

# FOULING IS A SAFETY PROBLEM

Excessive temperatures and pressures can result if fouling is not curtailed in various parts of the plant

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Our plant has had a fouling problem which has been with us since startup and which tends to become more and more serious. This fouling occurs in the heat exchangers immediately downstream of the secondary reformer. In our plant we have two waste heat boilers. All the gas passes through the first one. Immediately downstream from it, is another waste heat boiler which has a bypass on it. The bypass is used to control the temperature going to the high temperature shift converter. The fouling not only encompasses these two exchangers but also includes fouling of the high temperature shift converter.

The problem is not unique to our plant. In the last two or three years I have been, in effect, surveying the industry. I have talked with people who represent 15 - 20 plants. It seems that everybody has this problem in all degrees of intensity. The problem became serious mainly when the ammonia industry got into higher pressure reforming and higher temperature secondaries. I thought I would mention here the safety aspects.

As one starts operating a plant at maximum rates, it becomes a safety problem. Even at reduced rates, as these exchangers foul, it becomes a safety problem. These exchangers have design temperature limits. Inside a piece of pipe, there is one temperature, and outside, another. What is the design limit? Is it the internal temperature, the average temperature or the external temperature? One has to make a decision here.

## The failure is not instantaneous

There is another problem and that is the failure is not instantaneous. The metal fails as a result of creep as you operate at temperatures in excess of design for long periods of time. The exchanger or the pipe may not fail today, it may not fail next week, but it might fail a month from now. Just the fact that you operated at a certain temperature last week, doesn't mean it is safe to do it this week. You have to know how long you have been at the high temperature.

What are the alternatives when the waste heat boiler starts overheating? They have basically four. First, you can reduce rates. Whenever you reduce rates you get better heat transfer and the temperature goes down. This has been fairly successful. We find a small reduction in rates gives a significant drop in temperature. Recently we had occasion to cut to about 70% in plant rate and the temperature exit at this exchanger dropped something in the order

of 160 degrees. I was amazed that we could get 160 degrees drop with, in effect, a 30% reduction in rate.

Another way in which this temperature can be controlled or modified is by lowering the temperature of the secondary reformer. The lower the temperature going to the exchanger, the lower it is coming out. The operators found this in the plant very early. By lowering the secondary reformer temperature, they were able to hold the waste heat boiler outlet within design as it began to foul. This, however, cut into plant production and plant efficiency. The colder the secondary, the more methane you have going to the synthesis loop which in turn reduces plant capacity. So here again, you have a decision to make. Just how hot are you willing to run it? Another obvious solution is that you shut down and clean the exchanger. Nobody likes to do this. It takes from one day to one week to do this.

Another thing which has been done is to inject water into this exchanger, or just upstream, and shock it while running. This has been done at one or more plants with a moderate degree of success. It also has some inherent disadvantages. The exchanger has to be designed for this because impingement of water on linings and pipes at this high temperature can cause cracking and warping of the metal liners.

## Where does the foulant go?

Another problem is what happens to the fouling material. Since it is still in the system it just moves to the high temperature shift converter. So you have eliminated a problem in one area and created it in another.

What is this material? All the people I have talked to describe it as a very light gray-white powdery dust. Most people when they first look at the waste heat boilers expect a heavy coating like you get in a boiler, or a thick scaling, but it is really a light dust.

We have inspected the second exchanger in this series, and have found everything from a very light dust to a hard scale. In one case it was as hard as a cement. We had occasion to try and drill out some tubes. In certain rows of these tubes we could hardly drill. In fact, we gave up on the drill in some instances, the material was so hard. But, for the most part, I think it can be described as a light, white to gray dust.

Generally, silica is the most predominate component. There are

reported analyses with significant quantities of sodium, calcium, aluminum, iron and nickel. I have heard of one X-ray diffraction analysis which described the majority of the material as a sodium silicate complex.

Some of the ways these exchangers have been cleaned are of interest. In some of the designs, the process gas is on the tube side. In these cases, a wire brush has been extremely effective. In others, where the fouling has been on the shell side and where it has been possible to remove the bundle from the exchanger, a steam jet has been fairly effective. Hydrojet has also been effective. Chemical cleaning has also been used. If you want to get an extremely clean surface, you almost have to resort to chemical cleaning. Here again, this is quite time-consuming. There is more experience on steam cleaning or jetting than on chemical cleaning.

