reduction reaction available:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

and therefore the metal corrodes in the active state. But the rate of hydrogen evolution is small and therefore the corrosion rate is small, too. If the solution becomes aerated, reduction of dissolved oxygen

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

starts to predominate as shown by line 1 in figure 4.7. In this case one has borderline passivity.

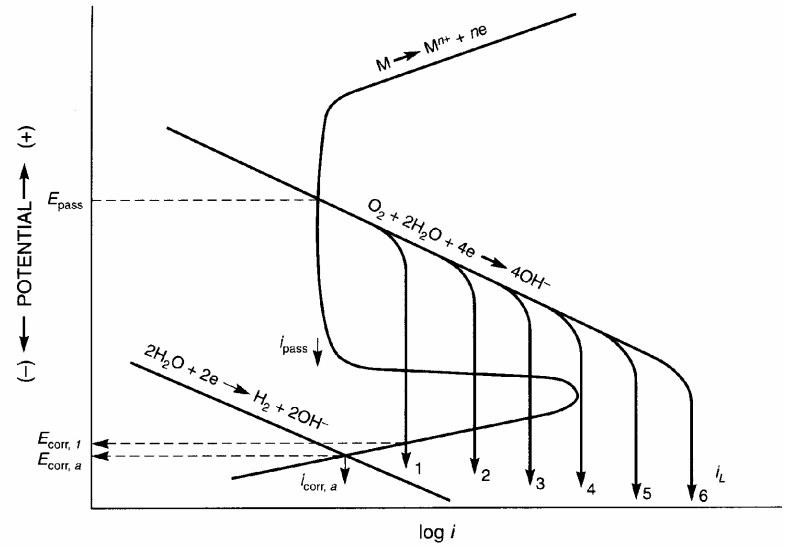

FIGURE 4.7 Effect of deaeration, aeration, and stirring on corrosion of active–passive stainless steel in neutral saltwater.

But agitation of the solution leads to an increase in the limiting diffusion current from 1 to 6, and the system gets in the passive state. In figure 4.8 a the corrosion rate from figure 4.7 is plotted against the solution velocity (agitation). For comparison figure 4.8 b shows the same plot for a metal that does not form a passive film. There the corrosion only shifts from concentration to activation control.

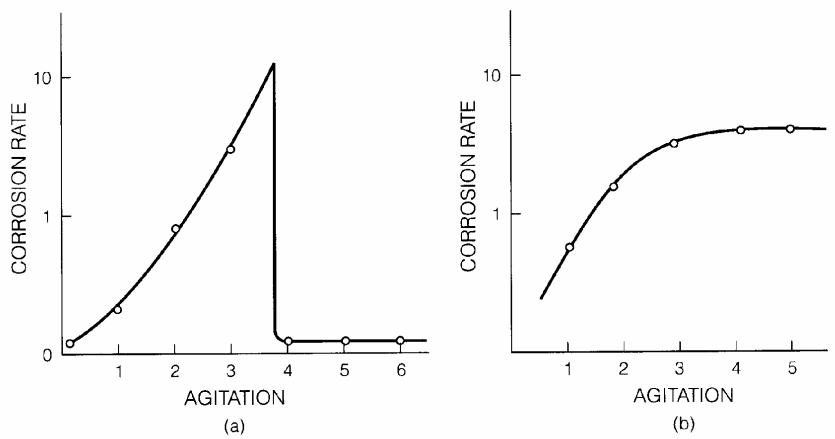

FIGURE 4.8 Effect of stirring or solution velocity on corrosion rate for (a) active–passive stainless steel, derived from Figure 4.6, and (b) normal active metal, reproduced from Figure 3.13b.

Experimental Apparatus and Procedures:

Potentiostatic and potentiodynamic procedures are used to measure the anodic polarization behaviour of metals. A potentiostat automatically adjusts the applied polarizing current to control potential between the working electrode (WE) and the reference electrode (REF). A schematic of such a system is shown in figure 4.10.

