
Question 3: Carbonate stress corrosion cracking (CSCC) has been identified as a cause of failure in FCC main fractionator overhead systems. What changes in feed quality, unit operation, or configuration would lead to increased risk of CSCC? What parameters do you monitor to determine whether a system is susceptible to CSCC? Has the problem been significant enough to warrant either comprehensive PWHT in potentially affected areas or localized PWHT when problem areas are identified?

THOMPSON (Chevron)

Carbonate stress corrosion cracking, CSCC, is characterized by inter-granular, sometimes branchy, scale-filled cracks. It is believed that ammonium carbonate is the main contributor to the cracking mechanism. Scale is typically black magnetite, and the corrosion, as far as the corrosion product, and sometimes iron carbonate, which is unlike the sulfide stress corrosion cracking that occurs with iron sulfide.

Chevron finds that the work by Kmetz and Truax published in 1989 still holds true. The conditions under which CSCC are a threat include susceptible material, which would be carbon steel that is either not post-weld heat-treated or poorly post-weld heat-treated; pH levels above 9.0 and carbonate concentrations above 100 ppm; or pH levels between 8.0 and 9.0 and carbonate concentrations above 400 ppm; and finally, electrochemical potentials between -500 and -600.

Stainless steels are basically immune to carbonate stress corrosion cracking and some facilities have used that as a way to solve the CSCC problem. We basically monitor the parameters of pH and carbonate levels to determine if we are in the range where CSCC is a problem, especially if we have non-post-weld heat-treated equipment. It is easier to monitor pH than anything else. And if we have a good sense of the carbonate ranges, pH may be the only parameter that we monitor.

Higher nitrogen levels will lead to higher ammonia. And of course, this result will increase the pH, which could lead to CSCC. Similarly, anything that promotes CO₂ will increase the amount of CO₂ that is available. We found in the 80s, when we went to complete combustion on many units, that series of events really tipped us into the range where CSCC was a problem.

We know that there are a number of companies that look at the sulfur/nitrogen ratio and we find that this ratio can be useful. Nevertheless, we use pH measurement and carbonate measurements as the defining parameters for monitoring.

Regarding the use of post-weld heat-treat as a mitigation against carbonated stress corrosion cracking, we are convinced that it is very effective if the heat-treatment is done properly and there are no unusually applied external stresses. We found that we needed to go to a more severe post-weld heat-

treat than is typical—for example, what the code would require—and we have to have better temperature measurement, wider bands, and things like that.

Our standard practice is to call for post-weld heat-treat for all new systems that are subject to CSCC and also on systems where we might be changing conditions where that could be a factor. Since implementing these procedures, we have not had an incident in over 10 years now.

WALKER (UOP)

The question mentions that CSCC was found in the main fractionator overhead system, but I would like to point out that carbonate stress corrosion cracking has also been reported in the gas concentration unit although only in locations where there can be an aqueous phase. So you would not expect to see this in, say, the debutanizer, but you might see it in something like a high-pressure condenser.

The problem is most pronounced in hydrotreated feed derived from high nitrogen crudes, such as Californian or Nigerian. Hydrotreating is very effective at reducing sulfur but less effective at reducing nitrogen. So if you start with a high nitrogen gas oil and severely hydrotreat, you can wind up with an FCC feed that has a very high nitrogen-to-sulfur ratio and subsequent high pH.

Most of the equipment in the main column and gas con is already heat-treated because it operates in wet H₂S service. Consequently, the carbonate stress corrosion cracking is generally limited to the piping, which is normally not heat-treated, even in wet H₂S service. I would like to also point out that this problem is fairly uncommon. Since first reported, we have only had one of our grassroots units deemed at risk for this, which justified unilateral post-weld heat treatment.

ASDOURIAN (Sunoco Inc.)

Sunoco FCCUs typically do not process hydrotreated feed; therefore, the naturally occurring sulfur-to-nitrogen ratio, which has been linked to this phenomenon, is not being altered. We have not observed CSCC at any of our FCCUs. Our FCCU overhead systems have had enhanced inspection programs in place for corrosion and cracking for quite some time.

