

An electrochemical evaluation of the corrosion resistance of 14Cr steel

by M.J.U.T. VAN WIJNGAARDEN* and R.F. SANDENBERGH†

SYNOPSIS

The corrosion characteristics of a new steel, 14Cr, which is a modification of the well-known 3CR12, in aqueous sulphate solution were studied through polarization diagrams and a computer analysis based on the polarization-resistance technique.

It was found that the corrosion rate of 14Cr steel is independent of pH for pH values above 6, but, below a pH value of 4, the corrosion rate increases sharply with decreasing pH. In air-saturated solutions of neutral and mildly alkaline pH, the corrosion rate is approximately 60 μm per year. The 14Cr steel shows a twentyfold improvement in corrosion resistance over that of 3CR12 in sulphate solutions at pH 2.0. This is considered to be due to the beneficial effect of its higher chromium and nickel contents.

SAMEVATTING

Die korrosiekarakteristieke van 'n nuwe 14Cr-modifikasie van die bekende 3CR12 in 'n waterige sulfaatoplossing is bestudeer deur gebruikmaking van polarisasiediagramme en 'n rekenaaranalise gebaseer op die polarisasieweerstandtegniek.

Dit is gevind dat die korrosietempo van die 14Cr-staal onafhanklik is van pH by pH-waardes groter as 6 terwyl by pH-waardes kleiner as 4 die korrosietempo skerp toeneem met afname in pH. Die korrosietempo in neutrale en matig alkaliese oplossings is ongeveer 60 μm per jaar. Die 14Cr-staal toon 'n twintigvoudige verbetering in korrosiebestandheid in vergelyking met 3CR12 in sulfaatoplossings met pH van 2,0. Dit word toegeskryf aan die voordelige invloed van die hoër chroom- en nikkelinhoud.

Background

Middelburg Steel & Alloys have made a significant impact on the South African and international steel markets in recent years with their development of 3CR12, which is a low-cost corrosion-resisting steel. Their prime objective in developing 3CR12 was to produce an alloy with adequate corrosion resistance in mildly corrosive environments, with good weldability, and with an alloy content that would make the steel economically competitive. Thus, 3CR12 fills the gap between the higher-alloyed stainless steels at one end of the market and the carbon steels at the other end. The duplex structure of the steel at high temperatures causes a second phase to form in the heat-affected zone¹, resulting in effective grain refinement and so overcoming the weldability problem in conventional ferritic stainless steels.

In general, it can be said that a minimum chromium level of about 12 per cent is necessary for 'stainlessness'. This minimum chromium level depends upon the corrosivity of the environment: the higher the corrosivity, the higher the minimum chromium level. It is reported¹ that the 12 per cent chromium content of 3CR12 results in relatively high corrosion rates in more-aggressive corrosive environments. With these aspects in mind and in order to improve the corrosion resistance of the steel, Middelburg Steel & Alloys developed a 14Cr modifica-

tion of 3CR12. The purpose of the study described here was to investigate the corrosion characteristics of the new 14Cr steel in sulphate solutions.

Electrochemical Evaluation of Corrosion

The influence of alloying on the corrosion properties of materials can conveniently be characterized by electrochemical methods. Full polarization diagrams are used in the prediction of corrosion behaviour in a variety of environments, while Tafel extrapolation and the polarization-resistance technique are used in the prediction of corrosion rates in a specific environment.

By the Tafel extrapolation technique, the corrosion rate is obtained from extrapolation of the Tafel lines to the corrosion potential. This extrapolation is often difficult to apply to stainless steels because of the active-to-passive transition that occurs. Furthermore, for Tafel lines to be obtained, the test electrode has to be polarized over a wide potential range, resulting in excessive disturbance of the equilibrium of the system. The polarization-resistance technique overcomes these problems to a certain extent since only the potential region close to the corrosion potential is studied. However, calculation of the corrosion rate from polarization-resistance measurements still requires a knowledge of the appropriate Tafel constants, as can be seen from the following equation²:

$$\text{Corrosion rate} = C \cdot \frac{b_a b_c}{b_a + b_c} \cdot \frac{dI}{dE}, \dots\dots\dots(1)$$

* Lecturer.

† Associate Professor.

Both the above of the Department of Materials Science and Metallurgical Engineering, University of Pretoria, Hillcrest, Pretoria 0083.

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where

- C is a constant,
- b_a and b_c are anodic and cathodic Tafel constants,
- I is the applied current,
- E is the potential, and
- dE/dI is the polarization resistance.

Mansfield² has shown that both the polarization resistance and the Tafel constants can be determined simultaneously from a slightly expanded polarization-resistance measurement, which makes the polarization-resistance technique extremely useful in corrosion research. The simultaneous determination of polarization resistance and Tafel constants can be achieved most directly by computer analysis of the polarization curve in the vicinity of the corrosion potential^{3,4}.