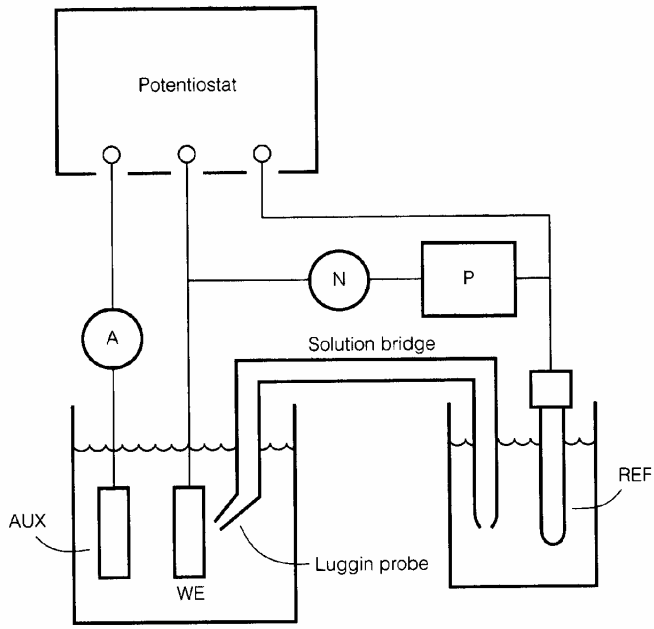

FIGURE 4.10 Controlled potential circuitry utilizing a potentiostat.

The current I polarizes the WE to the prescribed potential with respect to REF. In this setup no current passes through the REF, which has a constant potential. The result of such a measurement is shown in figure 4.11.

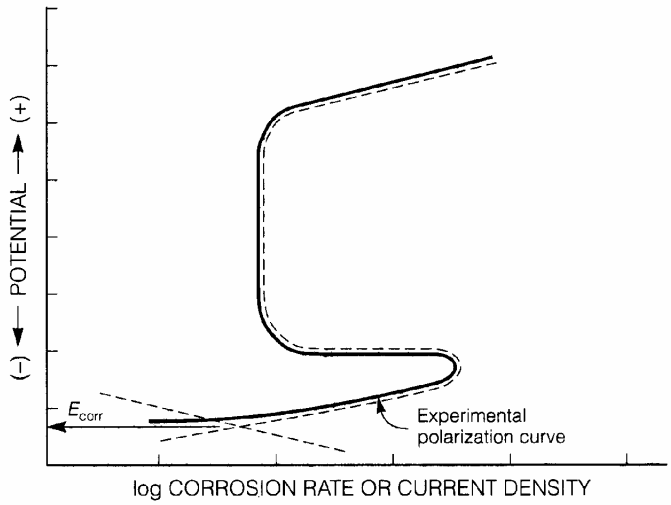

FIGURE 4.11 Polarization of an active–passive alloy with controlled (potentiostatic) potential.

In the measurment the potential is increased from E_{corr} in the active state in steps. After a step

the current is recorded and so on. In a potentiodynamic setup the potential is continually increased, while the current is continually measured at the same time. The result is the same as in the potentistatic experiment. An example of a real system is shown in figure 4.12. The potentiostatic polarizatzion cures of Fe and Fe-10.5Cr are shown.

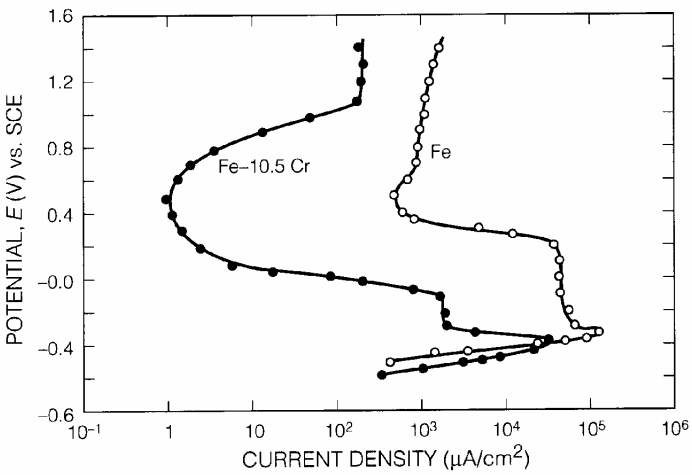

FIGURE 4.12 Potentiostatic anodic polarization of pure iron and iron-10.5% chromium alloy. *(Adapted from Steigerwald and Greene[6].)*

Anodic polarization curves are affected by the rate of polarization (scan rate in Vs^{-1}) (see figure 4.13) and by differences in the measured samples (see figure 4.14).

