Case Studies of Corrosion Failures

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Introduction
Hello, my name is Charles Zona, and I would like to welcome everyone to today’s McCrone Group webinar. Our presenter is Wayne Niemeyer of McCrone Associates. Wayne is going to talk to us about some case studies of corrosion failures.

Before we get started, I would like to tell you a little bit about Wayne’s background and experience. Wayne is a Senior Research Scientist with McCrone Associates and has over 40 years of experience. He specializes in X-ray microanalysis of small particles using energy and wavelength dispersive spectrometry methods (EDS and WDS) with the scanning electron microscope (SEM) and electron microprobe (EPMA). Wayne has extensive and diverse analytical capabilities developed during a long career in a research and development capacity for a major packaging manufacturing company prior to joining McCrone Associates in 1992.

Wayne Niemeyer (WN):
Thank you, Chuck, and welcome, everybody. I am certainly appreciative of the fact that you took time out from your busy schedules to join us today. I am going to talk to you a little bit about corrosion. We mostly associate corrosion with metals, but other degradations can occur on plastics, glass, and so forth, but we are going to talk about mostly metal corrosion.

As we know, metal corrosion has been a major issue and problem for many, many decades, probably even centuries. So, I am just going to bring you back up to the 21st century, and talk to you about two case studies that I thought were particularly interesting in some of my work here at McCrone.

Corrosion takes eight forms:
1. Uniform attack is when the corrosion just proceeds into the metal surface in uniform thickness and at a uniform rate.
2. Galvanic, or two metal corrosion is when two dissimilar metals are in contact with one another in the corrosive environment, and one metal corrodes in preference to the other.
3. Crevice corrosion is with one metal that has some crevices in it—scratch es, cracks, whatever—that would cause some corrosion action in those areas.
4. Intergranular corrosion is where the corrosion follows the grain boundary paths of the crystal grains in metals.
5. Pitting corrosion has a very rapid corrosion rate. It is very localized in the metal. The surrounding area does not corrode, and the pitting action continues on into the depth of the metal very rapidly.
6. Selective leaching is where one element of the metal alloy is selectively corroded and leached away. This is commonly found in brass, where the zinc is selectively leached away in a process known as dezincification.
7. Erosion corrosion is when the metal is exposed to some kind of flowing liquid; that’s the corrosive agent. So, there’s going to be not only the corrosion, but also the erosion by the liquid passing across it.
8. Stress corrosion occurs when the metal is under some sort of a stress. It could be bent, it could be pinned down or bolted down and stresses put into it that way. Corrosion sites where the stresses are the highest will be the areas that will corrode.
Today, I’m going to talk to you about intergranular corrosion and pitting corrosion from two projects that I had here that were quite interesting, and have some really unusual results.

So, here’s the first one. This is a stainless steel rod that is used for liquid fills in a manufacturing plant. These rods were prematurely breaking while they were in the assembly line machine, and they caused the entire line to shut down as a result. We were asked to determine the mode of failure and identify potential causes of the failure.

This is a scanning electron microscope image—in the center of the field of view here, showing the fracture face of one of the rods. The upper left-hand corner is the interior wall of the rod, and the lower right-hand corner is the exterior of the rod. We can see that the rough fracture face proceeds all the way across the full thickness of the metal. As we zoom up in magnification, in the lower right-hand side of the frame, here, we can start to see what’s happening. The crystal grains have grain boundaries, and we can see in most areas that these grain boundaries have been dissolved away, and are loosening the structure; losing strength, losing integrity. The crystals are starting to pull apart. We can see that in the fracture face, the crystals pulled apart very cleanly, for the most part. The opposite side fracture face has a similar appearance.

We can also see in the crystals some of the dark circular regions that appear to be pits within the crystals. This is a very severe corrosion attack that was going on.

