Question 49: In the past year, a sulfuric alkylation unit released a significant amount of sulfur dioxide to atmosphere when light hydrocarbon flowed from the reaction zone through the acid blowdown system and into the spent acid tank. What measures do you recommend for preventing this?

MULLINS (Marathon Petroleum)

Okay. Well, there's some S02 present in the system. The likelihood is high that the release contains significant amounts of atomized sulfuric acid: the sulfuric acid being atomized by the rapidly vaporizing C4s that would have been carried into the spin acid tank. We would recommend ensuring that the acid knockout drum be sized large enough to allow the hydrocarbons to disengage in the drum.

Secondly, it is recommended that the vapor system be sized to handle the release without creating backpressure that would force the contents of the knockout drum into the spin acid tank. And thirdly, we recommend the operating practice of keeping the liquid drained from the KO drum to the spin acid tank closed during normal operation.

HAZLE (NPRA)

Jay.

ROSS (Axens)

This is an example of technology that we do not license, but I'm indebted to our friends at Stratco DuPont for supplying the response to this question. In the normal design, I suppose the main issue here is under upset conditions or de-inventory in the reactor. It is possible that if great care isn't taken, you can overwhelm even a well-designed system. But in a normal design, I guess that would represent best practices: one that has a system involved with adequate residence time in settling devices where you anticipate the possibility of some hydrocarbon carryover; for example, in the acid separating device, which I think is shown here. This schematic is representative of some of the more modern units that are out there.

Most importantly, perhaps, is the design in the acid blowdown drum, which in older units has sometimes perhaps been neglected. It's important to have it nitrogen-blanketed in a three-phase separator in order to anticipate both liquid hydrocarbon, as well as the possibility of some light hydrocarbon (LPG)

carryover, such that enough residence time is provided for the light hydrocarbons to volatilize and, in fact, leave with the nitrogen and blanketing agent off to a scrubbing system, as this is operated on a flare header pressure.

Then further beyond that, when you do de-inventory and set off to the spent acid tankage, that system should also be nitrogen-blanketed with a scrubber system in place, both to avoid the explosive mixture possibility, with the blanketing and the scrubbing, so that you don't emit the S02 to the atmosphere. And again, a time when you have to take the most care, perhaps, is during unit shutdown at de-inventory, so as to take careful and proper precautions during the draining of these materials.

HAZLE (NPRA)

Those are the panel responses. It's time for your questions. As people carry a microphone to you, just raise your hand.

PETERSON (Stratco DuPont)

Randy Peterson, Stratco DuPont. One correction I would like to make about what Greg said is that there could be aerosol of acid out of the tankage. We don't really believe that this is true. There was a study done and presented about 15 years ago at the NPRA by Quest about how they tried to make sulfuric acid aerosol. In the study, it really was not ever shown to happen. We would see SO2 coming off, but the acid was so heavy and so viscous. So if there was any kind of aerosol, it would drop out very quickly outside of the tank. So an aerosol cloud with sulfuric acid is something we don't believe is possible.

HAZLE (NPRA)

Thank you. Other comments, questions. There's one up front.

PROOPS (Solomon Associates)

Kevin Proops with Solomon Associates. We may have to get Randy to help answer this one again. We haven't talked about layer-of-protection analysis (LOPA), per se, on this, but I'm wondering if Randy or the panelists have comments on instrumentation to help prevent this situation. For instance, was this incident caused by a faulty level transmission from the acid's alpha settler? Could high pressure in the acid blowdown drum have been sensed and helped prevent undercarry? Are there other potential fixes, or more LOPA that are instrumentation-driven, that are possible?

HAZLE (NPRA)

Jay. No? You're deferring? Deferring.

PETERSON (Stratco DuPont)

Yeah, I will answer that. I think Jay kind of hit the nail on the head. A lot of units out there that are 30, 40, and 50 years old do not have a lot of instrumentation or the appropriate instrumentation. The newer units do have level controls, and this was a result of not understanding the level controls that they had on the less modern control systems. Yes, a lot of hydrocarbon came to the blowdown drum and was pumped out to the tankage.

In our system, it is a three-phase acid blowdown drum. There's vapor, hydrocarbon, and acid. And if it's almost all hydrocarbon and just a little bit of acid, it still shows up as acid in the level gauges. So operators have to understand that with the three-phase drum, you need to have the acid level near the top of the baffle; otherwise, you might be pumping hydrocarbon. If it shows acid to the top of the baffle, then you know that it has to be pretty much acid because acid is three times the density of hydrocarbon. So that's the LOP. I mean that would have helped in this case.

UNIDENTIFIED SPEAKER

Is there training for this?

PETERSON (Stratco DuPont)

Oh, absolutely. Training is a big thing. Operators tend to forget, maybe, how to properly run these units, and over time—every five years or so—they should be retrained.

HAZLE (NPRA)

Any other comments? Other comments or questions? That was for the tape anyway. That was Randy Peterson, Stratco. Anyone else? Then we'll move on to Question #50. First response: Clever.

Tags

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