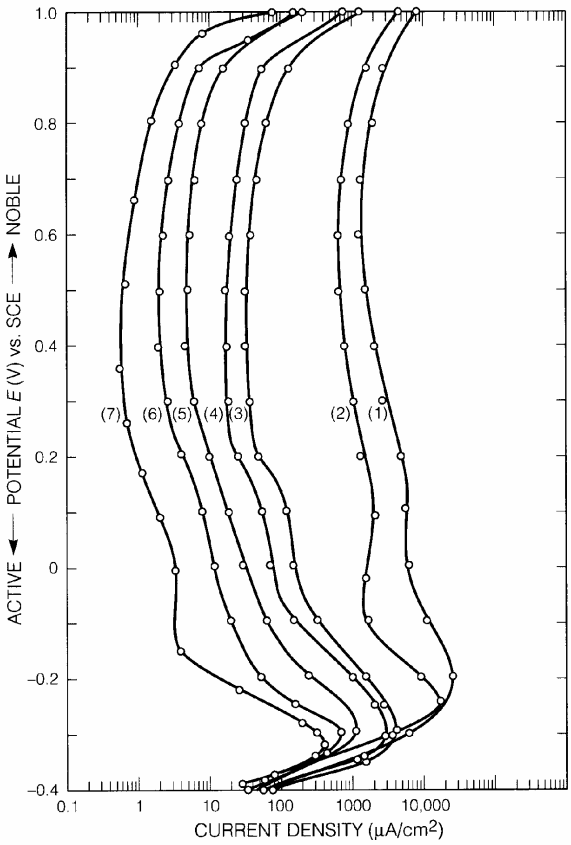

FIGURE 4.13 Effect of decreasing polarization rate (1) to (7) on potentiostatic anodic polarization curves for AISI 304 stainless steel in deaerated 1*N* H_2SO_4 at 25°C. *(From N. D. Greene and R. B. Leonard,* Electrochim. Acta, *Vol. 9, p. 45, 1964. Reprinted by permission, Pergamon Press.)*

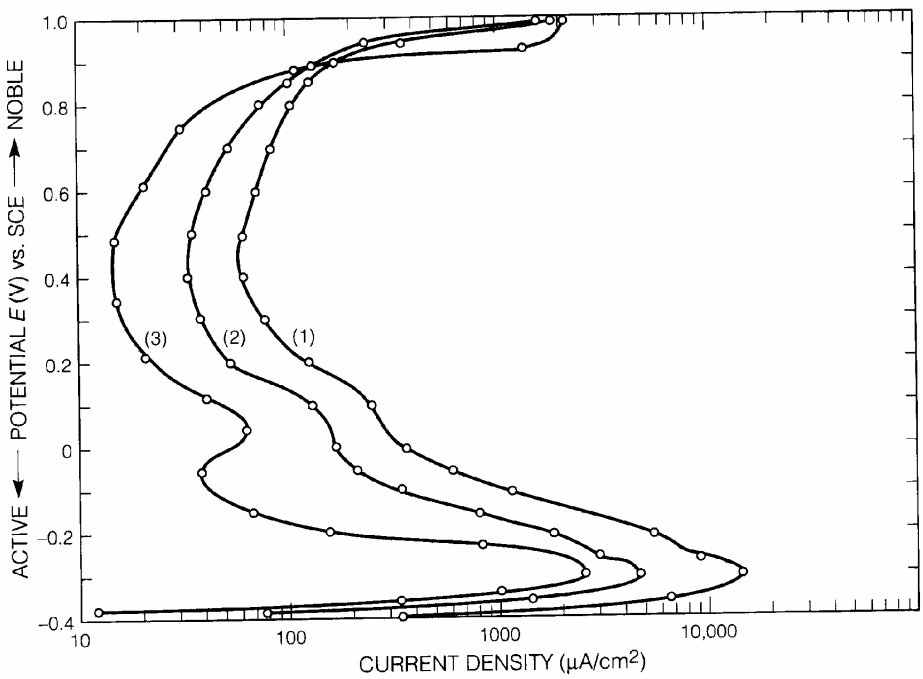

FIGURE 4.14 Effect of differing heats, (1) and (3), and differing specimens from the same heat, (1) and (2), on potentiostatic anodic polarization curves for AISI 304 stainless steel in deaerated 1*N* H_2SO_4 at 25°C; traverse rate 12 V/h. *(From N. D. Greene and R. B. Leonard,* Electrochim, Acta, *Vol. 9, p. 45, 1964. Reprinted by permission, Pergamon Press.)*

Potentiodynamic anodic polarization curves are used to judge corrosion resistance of alloys and the corrosivity of solutions. The experiments only need a couple of minutes. Potentiostatic measurements need a few hours, which is still short in comparison to the weeks or months needed for conventional testing. For example one can use the data to choose an alloy for different environments. The plots are shown in figure 4.16.

