambda_{CuK\alpha}=1.541838$  Å), a thin film attachment THA-1101 and counter monochromator CM-4121. The samples were scanned at a speed of 2.0 deg/min between 40 and 120° (2 $\theta$ ) at a tube voltage of 40 kV and a current of 30 mA.

## 2.4. UV-Vis-NIR spectroscopy

Reflectance of the samples and absorbance of the solutions spectra were obtained at room temperature using a UV-Vis-NIR spectrophotometer (Jasco Model V670) After 30 min immersion of alloy in tested solutions at 80 °C. The spectrophotometer was recorded from 220 nm to 2200 nm. Spectra were computer fitted assuming Savitzky-Golay smoothing and the second derivative used to improve the band's result, as well as to remove the base line shift [12-13].

## 2.5. Scanning electron microscopic and energy dispersive spectroscopy analysis

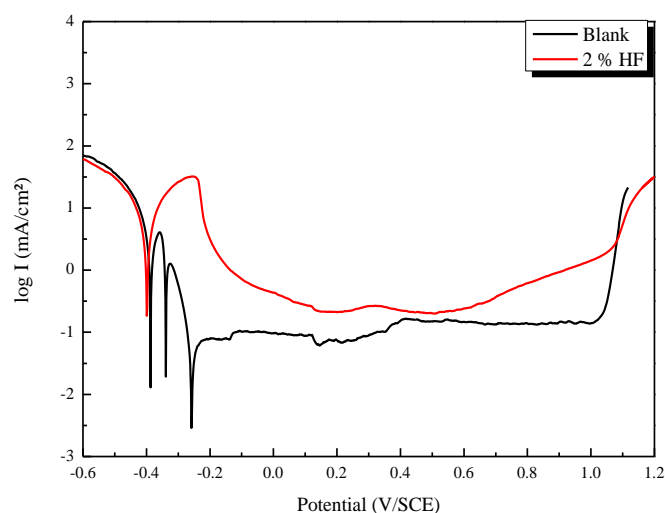
Scanning electron microscopic and energy dispersive spectroscopy analysis was performed on the alloy surface after 30 min of immersion in different conditions at 80 °C. The scanning

electron microscope (SEM) JEOL JSM-IT 100 was equipped with an EDX through an accelerating voltage of 20 kV.

### 3. RESULTS AND DISCUSSION

#### 3.1. Potentiodynamic polarization curves

Fig. 1 gives an idea about the effect of fluoride ions on the potentiodynamic polarization curve of White cast iron in the contaminated phosphoric acid solution at 80 °C. White cast iron doesn't exhibit analogous polarization curve at the presence and absence of fluoride. In the absence of fluoride, it is showing a wide potential domain of passivity, generally in the potential range between -0.25 and 1 V/SCE, and more than one corrosion potential appeared which is an indication of an unstable passive system [14,15]. The quick increase in current density at 1 V/SCE potential is a sign of the breakdown of the passive film, showing the transpassive region of White cast iron in the polluted phosphoric acid solution.



**Fig. 1.** The polarization plots of the white cast iron in the solution of polluted phosphoric acid were taken without and with the 2 wt.% HF at 80 °C

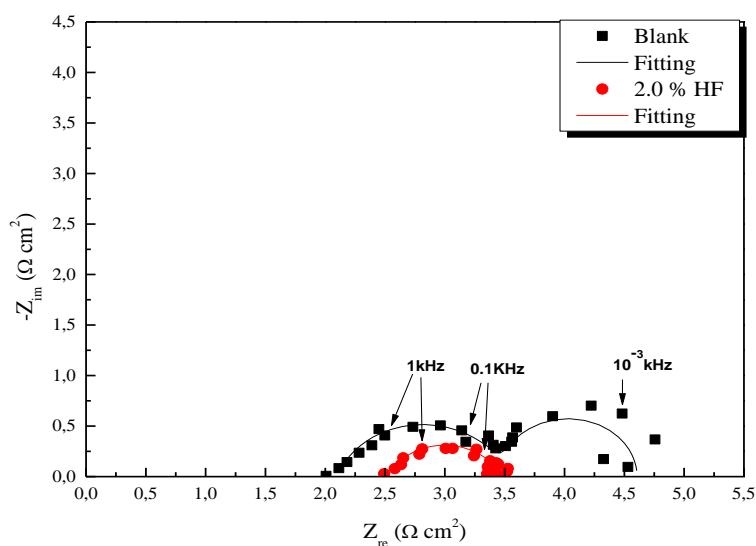
Furthermore, in the presence of fluorides, the anodic branch is modified, through an increase of the anodic current density, i.e. fluoride favors the kinetics of the anodic reaction, essentially the oxidation evolution reaction of iron to  $\text{Fe}^{2+}$ . Another observation, the higher current density value is registered within the passive region, and the short passive domain between 0.1 and 0.5 V/SCE, which are assigned the growth of unstable oxide films on the metallic surface. The critical current is around  $31.6 \text{ mA/cm}^2$  characterized by an enlargement of the active range, which could be attributed to an active dissolution of the alloy, and  $I_p$  value is seen about  $0.21 \text{ mA/cm}^2$ .

