

Effects of Contaminants on Molecular Sieves

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The widespread use of molecular sieve adsorption systems has introduced adsorption as a process tool to a host of new plants, and has introduced new processing parameters to many who were already familiar with adsorption systems employing silica gel, activated alumina or activated charcoal. Unfortunately, the "introduction" has not always included a comprehensive course in understanding the new system. Thus, it is not surprising that some operators have expressed concern or even disappointment over the behavior of the molecular sieves, either in terms of routine performance or because of bed life which was shorter than expected.

Among the most frequent problems encountered, and the single most important cause of premature bed aging, is contamination of the bed. This is usually caused by the entry, and adsorption, of materials which have a residual effect on the adsorbent even after normal regeneration. Obviously what this country needs, along with a better ten cent "nickel cigar", is a dissertation on the "Care and Feeding of Adsorption Systems". It is not possible to anticipate or predict performance under every situation which may be encountered, but it is hoped that the following information about the most common contaminants in molecular sieve adsorption systems will go a long way toward covering most problems and minimizing their effects by providing clues to prevention or quick cure. Although we have focused on systems employing molecular sieves, there is enough similarity in all adsorption systems that many items will be equally applicable to silica gel, alumina, etc.

Since contaminants, in the broadest sense, may be the cause of 90% of unsatisfactory molecular sieve adsorber operations, an awareness of these materials and an understanding of their effect on a system should help a number of process engineers and operators optimize their systems.

These "uninvited guests" come in all forms, solids, liquids, gases, and in many variations. The ones that are affecting you are the most important!

These that are hurting your neighbor are most important to him - there is no order of priority - so let's look at them at random.

1. Oil - This includes all the high boiling glop that comes along, from compressor lube systems, from the wells, from absorption plants, wherever. It is all the high boiling hydrocarbon material which enters a bed in the form of droplets or aerosol. At best, it will be adsorbed by the binder, or in the macropores of the molecular sieves. It is not completely removed during regeneration, and it eventually cracks, polymerizes, or otherwise goes through any number of reactions which result in "coke" formation. If its molecules are such that they can enter the micropores of the sieve, the coke is on the actual adsorption surface - blocking access to those materials the sieve is supposed to adsorb. If the molecules are excluded from the pores the "coke" forms on the external surface of the molecular sieve particles or in the macropores of the particles. There it blocks diffusion to the actual adsorption sites, or so impedes molecular diffusion within the macro pores that the kinetics of the system are slowed and the mass transfer zone becomes enormous. In either case, a decrease in dynamic capacity results and the sieves exhibit premature breakthrough of the "designed for" adsorbate. When this occurs on some types of thermally stable sieve, the heavy hydrocarbons can be removed by an actual "burn-off" under a controlled oxygen atmosphere. In some few systems, this is done "insitu", but in others the sieves must be removed from their towers and given the burn-off in an outside calciner. The availability of such equipment, cost of loading and unloading, investment in a spare charge to use during this process, and transportation costs all must be considered in establishing the economy of such a rejuvenation. Some sieves, including most of the available 3A grades do not have sufficient thermal stability to permit this type of treatment.

In systems where such contaminants exist, or are anticipated, efficient filter -separators or coalescers should be installed ahead of the adsorbers. Material coming through in aerosol form is much more difficult to remove than droplets or film moving along the pipe and equipment manufacturers specializing in high efficiency filtration equipment should be consulted for each specific case.



"The single most Important aging, is contamination of the bed. "

cause of premature adsorbent

2. Glycols, Diglycolamine (DGA), Di-isopropylamine (DIPA) and Associates

These materials, which frequently carry over from prior processing steps, behave much the same as heavy oils. They are quite readily adsorbed in the macropores, or even micropores of some sieves. During normal regeneration cycles they decompose and eventually go through various condensation or polymerization reactions which result in the deposit of heavy coke on the sieve surfaces, macropore blockage, and in severe cases the cementing of molecular sieve particles together to form large chunks. In mild cases the result is loss of access to adsorptive surface, and in the case of chunk formation, channeling of gas flow results. The channeling is most severe during the normally low velocity regeneration portion of the cycle. Channeling during reactivation leaves areas of unregenerated sieve which may partially release their adsorbate during the subsequent adsorption period. This, coupled with channeling of the process stream, can lead to very early breakthrough. The prevention of gross carryover is usually achieved by optimizing the operation of the processing step which introduces the contaminants to the stream. When this is not possible, the use of filters or even water scrubbers may be indicated.