We can also use our energy dispersive X-ray spectrometry (EDS), which is an attachment that’s on most SEMs nowadays, that can provide the elemental composition of materials. Here, we’re looking at the fracture face, and within that purple rectangle is the region that we are analyzing for the elemental composition. The spectrum is shown on the upper right, and we can see that the elemental composition is mainly iron, chromium, and nickel, with a minor amount of manganese. This is typical of a 300 series stainless steel material. The oxygen content is around 13 percent by weight, and that’s fairly high, but that’s obviously from the corrosion reaction that oxidizes the metal as the corrosion proceeds.

We took the sample fracture and mounted it in a clear epoxy material, and then used standard metallographic grinding and polishing techniques to grind down into the steel rod so that we can get a look at the base metal all the way from the outer perimeter down into the inner perimeter. The dark “V” region in the center of that rectangle is the inner portion of the rod, and the perimeter around that “V” is the corrosion sites. The outer perimeter of the dark area is the outer perimeter of the base metal, which is the dark area.

Now we can take a look at the base metal and see what is going on underneath the corrosion areas in the fracture site.

Again, we look at the scanning electron microscope image in the backscattered imaging mode, where we can see compositional differences due to brightness and contrast differences that are due to average atomic number. Low atomic number materials appeared dark, higher atomic number materials appear lighter. Here we have the interior surface, the upper right-hand corner, that is, to the right the base of that “V,” and then outside to the exterior on the left-hand side where it is the outside portion of the rod. The base metal in between has this nice convoluted river-like pattern all the way through the whole thickness of the metal. This is very typical of intergranular corrosion, where the corrosion is proceeding around the perimeter of the crystals in the metal, producing this river-like pattern. Higher magnification, again in the “V” area on the interior part of the steel rod, is on the left-hand side, and we can see how the grains have started to separate and pull apart where the metal is definitely losing its integrity and falling apart. Further down toward the bottom of the image, where I have grain boundary corrosion highlighted here, we can see the dark gray areas around the grain boundaries, and the grains have not separated yet. So these are where the corrosion products are still intact, and that’s where we want to do our analysis to find out what the corrosive agents might be.

Higher magnification. again showing the grain boundary corrosion around the various crystal grains and lots of corrosion product to work with for analysis.

Here’s part of the analysis. The first thing we want to do is find out a little better composition of the alloy, and here we have a nice polished section of a crystal. We can get the EDS spectrum on the right, again showing the chromium, iron, and nickel composition. The quantified data is at the bottom in the table.
We find that the chromium, iron, nickel, and manganese, and trace of silicon, is typical composition for the 302 or 304 series alloys within the 300 series materials. I have highlighted the chrome, carbon, and oxygen in yellow to show you something else when we look at the corrosion product which are labeled two, three, and four.

Here’s an example from the corrosion product in Box 3, and the spectrum, accordingly, and the quantitative data of all three of the corrosion products down below in the table. I want to bring your attention to the fact that there is excess chromium in the corrosion products compared to the base metal. There is also a minor amount of sulfur in the corrosion products; there may be a trace of chlorine here and there. The chlorine and the sulfur are probably the corrosive agents—chlorides and sulfate salts. Chlorine, in particular, and all the halides, are extremely corrosive to stainless steel alloys, so that is a dead giveaway that these are the corrosive agents involved here.

The chromium level being so high was also of interest. We know that when stainless steel corrodes, the iron is usually selectively leached away in the acidic environments where most of the stainless steel corrosion would occur, but if we look at the iron to nickel ratios, we find that the ratio in the steel itself, on the crystal grain, is about 8 to 1, whereas in the corrosion sites it’s also about 8 to 1. That would indicate that the iron really isn’t leaching away; it’s staying at the same ratio with the nickel. It’s the chromium that’s different, and the chromium is much higher. We also see on the left, in the table, that there is a little bit of elevated carbon, and, of course, the oxygen is there, too. But the high chromium and little elevated carbon indicates that this might be from chromium carbide precipitates along the grain boundaries. Chromium carbide precipitates form during the steel manufacturing process, and if they are allowed to remain around the grain boundaries, it makes the steel much more susceptible to intergranular corrosion. In order to get rid of the chromium carbides, the steelmakers have to heat treat the steel, where the steel coil is heated up to, around, I think, 1950°F for several hours, which allows the chromium carbides to remigrate back into the bulk crystals, away from the grain boundaries, and that’s how they try to minimize that.