Experimental Procedure

The chemical compositions of the materials used in this study are shown in Table I. Samples (20 by 20 by 2 mm) were prepared from hot-rolled and annealed plate supplied by Middelburg Steel & Alloys. The 3CR12 was annealed at 770°C, and the 14Cr steel at 700°C. The surface of the samples was abraded down to 600-grit silicon carbon paper, and they were then degreased in methanol, cleaned in distilled water, and allowed to dry in air before being fitted onto the exposure opening (1 cm²) of the electrochemical cell (Fig. 1). The standard electrolyte was an aqueous solution containing 2000 p.p.m. of sulphate prepared from sodium sulphate and distilled water. The pH value was adjusted with sulphuric acid and sodium hydroxide. The solution was saturated with air, oxygen, or nitrogen, and gas was bubbled slowly through the solution throughout the experiment. All the experiments were conducted at a constant temperature of 25 ± 0,5°C.

TABLE I
COMPOSITIONS OF 3CR12 AND 14CR STEEL
(In percentages by mass)

Steel	C	S	P	Mn	Si	Ti	Cr	Ni	N
3CR12	0,022	0,005	-	1,24	0,45	0,15	11,4	0,63	0,007
14Cr	0,020	0,014	0,020	0,94	0,48	0,34	14,68	2,27	0,017

Electrochemical measurements were made 1 hour after a stable corrosion potential had been obtained. In the polarization-resistance technique, polarization plots were measured over a potential range of ± 20 mV from the corrosion potential at a scan rate of 10 mV/min. Full polarization diagrams were determined over a potential range of 2000 mV at a scan rate of 30 mV/min. The samples were prepolarized to -1000 mV for 5 minutes, after which scanning was started from that potential.

The experimental polarization plots were analysed according to a method based on a combination of the graphical and computer analysis described by Mansfeld⁵, the computer program being developed in such a way that it could be used on any advanced programmable calculator⁶. An IR-drop compensation, based on a technique described by Mansfeld², was incor-

porated in the computer analysis.

For each sample, three separate experimental polarization plots under identical experimental conditions were recorded. The results given in this paper are the average of those measurements. For each medium, a minimum of three full polarization diagrams was recorded, and good reproducibility was achieved.

Results and Discussion

The Effect of pH

The influence of pH on the corrosion rate of 14Cr steel as obtained from a computer analysis of the polarization plots, is shown in Fig. 2. The corrosion rate of the steel is independent of pH for pH values above 6. Below a pH value of 4, the corrosion rate increases sharply with decreasing pH. These results are similar to that discussed by Uhlig⁷ for steel in aerated aqueous solutions. The lower corrosion rates obtained in the present experiments at the higher pH values are due to the lower concentration of oxygen in the solution.

The influence of pH on the polarization diagrams of 14Cr steel is shown in Figs. 3 to 5. In general, the corrosion potentials shift to more-noble potentials with increasing pH, while the polarization curves as a whole shift to lower current densities. This trend corresponds to results obtained by El-Basiouny⁸ for both 10 per cent and 15 per cent chromium steels in sulphuric acid solutions. At higher pH values, the passive current density is independent of pH, as is shown in Fig. 5. In these media, the system passivates and the corrosion rate is determined by the passive current density. Thus, one expects the corrosion rate to be independent of solution pH at the higher pH values. This conclusion corresponds to the results of the computer analysis shown in Fig. 2.

The Effect of Dissolved Oxygen

A survey⁹ of the corrosivity of South African mine waters has shown that most mine waters have a dissolved-oxygen content of more than 5 p.p.m. Therefore, it is important that the practical implications of a higher oxygen content on the corrosion rate should be investigated. The influence of dissolved oxygen on the corrosion characteristics of 14Cr steel at pH 0,5 is shown in Table II as obtained from a computer analysis of polarization-resistance plots. The results obtained from the computer analysis are explained by the schematic polarization diagram shown in Fig. 6. The oxygen-reduction reaction is diffusion-controlled because of the limited solubility of oxygen in aqueous solution. The limiting diffusion current density of oxygen reduction is given by

$$i_L = \frac{-D n F C_b}{\delta}, \dots\dots\dots(2)$$

where

- i_L = limiting diffusion current density,
- D = diffusion coefficient,
- F = Faraday constant,
- C_b = bulk concentration of oxygen,
- δ = thickness of the boundary layer, and
- n = number of electrons involved in the reaction.

