

Effect of Cr(VI) - Fe(II) interaction on the corrosion resistances of iron at different pH in dichromate solutions

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Effect of Cr(VI) - Fe(II) interaction on the corrosion resistance of iron in dichromate solutions has been studied under different experimental conditions. The presence of dissolved oxygen (DO) in the solution decreases Cr(VI) reduction by Fe(II) at pH 4 which became quite noticeable at pH 7. This probably influences corrosion of iron to certain extent. A positive shift of OCP and measurements of a higher charge transfer resistances of iron in dichromate solution of pH 2 and 3 suggest the formation of a protective film on iron. Energy Dispersive X-ray Analysis (EDXA) of iron immersed in Cr(VI) solution indicated a greater involvement of chromium in the formation of a protective film at iron surface. On the other hand, the EDXA analysis showed a decrease in chromium concentration in the reaction product film on the immersed iron surfaces in Cr(VI) solution at pH 4 and above. A shift of OCP in the negative direction and the occurrence of lower charge transfer resistance at the above pH as compared to pH 2 and 3 is attributed to a decrease in the protective properties of the film.

Keywords: Iron, dichromate ion, corrosion resistance, Cr(VI) - Fe(II) interaction

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It is well known that chromate and dichromate ions, after reduction to Cr(III), can adsorb on an iron surface and remain there as hydrated Cr_2O_3 ^{1,2}. Once Cr_2O_3 covers the iron surface, it acts as passive layer and suppresses corrosion of iron to a certain extent. The rate of Cr(VI) reduction increases with the increase of pH, temperature and chloride ions concentration in the aqueous solution².

Numerous studies on the passivation of iron in the presence of chromate ions have been undertaken in the past and discussed in details¹⁻¹⁶. It is reported that pH and oxygen content of the solution change the composition of passive film^{4,6,7}. Due to occurrence of similar redox chemistry in the presence of ferrous iron, it is expected that chromium of dichromate ion after reduction as Cr(III) may incorporate in the passive film in similar fashion to that of reduced chromium of the chromate ion. However, no details about the nature of Cr(VI)-Fe(II) interactions in dichromate solution and its ultimate influences on the corrosion of iron with respect to pH, are reported in the literature. After carrying dichromate ion reduction by iron, the nature of the occurrence of corrosion or

passivation phenomena of iron can be explained with respect to pH.

Therefore, the main objectives of present investigation are (i) to estimate the molar ratios of Cr(VI) of dichromate and Fe(II) of ferrous solution that are required for the completion of Cr(VI)/Fe(II) redox reaction at different pH, (ii) to determine the nature of shift of corrosion potential of iron with the variation of pH in dichromate solution, (iii) to find out the trend of variations of charge transfer resistances of iron with pH in the dichromate solution and (iv) to analyse chromium and iron content in the reaction product film formed at different pH of dichromate solutions.

Firstly, reduction of Cr(VI) was investigated in the presence of ferrous iron at pH 2-7 by spectro-photochemical analysis. Since a competitive oxidation of Fe(II) to Fe(III) by DO may influence the Cr(VI) reduction reaction to certain extent depending on pH, Cr(VI) reduction by Fe(II) was measured in the presence and absence of DO in the dichromate solutions of above pH. Afterwards, the Open Circuit Potential (OCP) variations of iron with time and impedance were measured to know the nature of corrosion or passivation phenomena occurring at the

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iron interface in the dichromate solution. Lastly, incorporation of chromium in the reaction product formed at the metal/solution interfaces in dichromate solutions of above pH, was analysed by EDXA.

Experimental Procedure

Analytical studies

Stock solutions of potassium dichromate ($K_2Cr_2O_7$) and ferrous ammonium sulphate $[Fe(NH_4)_2SO_4]$ were prepared in 0.01 M concentrations for spectrophotochromal analysis. During absorption measurement the solutions were further diluted to required concentration. Following solutions were used for the Cr(VI) absorption studies: (i) 0.003 M ferrous ammonium sulphate; (ii) 0.001 M potassium dichromate; (iii) 0.003 M ferrous ammonium sulphate + 0.001 M potassium dichromate. pH of the solutions was adjusted by HCl and NaOH. All the solutions were prepared in triple distilled water. Absorption measurements were performed using Cintra-40 GBC make UV-visible double beam spectrophotometer at 28°C in 250-500 nm wavelength range. Cr(VI) solution was analysed by diphenyl carbohydrazide method¹⁷ at 540 nm wavelength utilising a microprocessor based spectrophotometer (Hach DR-2000 Model), while total chromium {Cr(III)+Cr(VI)} and Fe in the reacted solution was analysed by atomic absorption spectrophotometer(GBC-902 model).

