

Sulphur recovery operations: a discussion forum

Members of the Amine Best Practices Group (ABPG) offer their advice and experiences to questioners having problems with amine unit operations

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Amine Best Practices Group

The Amine Best Practices Group (ABPG) was formed in 1993 by several refiners, a consultant and an engineering contractor with the original goal of benchmarking amine unit operations. They soon realised there was a paucity of real-world data on which to base their benchmarks, so two industry-wide surveys were conducted to create a comprehensive database on amine unit operations.

The results and conclusions of these efforts have been discussed in two symposia, and reported in journals ["The cost of poor amine operations", Scott et al, *Hydrocarbon Technology International*, Summer 1995; "Amine unit cost elements", Scott et al, *Petroleum Technology Quarterly*, Summer 1997; "How efficient are refinery amine units?", Scott et al, *Hydrocarbon Processing*, April 1995].

Having satisfied the original mission of establishing amine unit benchmarks and defining some amine best operating practices, the group evolved into a continuing forum for discussing common operating problems in the overall sulphur recovery area. Questions and issues are routinely discussed via e-mail, and the members continue to meet informally once or twice a year to focus on key issues and to plan future activities.

This is one of an occasional series of articles which will report on some of these electronic Q & A sessions of the ABPG via its Data Exchange Network (DEN). It is not intended to be a comprehensive review of the subject matter, but rather a compilation of the real world experience of a number of specific sulphur recovery operators and engineers.

The current members of the ABPG, all of whom have participated in the following DEN exchanges, are:

Lou Beke, Mobil Technology Company; Frank Bela, Equilon Enterprises (formerly Texaco Refining & Marketing); Al Keller, Conoco; Bruce Kennedy, Petro-Canada; Greg Roach, Caltex Petroleum Services; Bruce Scott,

BSI; Lon Stern, Equilon Enterprises (formerly Shell Oil Products); Duke Tunnell, BSDT Seminars; Ed Wagner, Chevron Products Company, and Mike Zacher, BP Oil Company.

Individual company confidentiality policies prohibit identifying the actual source of the questions and the comments made, so participants are indicated only as responder A, B, C, and so on.

Questions and answers

—Q: We've experienced heavy fouling of our lean 25 per cent DEA header over the past 10 years, which I believe to be due to the polymerisation of amine degradation products. One recent deposit analysis showed 30 per cent iron sulphide, 60 per cent organics insoluble in methylene chloride and 10 per cent organics soluble in methylene chloride.

Our filter is a 10 per cent slipstream carbon bed which is changed every six months and seems to be effective in maintaining solution clarity and low foaming tendency. However, without a prefilter we must backwash every few days (on pressure drop) to remove particulates.

I speculate that an efficient prefilter will minimise premature blinding of the carbon pores, and thus improve the removal of amine degradation products which would otherwise tend to polymerise on the pipe walls. Is my logic correct?

—Responder A: Conventional wisdom says your logic is right; you do need a mechanical filter before and after the carbon bed. I'd say 5µ rating, nominal. The carbon bed is much too expensive to use as a particulate filter. The filter after the carbon bed is needed to remove carbon fines which might cause foaming.

You might get away without the after filter if you're careful about two things: doing a thorough condensate wash of fresh carbon to remove the fines generated by shipment and loading, and using a good, hard grade of carbon to prevent

breakup of the carbon particles making fines in service.

—B: One contributor to the sludge buildup in your plant may be sticky elemental sulphur. This is formed when soluble polysulphides in the rich amine revert to colloidal elemental sulphur as the H₂S is stripped off in the regenerator. We typically use a 10µ filter upstream of the carbon and a 5µ filter downstream.

—C: The 60 per cent insoluble in methylene chloride lab result you mentioned would be consistent with the elemental sulphur hypothesis.

—D: Based on your backwash frequency, your carbon bed is a very efficient particle filter. It's too bad you only filter 10 per cent.

I think your logic is sound. Our standard design has been a 25 per cent slipstream particulate filter, with about half of that going to the carbon bed. There is also a small postfilter, which typically is only changed a couple of times following carbon changeout. With minor variation, this is what I hear every year at the NPRA Q&A. Our surveys seem to confirm this approach, also.

A new amine unit we're designing will have full flow particle filtration on the lean side, with 10µ cartridges. This will be followed with about 30 per cent carbon treating and a small postfilter.

—E: Our normal arrangement is to filter a minimum of 10 per cent of the lean amine: typically a cartridge filter, followed by a carbon bed, followed by a cartridge postfilter to catch carbon fines. I encourage new projects to go for more than that norm, for example, 25–35 per cent cartridge filtration at 5–10µ followed by 10–20 per cent carbon treatment.