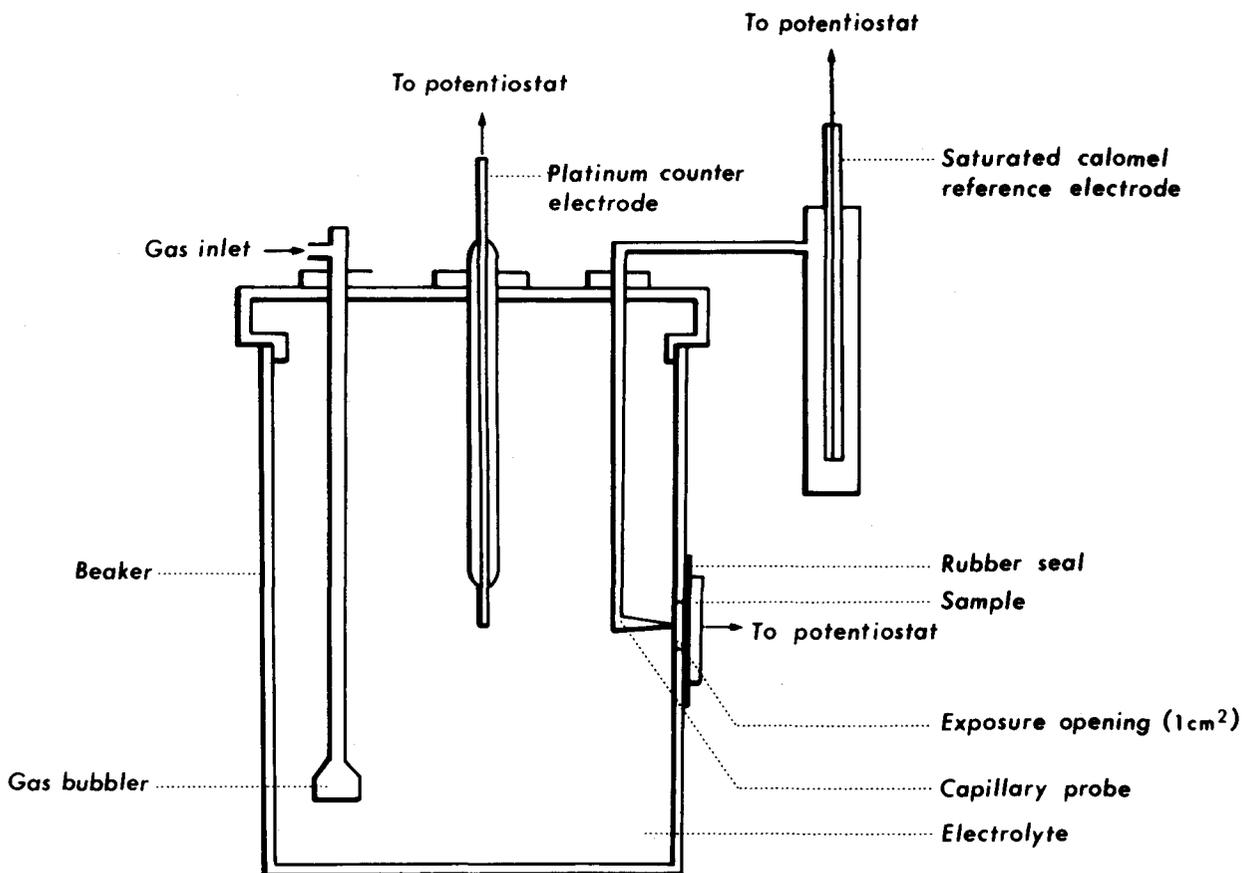


Fig. 1—Schematic diagram of the cell used for the electrochemical measurements

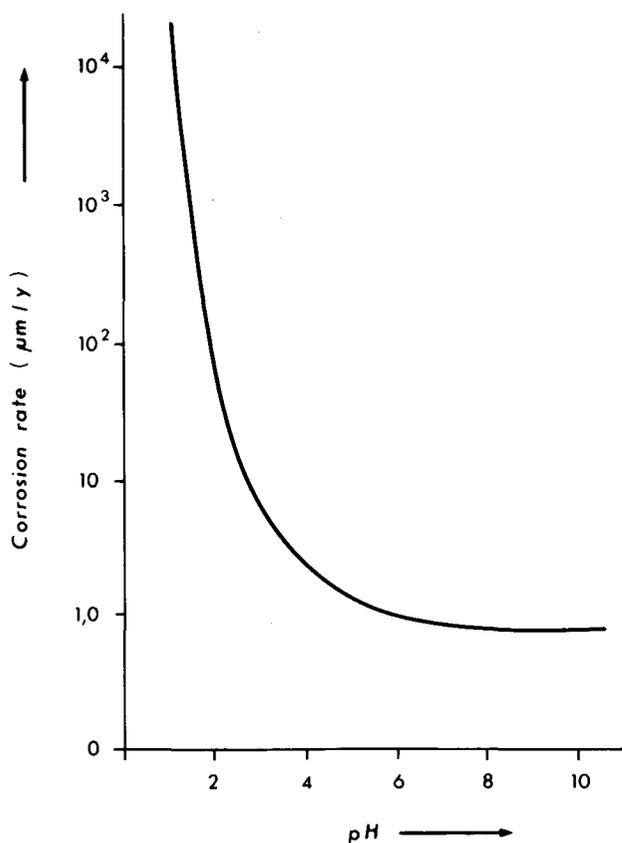


Fig. 2—The influence of pH on the corrosion rate of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C (obtained from a computer analysis of polarization-resistance plots)