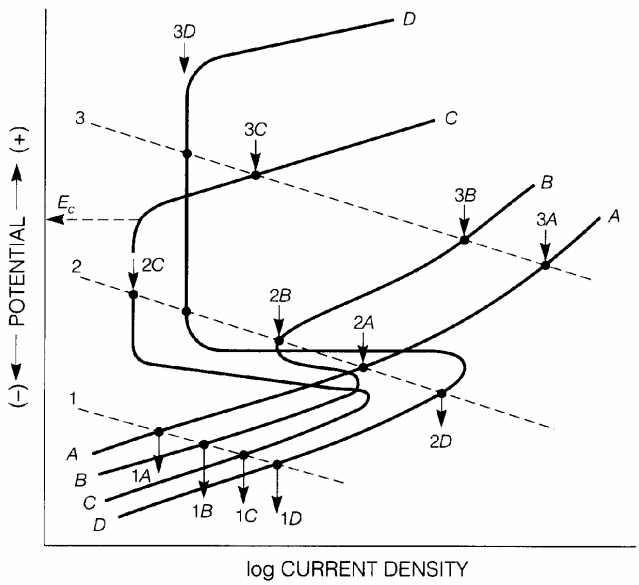

FIGURE 4.16 Schematic anodic polarization curves for hypothetical alloys *A, B, C,* and *D,* illustrating evaluation in various chemical conditions: 1, reducing; 2, moderately oxidizing; 3, highly oxidizing.

There are 5 parameters that may be used to judge an alloy:

1. In the active state, corrosion rate is proportional to the anodic current density whether or not the alloy is of the active-passive type.
2. The current density (rate) of reduction must exceed the critical current density for passivation to ensure low corrosion rate in the passive state.
3. Borderline passivity should be avoided in which either the active or the passive state may be stable.
4. Breakdown of the passive film in oxidizing conditions due to transpassivity or initiation of localized corrosion should be avoided.
5. The passive state in oxidizing conditions is essential for corrosion resistance, but reasonably small variations in the passive current density may not be significant.

A real world example is shown in figure 4.17. Hastealloy B is Ni-25Mo, C is Ni-15Cr-15Mo-5Fe and C-276 has low Si and C impurities. One can see that the latter has the best passive region. For use in the active region one would use alloy B as it does not contin expansive Cr. Apparently is the anodic polarization very sensitive to impurities.

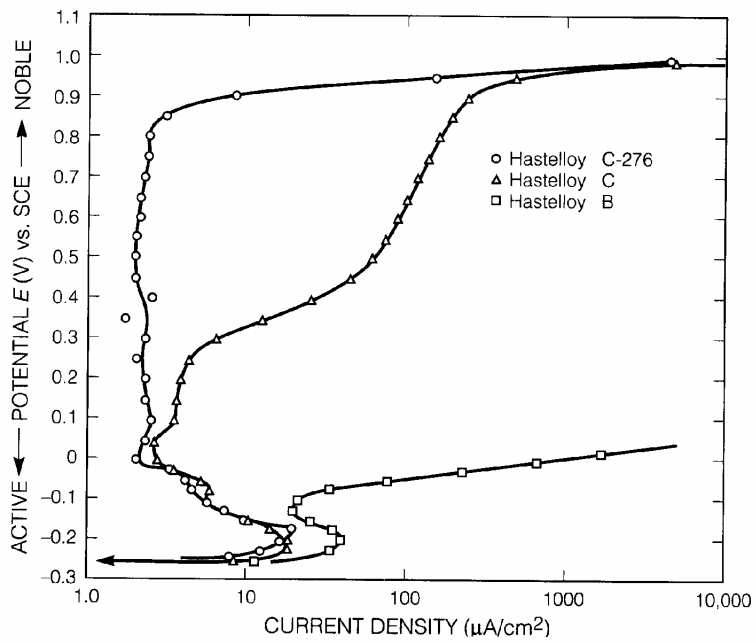

FIGURE 4.17 Comparison of potentiostatic anodic polarization of nickel alloys in 1 N H_2SO_4, ambient temperature. *(By courtesy of F. G. Hodge, Haynes International.)*

The influence of the solution is shown in figure 4.18. In this case one can see that the addition of chloride to the solution has a profound effect on the anodic polarization of steel, whereas hastealloy C is less affected. But in chloride free solutions the steel performs better.