What do we have here from this work? We know the fracture was definitely caused by intergranular corrosion. We know that there was some minor sulfur and trace chlorine in the EDS data indicating sulfate and/or chloride as the corrosive agents. The steel rod is very similar to a 304 series stainless steel alloy. I said before that 302 might be involved here, too, but in the industrial world, the 304 series alloys are really, really popular, so this is probably a 304 stainless steel.

Now there are apparent chromium carbide precipitates in the grain boundaries, indicating improper heat treatment, thus making them more susceptible to the intergranular corrosion attack. With these in mind, we contacted the client to discuss this further. Well, we were told that steel rods were really supposed to be a 316 alloy stainless steel, not 304. Their supplier apparently gave them the wrong alloy, and unfortunately the 304 alloy is, in general, much more susceptible to intergranular corrosion than the 316 alloy. The 316 alloy has a little molybdenum associated with it, and that also helps in minimizing the corrosion reactions. Obviously, they would have to replace any of the remaining rods on their line with the correct alloy.

Number two, apparently, the rod was not heat treated properly, and the chromium carbide precipitation might have been an issue. So, for future rod purchases, they really need to specify the heat treatment requirement, and have their supplier provide certification records for each batch of rods. The 316 alloy also will have chromium precipitates in it, and they have to be careful with that, too. Although this 316 alloy is much less susceptible to intergranular corrosion, it’s still a good idea to be heat treated to get rid of the chromium carbides and minimize the intergranular corrosion even further.

Number three, the client uses an organic acid strong oxidizer cleaning solution where they clean these rods during normal maintenance periods. They recently increased the concentration of the solution. We all know that more is better, right? Not necessarily. Unfortunately in this case, the organic acid that they were using is a known cause of intergranular corrosion on stainless steel alloys, so they either have to go back to the original concentration, or replace the cleaner, perhaps, with another solution that doesn’t cause intergranular corrosion in stainless steel. Now if the rods are the 316 alloy, as they’re supposed to be, and they’ve been using this cleaner for many, many years at the original concentration, they’re probably okay. Increasing the concentration? Maybe it can be a little more susceptible in the 316 alloy, so it’s best to be safe and go back to where you were when it was working fine.

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**Polished Cross Section Showing Typical Intergranular Corrosion**

**SEM BEI Composition Image**

Example from the corrosion product in Box 3.
Here is the second case. We were embarking on a really in-depth investigation that took a couple of months to try to determine the cause of an unusual cratering problem on the interior coating of drawn and iron (D & I) aluminum beverage cans. You will notice on the inside of the aluminum cans the aluminum was not exposed; it is coated with a clear material—a clear lacquer—to protect the aluminum from corrosion by the product.

In this particular case, we really discovered a surprising set of circumstances that led, eventually, to the successful resolution of this problem. I want to acknowledge Frank McDonough from Quaker Chemical Company who was there at the time, and was one of our main contacts; Mike Shuster from Ball Packaging International, at the time of this incident, he was a plant manager at the facility. You can download the entire article, if you'd like, for all the details; it is Microanalysis of Craters in Organic Coating Aluminum Cans that we published in February, 2006.

Okay, let’s define cratering: It is the formation of small, bowl-shaped depressions in the coating film; these depressions frequently have some liquid droplets or other bands of materials, or specks of materials, at the center, and then raised, circular edges. In other words, the coating will pull away from the contaminant on the surface in a radial manner, form a nice circle around it, and as it is pulling back, it’s forming a rim at the perimeter.