—Q: We are installing a new amine system and are considering full flow filtration of the rich solvent. What are your comments on rich versus lean amine filtration?

—A: We have about half and half rich and lean filtration. My experience with

both rich and lean filtration tells me there is no real difference between the two. What counts is how well the amine is filtered: micron rating of the filter, attention to changeouts, and so on.

I also don't see any real savings for refiners who increase micron rating of their filters or delay filter changes in an effort to reduce costs. All that does is to make the amine dirtier so that equipment fouls faster.

—B: In theory, rich amine filtration should be more efficient than lean because of the chelation of iron by the amine molecules in the lean holding some of the iron in solution. In the rich amine the high level of H₂S causes the chelated iron to precipitate. The difference is very small, however, probably only a few tens of ppms.

—C: We believe there is a possibility, via O₂ or SO₂ intrusion into the amine system, of forming colloidal elemental sulphur, which is subsequently converted to soluble polysulphide upon exposure to H₂S in the absorber. When the polysulphide is stripped of H₂S in the regenerator it reverts to solid elemental sulphur. Thus, the lean is turbid and the rich is clear.

In order to remove the sulphur, we always filter on the lean side in plants where we suspect this sulphur-polysul-

phide cycle is at work. We've confirmed the presence of elemental sulphur by dissolving a substantial part of the filter deposit in carbon disulphide. Evaporating the disulphide leaves sulphur crystals behind.

—D: Four years ago we replaced a slipstream lean filter with a full flow rich filter. Before the change we were constantly fighting fouling in the regenerator and plate-type rich/lean exchangers. Since the changeout the system has remained relatively clean. The rich filter utilises 20µ cartridges which are typically changed four to six times/year, based on pressure drop. A 30 per cent slipstream carbon bed was also installed at that time, but the amine has been so clean that the operators have elected not to commission it.

—E: We do all of our filtration on the lean side, because of safety and odour concerns. We would agree that attention to filter changeouts and maintenance is more important than where the filter is in the system. In our survey well less than 20 per cent of the responders had filters on the rich amine side; the large majority of plants filter lean amine.

—Q: What special procedures, if any, are required for changeout of rich amine filters to protect workers from

potential H₂S exposure?

—A: In the few locations we have that are still using conventional cartridge filters in rich service, the rich amine is displaced with nitrogen, then backflushed with hot condensate into the amine system. Fresh air gear is worn when initially opening the vessel and then until no longer warranted on the basis of sniff tests.

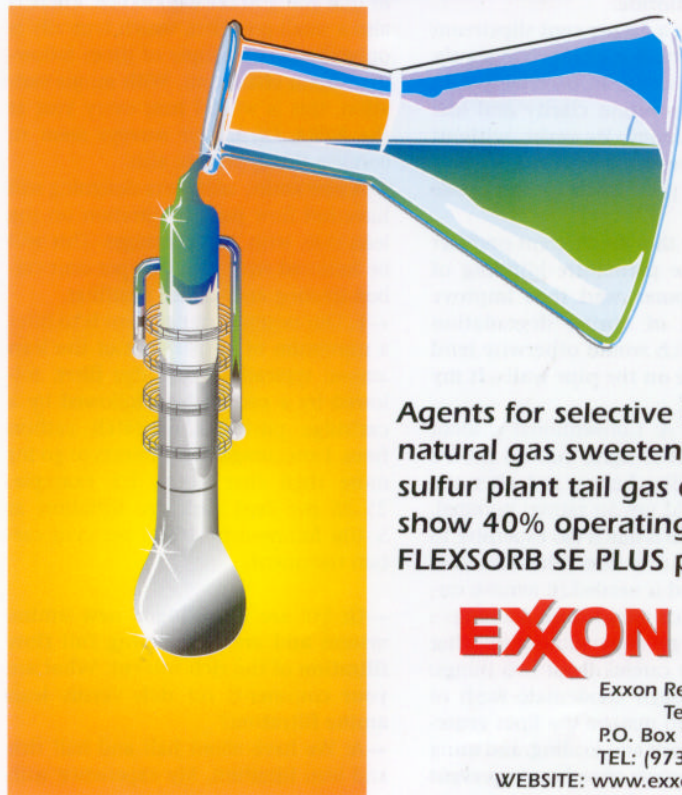
Most of our plants have converted their rich filters to backwashable systems which can operate for about a year before they need to be opened. The operators and mechanics sure like not having to open those filters.

—B: I have no first hand experience with rich filtration, but would be reluctant to displace the filter into the amine system with hot condensate for fear of redispersing some of the "shoe polish". I would cool the condensate.

