A client was having an unusual problem in their boiler feedwater tank. The pH would get very low. The lowest reading was 2.3!!! This is within the free mineral acidity range. Even more unusual was there was no distinguishable pattern to the event. The pH would be running along normally, and then suddenly take a dive.

Below is a diagram of the boiler system including the products used. Amines were not an option at this facility, which is one of the reasons we installed RO. Take a look at the diagram before you read the rest of this case study and think about all the factors that could affect the feedwater pH.
We had the greatest minds in the company working on this problem: Dave Christophersen, James McDonald, Jack Novotny, Chris Howell, and Matt Haikalis. Each came away scratching their heads until one of them just happened to be there at the right time for the eureka moment to strike.

The boiler system is a very low use boiler with the steam used to heat domestic water, heat food-related equipment for testing, and humidification. Neutralizing amines are not allowed due to employee sensitivity to them in the humidification steam. As a result, a dealkalizer was previously installed to reduce the amount of carbonic acid formed in the condensate return. The dealkalizer was replaced with a more efficient RO system. The low pH excursions had occurred with both the dealkalizer and RO.

What factors can affect feedwater pH? Let's discuss them one at a time.

**Faulty Equipment**

The pH meter itself was suspected first. A second, then third, then fourth meter was tried with the same results. M-Alkalinity indicator turned orange indicating the pH was indeed less than 4.3. The pH meters were working fine.

**Carbonic Acid**

Carbonate-based alkalinity in the boiler breaks down under the high heat and pressure and is released with the steam as carbon dioxide. Carbon dioxide dissolves into the condensed steam to form carbonic acid which lowers the pH of the condensate.

RO permeate is stored in a permeate storage tank with the water constantly recirculated so the makeup line to the feedwater tank is constantly pressurized. The recirculated line exits above the water level in the permeate storage tank. This results in air being mixed into the high purity permeate constantly. There is enough carbon dioxide in the air to depress the permeate pH below 7. The RO permeate storage tank pH was always in the 6's and above. We changed the RO setup so the recirculation pump only ran when the feedwater tank called for makeup. This had a minimal effect on feedwater pH, but did have a positive affect on condensate pH.

Under saturated conditions, carbonic acid can reduce the pH of water down to approximately 4.3 at most. The lowest you'll probably see in the field is in the 5's since you will rarely be dealing with saturated conditions. The pH's seen in the feedwater were much lower than this. Carbonic acid may have contributed to the low pH, but was not the cause of lowest pH's.
Condensate Contamination

The boiler is used to heat city water for domestic purposes, humidification, and testing food-related equipment. A leak in the domestic hot water heat exchanger would not explain the pH excursion, and no hardness was present in the feedwater. The humidifiers were completely turned off during the vast majority of the pH excursions and would not explain the pH excursion. The condensate lines were followed numerous times with no food-related equipment connected to the system. Even if a low pH solution was being tested in the food-related equipment, there was no way for it to get into the condensate system.

Bad Product Batch

The products used were a phosphate/polymer combination, bisulfite, and caustic. We tested the pH's of all of these and found them to be within specification (pH of 6 and higher). Also, the pH excursion happened on different batches of the products.

Product Interaction

The customer asked if there was any reaction with the chemical products that could be happening to lower the pH. These products contain sodium bisulfite, cobalt sulfate monohydrate, sodium hydroxide, polymer, and sodium hexametaphosphate, and the feedwater tank metallurgy was stainless steel. There are no known interactions between these products to produce free mineral acidity like we were seeing. The customer even mixed these products with feedwater in various combinations and could not reproduce the low pH.

Flue Gas Inleakage

In our frustrated attempts to find an answer, we even considered flue gas inleakage. If flue gas got into the boiler water and returned to the feedwater tank via the condensate, some of the combustion gases could form acids in water. This was a very, very remote possibility, though, with almost zero chance of happening. The water pressure is higher than the flue gas pressure. When the boiler is turned off, there is still a natural draft through the fireside as the unit cools off and hot gases rise through the system. Even if a slight vacuum formed on the cooling boiler and there was a hole in a tube, there would have been very little flue gases left to draw in. There were never any indications of leaking tubes in the inspections, and the condensate pH was always in the 6's and above.
Sabotage

We did a mass balance of everything going into and out of the feedwater tank.

- RO Makeup - pH >6
- Condensate - pH >6
- Q2002FDA, Q1134, Caustic - pH >6
- Feedwater - pH in free mineral acidity range at random times.

What was going on? The pH "in" should reasonably equal pH "out". Water chemistry does not occur for no reason. There had to be a reason. The plant had gone through some downsizing and job shifts in the recent years, and there was the possibility of grudges being held against those not forced to change jobs. We searched the room for anything that could be added to the feedwater tank that could drop the pH so low. Besides motor oil and a bottle of phenolphthalein, we could find nothing. The operator put various little marks and checks on the feedwater tank cap, product caps, door, etc. to see if anyone was messing with this unmanned boiler room. The pH would still randomly drop with no indication of tampering.

Not only were we flustered about the cause of the low pH, we were also flustered by not being able to tell exactly what chemical was causing the low pH drop. Our normal battery of tests would not reveal any impurities in the water that did not have a rational explanation. Chlorides, sulfates, phosphates, etc. could all be from the boiler chemicals used or type of makeup water pretreatment. Feedwater conductivity was not that high; so whatever it was, it didn’t take much.

Eureka Moment

The customer was not happy with us not being able to solve this annoying problem. They were beginning to see leaks around the threading of their feedwater piping and were starting to hold up future projects until we solved it. Our Technical Director visited the plant during one of the low pH excursions in a last attempt to figure it out. While looking around, the customer mentioned that he might want to cover his ears because the air compressor was about to blow down to the drain. That simple warning started the puzzle pieces fitting together… drain… air… feedwater tank vent… vented to same drain… EUREKA!!!

The Technical Director asked the operator to cut the vent line so it wasn't directed to the drain. When he put his hand on the end of the vent line, he could feel it pulling a vacuum when the feedwater tank took on fresh, cool makeup water. What was happening was that when the feedwater tank took on makeup water, it would cool the vapor space above the feedwater in the tank and form a negative pressure. Because the vent line was routed to the
drain, it would suck in the compressed air and sewer gases when conditions were right. The compressed air's carbon dioxide would have depressed the pH as mentioned above, and the sewer gases would depress the pH to the free mineral acidity range. Conditions had to be just right for this to happen though which explained why we couldn't see a pattern. The customer later routed the vent line to outside the building, and we haven't seen a low pH excursion since.

**Moral of the Story**

The solution was simple but easily overlooked. When considering a problem, start with the obvious causes but don't forget to look at all factors. Sometimes the smallest one can cause the biggest problems.