EFFECT OF MEA VARIABLES ON CORROSION

Optimum operating conditions and minimum corrosion can be achieved with proper attention to major solution and process variables in monoethanolamine units

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There are very few ammonia plants that have been in operation for periods of say two to four years which are not operating significantly over designed capacity. Most companies are not satisfied until they have exceeded design production rates. The first thing most firms do when they get a unit up to design is to start figuring out how they can debottleneck the unit to increase the capacity. It doesn't take long for some companies to get into a position where they may be 30-40 over original design production rates due to these debottlenecking modifications. Unfortunately, most of the debottlenecking operations do not apply to the monoethanolamine treating system, with the result that as production rates are increased the MEA systems become increasingly more overloaded.

It is unreasonable to expect a synthesis gas purification unit to operate without corrosion when original design conditions are significantly exceeded. Under circumstances such as this, moderation in the original choice of design conditions is particularly advantageous because it will allow some flexibility for increasing capacity of the system by increasing acid gas loadings, solution strength, and materials of construction.

Minumum corrosion with carbon steel

Some general recommendations concerning the major solution and process variables will now be given on the basis the plant is designed for minimum corrosion while maximizing the use of carbon steel as a material of construction.

MEA concentration: Under the category of solution and process variables, monoethanolamine (MEA) solution strength is one of the simplest to control. We recommend the use of 15 wt. % MEA in the original design to maximize the use of carbon steel as a material of construction in hot portions of the plant if possible. We strongly recommend that you avoid MEA concentrations in excess of 20 wt. % MEA regardless of the materials of construction used.

Loading of MEA solution: Acid gas loading of the rich MEA solution is another very important process variable. Plant experience has indicated that much less corrosion is experienced if solution loadings can be maintained below levels of 0.4 mols of CO_2 /mol of MEA, and preferably at a level of 0.35 mols of CO_2 / mol of MEA. Higher acid gas loadings can be achieved but extensive use of stainless steel would be required. This is particularly true where the solution is in hot service or where heat exchange is taking place.

There were some particularly interesting results obtained by Fochtman, Langdon, and Howard published under the title of "Continuous Corrosion Measurements" in Chemical Engineering, 70, No. 2, 140-142 (1963). These gentlemen worked on a project evaluating MEA process variables in CO_2 recovery systems for a private firm. Their data indicated a quadrupling of the corrosion rate when the CO_2 loading of the rich solution was increased from a level of 0.35 mols of CO_2 /mol of MEA to a level of 0.42 mols of CO_2 / mol of MEA. This was an empirical study that was run in a dynamic pilot plant. However, even though the corrosion rates indicated were empirical, the rates do indicate that the additional loading indicated is extremely expensive from the standpoint of corrosion.

Regeneration temperature: Many plants will increase the temperature of the lean MEA in their regenerator reboilers to temperatures as high as 260°F. in order to obtain a more complete stripping of CO_2 from the lean MEA solution. It is the feeling of some people in the industry that the benefits obtained from increasing the stripper temperatures to this level are not warranted by the problems incurred from solution degradation and reboiler corrosion over those experienced at levels of around 245°F. Where higher temperatures are used, serious consideration should be given to the use of materials of construction such as the stainless steel and Monel.

The amount of backpressure maintained on the stripper column is the primary factor in the temperature of regeneration. The amount of extra carbon dioxide stripping obtained by the use of higher-than-normal temperatures in the MEA stripper regenerators does not appear to be economically justified basis possible lost production from the unit due to corrosion.

D. Speed's presentation on results of a survey of corrosion in synthesis gas purification systems of various ammonia plants has indicated that many of the plants which were operating in the upper limits of the regeneration temperature ranges reported were the same ones which were having extensive corrosion problems.

Heating mediums: Particular care should be taken when hot synthesis gas is used in conjunction with steam as a heating medium to be sure that the temperature differential between the heating medium and the amine solution does not become excessive from the standpoint of heat flux on the tube surfaces.

Operators supposedly using 45-50 lb./sq.in. gauge saturated steam in the MEA regenerator reboilers sometimes report extensive pitting on the reboiler tube bundles. Superheat unknowingly left in the steam is often found to be the cause of severe flashing of CO_2 off the reboiler tube surfaces.