—C: Where we have rich filtration our procedure for clean up is to take the filter off line and flush it with lean amine to the rich return line. This is followed by a cold condensate wash into the rich line. We then pressure the condensate out with nitrogen.

—D: We initially displace the rich cartridge filter with lean amine, then nitrogen pressure the lean into the rich amine line.

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—E: Rich filter changeout is a fresh air job for two operators. The procedure is to displace amine with condensate, then drain the condensate to the sump. We don't rinse with lean amine or nitrogen purge the filter housing.

—Q: One of our plants completely dissolved their bag filters on two occasions. All that remained were the metal retaining ring and paper tag saying the filter was 10µ polyester. The filters normally operate at about 185°F, with excursions to 195°F. In both cases startup upsets carried crude oil over into the amine system, so this obviously may have been a factor. We tentatively plan to switch to polypropylene. Advice?

—A: We experienced a similar problem at one of our plants, where lean DEA is filtered at 210–220°F. Based on our experience I don't think you're dissolving your filters; I think you're melting them. We have found that string-wound cotton filters can take that kind of temperature.

—B: Polypropylene may go soft at 185 to 195°F as well; our polypropylene-lined pipe in amine service is limited to 175°F. Consider fibreglass as an alternative material. In general, I think filtering at high temperatures is unproductive, as some of the iron sulphide appears to dissolve or dissociate at high temperatures. I would suggest changing the filter location to a cooler spot in the system.

As a side comment, I would note that we have not had good experience with bag filters in general, and prefer to use cartridge filters instead, regardless of service temperature.

—Q: Is there an analyser available for detecting hydrocarbons in amine to warn of contamination or confirm its source before it upsets the regenerator? We have multiple contactors linked to one remote regenerator, and we never know who is hitting us.

—A: I don't know of anybody with a successful hydrocarbon analyser for this service. It would be a tough analysis because the amine itself is a hydrocarbon. You might look at an RVP analyser, which would pick up LPG contamination. I know of several refiners who have flow monitors, or even alarms, on the flash drum vent line as a warning of hydrocarbon excursions. Some also use flash drum pressure increase as a warning.

—B: If you find such an analyser that is quick and accurate, let me know: I want to invest in the company because it will make millions. The one safeguard we do frequently include in plant designs

is a low level trip, separate from the level controller, on the contactor level control valve. This offers some protection from loss of level resulting in a hydrocarbon blow-under into the rich amine.

—C: We have success only in the lab with hydrocarbon identification, and are aware of no online instrument. I would like one of these analysers: we lost some 200 000 pounds of amine last year due to hydrocarbon contamination problems. These were aromatics, and were too soluble to come out in the flash drum.

—D: Our hydrocarbon detector is our sulphur plant.

—Q: Has anyone tried sand filters in amine service?

—A: I've never seen it tried, and would not expect it to work very well. They're good coalescers, but not very good filters for fine particulates.

Suggested filter aid

—Q: We operate a large pre-coat filter in an amine system. Someone suggested using ion exchange resin as a filter aid. The idea was to remove heat stable salts at the same time as removing solids.

—A: That's an interesting idea. Let's run some numbers on it. If we assume a system with 100 000 gallons of solution containing 20 000ppmw of anions, we have about 16 000 pounds of anions. To get out of the corrosive range you would want to remove about three quarters of the anions, or 12,000 pounds.

We figure the nominal loading is about 0.05 pounds of anion per pound of resin, so you'd need about 240 000 pounds of resin at a cost of almost \$2 million. Since the resin is not being regenerated, you'd probably be better off using the cash itself as the filter aid.

On top of the cost factor, the resin is normally supplied in the chloride form, so you'd replace the heat stable salt anions with chloride anions, which would cause even bigger problems from cracking and corrosion.

—Q: What amine chloride limit do refiners consider necessary to avoid stress corrosion cracking of stainless steels? We normally hold to a limit of 500ppm, but have one unit with 700–800ppm chloride ion which runs at very high acid gas loadings and so depends on a good corrosion inhibitor. The inhibitor contains some chlorides, which contribute to the problem. Switching to a less effective inhibitor to reduce chlorides will likely increase general

metal loss. What is the real limit?

—A: We had a unit which ran consistently at over 1000ppm chlorides, with peaks up to 2000, and saw no evidence of cracking in the stainless column internals or exchanger bundles. As a result of that experience, we raised the company limit from 300ppm to 500ppm.

There's not much published data above 500–600 ppm on which to base a next step. Personally, I feel comfortable with chloride levels as high as 1000ppm, but I would certainly do some inspection for stainless cracking at each turnaround.