## Shutting down cleans equipment

In our plant we have not had occasion to remove and clean the exchanger which causes most of the problems. We have found a temporary measure which has gotten us by, which involved shutting the plant down. We found out very early if you shut the plant down and start it back up you have removed a lot of this fouling. In the early days we found we got a moderate degree of success just by shutting down. Later on, we found a better technique. Once we had taken the air and the gas out and had cooled down to a moderately low temperature, something like 500 degrees, then we would inject water upstream to the exchanger to make sure that the steam was at its saturation point. By using wet steam, we got very effective cleaning. When we came back on line the effluent gas would be several hundred degrees cooler than before. This has one advantage, that when we shut down, we always vent our gas upstream of the high temperature shift converter. So when this material sloughs off, it goes out the vent instead of into the shift converter.

We have also experienced fouling in our high temperature shift converter. Very early in startup we observed the pressure drop across the top bed was building very rapidly. One day it was one lb./sq.in., the next day it was 3, the next day it was 5, and pretty soon, it was up to 10 and 12. With a 12 lb./sq.in. maximum limit, we were reluctant to chance damage to the catalyst supports. To prevent damage, we began cutting rates. It didn't take but one to two days before our rates were so low that we decided we had to do something about it. The obvious thing was to change out the catalyst. We happened to make a fortunate phone call to a catalyst vendor and they said, "Yes, somebody else had that problem, and they solved it by back flowing the catalyst." So we shut down, opened up the top manway, put all the steam we could get into the bottom of the shift converter, blew some clouds of white dust out, crossed our fingers, put the manway back on and started up. Fortunately, this solved the problem. We have back blown it once since then when we had the occasion. This has proved to be a fairly effective technique.

Catalyst fouling showed up in our plant also as loss in activity of the catalyst. Back in this early period with less than a month's operation, the activity was quite low on the shift converter at the same time the pressure drop was building up. I don't think this is anything unusual. We figured we were channeling. Following back blowing, we noticed an appreciable recovery in catalyst activity. Right now with something in the order of nine or ten months onstream time, we are again running into pressure drop and low catalyst activity in this bed. I don't know whether back blowing is going to be as effective this time as it has been in the past, but it is a little bit more palatable to be changing out catalyst after a year than after a month.

## Where does the foulant come from?

Where is all this deposit coming from? Is this something we are going to have to face from here on out?

There are really four different places - probably five or six - but four main places from where this can come. The first one is steam. In some of the older ammonia plants this was a definite source. It was traced back to the water purity. Calcium and silica were definitely getting into the process by route of the steam. Some other ammonia plants, where they import steam, have been able to correlate temperature rise in this exchanger with the amount of steam they have imported. In our plant we don't have any import steam. It all comes off the plant itself, so we don't have the concern of importing low quality steam. We ran some tests on our steam and found it to be very good. The last set of analyses I saw on sodium was 10 to 15 parts per billion sodium which means total impurities are under 50 parts per billion. We have ruled out steam in our plant, but I would advise other people not to rule it out as a source because it can be.

Air was another thing with which we became concerned. What do you bring in with the air? We happen to have an unfortunate location in that we are right next door to a cement plant. And it gets dusty! Back in the design stage we put in back-up filters, so we go through a double filtration of our air. I have been trying to look at a correlation between when the wind is blowing in our direction and when it is blowing in the other direction. I can reach no conclusion on the fact that fouling can be coming from the cement. I can't rule it out, but I can say that of the other 15 to 20 plants I have looked at, they have all had fouling problems and they are not located next door to a cement plant. So, hopefully, our problem is similar to theirs.

Catalyst is another source. Most catalyst vendors have done a lot to improve their catalysts in the last few years. I have a tendency to write this as a fairly low source, although you can't completely eliminate it - I think in the early stages there is some dust as a result of loading the catalyst. It has to be blown out - I don't think it is a pronounced problem, but it is one that has to be considered and I think most catalyst vendors have given this considerable thought and are trying to help out.

## Secondary reformer is main source

The place that seems to be the biggest fouling source is the secondary reformer. The lining in the secondary reformer seems to be one of the places that everybody suspects. One of the reasons we look to this is that in plants that have had problems, after six months to a year this problem tends to get less and less. This points to either initial dirt in the system which has to migrate out, or something like the liner of the secondary which has silica in it which tends to leech out and deposit in this exchanger. After a certain amount of leeching it tends to go away.

So far, we have had only one week of operation where the exchanger effluent temperature has held constant. That is encouraging. After watching the temperature rise on occasions from 5 degrees to 15 degrees a day, any period where you can go for a week at a constant temperature level leaving this exchanger is encouraging. I don't know the answer. I think the problem is going to go away, but in the meantime, I wonder how many more shutdowns will we have to make to get rid of whatever it is. How close can we run this plant the maximum temperatures and still be safe? I am just waiting for the day that it goes away so I can forget this problem.