3. Amines, and the Amine Portions of the Previously Discussed DGA, and DIPA

Amines themselves, when adsorbed by the sieves, will decompose during regeneration and contribute some hydrocarbons to produce coke. In addition, the ammonia formed will chemically attack the silica in the most commonly used molecular sieve "binder systems" and weaken the physical structure of the particles. When water is also present, the ammonia may affect an ion exchange with the cation in the molecular sieves (especially the K in 3A) to form an unstable hydrogen sieve crystal structure. The displaced cation may actually be washed from the system by subsequent liquid carryover, or it may migrate to the pore openings and block access to the pores by the

normal adsorbates of the system. The hydrogen form of the sieves, being quite unstable, will shortly collapse leaving a mass of amorphous "clay" in place of the molecular sieves. Again, optimizing the operation of the sweetening unit will minimize such carryover, but large scrubbers and water washes are recommended to further reduce the level of such contaminants. Make-up water for the amine system should be added on the top trays of the contactor to reduce vapor phase carryover.

4. Heavy Sulfur Compounds – and an Unexpected Cohort, O²

Many molecular sieve adsorbers are designed to remove sulfur compounds from hydrocarbon streams. Unfortunately, all sulfur compounds are not designed for easy removal from the sieves. Heavy mercaptans and other large molecule, high boiling, sulfur compounds, are not efficiently removed during routine molecular sieve regeneration cycles. As a result, they tend to build in concentration as a bed ages and produce a capacity reduction much as do the previously mentioned heavy oils.

If there is any oxygen in the system, or in the regeneration gas, it will react with H² S and some other sulfur compounds on the surface of the sieves and deposit elemental sulfur. In extreme cases this will not only block macro and micropores but also the space between the sieve particles, resulting in one large "lump" which may have to be removed with pick and shovel. By the way, don't say "who would have oxygen in a hydrocarbon stream?" unless you've looked lately. Some of your best friends (or suppliers) won't tell you! The best preventive for fouling by heavy sulfur compounds, once the O² has been cut off, is not so easy to prescribe. If the source can be controlled, once it is identified, fine! If not, you may have to resort to controlled oxygen bum-off, similar to that mentioned for removing carbon, but watch that stack gas!

Complications resulting from oxygen in a hydrocarbon system are not limited to the production of sulfur. Reaction with the hydrocarbons present, especially during the high temperature portion of the regeneration cycle, can result in heavy coke lay down and fouling of the sieves.

Since oxygen can enter a system by a number of routes, some almost unbelievable, it's a good idea to request an oxygen determination during any routine stream analysis. If only trace amounts are detected early, and the source is discovered and cut off, it should be possible to prevent severe damage to the sieves.



*"Efficient
coalescers should be
adsorbers. "*

*filter-separators or
installed ahead of the*

5. Well Treating Compounds, Mud, Corrosion Inhibitors, and Unidentified Companions

This motley collection of adsorbent enemies is lumped together because none really justifies individual treatment. They usually show up sporadically and then disappear before you can tag them. They may be acids, amines, phosphates, etc. and their effect on the adsorbent is as varied as their lot. The end result, and what you pay for, is loss of capacity. Sometimes they may be controlled by more judicious use at their source - twice as much is not always twice as good, etc. Sometimes efficient scrubbers or coalescers will get them, and sometimes in isolated cases, when you have no control of the source, you just have to "grin and bear it".

6. Particulate Matter

Aha! Before you read any further, you say filter! Three points for a correct answer, but where do you put it? In some cases, the direct result of particulate matter may not be in the adsorber. Coming through a gas system, the solids may raise hob with an amine plant - and the resultant foaming and carryover will be what really hurts the adsorbent - so catch it at the gate!

When there is no other process system ahead of the adsorbent bed, the packed tower itself will act as a pretty good filter - but at the expense of pressure drop, good fluid distribution, and a consequent loss of adsorption efficiency. In new plants, this type contaminant may be mill scale, rust or other debris from the construction, new pipes, or equipment up stream. It's a good idea to blow all this accumulation out of the system before the final flanging of an adsorber.