Moreover, the presence of fluoride retards the formation of the oxide film and results exceeding in the oxide films dissolution at the potential near to 0.5 V/SCE. This value is near to potential oxidation of  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$  which may explain this drastic phenomenon [16], and the trans passive potential is similar to without fluoride at 1 V/SCE; this suggested that passive layer partially breaks down at 0.5 V/SCE before the breakdown of the film completely at 1 V. This partially chemical breakdown may produce via the interaction of fluoride ions with the metals of the alloy that catalyze the dissolution of iron and chromium. Many research papers were examined the aggression of ions like chloride and sulfide, fluoride, through different mechanisms whether the incorporation into the oxide film or the accumulation at the metal oxide interface; and often remaining adsorbed on the dissolving metal surface; Complexing of metal cations on the surface of the film. Generally, the interpretation of each mechanism depends on many parameters such as the solution environment and the nature of material and temperature, etc. [13,14,17,18].

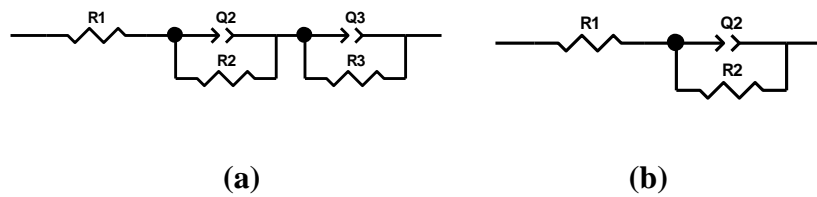
### 3.2. Electrochemical impedance spectroscopy measurements

Fig. 2 shows the Nyquist plots of white cast iron were traced over 30 min in the blank solution and blank +2% HF. The equivalent electric circuits were used to fit the results are presented in Fig. 3. It can be observed that the fluoride changes the impedance curve of alloy, in comparison with the reference solution. In the blank solution, the Nyquist plot of the sample shows two capacitive loops and its equivalent electric circuit is shown in Fig. 3a.

Furthermore, the  $R_1=R_s$  represents the electrolyte bulk resistance and the first loop at high frequencies related to the charge transfer resistance ( $R_2=R_{ct}$ ) in parallel with  $CPE1$  (the constant phase element) ascribed to double layer capacitance.



**Fig. 2.** The Nyquist plots of the white cast iron in the solution of polluted phosphoric acid were taken without and with the 2 wt.% HF at 80 °C