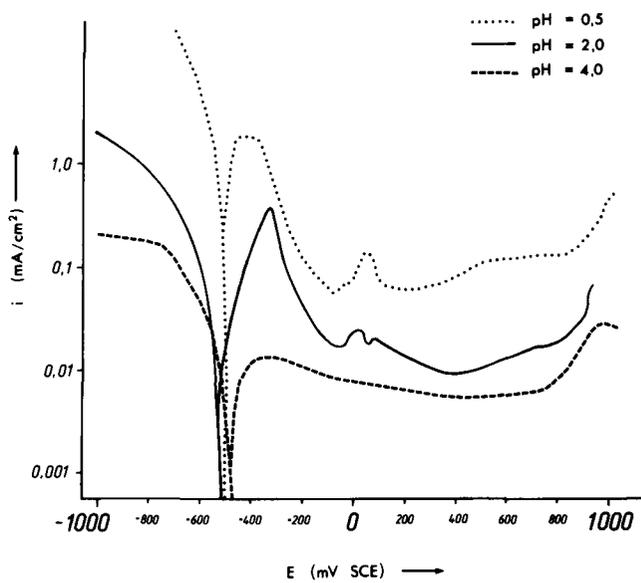


Fig. 3—Polarization diagrams of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, at pH 0,5, 2,0, and 4,0, and at a scan rate of 30 mV/min

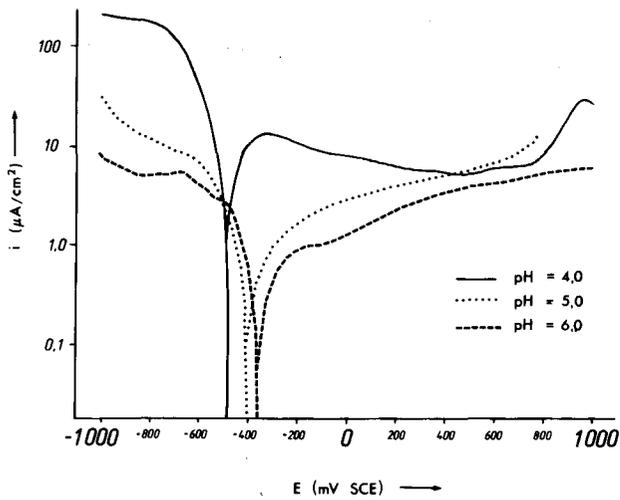


Fig. 4—Polarization diagrams of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, at pH 4,0, 5,0, and 6,0, and at a scan rate of 30 mV/min

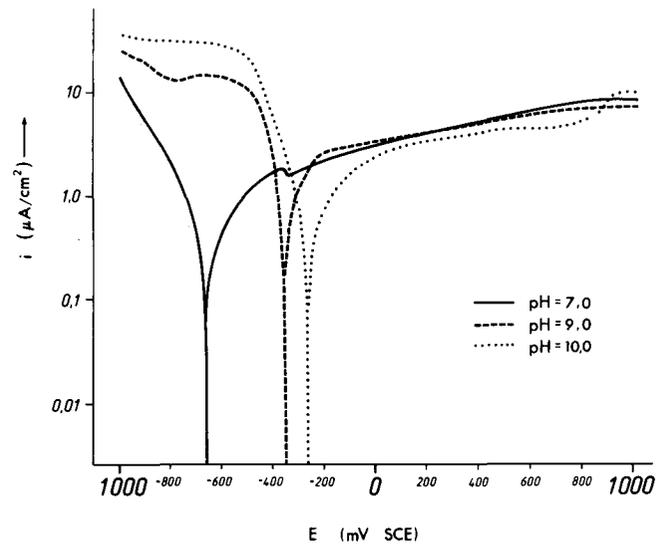


Fig. 5—Polarization diagrams of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, at pH 7,0, 9,0, and 10,0, and at a scan rate of 30 mV/min

TABLE II
THE INFLUENCE OF DISSOLVED OXYGEN ON THE CORROSION CHARACTERISTICS OF 14CR STEEL
Conditions: Aqueous solution containing 2000 p.p.m. of sulphate
Temperature 50°C
pH 0,5

Solution	Corrosion potential mV (SCE)	Anodic Tafel constant mV	Cathodic Tafel constant mV	Annual corrosion rate, μm
Oxygenated	-462	60	160	$19,22 \cdot 10^3$
De-aerated	-480	40	40	$12,02 \cdot 10^3$