OCP and impedance measurements

OCP and impedance of iron were measured in solutions of pH 2-7 containing 20 mg/L Cr(VI). For this, a stock solution of 1000 mg/L Cr(VI) containing dichromate solution was prepared by dissolving required quantity of $K_2Cr_2O_7$ in triple distilled water. Working solutions (20 mg/L) of Cr(VI) were made by successive dilution of the stock solution. A rectangular flag shaped iron (Armco grade) electrode (working area, 1 cm²) was polished till mirror finish by using different grades of emery paper. The OCP of iron was recorded against a saturated calomel electrode (SCE) as reference electrode immediately after immersing the electrode in dichromate solution. Impedance measurement, using PARC-Model 398 electrochemical impedance system, was performed employing three electrodes system, using working electrode as iron (working area, 1 cm²), saturated calomel reference electrode (SCE) and a platinum foil (2 cm² area) as a counter electrode. All the impedance measurements of iron were carried out under OCP condition by applying a sine potential signal of 20 mV

AC amplitude in a frequency range of 10 mHz to 10 KHz.

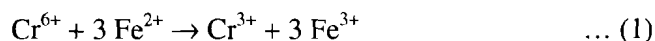
EDXA measurement

For the determination of the elemental composition of the reaction product film, a well polished rectangular iron specimen (dimension 1 × 1 × 0.1 cm) was immersed vertically in 20 mg/L Cr(VI) bearing dichromate solution. After 24 h the immersed sample was removed and kept in desiccator. Analysis of chromium and iron of immersed samples was made by Energy Dispersive X-ray Analysis (EDXA) (Link ISIS 300 Model) a week after immersion.

Results and Discussion

Cr(VI) reduction by Fe(II) at different pH

In the Cr(VI) reduction to Cr(III) by Fe(II) the overall redox reaction can be expressed as



To verify this, Cr(VI) and Fe(II) in 1:3 molar ratio were mixed at pH 2-7. Afterwards, absorption spectra were recorded for Cr(VI) ion. When absorption spectra was measured in the mixed solution of Fe(II) and Cr(VI) (3:1) ratio, the corresponding peak due to Cr(VI), was completely absent (Fig. 1). This verifies the concept of Cr(VI)/Fe(II) redox reaction as per given reaction 1 above that three equivalents of Fe(II) are essential for the reduction of one equivalent of Cr(VI). After absorption measurement, unreduced Cr(VI) present in the solution was analysed. It is worthwhile to mention that no Cr(VI) was detected in the mixed solution and total chromium was present as Cr(III) in the mixed solutions of pH 2 and 3. In case of mixed solution of pH 7, a considerable decrease in

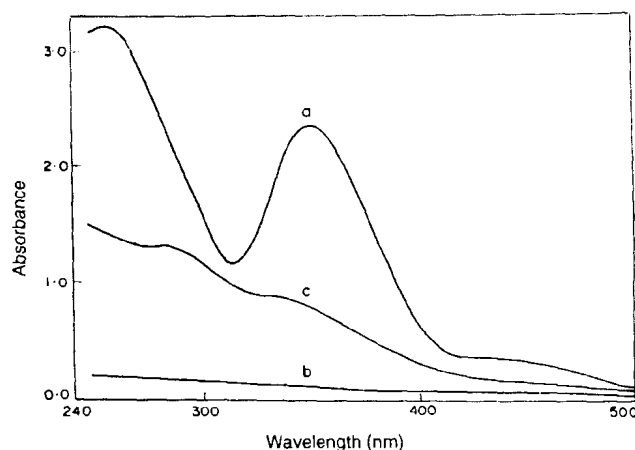


Fig. 1—Absorption spectra: (a) 0.001 M Cr(VI), (b) 0.003 M Fe(II) and (c) 0.001 M Cr(VI) + 0.003 M Fe(II) at pH 3