Common causes of craters:
- Gel particles
- Dirt fibers
- Undissolved silicone (really bad)
- Overspray from different types of paints
- Filter aids from some of the paint lines, the coating lines—a lot of them use diatomaceous earth as a filter aid
- Oil droplets from air lines or machinery are also quite common

The silicone and the oil droplets are really bad if they get onto the metal or any other substrate when you’re trying to apply a water-based coating over it. Water-based coatings are not compatible with silicones and oil.

Here is a typical crater in a paint film. This is a stereomicroscope image of the top; it’s a white paint on the black plastic substrate. You can see how it pulled away from that brown object in the center; it makes a nice circular region around it, and then we can go into the area with our SEM/EDS analysis and find out what that dark brown material is. It turns out it’s iron oxide with a little bit of chromium, maybe a trace of nickel, some manganese, possibly a low alloy steel type of composition. For the average person, this is just a piece of rust.

In the process of the drawn and iron can that we were working with, this is a simple schematic of the entire line. Aluminum coil is fed into a machine that cuts a blank and draws a cup, and then the wall ironing process, or body maker process as it’s often referred to, produces the wall from the cup by thinning the wall metal and expanding it out to elongate it. Then the open edge is cut down to the proper height of the can, and then it’s washed and chemically treated to remove the emulsion oils that are used for the wall ironing process. Then they apply an outside coating, cure it in an oven, then they can apply the label over the outside of it, cure those inks in an oven, and then finally lubricate the open end, neck it in with another machine to create a flange that is used to attach the aluminum end to it when it’s filled at the customer location. Finally, the cans are palletized for shipment.

Our problem was noticed when the craters were seen at the inside lacquer oven cure, as the cans were coming out. That’s where the quality control people first noticed the craters. In that case, they knew ahead of time, at that point, that these craters were being formed by something getting on there prior to the inside lacquer, so somewhere upstream in that process.

Normally, you have to look at just about every step of that process to find out where something might be contaminating the metal. In this particular case, the cause was seen all the way back up at the wall ironing process, where the oil emulsion lubricant system and cooling systems are used to pass through the tooling of the body makers to provide the lubrication, and also cool the tooling as it’s going through. This is really one of the last places we would look for something like this; I guess that is why it took so long to figure it out, to get all the way back to that point. But here is what we found.

This is a scanning electron microscope image of one of the craters against the backscattered electron image. The dark area around the outer surface—or the outer part of the image—is the coating, which is actually a clear coating, and then the crater floor is the exposed aluminum from being pulled back by the coating from the material in the center of it. Zooming up in magnification, we can see that this is not deposited material; this is actually a corrosion pit. We see the bridging over the center of it, and then in the rounded edges, a little bit of corrosion product, perhaps in the upper left corner—the small particulates. So, this was quite unusual. This is a very, very rapid pitting attack in the aluminum. Now we need to find out where that’s coming from.

When we ran our EDS analysis in the crater areas around the floor of the craters and in the edges of the pits...
looking at corrosion products, we came up with very little information. We found a little bit of calcium, a little bit of sulfur—these are logarithmic scales on the spectra to highlight the small amounts of the materials that are there so we can see them better in the spectra. The magnesium and manganese are part of the aluminum alloy, it's a 3000 series aluminum alloy. The carbon and oxygen, of course, are part of the corrosion product of the aluminum oxide, and carbon is usually, pretty much, ubiquitous all over the place anyway in EDS analysis, so we resorted to something a little more sensitive.