**Fig. 3.** The proposed equivalent electrical circuits (a) blank solution; (b) in the presence of 2.0% of HF

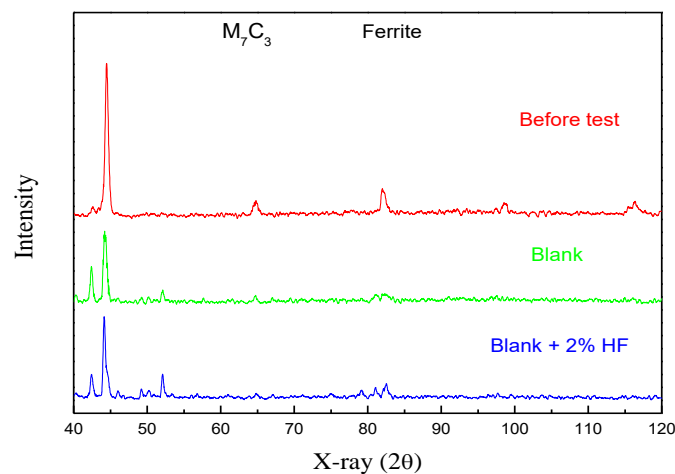
At lower frequencies, the second loop ( $R_2//CPE_2$ ), may be due to the relaxation of the surface coverage by intermediate species at the metal/electrolyte interface [20]. These results directed us to suggest that the mechanism of interaction performed by two processes, the charge transfer and the adsorption.

**Table 2.** Impedance parameters of white cast iron in contaminated  $H_3PO_4$  solution, without and with the 2 wt.% HF at 80 °C

	$R_1$ ( $\Omega\text{ cm}^2$ )	$Q_2 \times 10^4$ ( $\Omega^{-1}\text{ s}^n\text{ cm}^{-2}$ )	$n_2$	$R_2$ ( $\Omega\text{ cm}^2$ )	$Q_3 \times 10^3$ ( $\Omega^{-1}\text{ s}^n\text{ cm}^{-2}$ )	$n_3$	$R_3$ ( $\Omega\text{ cm}^2$ )
Blank	2.100	15.7	0.80	1.4050	73.21	1	1.102
2% wt. HF	2.519	28.5	0.74	0.9557	—	—	—

### 3.3. X-ray diffraction (XRD) analysis

Fig. 4 shows XRD traces of the alloy before and after immersion in test solutions. The analyze of the results exhibit that the microstructure consists only of eutectic  $M_7C_3$  carbides in the ferrite matrix.



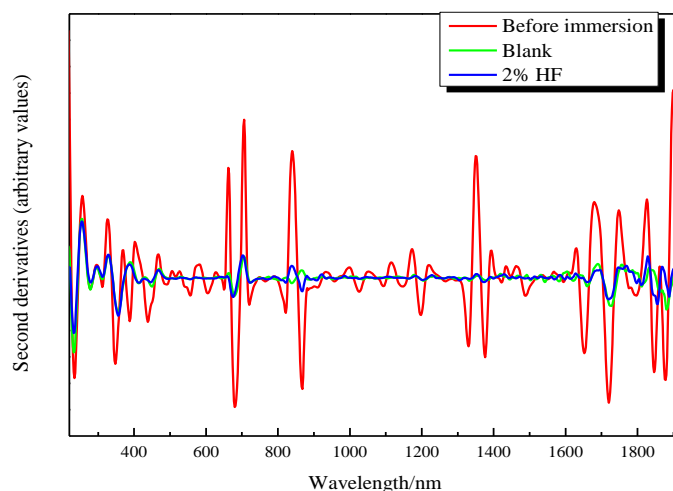
**Fig. 4.** X-ray diffraction traces of the white cast iron before and after the test, with and without 2 wt.% Fluoride at 80°C

Moreover, the presence of fluoride in the solution allowed the sample to show one capacitance loop matches to the charge transfer resistance  $R_t=R_{ct}$  and the constant phase element (CPE1) (Fig.3b). The change reflects a variation in the interaction process of the alloy with its environment, means the fluoride renders the material to interact with one process. The results of the experimental test are resumed in the table 2. It is apparent, from the registered values that the polarization resistance decreased in the presence of fluoride, which weakens the protection of alloy.

After the immersion in both solutions, the high decrease in the percentage of ferrite is detected compared to eutectic M7C3 carbide. That implies that the material might be under the selective corrosion, and the ferrite was more corroded and destabilized. It has been reported by Ref. [21] that the inter-granular corrosion of an chromium cast iron easily takes place in a strongly acidic medium, and the phase that resists to corrosion, protrude out of the matrix. This explication may interpret the X-ray diffraction results. Furthermore, the inter-phase corrosion between the eutectic carbide and the eutectic matrix may act an essential part in the corrosive modes, and for this reason, the corrosion resistance of chromium white cast iron is weakened.