peak height (~0.85%) of Cr(VI) as compared to peak height of Cr(VI) at pH 3, was recorded (Fig. 2). On analysis, 10 to 12 % unreduced Cr(VI) of the total Cr(VI) mixed with Fe(II), was found. This confirmed the reason for decline of absorption peak height of Cr(VI). The decrease in the Cr(VI) reduction rate at pH 7 is the result of a preferential competitive oxidation of Fe(II) by DO. The effect of dissolved oxygen on the Cr(VI) reduction has been reported recently by Singh and Singh¹⁸. According to them, the presence of DO influences the dichromate ion reduction at pH 4 itself with a low magnitude but its effect becomes quite significant at pH 7 due to competitive oxidation of Fe(II) to Fe(III) by O₂.

The beginning of precipitation reaction at pH 4 is likely to develop turbidity in the mixed solution as a yellowish colouration was observed immediately after mixing of Cr(VI) and Fe(II) solutions at pH 4. At pH 5 and above, a clear precipitation was observed. Early and Rai¹⁹ also observed precipitation at the above mentioned pH of mixed solution of Cr(VI) and Fe(II). They identified the precipitate with empirical formula Fe_{0.75}Cr_{0.25}(OH)₃(s) formed at pH 3.91-11.6. Weng *et al.*²⁰ carried out detailed analysis of Cr(III), Cr(VI), Fe(II) and Fe(III) ions in Cr (VI)/Fe(II) redox process at different pH and observed a strong influence of pH on the precipitation reaction. They measured a steep decrease in the concentration of soluble Fe(III) and Cr(III) after pH 4. These data are in good agreement with the observation of start of precipitation reaction at pH 4 and above, in the present study.

OCP variation with time

OCP of the iron was measured in 20 mg/L Cr(VI) containing solutions at pH 2 to 7 for two hours of immersion. Fig. 3 illustrates the trend of OCP variations with time at pH 3 and 4. As seen in Fig. 3, OCP tend to shift in the positive (anodic) potential region at pH 3. Similar trend of OCP variations was observed at pH 2. However, an opposite trend of OCP variations was observed at pH 4 and above. Since the shift of corrosion potential in positive potential region is an indication of passive or protective film formation on the metal surfaces, it can therefore, be assumed that a protective layer forms on the iron surface in the dichromate solution of pH 2 and 3. On the other hand, change of corrosion potential in the active or negative potential region at pH 4 and above could be due the occurrence of instantaneous corrosion reaction. The steady E_{corr} values of the iron obtained after 50 to 60 min of exposure at each pH,

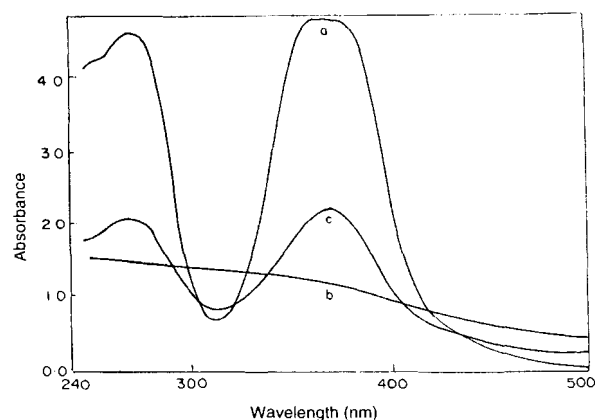


Fig. 2—Absorption spectra: (a) 0.001 M Cr(VI), (b) 0.003 M Fe(II) and (c) 0.001 M Cr(VI) + 0.003 M Fe(II) at pH 7