These inspection methodologies include wet fluorescent magnetic particle inspection for environmental cracking. Our associated sour water strippers are post-weld heat-treated to mitigate potential metallurgical impact of carbonates since this can manifest itself in those systems. The primary control that is used is post-weld heat-treatment of the welds. The post-weld heat-treatment, we have found, has also improved the resistance of welds to wet H₂S and cyanides attack, which is common in these types of systems.

WARDINSKY (ConocoPhillips)

ConocoPhillips has experienced carbonate stress corrosion cracking in one FCC main fractionator overhead and wet gas compressor system in which intergranular and base metal cracks were discovered in 78 welds. This unit runs 100% hydrotreated feed with a high nitrogen content. Eighteen full-separation clamps were installed until the affected piping could be replaced at the next turnaround.

SHELLY ROMMELMANN (Washington Group International)

Aside from clamping, if you have a couple of years until the turnaround and you are operating in a carbonate stress corrosion cracking range, what can you do operationally to alter the pH without using mass quantities of water for dilution or harsh chemical addition?

WARDINSKY (ConocoPhillips)

I think the unit in question that experiences this within our system probably looked at various chemical additives, such as ammonium polysulfide (APS) and filmers that would protect the surface of the metal. Obviously, they implemented more elaborate lab testing and started looking at pH and monitoring carbonate levels in the sour water.

THOMPSON (Chevron)

I would say that without implementing some proactive responses, such as selective heat treating and things like that, it is going to be difficult to address CSCC without some sort of a turnaround. Usually, you are in a position where oftentimes you cannot change the chemistry enough to be able to get yourself out of the range. That is very unit-specific; however as Mike mentioned, there may be the opportunity to, for example, switch from APS to a filmer as a way to control corrosion if you are just marginal.

For example, one of the things we found a little bit disturbing is that we even had cracking at places where pipes were supported in pipeways. This was completely outside of weld zones. So sometimes this occurs in locations where you would not even expect it, making it very difficult to do enough monitoring and really pick up all the locations where you might be at risk.

SAM LORDO (Nalco Energy Services)

I do not have anything to add to the panel's response, but there is a NACE Task Group that is looking at this issue. It is TG347 and they will be issuing a report. They have actually done a survey of the industry. As you have heard, there are a lot of things that go into this carbonate cracking that are not well understood and rules of thumb do not always apply across the board. So what they have done is they have surveyed the industry and tried to capture all the incidences out there that have occurred and what

are the parameters around them. Also, I would like to note that in several locations, we have been successful when applying a filmer in places where carbonate cracking has been known to occur.

REZA SADEGHBEIGI (RMS Engineering)

You can reduce the amount of the ammonia produced in overhead by cutting back the riser temperature or basically slowing down the severity of the cracking. That can be done by reducing riser outlet temperature and maybe by putting in more active catalyst. That way, you slow down the cat circulation, yet do not lose that much on conversion. Also, that person who asked that question needs to look at the air distributor, as well as the catalyst withdrawal system regen catalyst. If you are dragging all of the CO₂ down with the flue gas into the reactor, then you must have a mild distribution problem. Normally, you have the flue gas coming down and there is a ratio of the nitrogen to CO₂. If that CO₂ is higher than it is supposed to be, then you can look it up at the sponge absorber off gas. Normally, a sponge absorber off gas has somewhere between 1% and 2.5% CO₂ in it. If you see that number has gone up, then you have to look at your regenerator to see how air and a regenerator catalyst withdraw nozzle are working out. So by reducing cat circulation rate and reducing riser temperature, you reduce the ammonia. And at the same time, you reduce the amount of entrained CO₂ that goes down into the reactor.

WARDINSKY (ConocoPhillips)

I want to mention that I believe the corrosion community is divided on whether APS has any mitigating effect on the carbonate stress corrosion cracking. About half of them believe it works and the other half do not. That is maybe one of those things that will come out of the NACE Task Force.

I was thinking more about this question. I believe that the unit where we experienced it did try to raise their water wash rates to try to reduce the pH. This is a unit that if you cut back riser outlet, you are going to make more slurry; and so, you are going to hit some constraints somewhere else. That is probably easier said than done. They basically just held on for two years until their next scheduled turnaround.

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