### 3.4. UV-vis-NIR spectroscopy

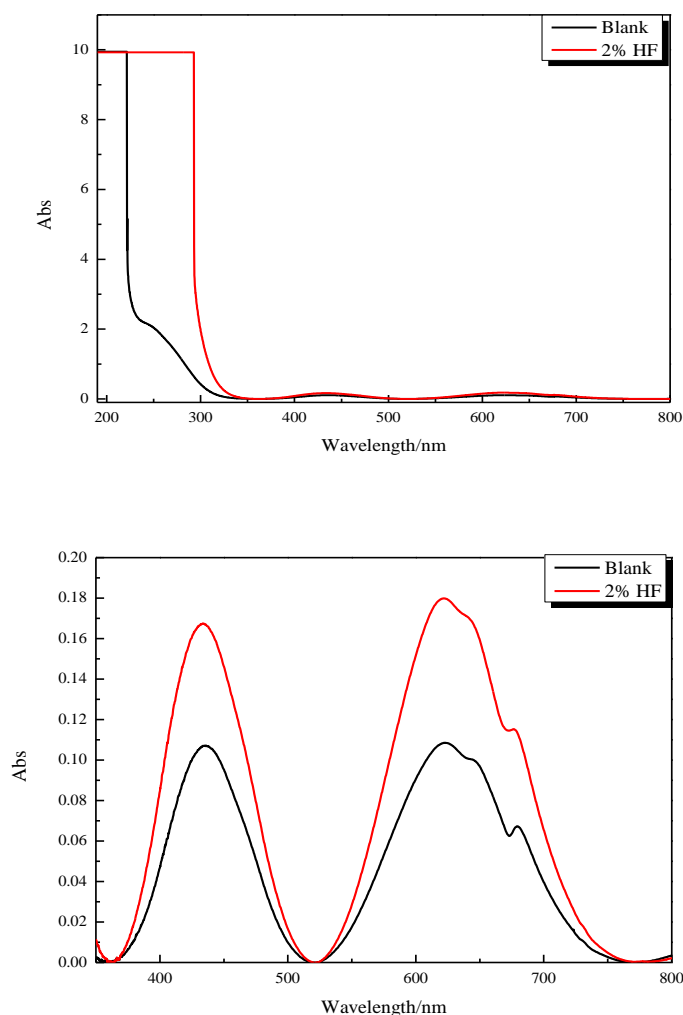
The chemical composition of the surface after exposition at  $E_{OCP}$  in polluted phosphoric acid solutions with and without HF ions was evaluated by UV-Vis-NIR measurements. Figure 5 shows the absorbance spectra of the samples obtained after 30 min of immersion.



**Fig. 5.** UV-Vis-NIR spectroscopy of white cast iron surface before and after the immersion for 30 min, in contaminated  $H_3PO_4$  solution, with and without 2 wt.% Fluoride at 80 °C

The aim of this part is to investigate and illustrate the nature of the corrosion products formed on the surface alloy. The measurements were recorded before the immersion in the base electrolyte with and without the fluoride. Before the immersion, the specter of the alloy surface

shows that the main component elements are the iron and chromium[13,22-25]. Further, the amplitude of the peaks only decreases when the material was immersed in the solutions, which suggests a decrease in the composition elements that contain in the surface alloy and it's a signification of the dissolution mechanism caused by the acid environment and the halide ions. Moreover, the peaks within 500 and 2200 nm have a higher amplitude reduction than that between 220nm and 500 nm. In correlation with XRD analysis, these peaks may be the iron compounds [26] of the ferrite phase and iron chromium compounds (carbide  $M_7C_3$ ), respectively, this may be an indication of the inter-phase corrosion of the alloy surface. Also, the specter of the surface alloy in the presence of fluoride shows a little decrease in the amplitude of the peaks compared with the effect of the blank solution; this remark may mean that the fluoride has influence the dissolution mechanism.