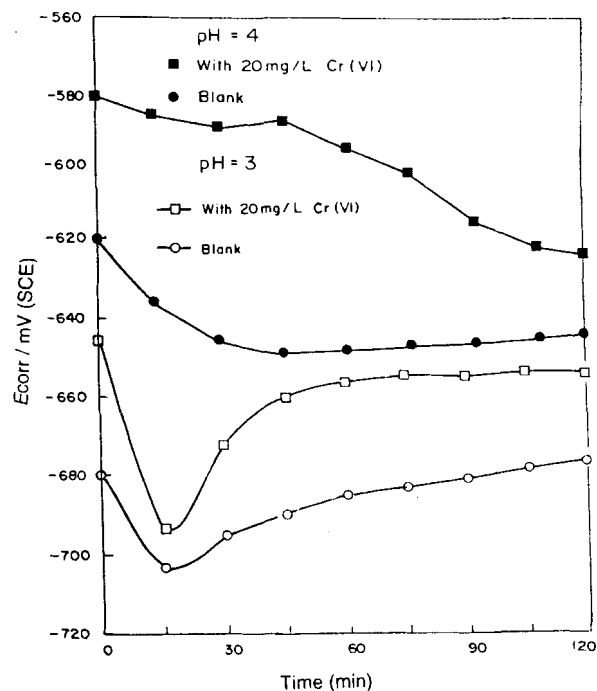


Fig. 3—OCP variations of iron with time, with and without Cr(VI) at pH 3 & 4

Table 1—OCP and charge transfer resistance (R_p) of iron in 20 mg/L Cr(VI) containing dichromate solutions in different pH

pH	OCP(mV)(SCE) in blank	OCP(mV)(SCE) in Cr(VI)	Charge transfer resistances R_p (Ohm)
2	-618	-595	280
3	-690	-672	245
4	-645	-630	155
5	-595	-615	110
6	-525	-535	105
7	-458	-468	85

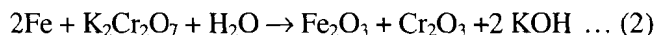
are summarised in Table 1. A positive shift of OCP around 23 and 18 mV of iron in the dichromate solutions of pH 2 and 3 respectively suggests the

formation of somewhat more protective film at the above pH.

Impedance measurement

The impedance measurements on iron were carried out at OCP in 20 mg/L Cr(VI) containing dichromate solution at pH 3 to 7. Figs 4-6 show Nyquist plots obtained for the iron immersed in dichromate solutions at pH 3, 4 and 7, respectively. The Nyquist plots describe the typical feature of charge transfer with existence of passivation or corrosion process. The charge transfer resistance (R_p) obtained from the Nyquist plots at different pH, is given in Table 1. Occurrence of more than 100 ohms R_p at pH 3 in comparison to pH 7 indicates the existence of a corrosion resistant film at pH 3. Involvement of chromium in the film could be the main reason for the development of corrosion resistance at the iron surfaces. A positive shift of OCP at pH 2 and 3 is in agreement with the impedance analysis results. At pH 4, interestingly, two types of semicircle were observed (Fig. 5). Representation of two semicircles in Nyquist plots generally determines the two-step mechanism of electrochemical reaction involving an adsorbed intermediate^{21,22}. It has been suggested²²⁻²⁴ that if electrode is completely blocked, the frequency response when plotted as a Nyquist plot may be represented in one semicircle. However, if there is partial coverage of the surface, the frequency response may appear in two semicircles. It can therefore be inferred that the surface coverage due to protective film formation is effected at pH 4. At pH 7, the semicircle became nearly in a depressed form as shown in Fig. 6, a characteristic of the occurrence of corrosion.

At pH 4 and above, a mixed hydroxide $\{\text{Fe}_{0.75}\text{Cr}_{0.25}(\text{OH})_{3(s)}\}$ ¹⁹ probably forms at the surface of iron after Fe(II) oxidation to Fe(III) by Cr(VI). Since above precipitate is not adherent in nature it developed turbidity at metal/solution interfaces. But at pH 2 and 3, reaction product is mainly a passive oxide film comprising hydrated Fe_2O_3 and Cr_2O_3 which may form as per the following reaction



Since Cr^{3+} and Fe^{3+} meet the crystalline structure criteria of having same charge density and nearly the same ionic radii, 0.63 and 0.64 Å, respectively²⁵, formation of inseparable mixed oxides between iron and chromium is possible. The passive oxide film

