Question 77 What is your experience with cooling water exchangers in an HF alkylation unit? How long do you go between cleanings? Do you have a special water treatment program for cooling towers dedicated to the alkylation unit?

KAISER (Delek Refining Ltd.)

In my experience, the cooling water exchangers in an HF alkylation unit are really no more problematic than any other exchanger in the refinery when you're looking at the waterside only. If you have an exchanger in the HF alkylation unit that suffers from low flow or it's at the end of a header, trapped scale, and there are certainly critical exchangers inside the alkylation unit that you want to keep clean, it's really no different if it's in the alkylation unit or in some other unit in the refinery. You're going to have water problems and that's going to generate issues for you.

Generally, what I've been able to see is that most of those exchangers will tend to make two to three years. Some of them will go longer than that—four to five, depending on what service they're in. The things that I've seen is that we'll typically have process-side corrosion issues that generate leaks and that would force us to take that exchanger offline for repair any cleaning before we had significant enough fouling on the waterside solely to force a cleaning by itself.

Both alkylation units that I have experience with have their own dedicated cooling towers. Whether that's by choice or by design, I'm not sure. What it does allow you to do is minimize the impact of any leaks upon any other process unit or refinery. And certainly when you have a leak in any acid service, be it sulfuric or HF, the key is to track down which exchanger is leaking rapidly and isolate that from the cooling water system so that you minimize damage to your cooling water circuits. Most refineries will tend to monitor pH, ORP (oxidation reduction potential), fluoride, or some combination of these, either on a shift or continuous basis, to help them determine when they have a leak.

Most cooling towers will operate a fairly standard cooling water package. They'll use phosphates for corrosion control, polymer dispersants, and various other bits and pieces of chemicals. It's nothing really any different than what you would use in any other cooling tower in the refinery. METKA (Sunoco, Inc.)

Sunoco has a separate cooling tower at the HF alky complex as well. Our experience is very similar to what was just discussed. We don't have a special chemical treatment program. We do perform additional pH monitoring for leak detection, and the process side can limit the run for several services. ZMICH (UOP LLC)

I would like to share some thoughts provided by our Tech Service experts in our Engineering department. At UOP, we have seen corrosion in cooling water exchangers and

alkylation units on both process and water side. Typically, the corrosion rate on the process side of the reactor bundles and on the acid cooler bundles is relatively low at normal conditions, but excessive temperature or higher concentration of percent water in the circulating acid can cause corrosion and plugging on the process side.

Refiners have reported corrosion rates on the process side of water cool condensers, especially if the water content of the circulating acid is high. Low water flow rate can lead to fouling of the tubes from biological growth or calcium scaling, both of which can lead to under-deposit corrosion. Inadequate treatment or blowdown of the cooling water can also cause corrosion on the water side of these

exchangers.

An important point is UOP strongly recommends a separate cooling water tower for HF alkylation service, and I believe we include that in our new unit design specifications.

Finally, at UOP, we have seen some new unit activity for alkylation units. Generally speaking, permitting does not prohibit installation of an alkylation unit; but if one is considering addition of an alkylation unit, it should go through what's considered a quality-risk assessment.

MIKE FACKER (Western Refining Company)

We have a couple of heat exchangers, water coolers, ahead of our KOH, and there's a temperature limitation there. I am wondering how people try to limit their temperature at that point, whether you try to do it on the water side and take your fouling there. I understand there's about 100°F limit you want to go into your KOH system. Are you all familiar with that part of the treating or do you know what you do for temperature control there?

KAISER (Delek Refining Ltd.)

What service are these in?

MIKE FACKER (Western Refining Company)

This is behind the alumina.

KAISER (Delek Refining Ltd.)

Is this on propane or alkylate?

MIKE FACKER (Western Refining Company)

Well, we have both propane and butane. The coolers go under the KOH and it is HF, yes.

KAISER (Delek Refining Ltd.)

And this is off your isostripper and depropanizer towers?

MIKE FACKER (Western Refining Company)

Right.

KAISER (Delek Refining Ltd.)

There's generally not a better cold-sink anywhere than the cooling water, and cooling water is typically used there, from what I've seen. No, there's not a whole lot you can do other than take the hit on the water side and suffer through some high skin temperatures. The thing that you ought to try and do as best you can is to work with your water vendor and do your best to keep the cooling water as clean and solids-free as it can be. You might have to give up some cycles on your cooling tower, get the total dissolved solids down, and keep a close eye on your phosphate.

The other thing that your water vendor ought to be able to do is help you understand what your failure mechanism is. Is it the calcium carbonate? Is it silicate carbonate? Then, maybe the vendor can tailor the water treatment program a little bit more specifically around these particular exchangers if they foul out. The best case situation, which you probably don't have, is parallel exchangers where you'll be able to switch back and forth between the two and just plan on a routine cleaning before the deposition gets bad enough to precipitate an under-deposit corrosion.

METKA (Sunoco, Inc.)

That particular service has not typically been a problem for us on the process side, but it has had some issues on the water side. In some of these problem services, we've had the opportunity to install some piping connections and we've put a little rental booster pump in for the summer operation to increase the pressure and get a little bit more water flow. We have also used the same methods to address water side issues that Allen discussed: adjusting the chemistry and working with the water vendor to try to help prevent it in the first place.

DARYL DUNHAM (UOP LLC)

The particular issue on the cooler ahead of the KOH treater is pretty widespread, and I'll try and explain how this works. It's a very common problem. When you're removing organic fluorides in the LPG

Defluorinators, both on propane and butane, the Defluorinators make water as a byproduct. The KOH treater is intended to remove the water. Now in between, you condense and cool the LPG before it gets to the KOH treater. If you have relatively high organic fluorides, you make a lot of water. And if you cool the stream below the water dew point or fallout point, it will form a separate phase. When it forms that separate phase, it will do that on the coldest surface, which is usually the tube wall in that cooler. When it forms that separate phase, any HF present will go with water. So you have a very small amount of water, usually it's droplets that form with maybe a couple ppm HF coming out of the LPG. So now you have a weak acid and it eats those carbon steel tubes.

So the first indication you'll see is pitting of the bottom row of tubes in that condenser. And if it goes far enough, you'll get holes in those tubes and you can get corrosion in the shell.

You can get corrosion in the downstream piping. A lot of people have tried to solve this by putting in Monel tubes in the condenser, and then you start eating the condenser shell. And then if they put in a layer Monel on a condenser, then it starts eating the outlet piping. And so they put in Monel outlet piping, and it starts eating the inlet nozzle on the KOH treater.

A couple of things that we've seen refiners do to try to solve this problem is: One, they'll pinch the water flow trying to limit the outlet temperature so you don't reach the dew point. One refiner has put in a coalescer downstream of the water cooler to knock any free water out before it eats any more piping up. We had one refiner that had an innovative approach of injecting steam into the cooling water to raise the cooling water temperature so they didn't reach the dew point on the exchanger tubes.

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