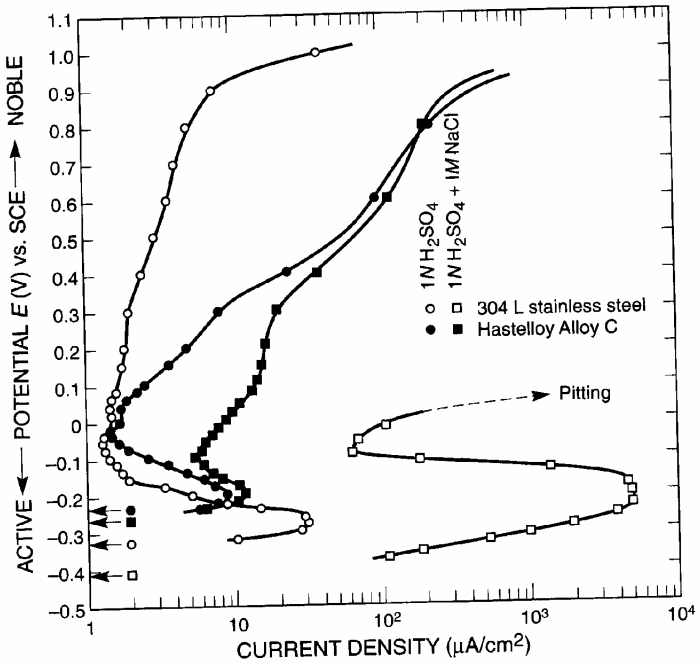

FIGURE 4.18 Effect of added chloride on potentiostatic anodic polarization of stainless steel and nickel Alloy C in sulfuric acid. *(Adapted from Green and Judd.[10])*

There are of course limitations to the data achieved by potentiodynamic anodic polarization. Under plant conditions additional processes can occur that influence the corrosion resistance of a material. Passive current density and corrosion rates can change over time. Therfore only qualitative predictions can be made. Then more extensive in-plant exposure tests are necessary.

Anodic Protection:

If an active passive metal is maintained in the passive region with a potentiostat its corrosion rate will be low at i_{pass}. With the electrical parts scaled up to plant size this is called anodic protection. The metal needs to have a broad passive region, as a wrong potential outside of the passive region would lead to increased corrosion. The method so far is only used for storage tanks for very corrosive acids (e.g. sulfuric acid (steel), phosphoric acid (stainless steel) and nitric acid (nickel)).

Properties of Passive Films:

The properties of passive films are unfortunately rather elusive. While potentiodynamic anodic polarization contains a lot of information, it is not possible to delineate the mechanism of the transition to the transpassive state. Passivity has been investigated for about 140 years,

but still not much is known about the structure of the films. It is clear that the films contain some water and most films are more likely hydroxides and not oxides. Surface analysis of the films is a problem, as the morphology of the film can change, when it is transferred into the vacuum. Water bound in the structure can be lost and this may lead to or change crystallization. Due to the fact that passive films are very thin most of them show semiconducting behaviour. For some cases it has been shown that the passive film is amorphous (e.g. Fe, Al). It has been shown recently [Mamun A, Schennach R, Parga JR, Mollah MYA, Hossain MA and Cocke DL Electrochimica Acta, **46** (22) 3343 (2001)] that oxygen evolution can initiate crystallization of the passive film on zirconium, which coincides with the passive transpassive transition.

Galvanic and Concentration Cell Corrosion

A galvanic cell is formed, when two different metals are connected electrically, while both are immersed in an electrolyte. In this case one of the two is corroded preferentially by galvanic corrosion. When different solution concentrations are present on the same metal surface, a concentration cell is formed, which leads to preferential corrosion, too. When attack on the junction of two dissimilar alloys is limited to one of the two, one usually has galvanic corrosion. The preferentially corroded alloy is the anode in the galvanic couple and the unattacked alloy is the cathode. The cathode may be damaged by hydrogen or by cathodic polarization out of the passive into the active zone.

Any metal or alloy has a unique corrosion potential E_{corr} immersed in a corrosive electrolyte. When two metals are coupled, the one with the more negative E_{corr} will lose electrons, which leads to an increased corrosion rate. The anodic dissolution, or corrosion reaction is

$$M \rightarrow M^{n+} + ne^-$$

for the active metal. The rate for the more noble metal N is decreased due to the excess electrons from M.

$$N \rightarrow N^{m+} + me^-$$

N is the cathode of the galvanic cell and M is the anode. The corrosion rate decrease in the cathode is the basis of cathodic protection by a sacrificial anode.

The corrosion potentials of different metals and alloys in a specified electrolyte give a galvanic series. Such a series gives a qualitative prediction, which alloy or metal will corrode first in a galvanic couple. But the quantitative corrosion rate can not be predicted from this series, as the influences of solution velocity and temperature are neglected. And the series is not necessarily the same for a different electrolyte, although people sometimes try to draw conclusions from the seawater series for different electrolytes.

Area Effects:

A large ratio of the cathode to anode surface area should be avoided. For small anodes the galvanic attack is concentrated and penetration of the attack through the metal is faster. A larger anode surface will give a more uniform attack and will slow down the rate of penetration. A classic example are storage tanks with new stainless steel bottoms and coated sides made of normal steels. The galvanic corrosion penetrated the sides quickly, due to small