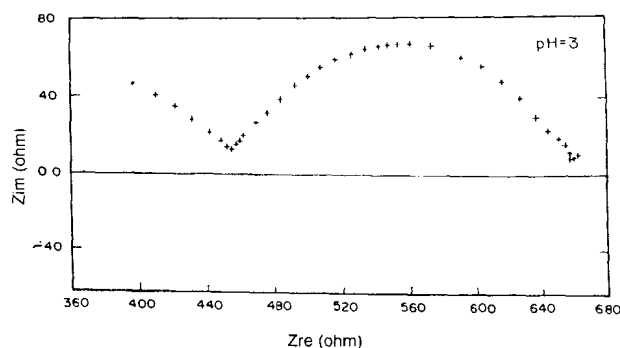


Fig. 4—Nyquist plot of iron in 20 mg/L Cr(VI) bearing dichromate solution at pH 3

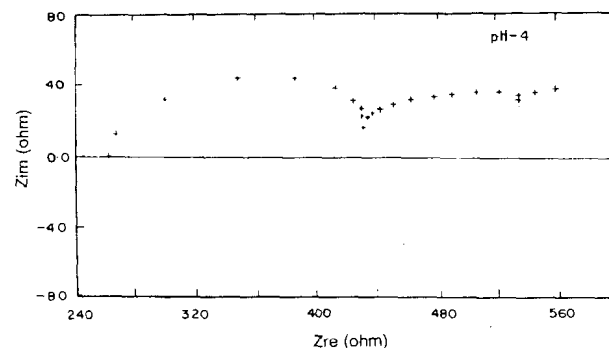


Fig. 5—Nyquist plot of iron in 20 mg/L Cr(VI) bearing dichromate solution at pH 4

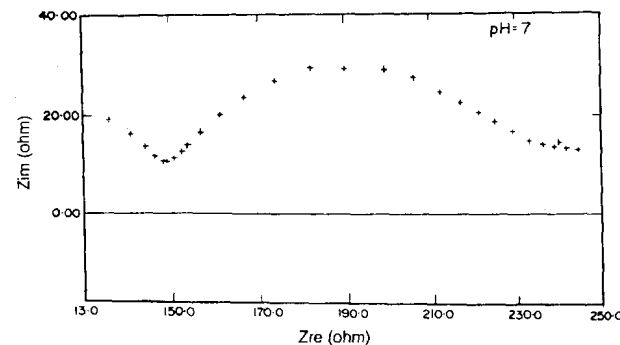


Fig. 6—Nyquist plot of iron in 20 mg/L Cr(VI) bearing dichromate solution at pH 7

may also contain an amorphous layer of hydrated chromium oxyhydroxide $\{\text{CrO}_x(\text{OH})_{3-2x} \cdot n\text{H}_2\text{O}\}$ ²⁶.

Chromium determination by EDXA

Since EDXA is not a surface sensitive technique as analyses are done from up to one micron below the surface, so no EDXA sensitivity for chromium was detected for those specimens which were kept for the OCP measurements up to two hours of immersion. When specimens were kept for 24 h under immersion condition in 20 mg/L Cr(VI) dichromate solution, a

clear EDXA peak corresponding to chromium was observed. Appearance of such peaks was mainly due to the formation of a somewhat thick chromium bearing protective or corrosion product film which could be able to response EDXA sensitivity for chromium. The EDXA spectra obtained for 24 h immersed specimens in the dichromate solutions of pH 2 and 7, are given in Figs 7 and 8, respectively. As seen in Fig. 7, a distinct peak of significant height related to chromium, occurs for the specimens immersed at pH 2. Similar chromium peaks of slightly reduced height were found on 24 h immersed iron in dichromate solution of pH 3. This shows the incorporation of chromium in the reaction product film formed on the iron in the dichromate solutions of pH 2 and 3. However, the heights of the chromium peak was found to reduce considerably at pH 4. At pH 7, no chromium peaks were observed (Fig. 6). The elemental distribution of iron, chromium and oxygen obtained by EDXA and relative oxide concentrations of Cr and Fe, are given in Table 2. Elemental analysis data clearly show the inclusion of more than 1 % chromium in the surface film formed at pH 2 and 3. At pH 4, chromium enrichment in the surface film reduces considerably because only 25% chromium as compared to pH 3, was measured by EDXA at pH 4. Incorporation of chromium in the surface films further reduces at pH 5 and its presence becomes almost non detectable at pH 6 and 7. Presence of a noticeable level of chromium in the reaction product film formed at pH 2 and 3 is mainly due to its involvement with iron at the surface itself. EDXA though, not a surface analysis technique, supports the observations based on OCP and impedance measurements. At pH 2 and 3, after Cr(VI) reduction, Cr(III) involves with oxidized Fe(III) on surface itself and both make their respective oxides, Fe_2O_3 and Cr_2O_3 (reaction 2).