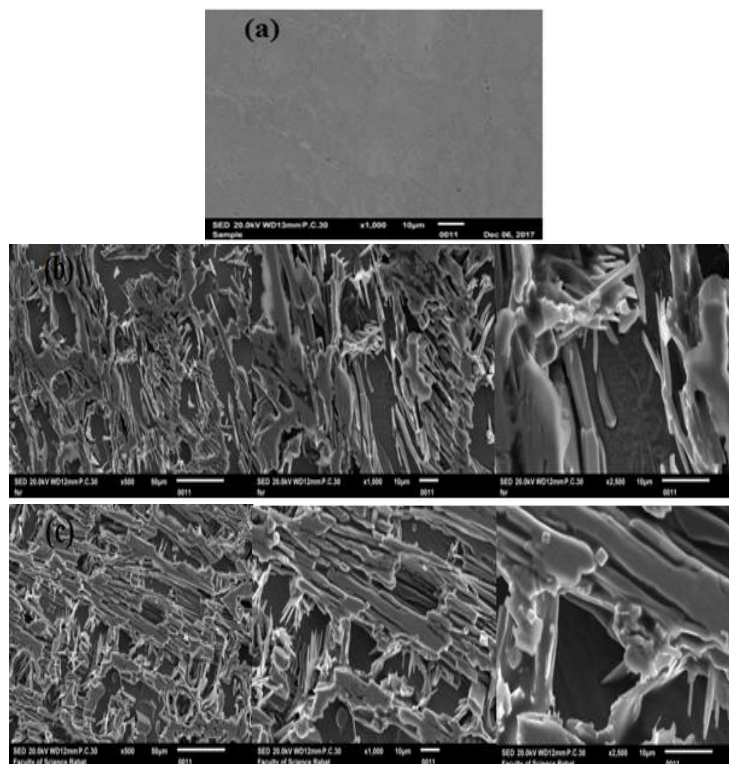
**Fig. 6.** UV-Vis spectroscopy of white cast iron surface before and after the immersion for 30 min, in contaminated  $H_3PO_4$  solution, with and without 2 wt.% Fluoride at 80 °C



Furthermore, UV–Vis spectroscopy allows to detection of iron and chromium species and phosphate anions in the solution. This information is important to understand the effect of fluoride on the corrosion of alloy. The UV-Vis spectra of solutions reveal the absorption bands at 245 and 436, 623, 645, 680 nm, and intense absorption in the UV domain. In agreement with the results of many studies [27-29], these bands were assigned to water and phosphates ion, iron and chromium complexes. After the addition of fluoride to the solution, an increase of the absorption peaks, and the spectra profiles remain similar. Also, As comparatively shown in Fig. 6, the absence of absorption bands at 350 nm assigned to Cr (VI) structure. These analytical responses indicate that HF promotes the dissolution of iron III and Chromium III together, without inducing the oxidation of Cr (III) to Cr (VI) at OCP. In addition, the neglect able two peaks of iron III Phosphate ions has also been confirmed at 645 nm and 680 nm.

### 3.5. Scanning electron microscopic and energy dispersive spectroscopy analysis

The SEM of the metal surface was performed after 30 min of immersion at 80 °C. The samples were immersed at free OCP in blank solution and the presence of 2% HF. In both cases, the pictures show that the base structure is influenced more than carbide by corrosion, suggests that ferrite displays an exceed activity, which increases the matrix dissolution fig.7.