We wanted to find out what the corrosion products are, and the EDS analysis did not give us much information, so we switched over to secondary ion mass spectrometry, known as SIMS. Here, a sample is bombarded with a beam of particles—it is a plasma beam of primary ions, and then, as they go into the surface of the sample, they produce secondary ions that are ejected or sputtered from the surface. This is kind of a destructive technique on a microscopic scale. The secondary ions that are ejected are collected through a mass analyzer and into the detector to produce a spectrum of atomic mass versus counts. The nice thing about SIMS analysis is that it is capable of detecting all elements of the periodic table with part per million detection limits, whereas EDS analysis has detection limits of about 1,000 ppm for most elements, and then when we get into the lighter elements, like nitrogen and fluorine, the detection limits are up in the percent range.

So, this is the SIMS instrument that we used at the time, and it's a very complex instrument. Toward the left of center there is a round circular gray area: that's where the sample is put into a chamber. It's an ultra-high vacuum system, and the primary ion gun is up at the top. Then the samples are sputtered, go through a mass analyzer magnetic system in the back, and, finally, up to our detector to produce the spectrum.

This is basically how it works. The primary ion beam coming down from the upper left strikes the sample and sputters things away; we get all kinds of stuff coming out; we have secondary ions, we have atoms, we have electrons, but we're interested in collecting those secondary ions in the mass spectrometer system. The samples go through the mass analyzer and then finally into our detector. The primary ion beams can be oxygen, argon, cesium, and gallium. For most purposes, people use the oxygen and the argon beams. Cesium is often used for depth profiling, but that's a different subject.

Here's the spectra from the crater floor and the pit. The crater floor on the left is showing boron at about 20 counts, and on the right hand side, where we have—inside the pit, we find boron approximately 100 times more, at 2000 counts. This really stood out from pit to pit. This is a very common effect that the boron was quite high within the corrosion pits. Also, the SIMS detected the calcium, which is kind of in the middle of the spectrum, and iron over a little bit more to the right, about three-fourths of the way through the spectrum to the right. We did find the calcium by EDS; we did not see the iron, and we did not see the boron. So now we have some additional information to work with here.

We can also do SIMS ion maps, and this is similar to up elemental dot maps—if you're familiar with that from the scanning electron microscopes, they are also known as X-ray maps. We can also do ion maps to see what elements are associated with one another. Within these pits, we found that the calcium, the boron, and the iron were really highly associated with one another. That was a major clue for what we needed to continue on in our investigation.

During all of this time, concurrently, the plant, of course, was reviewing everything they could to try to troubleshoot the problem.

Quaker Chemical Company was also analyzing the lubricant emulsion systems. They always take and retain samples throughout the course of the year in order to do a bunch of other analyses back at their lab to make sure that the lubricant coolant system is still within operating specifications. Here are some comments that came from the plant personnel: "There seems to be a pattern initially of high ME measurements." ME is metal exposure. This is a quality control test that’s used in the production plants to determine the amount of metal that is actually exposed on the finished coated can. Of course, with craters coming into play, the metal exposure was much higher, so they
started reviewing the whole process chemistry in the plants, and they noticed that there were some excessive makeups of water on the closed loop of the cooling tower system.

The cooling tower is used to cool the lubricant coolant system that makes the cans, the body makers on the wall ironing systems. The coolant system in this plant, I believe, was around 6000 gallons, servicing, I think, 15 or 20 body maker machines. There’s a lot of heat that comes in the tooling from the wall ironing process where the metal is thinned down and elongated, and that produces a lot of heat. So, this closed loop cooling tower system keeps the temperature of that lubricant cooling system down to about 100–110°F. The operators of the body makers also noticed that the coolant had sporadic color changes, it was similar to the color of the dye that is used in the cooling tower water. Borate salts, such as amine borate, are often used as corrosion inhibitors for iron piping in water systems, it’s a great corrosion inhibitor for iron. When the production personnel dumped out the lubricant coolant during the changeover, they did replace a cracked heat exchanger used to circulate the cooling tower water. The cooling tower water turned out to be very highly alkaline, which isn’t so corrosive to steel, but it’s very, very corrosive to aluminum. The pH of the cooling tower water was on the order of 10.5. Aluminum corrodes very aggressively when the pH gets above about 9. So, that is it. The cooling tower water was leaking into the cooling system causing severe corrosion on the aluminum cans; that is the final conclusion that we came up with.

