ArcelorMittal Breaks Down the Physics of Corrosion

Automakers and other users of rolled steel know that a surface is well protected but have concerns at the edges when pieces are cut from a roll – and where paint delamination can start. Simulations are helping steel manufacturers determine which methods prove most effective in protecting edge cuts.

BY CHRISTIAN ALLÉLY AND TIAGO MACHADO AMORIM, ARCELORMITTAL, FRANCE

Steel makers have made great strides in developing products that resist corrosion. Even so, the US Department of Transportation published a study in 2002 that listed the total annual direct cost of corrosion at $23.4 billion due to increased manufacturing costs, repairs and maintenance and corrosion-related depreciation of vehicles.

Automakers spend a great deal of time working with suppliers to come up with the most corrosion-resistant steel. It's no surprise, then, that the largest steel manufacturer in the world has a dedicated team devoted exclusively to the study of corrosion, ways to combat it and to develop new products — and they've found that multiphysics modeling provides them with invaluable information towards this goal. This company is ArcelorMittal, which had revenues of almost $125 billion in 2008, and crude steel shipments exceeding 100 million tonnes, representing around 10% of world steel output.

Protect the Gap

Steel surfaces are coated with a thin layer of molten zinc to create what we know as galvanized steel. The exposed zinc reacts with oxygen to form zinc oxide, which in turn, reacts with carbon dioxide to form zinc carbonate, a fairly strong material that helps stop further corrosion. A problem arises, though, when steel is cut into the desired lengths during manufacturing. At the cut edge, the steel substrate and zinc coating are both exposed.

Zinc is electrochemically more reactive that steel. When the two are in contact with each other and a moisture layer, then the zinc will act as the more reactive metal and sacrifice electrons to dissolve as zinc ions in the moisture layer (reacting with hydroxide ions to form the corrosion product). This is known as galvanic protection, and ensures that the steel will not corrode, as it acts as the noble metal in the electrochemical circuit. Yet, when enough of the zinc has disappeared, the

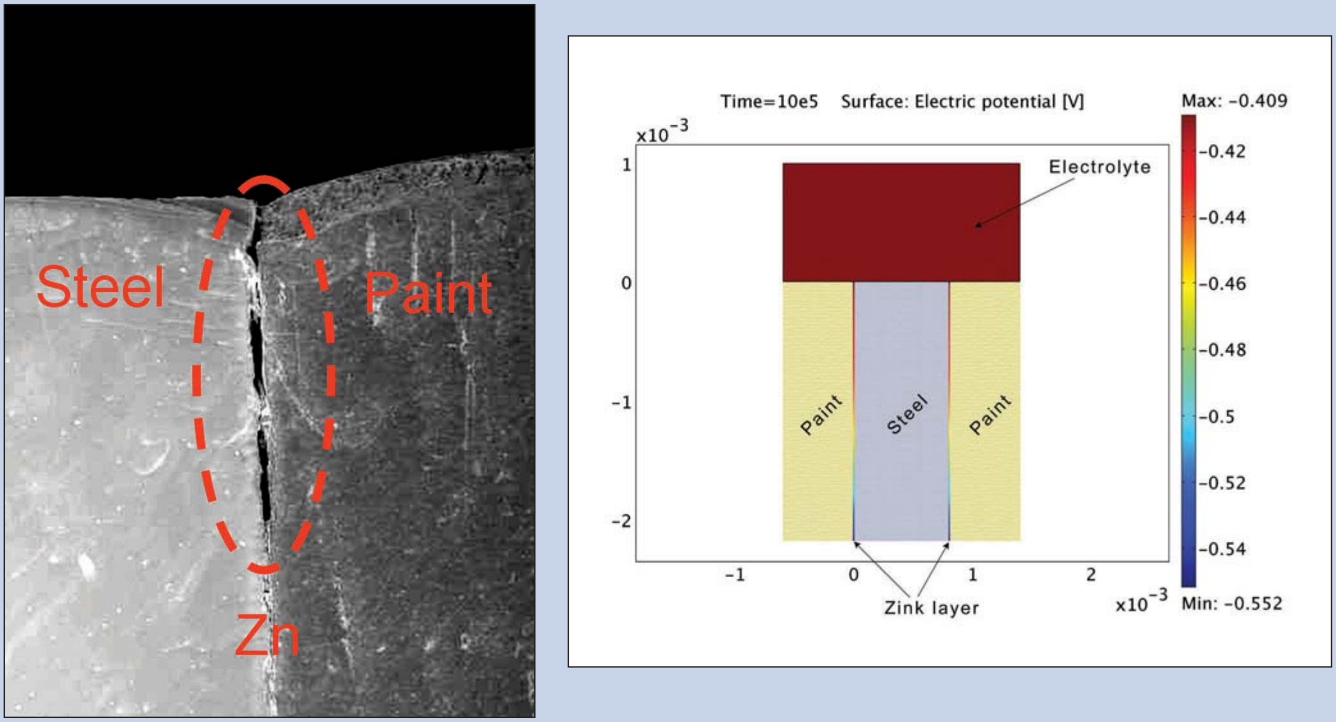

Figure 1: Photograph (left) looking at the cross section of the cut of galvanized steel. The ring indicates where the sacrificial zinc layer has already disappeared, leading to potential delamination of the paint coating from the material. The model simulates the disappearance of the zinc layers (right).

