Executive Summary

**Dealing with Non-Detects in Air Emissions Testing – (Part 2)**
By Scott Evans, CleanAir Engineering

In Part I of this series, we defined the Method Detection Limit (MDL) as a function of the variability of the measurement process (MP) at or near zero, the importance of the matrix blank in determining MDL estimates as well as the difficulty of determining matrix blanks for air emission measurement methods. Finally, we discussed a solution to this problem using repeated measurements with paired sampling trains.

In part two, we will discuss how to handle and report air emission test data that are below the detection limit. There are a variety of techniques that are traditionally used when reporting data below the detection limit. However, all of the techniques rely on “data censoring.” Data censoring occurs when the true value of the measurement data are replaced by a fabricated value. Even though it is commonplace within the EPA reporting regime, data censoring is a very controversial topic within laboratory and metrology circles. *Full Story...*

**Impact of Biomass Co-Combustion on SCR DeNOx Operation**
By Hans Jensen-Holm, Joakim Reimer Thøgersen, and Nathan White, Haldor Topsøe A/S

With increasing requirements for reductions of CO₂ emissions from the power-generating industry, there is a considerable interest in the utilization of biomass and municipal and industrial waste in power plant boilers. Combined with still tighter limits on emission of NOx, the use of biomass fuel represents a challenge to the designers of Selective Catalytic Reduction (SCR) units since the useful life of the SCR catalyst can be significantly reduced. The mechanisms responsible for the catalyst deactivation are discussed as well as a number of SCRs implemented to meet these new challenges. *Full Story...*

**Commercial Experience of Ammonia-based Flue Gas Desulfurization Technology**
By Amy P. Evans, Director of Technology, Marsulex Environmental Technologies Corporation

A process for flue gas desulfurization, using ammonia as reagent (AS-FGD) that produces ammonium sulfate (AS) crop fertilizer, was developed by General Electric Environmental Services, Inc. in the early 1990’s and subsequently acquired by Marsulex Environmental Technologies (MET). The AS-FGD process is similar to conventional open spray tower FGD in terms of operational reliability, SO₂ scrubbing performance, and absorber equipment/configuration. Principal differences of the AS-FGD compared to conventional include system chemistry, reagent handling, dewatering, elimination or significant reduction of wastewater, elimination of CO₂ generation within the absorber, and economic benefits from the sale of the fertilizer by-product. *Full Story...*
Dealing with Non-Detects in Air Emissions Testing (Part 2)
By Scott Evans, Clean Air Engineering

Introduction
In Part I of this series, we defined the Method Detection Limit (MDL) as a function of the variability of the measurement process (MP) at or near zero, the importance of the matrix blank in determining MDL estimates as well as the difficulty of determining matrix blanks for air emission measurement methods. Finally, we discussed a solution to this problem using repeated measurements with paired sampling trains.

In this part, we will discuss how to handle and report air emission test data that are below the detection limit. Based on the work of Currie (Currie 1968), data near zero can be classified into three categories or regions – Region I (from zero to the MDL or \( L_D \)), Region II (from \( L_D \) to the Limit of Quantitation, \( L_Q \)), and Region III (above \( L_Q \)). The relationship of these regions is shown in Figure 1.

![Figure 1. Relationship of Detection Related Limits and Associated Regions (from Currie 1968)](image)

In this Part, we will address data that falls into Region I – below the detection limit. Data in Region III are simply reported as is, with no special treatment. Data in Region II will be covered in Part III of this series.

Reporting Results Below the Detection Limit
There are a variety of techniques that are traditionally used when reporting data below the detection limit. However, all of the techniques rely on “data censoring.” Data censoring occurs when the true value of the measurement data are replaced by a fabricated value. There are three values commonly used for this purpose – zero, the detection limit, and one-half the detection limit. The value that is used may be specified in the applicable method or may be left to the discretion of the testing body. For example, in reporting dioxin/furan data under 40 CFR 63 Subpart EEE, the standard requires substitution of zero for measured values below the detection limit. The same regulation allows substitution of one-half the detection limit for metallic constituents of incinerator feed stocks. For many methods and applications, EPA’s Office of Air and Radiation prefers substitution of the MDL for values less than the detection limit.

Even though it is commonplace within the EPA reporting regime, data censoring is a very controversial topic within laboratory and metrology circles. Many studies have been done involving the reliability of results using censored data and techniques for data censoring as well as other types of data substitution (i.e. various statistical estimation procedures).

Data censoring is controversial for two reasons: 1) It inevitably biases the data either high or low depending on the substituted value, and 2) it obscures real information contained within the data.