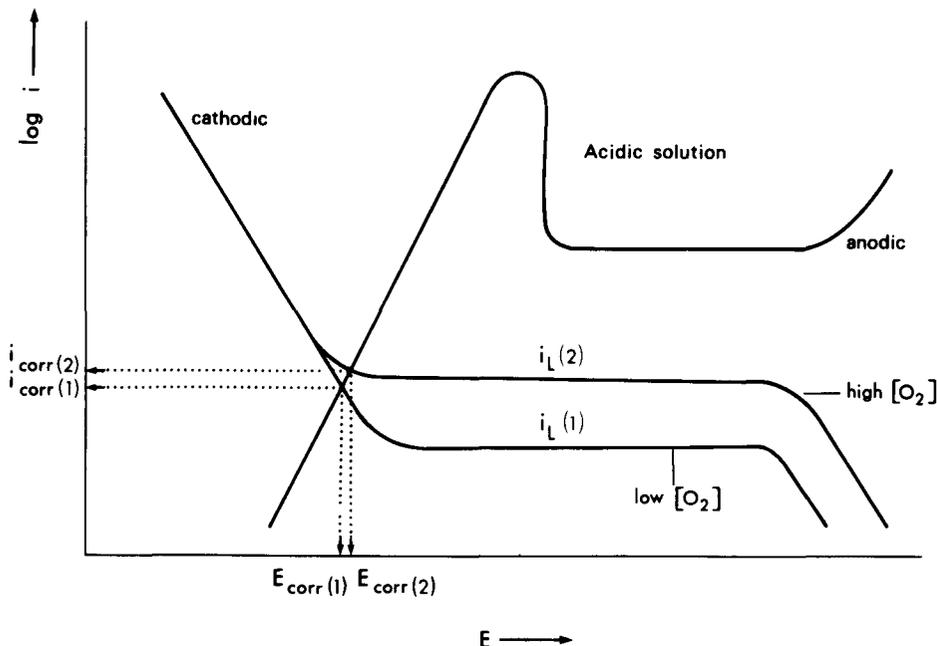


Fig. 6—Schematic representation of the influence of oxygen on the corrosion characteristics of 14Cr steel in acidic solution

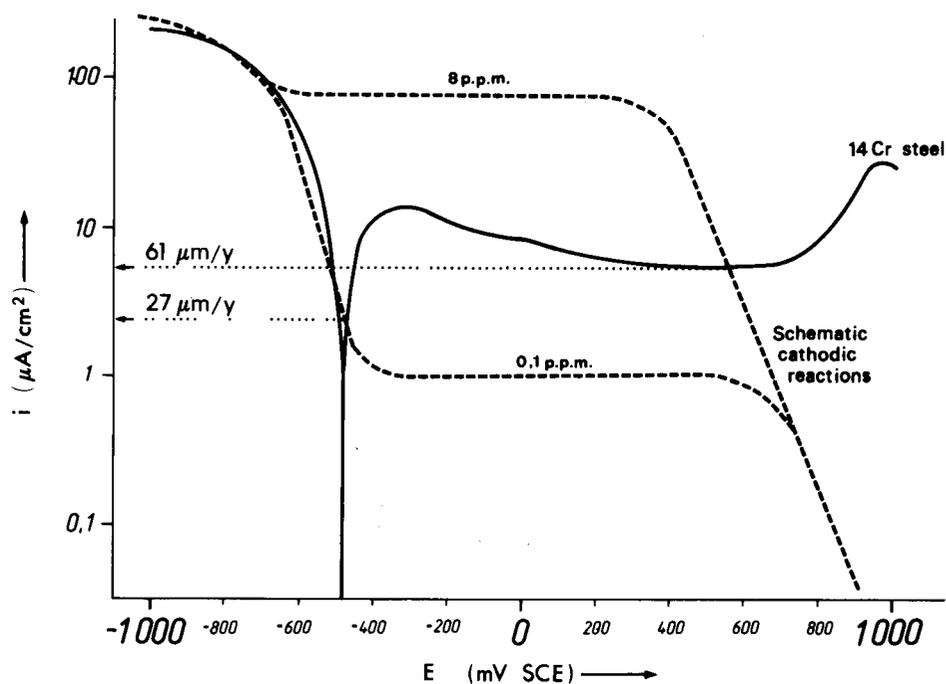


Fig. 7—Polarization diagram of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C and pH 4,0, and schematic cathodic polarization characteristics at different oxygen levels

TABLE III
THE CORROSION CHARACTERISTICS OF 3CR12 AND 14CR STEEL
Conditions: De-aerated aqueous solution containing 2000 p.p.m. of sulphate
Temperature 25°C
pH 2,0

Steel	Corrosion potential mV (SCE)	Anodic Tafel constant mV	Cathodic Tafel constant mV	Annual corrosion rate, μm
14Cr	-450	240	110	73,5
3CR12	-570	90	75	1471