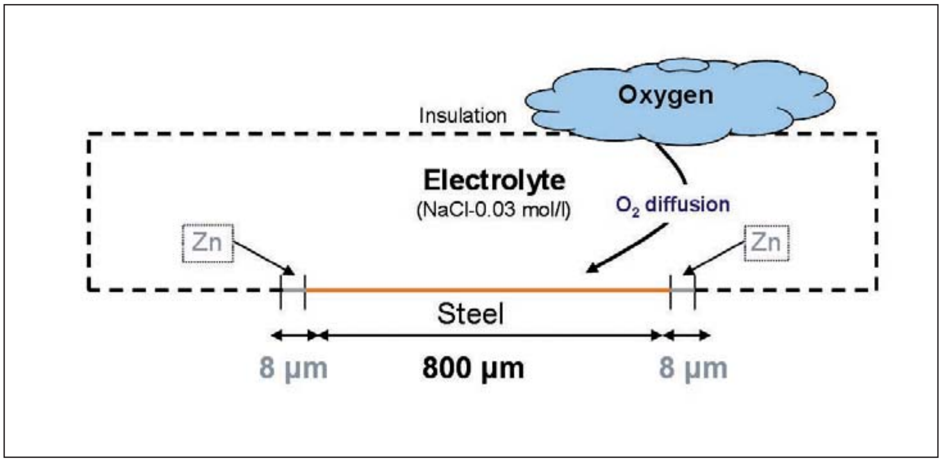

Figure 2: The physics of the corrosion model. Oxygen dissolves in water, such as a rain drop, and this in turn ionizes to hydroxide ions. The zinc metal loses electrons and dissolves as zinc ions. The electrons are then available in the steel to electrochemically react with hydrogen ions and complete the electric circuit.

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rate of its corrosion becomes hindered, and the steel then starts to corrode instead. This is especially the case when the disappearance of the zinc layer leads to difficulties for the participating ions to transport themselves through the moisture layer, such as in the gaps between the paint and steel, created by the corroding zinc. The steel starts to react with the atmosphere and the paint starts to delaminate; see Figure 2.

Researchers have found that a key variable that determines how quickly the gap develops and the paint delaminates is not the absolute amount of zinc but rather the relative thickness of the zinc to that of the steel (ratio of Fe/Zn). If the zinc layer is too thick, it not only consumes unnecessary amounts of expensive zinc, it can lead to problems during welding, and that material also generates hazardous pollutants. In contrast, a layer that is too thin provides effectively no galvanic protection.

The question is thus: what is the maximum ratio of Fe/Zn that guarantees protection of the substrate? Until now, the primary method of finding the best thickness was with accelerated corrosion tests in the laboratory, but that is not sufficient because tests are not only time consuming but are not always truly representative of a material’s performance in actual environments. Instead, our engineers want an explanation of what they observe so they can better address the issue. This has become possible only with modeling, which not only adds understanding but saves time and money because it is no longer necessary to perform a large number of laboratory tests to evaluate product performance.

Modeling Goals

As stated earlier, one of our goals was to understand the mechanism behind delamination and underpaint corrosion, and Figure 2 shows a diagram of the physics we model. In addition, there has always been considerable discussion as to whether the dominant process is cathodic or anodic corrosion. With the COMSOL® model we have a much better understanding of the underlying phenomenon and have determined that anodic corrosion arises more in products with good adhesion such as those we deal with, whereas cathodic corrosion is more important in systems with less adhesion.

In the anodic mechanism, coating thickness plays a critical role in the delamination rate. Thus, we also wanted to study the most effective and least costly thickness of the zinc layer. Our dynamic