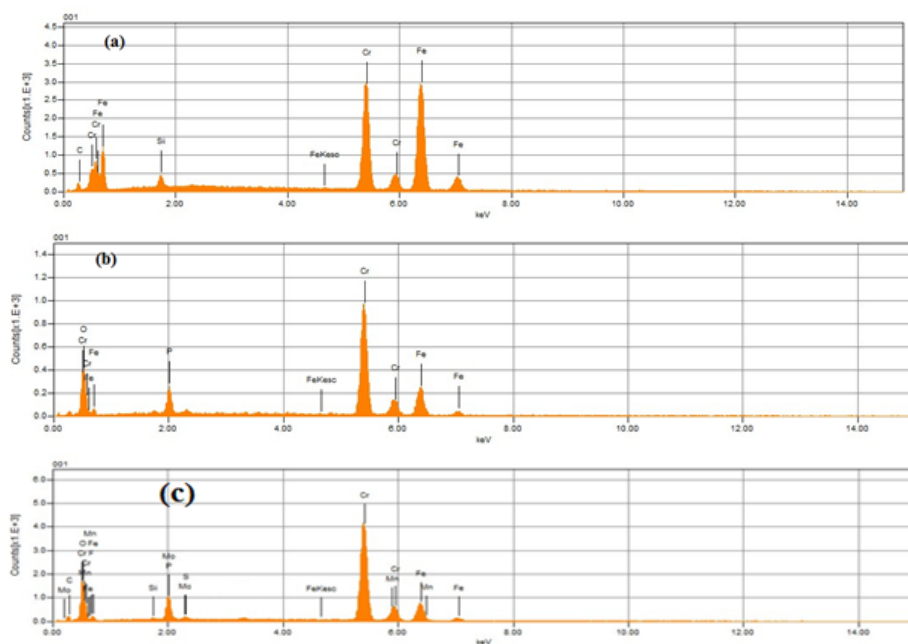


**Fig. 7.** Images of white cast iron surface, (a) before the test; (b) after 30 min of immersion in polluted  $H_3PO_4$  solution without HF, and (c) at the presence 2 wt.% of HF at 80 °C

Whereas the presence of fluoride, a special attack on ferrite matrix develops clearly, and the eutectic carbide protrudes out of the matrix more than in the blank solution. This investigation confirms that the white cast iron was under the inter-phase corrosion, which makes a large amount of carbide be extruded out of the matrix. That confirms the results of XRD and UV-Vis NIR analysis.

On the basis of the recent study [21], it was proposed that the inter-phase corrosion of Fe–Cr alloys caused by the free corrosion potentials difference between carbide and matrix [9]. This study leaves us to suggest that fluoride increase the difference of corrosion potential between the carbide and ferrite matrix, which accelerates the inter-phase corrosion. As a result, the corrosion products on the iron surface are continuously removed, as showing in the picture, which makes the fresh surface exposed to the corrosion medium.

The chemical composition of the surface alloy determined by SEM/EDX is given in fig 8. Before the immersion in the solutions, the surface of the white cast iron mainly consists of chromium and iron oxides, and a small amount of silicon and carbon. After the immersion in the corrosive solutions, at free potential and at 80 °C, the surface mainly consists of the chromium oxides and a high decrease in the iron amount. In the case of fluoride, the atomic ratio between the chromium and iron are elevated, and an immense decrease of silicon, which means that fluoride, increases the dissolution of iron and silicon.



**Fig. 8.** EDX analysis of white cast iron surface, (a) before the test, (b) after 30 min of immersion in polluted  $\text{H}_3\text{PO}_4$  solution without HF, and (c) at the presence 2 wt.% of HF at 80 °C

It's known that fluoride and phosphate ions enhance the formation fluoro-complexes with silicon [30]. Moreover, the surface of the white cast iron alloy also consists of phosphate metal complexes; this supported by the rise of the phosphor and oxygen contents. Consequently, the

addition of fluorides to polluted phosphoric acid causes strong dissolution of the layer formed on white cast iron. The chemical dissolution of the alloy is favored at irregularity of the surface as showed by the images.

#### **4. CONCLUSION**

The corrosion resistance of white cast iron was tested in the aggressive environment of phosphoric acid solution contains fluoride ions at 80°C. Fluoride promotes the kinetics of the anodic reaction and delays the formation of the oxide film. In addition, it increases the current density value in the passive region and reduces the passive domain, while causing the partial chemical degradation of the passive film at the potential close to 0.5 V/SCE. Fluoride makes the material interact with its environment by individual process and decreases the polarization resistance, which weakens its resistance to corrosion. The results of XRD analysis, display that the microstructure of white cast iron consists only of eutectic M7C3 carbides in the ferrite matrix and a high decrease in the proportion of ferrite is observed compared to eutectic M7C3 carbide after the immersion in the test solutions. UV-NIR spectroscopy of white cast iron surface and the test solutions showed that fluoride enhances the dissolution mechanism of alloy, through increases the presence of the Fe<sup>2+</sup>, Fe<sup>3+</sup>, Cr<sup>3+</sup> in the solutions. SEM analysis has shown that fluoride improves inter-phase corrosion by increasing the activity of ferrite relative to carbide, which increases the dissolution of the matrix. And this confirms the results of the DRX and UV-Vis NIR analysis.

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