—B: Our system runs at around 100 ppm, so we haven't had to worry about an upper limit.

—C: Our company guideline has been 1000ppm for some years now, with no apparent problems.

—D: We have two units which typically see chlorides build from 300 up to 3000 ppm over six months. The chlorides (and other heat stable salts) are removed by ion exchange at the end of the cycle, so the metal is not exposed to the higher concentrations for the entire period. We have seen no cracking of stainless steels, although some pitting is evident.

—Q: Let's talk about cleaning the equipment rather than the amine. Our coker gas DEA contactor, with random packing, is prone to chronic fouling which we presume is due to entrained light gas oil from the upstream sponge absorber. What is the experience with off-line chemical cleaning?

—A: We have historically used a hot water wash to clean the cracked gas absorbers. The procedure is to cycle between hot water with steam and cold water in an effort to thermally shock the gunk. Some of our units have tried commercial inhibited acid washes with some success. However, one recent acid cleaning resulted in losing some 304 SS trays due to high acid solution temperatures.

—B: We have successfully used inhibited sulphuric acid in some of our locations.

—C: Acid generally works well. Iron sulphide is readily dissolved in acid, and removing the solid material from the gunk usually breaks down the residual organics so they can be flushed away. One caution, however, is that the acid will liberate H₂S.

A common practice in the past was to add a minor amount of formaldehyde to the acid to sponge up the H₂S. Now that formaldehyde is taboo, the commercial cleaning contractors have

developed some equivalent materials.

One concern: you mention oil fouling, and if there's too much oily material the acid can't get to the iron sulphide and may therefore be ineffective. I've seen some success removing oily deposits from sour water strippers with a reformat wash. The aromatics seem to take care of the organics, leaving the iron scale behind. This may help if your deposit is mostly oil based. Warm soda ash solution might also be effective in removing oily deposits.

Is it possible to get a handful of the dirty black gunk in advance? You have a much easier decision if you've played with it in the lab first.

—D: We've had success chemical cleaning dirty absorbers with commercial outfits using a two-step approach: a warm, inhibited acid wash to remove the iron sulphide that is stabilising the gunk, followed by a warm soda ash wash to dissolve the oils, neutralise residual acid and also passivate the walls of the column. From our experience, solvent temperature is often more crucial than solvent strength.

—E: We've cleaned a coker wet gas amine contactor using 5 per cent inhibited sulphuric acid. The deposit was believed to be a mix of antifoam and iron sulphide that resembled black shoe polish. The cleaning was successful, so maybe we do know Shinola.

Follow up comment from the questioner: The coker contactor in question was subsequently circulated with a dilute KOH solution for approximately 8 hours, followed by an inhibited sulphuric acid solution for roughly 12 hours. During each phase, chemical strength and iron content were measured periodically. When three consecutive samples showed no change in the analyses, that phase was considered complete. Tower performance and pressure drop following the wash procedure was comparable to that of a clean tower.

—Q: What experience can you share regarding permanganate cleaning of equipment prior to opening for maintenance or inspection?

—A: I'm aware of one refiner that has done this several times and found it very successful. The procedure he uses is to first drain the system completely, followed by a condensate flush. It's important to get all the amine out of the system, as it is a strong consumer of permanganate.

This refiner's target is to flush until the condensate tests below 500ppm of COD. The system is then drained and filled with permanganate solution, which is recirculated and replenished

until it stays purple for an hour or so.

At this point the spent solution is drained to the effluent water treatment plant. He reports no problems with a little permanganate in the effluent water treatment facility.

This refiner mixes a 1 per cent solution by weight of $KMnO_4$ in hot condensate for most jobs, but will go higher if the equipment is extremely dirty. The solubility limit is about 5 wt%. The only real hazard seems to be the dust generated when unloading the solid permanganate from barrels.

—B: The only thing I'd add to responder A's comments is that the permanganate leaves behind a fine manganese dioxide sludge. This procedure is therefore only used when the equipment is to be opened to permit these solids to be removed.

The choice between permanganate and acid involves a tradeoff. A permanganate-washed column will be odour-free but will need some mechanical cleaning; an inhibited acid-washed column will have no residual sludge, but will have odours to deal with. We use both procedures, depending on the circumstances.

—C: No permanganate experience here. We typically use a 5 per cent caustic wash combined with a surfactant and some citrate. For severely fouled systems we hydroblast or discard packing.

—D: I haven't played with permanganate since my chemistry set days.

The authors wish to thank all members of the ABPG, first for their continued active participation in the DEN, and second for their assistance in selecting and editing these ABPG DEN postings for presentation to the users of amine treating plants.

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