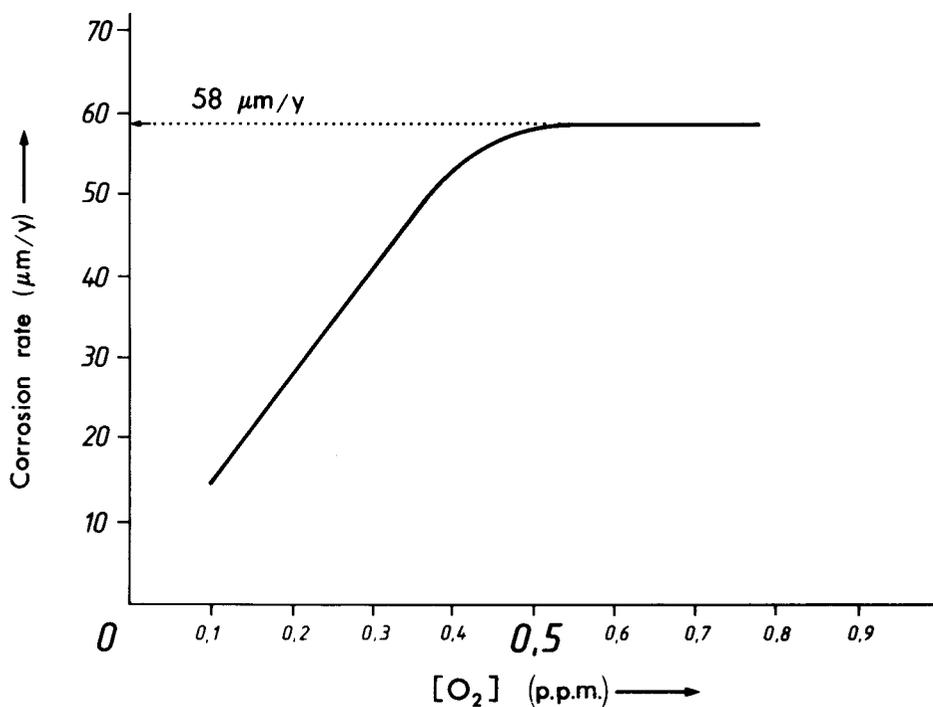


Fig. 8. Influence of oxygen content on the corrosion rate of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C and pH 7,0

The value of C_b will be low in a de-aerated solution, and consequently oxygen is not expected to contribute significantly to the reduction reaction. In an acidic solution of pH 0,5, the cathodic Tafel constant was equal to 40 mV, which indicates an activation-controlled reaction such as hydrogen reduction. If oxygen is bubbled through this solution, the oxygen content of the solution¹⁰ will be approximately 30 p.p.m. and the limiting diffusion current density of the oxygen reduction will be high. Oxygen reduction will now contribute significantly to the reduction reaction, which is confirmed by the cathodic Tafel constant of 160 mV when oxygen was bubbled through the solution.

Fig. 7 shows the polarization diagram of 14Cr steel in a solution of pH 4,0, as well as the schematic cathodic characteristics at different oxygen levels. In air-saturated, non-agitated aqueous solutions, the limiting diffusion current density¹¹ is approximately $100 \mu\text{A}/\text{cm}^2$. When

the oxygen current is low, the corrosion rate is determined by hydrogen reduction. In air-saturated solution, the steel passivates and a corrosion rate of approximately $60 \mu\text{m}$ per year is expected. This conclusion is confirmed by a shift in the stable corrosion potential from -440 mV (SCE) in a de-aerated solution to $+80 \text{ mV}$ (SCE) in an air-saturated solution. The influence of dissolved-oxygen content on the corrosion rate of 14Cr steel in a neutral solution is shown in Fig. 8. The corrosion rate of the steel increases with oxygen content up to 0,5 p.p.m., and then becomes independent of oxygen with a rate of approximately $60 \mu\text{m}$ per year. This is much lower than the $250 \mu\text{m}$ per year for steel in aerated neutral water⁷.

Comparison of 14Cr Steel and 3CR12

The corrosion characteristics of 14Cr steel and 3CR12 in an acidic solution, obtained from a computer analysis of the polarization-resistance plots in Figs. 9 and 10, are

Fig. 9—Polarization resistance of 3CR12 in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, pH 2,0, and a scan rate of 10 mV/min