Well, Quaker Chemical Company decided to take this a little bit further, just to sort of prove it. They did some simulation friction tests with a machine that is used to measure the lubricity of various coolant formulations on various metals. In this case, they were working with the same lubricant coolant that they would use in that production plant on a strip of aluminum. This is an SEM image of the aluminum after that test with fresh lubricant emulsion, and that’s a normal striation pattern that they normally would see on aluminum. Then they added some of the cooling tower water to it. Notice how now the striations are more rounded, even somewhat flattened out. Right in the center, look what we have: a nice deep corrosion pit. There’s lots of them on the surface of the aluminum. Then they took it even further and ran the cooling tower water by itself, and now we’ve got really severe corrosion on the aluminum; lots of fractures. The aluminum is just falling apart, basically, at that point.

To get a really successful conclusion to this really difficult problem that actually took several months of work to find all this out, it required a very strong partnership between the vendor, which in this case was Quaker Chemical Company, and the customer, in this case, Ball Metal Container, and it was based on their open communication, common goals, and mutual trust. It was very important in this particular problem that the plant manager, or the plant personnel, and Quaker
Chemical Company had a very strong relationship. There was not a lot of finger-pointing and shouting going on, it is all your fault type of thing. No. They had the common goal to try to resolve the problem. Worry about who is at fault later, just get the problem resolved.

Teamwork also came into this. Quaker Chemical Company brought us into the problem-solving team as the contract laboratory, and the three of us really had to work very closely together with a lot of communication back and forth: exchanging ideas, and exchanging data as we were generating it. We all had a very strong sense of urgency. It was great project organization, especially by Mike Schuster, the plant manager, and, of course, the execution that was done by the plant team, the production personnel at Quaker Chemical Company’s laboratory, and us. It’s an important factor for these types of things, don’t get into the finger-pointing mode and blame mode right away with your problems. Try to get it resolved first, then decide who’s at fault later, and who is going to pay for the damages, and all that good stuff.

So that’s the end of it. Thank you for joining us so will be taking questions, you can type those questions into the question box.

*Case 1: Organic Acid in Cleaning*

CZ: Looks like we have the first question rolling in, Wayne. From Liz, “Do you happen to know which organic acid was used in case one for the cleaning?”

WN: I knew that was going to be the question. Unfortunately, my client does not want me to divulge that information; I compromised and asked if could at least call it an organic acid. I think you probably have to look on the internet to find out what organic acids commonly cause intergranular corrosion on stainless steel, and you’ll probably find it pretty quickly.

CZ: Liz said, “That’s a bummer.”

CZ: Patrick: “Could you see the chromium carbides in the microstructure in case number one?”

WN: No, we did not. The scanning electron microscope that we were using would have had to go to really high resolution magnifications for that. That would probably be done best with the field emission scanning electron microscope. In this particular case, I was using a low vacuum microscope in backscattered imaging mode, which doesn’t have quite as good of resolution, and therefore, no, I couldn’t see individual particles. I just had to go by the amount of chromium that we found there, compared to the iron and nickel.

CZ: We have one from Connor, here. “Do you have any recommended reading for corrosion analysis, your favorite books or articles?”

WN: Let me go back to one of the original slides. Fontana and Green’s book *Corrosion Engineering* is an outstanding book. This was a textbook that was used at Ohio State University for their short courses that they were teaching the back in the 1990s. I see the copyright is 1967, so it is a pretty old book, but it’s an excellent reference for corrosion processes. Their chapter, by the way, on the eight forms of corrosion, I think is around 40 pages long.

CZ: Alright, well, I think that will do it for the questions. Thanks again everybody for attending and we will see you back here for another McCrone group webinar in the future. Thank you.