Question 23: When shutting down a reactor, what is your current Best Practice for measuring CO (carbon monoxide) in a mostly hydrogen/nitrogen atmosphere to assess the carbonyl concentration? Is the steel a potential source of zero-valence metal necessary for carbonyl formation? If so, does that cause a corrosion concern for equipment that normally operates in the temperature range favorable for carbonyl formation?

JOHNSON (Motiva Enterprises LLC)

From our experience, we have learned some lessons about properly measuring CO. Gases that have high concentrations of hydrogen, especially utilizing a ‘regular’ CO Dräger tube, can give a false positive. One of our observations is that using a carbon-free filter in front of the tube and ensuring that a couple of draws of air prior to trying to measure with the tube is most effective. Catching it in a Tedlar® bag helps as well. We also go test the streams we will be using for sweeping before we get into the shutdown phase of the unit in preparation for a catalyst change or turnaround. Testing these streams proactively to see if CO is present, as opposed to ‘reactively’ testing during the shutdown phase, has been effective for us.

PAPPAL (Valero)

The information and opinions expressed in this presentation are those of myself and do not necessarily represent the official policy position of Valero.

Nickel carbonyl is very difficult to measure. Its health effects are severe and the concentration at which it could be fatal is extremely low: in the ppb (parts per billion) range. My approach is to assume that it is present and handle the situation accordingly. From a Best Practice standpoint, the hydrogen source to the hydroprocessing unit should be changed to a non-CO containing hydrogen makeup gas stream well above the temperature at which nickel carbonyl forms. Brant already described all the difficulties of trying

to get an accurate CO measurement. A hydrogen gas makeup stream that cannot contain CO, based on the manufacturing technique for hydrogen, avoids this issue entirely. One guaranteed way to prevent nickel carbonyl is to switch to a non-CO-containing hydrogen source at a high enough temperature where the kinetics for nickel carbonyl formation are not very favorable. This approach provides a level of certainty in your atmosphere change and subsequent maintenance in the reactor system. If that is not possible, then we would assume that nickel carbonyl is present and take all the appropriate safety measures. The first approach is to prevent the formation of nickel carbonyl. If there is any doubt, take the proper safety considerations when entering the reactor.

JOHNSON (Motiva Enterprises LLC)

There is a second part to the question about the actual steel. We do not have any experience with nickel alloy steels being a source of nickel for the formation of a carbonyl. I just want to close a gap on the question.

PAPPAL (Valero)

The literature indicates that nickel carbonyl can form from finely divided stainless steel and finely divided iron. However, the operating experience indicates that this is not an issue. In talking with our metallurgists, there has not been any evidence found in our operations that formation of nickel carbonyl is a corrosion mechanism for stainless-steel pipe.

DAVID GRAY (INEOS Olefins & Polymers USA)

Can you tell me if, in your careers, any of you have ever experienced any fatalities from nickel carbonyl poisoning or did most of that happen back in the old-school days?

PAPPAL (Valero)

In my experience, there have not been any fatalities with nickel carbonyl.

DAVID GRAY (INEOS Olefins & Polymers USA)

Everyone knows it is dangerous, because it will kill you. I am just wondering when the last fatality occurred; because nowadays, the procedures are a lot better than they were 30 years ago.

PAPPAL (Valero)

Right.

VALERIE LAWSON (Norton Engineering Consultants, Inc.)

I previously worked for an operating company. While I do not know of any fatalities, I do know of several serious injuries that were caused in hydrogen plants rather than hydroprocessing units.

SCOTT McARTHUR (Phillips 66)

The only fatalities of which I am aware were part of an industry defining event. I think it was back in the 1960s. There were fatalities from that event during which there was CO coming in from an exhaust source. However, I do not know of any fatalities recently.

Another comment I want to make is that we recently had an incident where we had an atypical nitrogen supply routed to a reactor during a cooling phase, and that reactor had a trace amount of oxygen in it. Another learning for us was that we need to be careful about allowing oxygen into the reactor system which can generate CO in the reactor bed and then nickel carbonyl after that reaction. So, planning your hydrogen and nitrogen sources is important.

ANDREW MORELAND (Valero)

Has anyone seen a nickel carbonyl incident he or she would like to mention? I can share one experience we had several years ago. We had a low concentration of carbon monoxide in the hydrogen source used for cooldown, and we did detect nickel carbonyl with a Dräger tube. It was a big deal because the procedure calls for us to heat the reactor back up above the nickel carbonyl decomposition temperature. Those of you who are under pressure from turnaround managers know that heating the reactor back up will really slow down the turnaround process. We were not sure if this finding was real or not; but obviously, we treated it as if it was. It did cost us quite a bit of time in the turnaround. I wonder if anyone else can share a similar incident.

SPENCER YENDELL (Flint Hills Resources)

Yes, we had a similar experience during a reactor cooldown. We had makeup hydrogen introduced from one of our PSA (pressure swing absorption) plants after verifying the recycle CO content. We decided to heat the reactor back up to ensure that we did not have nickel carbonyl form in the unit. It was a

significant delay, but we determined it was necessary to mitigate the potential risk.

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