Despite the extensive studies on the corrosion behavior of pure Zn, galvanized steel, and Zn-Al alloy-coated steels which have been carried out over the past several decades, very little is known about the specific electrochemical reactions that occur on these surfaces. Most existing literature concerns only corrosion studies at the open-circuit potential and in the media of neutral and alkaline conditions. Because galvanized Zn and Zn-Al alloy-coated steels have been widely used in many industrial areas, particularly in building, appliance, and automobile industries, and because acidic air pollution and acid rain currently are a serious global environmental problem, it is important to systematically study the corrosion behavior of those materials under a wide pH range in the presence of different concentrations of corrosion aggressive species, such as chloride anions.

Although a general survey of the literature clearly indicates that the nature and mechanism of anodic dissolution of Zn, the composition and structure of the passive film, and the corrosion products formed are still the active subjects of debate, it is generally believed that in alkaline solutions, the dissolution-passivation of Zn involves a number of intermediate species as illustrated in Scheme 1.

\[
\begin{align*}
Zn + OH^- &= Zn(OH)_{ads} + e^- \tag{1} \\
Zn(OH)_{ads} + 2 OH^- &= Zn(OH)_3^{2-} + e^- \tag{2} \\
Zn(OH)_3^{2-} + OH^- &= Zn(OH)_4^{3-} \tag{3} \\
Zn(OH)_4^{3-} &= Zn(OH)_2 + 2 OH^- \tag{4} \\
Zn + 2 OH^- &= Zn(OH)_2 + 2e^- \tag{5} \\
Zn + 2 OH^- &= ZnO + H_2O + 2e^- \tag{6}
\end{align*}
\]

where Zn(OH) is assumed to be adsorb on the electrode surface and Eq. 2 is the rate-determining step. The composition of the passive film has been proposed to be Zn(OH)$_2$, ZnO, or the composed layer of the two. Qualitatively, Eq. 1-3 represent the processes that dominate in the initial dissolution and the beginning portion of the active dissolution regions. When the potential becomes less negative, Eq. 4 and 5 become increasing important. The formation and modeling of the anodic dissolution of zinc through adsorbed intermediates and ionic mass transfer accompanying anodic dissolution of zinc in alkaline solution have been recently reported.

In the presence of Cl$^-$, however, chloride can react with $Zn^2+$ and Zn$^{2+}$ to form various species such as soluble ZnCl$_2$ and ZnCl$_3$, and surface-confined $\beta$-ZnOHCl that leads to the formation of the main corrosion product of zinc hydroxychloride, $Zn(OH)_2$Cl. In situ determination of zinc corrosion products under different conditions by Raman and infrared reflection absorption spectroscopy has been reported. Influence of other anions, such as Br$^-$, I$^-$, SCN$^-$, and sulfur-containing anions, on zinc corrosion behavior have been also studied and found to cause pitting corrosion.

In the present report, cyclic voltammetric (CV) and potential scan/hold techniques have been applied to evaluate and to compare the corrosion performance of hard Zn, Zn-5% Al, and Zn-55% Al alloy coated steels in deaerated NaCl of 0.10 to 0.90 mol L$^{-1}$ solutions in the pH range of 2 to 12. Surface and cross-sectional images of the passive film on Zn and its composition were examined with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), respectively. Distribution of the solution and solid-phase zinc species as a function of pH was presented on the basis of the chemical equilibria calculations. Finally, a pitting corrosion mechanism based on our experimental data obtained from hard Zn is proposed.

**Experimental**

**Sample preparation.**— Three different coated steel sheets supplied by BHP (Australia) were selected for this study: hard zinc (with 0.1–0.3 wt % Al and < 0.01 wt % Ti), Zn-5 wt % Al (with < 0.5 wt % mischmetal, known as “Galval”, and Zn-55 Al wt % (with 1.6 wt % Si, known as “Zincalume” in Australia and “Galvalume” in the USA). The thickness of the coatings was between 20 and 30 µm. Samples were cut from the coated sheets and had dimensions of 100 × 200 mm. After being washed with ethanol and distilled water, all samples were dried at 303 K in a vacuum oven at 0.01 kPa for 20 min, and stored in a desiccator until use.

**Chemicals.**— All chemicals used were of analytical grade purity. NaCl solutions (0.10 to 0.90 mol L$^{-1}$) with different pH values were freshly prepared. The pH of the solution was measured using an HI 8314 membrane pH meter (Hanna Instruments Inc., USA) and adjusted by using 1.0 mol L$^{-1}$ of either NaOH or HNO$_3$ solution.

**Electrochemical cell and instrumentation.**— The electrochemical cell designed for this study is shown in Fig. 1. The testing sample (~100 × 200 mm, Fig. 1a) was sandwiched between two silicon O-rings (Fig. 1b), both of which had an inside diameter of 6 mm. The surface area of the working electrode, i.e., the area of the sample exposed to the electrolyte solution, was 0.283 cm$^2$. A saturated calomel electrode (SCE, Fig. 1d) and a platinum wire (Fig. 1e) were used as the reference and counter electrodes, respectively. Electrolyte solutions (~25 mL) initially contained in a 100 mL beaker were thoroughly degassed with high-purity N$_2$ (BOC, Australia) for at least 5 min before being transferred to the electrochemical cell.