7. Salt

Salt usually enters a desiccant bed dissolved in entrained water. Unfortunately, it does not leave when the water is vaporized and removed from the bed during regeneration. Thus, the solid accumulates and blocks pores, macropores - and in extreme cases -

all the voids between the molecular sieve beads. Once sufficient salt has accumulated to reduce adsorbent capacity below the minimum level required to maintain cycle times, it is usually necessary to replace the adsorbent. Unfortunately, there is no dependable way to recover desiccant capacity from such a unit. In extreme cases, and where a plant shut down for desiccant change must be avoided, a water washing can sometimes achieve partial capacity recovery.

Of course, the only adsorbers subject to such contamination are those treating gas from salt water bearing formations, and those treating LPG, propylene etc. from "salt dome" storage caverns. In such installations, the design of inlet scrubbers, separators coalescers, etc. is extremely critical to satisfactory adsorber service and adsorbent life.

8. Olefins, Diolefins, Aromatics, etc.

The vast majority of adsorbers operate in systems completely free of these reactive or high boiling hydrocarbons. But some systems, cracked gas dryers for example, get them as a steady diet. Obviously, in such situations, they can't be removed ahead of the adsorber; they must be tolerated. The problems they create are two-fold and the methods to minimize the two detrimental effects of their presence are in direct opposition to each other. We've got to compromise!

First let's consider the reactive molecules such as the diolefins. On any surface, in the presence of heat and some pressure, they will polymerize. The surface of molecular sieves during bed regeneration fits the bill. In addition, the surface of the sieves is somewhat catalytic, so the reaction is promoted. When such polymerization occurs inside the pores of molecular sieves, alumina, or other adsorbents the resulting polymer molecular is usually too large to "leave by the way it came in" or has such a high boiling point that normal regeneration temperature will not strip it from its resting place.

To minimize such adsorbent uling, special attention should be given to three factors in the design of the system:

A. Long Cycles

Cycle time should be long. This, of course, requires larger beds, but will prolong adsorbent life and save operating expenses. A longer cycle permits more gas processing per regeneration, and since it is mainly during regeneration that polymerization occurs, the rate of adsorbent fouling will be reduced. This, of course, is based on the fact that the amount of adsorbent is not a direct function of the cycle time, due to the presence of both equilibrium and mass transfer zones in an adsorbent bed. To maximize the advantage of such design, the beds should be operated on cycles determined by moisture analysis of the treated gas rather than on fixed time cycles. This assures maximum gas processed per cycle - or per unit of bed life - which is what saves adsorbent cost. Also, it loads the bed to the maximum water level consistent with specification product, and since water displaces the reactive and high boiling molecules, there will be a minimum "heel" of these materials left on the bed at the time regeneration starts.

B. Maximize Water Load

This last consideration minimizing the amount of "foulants" at the end of the adsorption period can be carried to the ultimate. That is, the bed can be operated to complete water equilibrium, assuring an absolute minimum of adsorbed hydrocarbons in the pores of the desiccant. This means the mass transfer zone, or rather the water which would normally be held in it, passes on out with the effluent gas. To prevent this water from entering the downstream system, there must be a second adsorber in series. The system, then, must be three beds, with two in series, and one on regeneration. While one adsorbs, the second acts as guard, catching the water from the mass transfer zone as it passes from the first. When the first is loaded to equilibrium, it shifts to regeneration, the guard bed becomes the primary dryer, and the freshly reactivated one assumes the guard position. As in the previous consideration, the cycles should be based on water breakthrough rather than time, only in this case the switch occurs when the water level in gas leaving the primary dryer approaches the level of the water entering.

C. Purge

Provide a purge at the beginning of the reactivation portion of a cycle, using the regeneration gas at ambient temperature. Follow the purge with a relatively slow heat up until final regeneration gas temperature has been reached 2-3 hours into the regeneration. This will remove a maximum amount of reactive molecules at minimum temperature, thus reducing their tendency to polymerize. In systems containing reactive molecules the final bed temperature is usually held on the low side of the range used for dehydrators, to further minimize polymer formation. With molecular sieve beads, the peak may be 375-425°F.