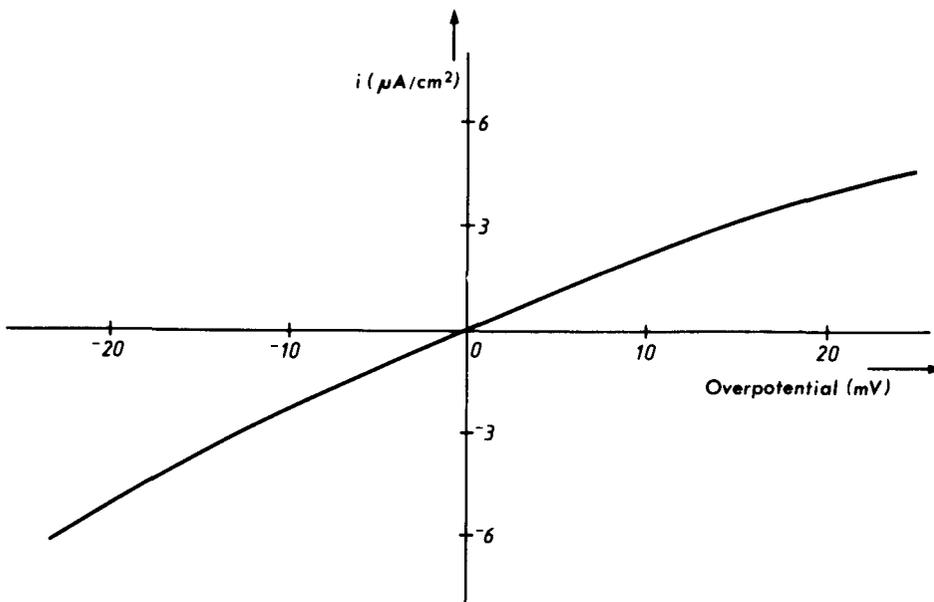
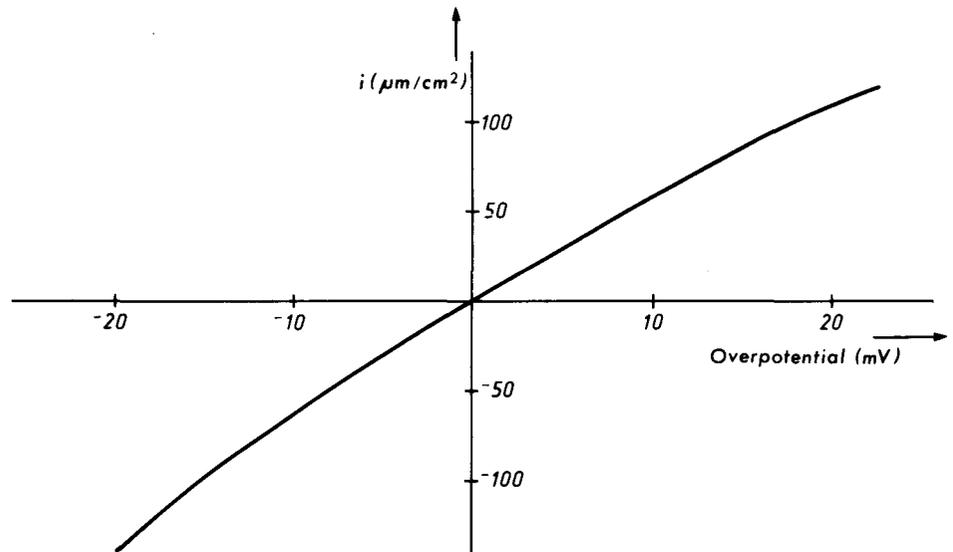
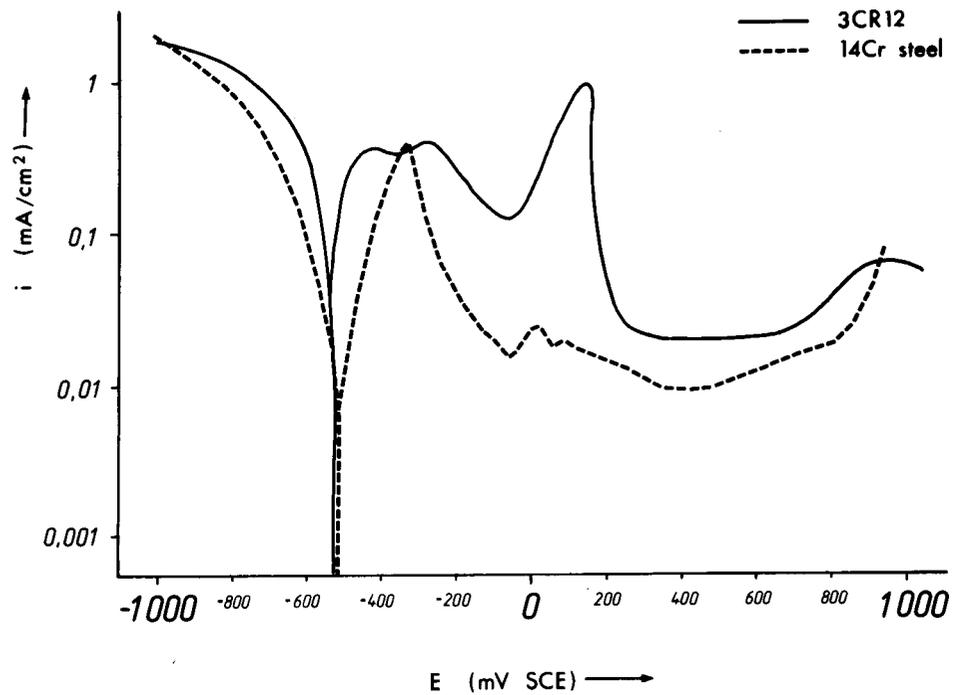