The major drawback of the EDXA was that the oxidation states of metal cannot be identified. To conform the incorporation of chromium as Cr(III) in the reacted surface film, Pratt *et al.*²⁷ conducted a detailed surface analysis including AES, EPMA, XPS, etc of Cr(VI) reacted metallic iron in dichromate solution and observed the presence of Cr(III) in the reaction product layer formed at the iron surfaces. XPS results by McCafferty *et al.*¹³, as well as Rosenfeld and co-workers²⁸ showed that the passive film formed on iron in chromate solution mainly consists of Cr(III) species without any evidence of the presence of Cr(VI) in the passive film.

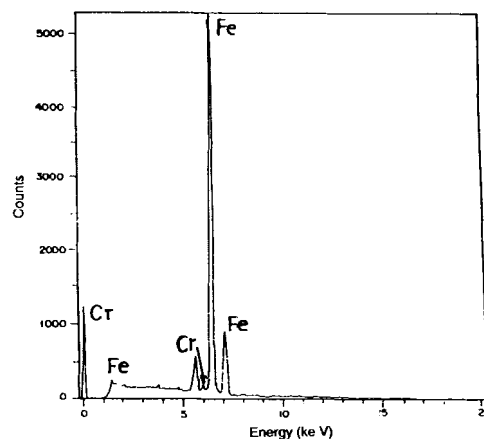


Fig. 7—EDXA of 24 h immersed iron in 20 mg/L Cr(VI) containing dichromate solution at pH 2

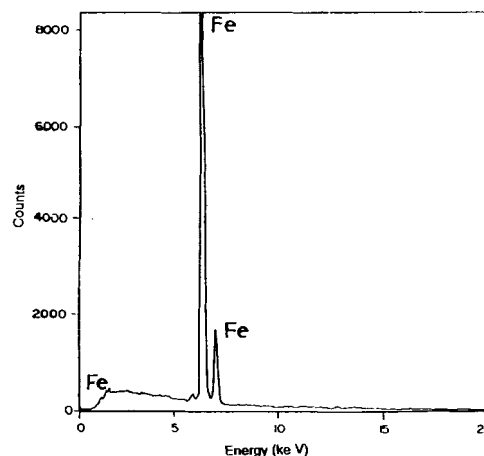


Fig. 8—EDXA of 24 h immersed iron in 20 mg/L Cr(VI) containing dichromate solution at pH 7

Table 2—EDAX analysis of chromium, iron and oxygen of 24 h immersed iron in 20 mg/L Cr(VI) containing dichromate solution of pH 2-7

Solution	Elements	Elemental percentage	Oxides percentage	
pH 2	iron	68.57	Cr_2O_7	1.95
	chromium	1.36	Fe_2O_3	98.05
	oxygen	30.09		
pH 3	iron	68.87	Cr_2O_7	1.53
	chromium	1.05	Fe_2O_3	98.47
	oxygen	30.08		
pH 4	iron	69.31	Cr_2O_7	0.39
	chromium	0.27	Fe_2O_3	99.61
	oxygen	30.07		
pH 5	iron	68.57	Cr_2O_7	0.17
	chromium	0.12	Fe_2O_3	99.83
	oxygen	30.07		
pH 6	iron	69.81		
	chromium	ND	Fe_2O_3	99.97
	oxygen	30.07		
pH 7	iron	69.81		
	chromium	ND	Fe_2O_3	100
	oxygen	30.06		

Conclusions

Present study indicates the occurrence of two distinct types pH dependent Cr(VI)–Fe(II) interactions at the iron surface in the dichromate solution. At pH 2 and 3, Cr(VI)–Fe(II) interaction occurred at the metal/solution interface itself. This results in the formation of a chromium enriched protective oxide film on the iron surface. At pH 4 and above Cr(VI)–Fe(II) interaction at metal/solution interface seems to decrease. This ultimately reduces the corrosion resistance of iron and corrosion becomes more pronounced at pH 4 and above.

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