Unfortunately, the "gentle approach" to regeneration may promote the second problem associated with treating high boiling olefins and aromatics. It may allow a "heel" of high boilers to accumulate in the bed until they reach a concentration that can seriously reduce performance. When this occurs, and it will vary with each system, the bed should be given an extra, high temperature, "cook-out" following a normal regeneration. The temperature to be attained in this special cycle will depend on the stability of the adsorbent in the system. Davison type 3A molecular sieves will tolerate bed temperatures as high as 500 - 550° F with no thermal damage, while special modifications of the type 3A may tolerate temperature high enough to actually "burn-off" accumulated coke by the addition of controlled amounts of oxygen. Such "burnoff" is usually controlled at 750 - 850°F.

Water

Unlikely as it may seem at first, water can be a serious contaminant in an adsorber, either because of the quantity present, or because of any quantity present. The overload situation occurs when the feed carries more water than is anticipated under design conditions. In a closely designed system, the problem is in

almost direct proportion to the "excess". However, even systems that are designed for water saturated feed will be severely overloaded if some liquid water, mist or droplets, enters the bed. The answer to this "liquid invasion" may be as simple as bigger and better separator -scrubbers ahead of the adsorber. In any event, stopping liquid water is a mechanical problem that can be solved if the importance of optimum dryer operation warrants it.

In the case of feed containing a higher than anticipated percentage of saturation, the solution may be total, partial, or "live with it occasionally", depending on the frequency of occurrence, and on the extent to which water can cause trouble downstream.



"Unfortunately, all sulfur compounds are not designed for easy removal from the sieves."

One obvious answer is to design for 100% saturation regardless of what the "normal" feed may be. This solution could seem expensive, but may be warranted on occasion. A solution almost as good, and at some saving in adsorber size is to design the adsorber for the expected load, but design the regeneration system so that the cycle can be drastically shortened in the event there is an occasional surge in water content of the feed. A water monitor, to indicate bed switching time, is a necessary part of this system. It may be an automatic system with the probe a few feet, (1-3), up in the bed at the exit end, or it may be only an indicating system in the feed stream which will display the water content for an operator so that he can compensate by manually changing the cycle time.

The presence of water, where none is expected, can have numerous consequences - mostly bad. Since molecular sieves will adsorb water in preference to any other molecule the water will take space required by the adsorbate for which the system was designed, CO² for example. The result will be a premature breakthrough of the "design" adsorbate, water in the regeneration system, (which may be as serious as water in the product) and possibly an incompletely regenerated bed on the next cycle. This latter is the likely consequence of the regeneration system providing less energy than is required to remove all the water, since most "non-water" adsorbers are designed with smaller regeneration systems than would be required for a comparable dehydrator.

Water monitors in the feed gas can give early warning in such systems, but once the water has entered the bed, it is usually necessary to shut down normal operation, go through a prolonged regeneration, or series of regenerations, or in severe cases replace the molecular sieves.

10. The Inevitable

Of course, there is that ultimate menace - the one we all must face - old age. This will eventually reduce capacity of a molecular sieve unit to such an extent that the adsorbent must be replaced. The rate of aging, and the time for replacement, are highly individual characteristics of the type of service, the particular system, design, and feed characteristics. In order to anticipate replacement and plan for it during a scheduled shut down or turn-around, you should periodically test your unit and determine its capacity. This applies only to units operated on time cycles, of course, since monitor switching actually tests a bed each cycle. When several test results are plotted on a capacity, or cycle time, vs. number of cycles basis, you can usually extrapolate to find when the shortest cycle possible with existing regeneration equipment will be reached. At that point, or during the nearest regular plant turnaround preceding that point, you must plan an adsorbent change out.

The details of making such tests will vary with the system and they are most conveniently made on systems that have effluent sample taps in the discharge position of the bed. (A point to remember when a new plant is designed). We, at Davison, will be glad to make specific suggestions about testing any system, and will evaluate samples of the molecular sieves if they can be obtained from the unit. A combination of test data from the operating plant, and adsorbent analysis, over several periods, could provide a very complete profile on the aging curve. It is hoped that the preceding information will assist you in making that curve as gentle as possible.