Fig. 10—Polarization resistance of 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, pH 2,0, and a scan rate of 10 mV/min

Fig. 11—Polarization diagrams of 3CR12 and 14Cr steel in a de-aerated aqueous solution containing 2000 p.p.m. of sulphate at 25°C, pH 2,0, and a scan rate of 30 mV/min



summarized in Table III as obtained from a computer analysis of polarization-resistance plots. The higher anodic Tafel constant, as well as the more-noble corrosion potential of 14Cr steel, is considered to be due to the beneficial effect of its higher chromium and nickel contents. Both these aspects mean a lower corrosion rate, which is consistent with the significant difference in the corrosion rates of the two steels: 14Cr steel shows a twentyfold decrease in corrosion rate over that of 3CR12.

The improvement in corrosion resistance of 14Cr steel is also due to a shift in polarization to lower current densities, as shown in Fig. 11. The fact that a smaller shift in corrosion potential is obtained in the polarization diagrams than indicated in Table III is probably due to the potentiodynamic method used in the determination of the polarization diagrams. As indicated by the polarization diagrams, no significant difference in corrosion resistance between the two steels would be expected in mildly corrosive environments since the passive current densities are virtually the same.

Conclusions

- (1) The corrosion rate of 14Cr steel is approximately independent of pH at pH values above 6. Below a pH value of 4, the corrosion rate increases sharply with decreasing pH.
- (2) In neutral and mildly alkaline media, oxygen reduction is the dominant cathodic reaction. The corrosion rate of the steel increases with oxygen content up to 0,5 p.p.m., and then becomes independent of oxygen with an annual corrosion rate of approximately 60 μm .

- (3) The 14Cr steel shows a twentyfold improvement in corrosion resistance over that of 3CR12 in sulphate solutions at pH 2,0. Therefore, 14Cr steel may find application in more-aggressive corrosive environments, where the corrosion resistance of 3CR12 is unsatisfactory.

Acknowledgements

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Analytical chemistry

The Analytical Division of the Royal Society of Chemistry has chosen Bristol as the site for the SAC 86 International Conference on Analytical Chemistry. On this occasion the SAC Conference is to be combined with the Biennial National Atomic Spectroscopy Symposium (BNASS—organized by the Atomic Spectroscopy Group of RSC/AD and the Spectroscopy Group of the Institute of Physics). SAC International Conferences are organized triennially, and still bear the initials of the Society for Analytical Chemistry, which was responsible for the initiation of these Conferences. BNASS is the third in this jointly run series, which is organized on a two-yearly cycle. The 3rd BNASS will be formally opened on Wednesday, 23rd July, 1986, and will continue on 24th and 25th July.

The scientific programme will be organized around plenary, invited, and contributed papers and posters covering the whole field of analytical chemistry, and all aspects of atomic spectroscopy. As at previous conferences, special symposia on particular analytical themes will be organized by RSC Groups and associated bodies. The programme will include workshops, where research workers can demonstrate new apparatus and techniques. Update courses are also planned, to provide all-day tutorial and

practical demonstration sessions. The latter will be held on the Wednesday, as an alternative to a scientific or cultural visit, or to the 3rd BNASS programme.

An exhibition of commercial apparatus, equipment, and books will be a feature of the Conference. Lecture-free times will be organized to facilitate attendance at the exhibition.

The Conference is sponsored by the International Union of Pure and Applied Chemistry (IUPAC) and the Federation of European Chemical Societies (FECS event no. 78). IUPAC sponsorship implies that entry visas will be granted to all *bona fide* chemists provided application is made not less than three months in advance. If a visa is not granted one month before the meeting, the IUPAC Secretariat should be notified without delay by the applicant.

Further information is available from
Miss P.E. Hutchinson
Secretary of the Analytical Division
Royal Society of Chemistry
Burlington House
London W1V 0Bn
England.

Waste management

The Eighth Annual Symposium on Geotechnical and Geohydrological Aspects of Waste Management will be held at Colorado State University, Fort Collins (U.S.A.), from 5th to 7th February, 1986. In recent years, much interrelated geotechnical and geohydrological technology has been developed for the management of waste materials, including mill tailings, low-level waste, and hazardous waste. For that reason, the Symposium will include papers and presentations dealing with this technology as it is related to the management of all waste materials.

Five mini-courses relating to the engineering and design of waste-disposal systems will be offered on the three days prior to the Symposium (2nd to 4th February, 1986). The mini-courses will be presented to offer attendees a selec-

tion of topics designed to transfer the latest technology in waste disposal to those involved in the waste-disposal industry. The course instructors will prepare a self-contained written version of the course content for distribution.

The Symposium will deal with the following topics:

- Uranium mill tailings
- Low-level waste
- Hazardous waste
- Other mine wastes.

Further information is obtainable from Colorado State University, Office of Conference Services, Rockwell Hall, Fort Collins, Colorado 80523, U.S.A.