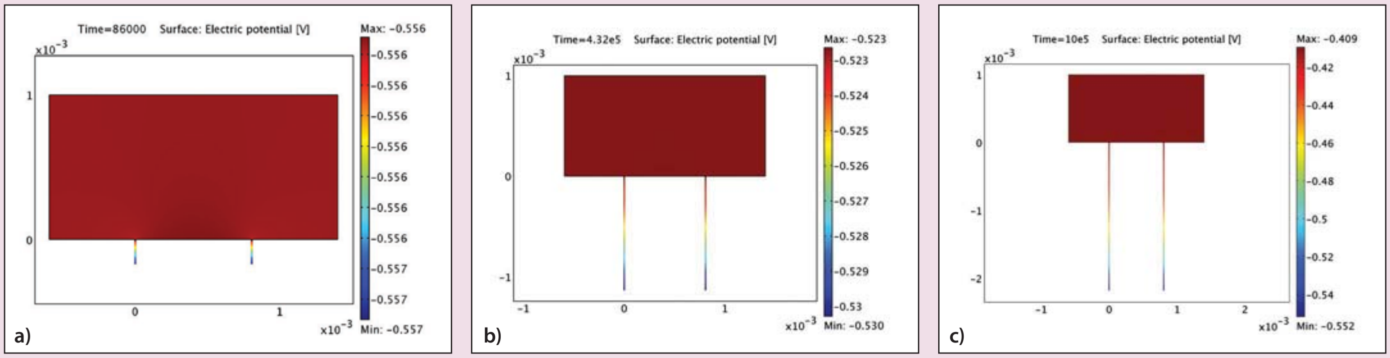
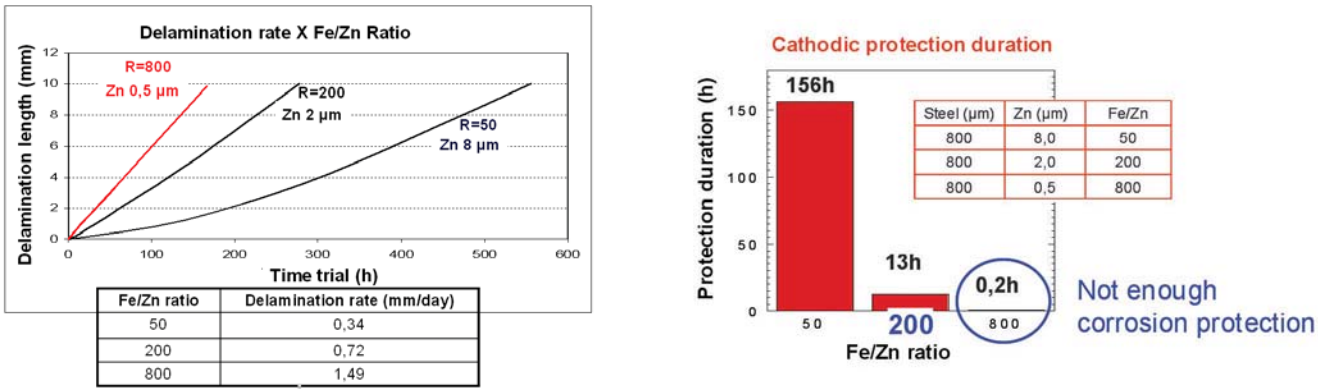


Figure 3: COMSOL model of electrochemical potential and zinc consumption after 1 day (a), 5 days (b) and 11 days (c) of exposure to salt spray.



Fe/Zn ratio	Delamination rate (mm/day)
50	0,34
200	0,72
800	1,49

Steel (µm)	Zn (µm)	Fe/Zn
800	8,0	50
800	2,0	200
800	0,5	800

Figure 4: COMSOL results help determine how thin we can make the zinc layer without losing cathodic protection.

model allows us to follow the delamination front as a function of corrosion time (Figure 2b).

We are starting to get some very good information. We know, for instance, that for a given thickness of steel, the delamination rate increases with a decrease in the coating thickness. The model also allows us to analyze the evolution of the electrolyte potential at the steel surface as a function of zinc corrosion. In this way it becomes possible to determine the duration of cathodic protection by calculating the time necessary for the steel surface's potential to achieve Fe equilibrium potential — which is the time after which steel dissolution can start to occur. And while the results are based on some simplifications, the trends are relevant. The results confirm that a ratio of Fe/Zn = 800 does not confer an acceptable corrosion protection to steel; the protection well is lost after only a few minutes.

Such knowledge has already helped us in practical applications. Before we had the model, our production engineers wanted to save money and deposit only a few hundred nanometers of zinc. However, our model showed that doing so makes no sense because this amount provides almost no anodic protection. In the same way, our model allows us to give recommendations for optimizing the zinc thickness according to the final use of the coated product.

About the Authors

Christian Allély (left) holds a Ph.D in Electrochemistry from the University of Paris. In 1990 he joined ArcelorMittal R&D where he is currently a corrosion expert in the Automotive Product Research Center and responsible for the management of European projects on corrosion of coated steels. Tiago Machado Amorim is a Ph.D Student in Christian's team modeling corrosion protection.

Future Projects

This was our first entry into mathematical modeling, and we spent quite some time evaluating various software. We read a number of interesting scientific articles that mentioned COMSOL and investigated it. We found that with COMSOL you don't have to be a modeling expert to get very useful results.

The current model works with stationary corrosion conditions, but an automobile faces continually changing conditions that vary in the amount of humidity and salt content. We plan to expand the model to handle these situations. We also want a tool that will allow us to model the electrochemical behavior of new coatings that consist of other zinc compounds that allow for a thinner layer. In these first efforts we are focusing only on the coatings and not on different grades of steel, even though this is also an important aspect to consider because auto parts do not all use the same types of steel. We plan to start looking at high-strength and specialty steels in this context. In addition, we would like to simulate corrosion products' precipitation, cyclic corrosion conditions and simulate alloyed coatings — aspects we intend to address in the coming years. ■

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