Insufficient steam causes stripping of CO_2

Speaking of stripping of carbon dioxide from the amine solution in the reboiler, this is also quite common where insufficient steam or heat is being used to obtain the boilup necessary to maintain the stripping zone in the stripping column rather than in the reboiler. The best way to accurately check whether or not a significant amount of CO_2 stripping is being done in the reboiler is to check a sample of the amine solution to the reboiler and a sample of the amine solution out of the reboiler for CO_2

loading. Since reboiler tube bundle corrosion is so common in all synthesis gas purification plants, it is strongly recommended that sample points be installed on the still-to-reboiler line so that a check can be maintained on the amount of stripping done in the reboiler. It is quite often misleading to merely check a sample of the lean solution since one plant can have a CO_2 loading of the lean MEA solution comparable to another and yet it will be doing up to 30 or 40% of the acid gas stripping in the reboiler versus 10 or 15% in the other plant. Stainless steel and Monel are no panacea for the corrosion problems incurred where excessive acid gas stripping off reboiler tube surfaces is involved.

MEA reclaiming: Removal of soluble contaminants such as MEA degradation products is very important, since some of the degradation products act as iron chelating agents. Removal of these contaminants by means of a semi-continuous batch distillation of a sidestream of the hot lean MEA solution is relatively simple. The amount of MEA reclaimed in a synthesis gas type operation should be in the 2-3% range.

Analytical procedures: All ammonia plants using MEA for treating of synthesis gas should institute a routine program for analysis of plant MEA solutions. Determination of MEA and carbon dioxide content of the lean and rich MEA solutions, as well as the still-to-reboiler MEA solution, should be determined at least once a day. It is eye-opening to learn how many firms with large investments in ammonia synthesis gas plants do not take the trouble to analyze their amine solutions on a routine basis. Such analyses can indicate current or potential processing problems. Any plant which does not have the capability to perform routine sample analyses can purchase the necessary analytical equipment at a minimal cost. Plants that have been experiencing corrosion in the synthesis gas purification systems and have not been analyzing their MEA solutions, will probably find either high quantities of degradation products or excessive acid gas loadings of the amine solution.

Careful consideration and attention to the major solution and process variables discussed here is necessary to achieve optimum operating conditions while minimizing corrosion.

Discussion

William Long (Foster Wheeler Corp.): I have a small survey of some plants that we have gone back and examined after anywhere from four months to two years running. I think we can get a little bit more of a definitive picture of what is going on, if I can read these.

Plant A ran two years with 1.3 standard cubic foot of CO_2 per gallon of MEA in the lean solution. Process gas temperature was 360°to 380° and after a two year run there was severe corrosion on the top of the reboiler tubes. Actually two of the tubes have been pitted right through.

The customer rotated the bundles 180° and went back into operation. He replaced one of the stainless steel bundles with a Monel bundle. He lowered his process gas temperature to 330°, a drop of over 30 degrees from his former operation, and there was absolutely no corrosion after a year and one-third subsequent run.

We have had three more customers with lean solution loadings of about 1.3 and as long as the temperatures were kept below 350 F, there was no significant corrosion in the reboiler. All these reboilers were 304 welded stainless steel, solution annealed tubes.

In the four units surveyed, operating six months, because of reduced capacity and thus reduced process gas to the reboiler, the lean solution was running at a 2.0 standard cubic foot of CO . Evidently very little stripping was being done in the regenerator and after these six months of operation, severe pitting occurred in the reboiler tubes. This was at a process gas temperature of 344°. Since the customer has gone to full capacity and his lean solution loading has come down to 1.3, we know of no problems.

A fifth unit with only two months of operation, where the customer was by-passing process gas around the reboiler and again was not stripping in the regenerator tower (his lean solution loading was 1.8) had severe pitting at the 304 stainless steel tubes, approximately one-quarter of the depth of the tube.

I think what we have established from this short survey is that at loadings above about 1.3 in the lean solution of the reboiler, and at temperatures approximately 350°or greater rapid corrosion of 304 stainless steel will occur irrespective of the reclaiming operation, since one of these units has operated three years with absolutely no reclaiming, while in the other units there was very spotty reclaimer operation.

I do agree that the reclaimer is an important variable but I think we have satisfied ourselves with this survey that the two most essential variables are the gas loading of the boiler and the temperature of the heating medium.