Many studies have been performed on the bias inherent in censored data (see for example Helsel 2005, Travis 1990, Helsel 2006). From EPA’s standpoint, substitution of the detection limit for all data less than \( L_D \) provides the “worst case” scenario, that is, data biased high. While this may give the regulators a warm feeling, it may not be the best solution for sources that
sources that must report higher emissions than are scientifically justified. For some large sources, this can be very significant. For example, on a large electric power plant, every 1 ppm of ammonia reported in the gas stream represents an additional 5 tons of ammonia emissions each year. Small numbers can add up quickly on large sources.

The second issue, that censoring obscures information contained within the results, is an even more important factor. Yes, there is information contained in data below the detection limit. The idea that all data below the detection limit are noise is a myth that needs to be busted once and for all.

It is important to remember that the \( L_D \) value is not any kind of inherent, absolute physical limitation of the measurement process. It is a statement of arbitrary risk levels and assumptions that are the result of political or institutional policy rather than technical limitations. This must be made very clear if we are to make any progress on understanding and reporting low concentration data.

To help understand the idea of the detection limit in more depth, let us return to the blank distribution we discussed in Part I. I want to make it clear to all the detection limit savvy readers that we are going to discuss these ideas conceptually and as such I am going to make some simplifying assumptions in order to make the main ideas clear. Most importantly, I am going to use a single distribution to describe the detection limit.

The proper technique to determine a detection limit involves two distributions – the blank distribution, which we have already encountered, and the measurement process distribution. It would look like Figure 2.

This dual-distribution concept (Figure 2) will be further discussed (perhaps) in a future article. However, for now we will limit our discussion to a single distribution – the blank distribution.

Let’s take a look at the blank distribution introduced in Part I again. You can see in Figure 3 a nice bell shaped curve with most of the values clustered around zero and fewer values as you move away from zero – just as one would expect if measuring nothing. The scatter around zero represents the random noise of the measurement process. I should note here that although the blue curve looks like it ends at about 15, it actually goes on to infinity. You will never get a value that is “past” the curve.

The nice thing about expressing the measurements as a distribution rather than as individual measurements is that one can then make probability-based predictions from the distribution. For example, the zero line divides the distribution exactly in half. Since the noise is random, any result from the MP when the true value is zero has about a 50% chance of being greater than zero (and of course about a 50% chance being less than zero). I say “about” because we have to remember that the distribution is only an estimate or model of the actual data.

As we move away from zero, we can choose a value that gives us any split we want. For example, see Figure 4. Here a line is drawn so that 95% of the data are to the left and 5% to the right.
Now let’s talk about what Figure 4 means in terms of a detection limit. Let’s assume that we have done multiple blank determinations and have come up with the distribution shown in Figure 4. Now we apply our measurement process (reference method, analyzer, etc.) to a stack. We obtain a result of 10 (the dashed line). We know that about 5% of the time, when we measure blanks we get readings of 10 or more. So the question is… Is this value “far enough” from zero to allow us to state that the compound of interest is actually present and we have not just measured zero? As you can see, this is not a technical question – this is a judgment call. That is what every detection limit determination is – a judgment call based on what some person or some organization has decided is “far enough.”

In this particular case, if we state that we have detected the compound, we only have a 5% risk of being wrong because only 5% of the zero values are 10 or more. Another way to say this is that our false positive risk (the risk of deciding a substance is present when it actually is not) is 5%. Alternatively, (if we were an optimist) we could say we had a 95% chance of being right – hence the common term 95% confidence limit. We will not consider false negatives here. That is where the second distribution discussed above comes in.

These are the risks that are taken into account when someone decides what the detection limit of a method should be. When a number is shown as the detection limit, it is simply the tangible representation of the risks and assumptions that someone has arbitrarily chosen. If we choose 10 to be the detection limit for the measurement process above, it does not mean that the process cannot measure below 10. It most certainly can. It does not mean that any measurement below 10 is random noise. It simply means that someone decided that the false positive risk for this MP must be 5% or less.

Very often the criteria for a detection limit specifies a false positive risk of 1% (or optimistically 99% confidence). Very confident, indeed. This sounds like a good thing. More confidence is better, right?

Well, yes and no. Here is where data censoring becomes a problem. Let’s take our measurement process from the previous example and arbitrarily assign a false positive risk of 1%. See Figure 5.

This puts our detection limit at about 15. Once again, we apply our measurement process to a stack and get a result of 10. If we follow traditional data censoring and report this as “less than the detection limit”, we would report the value of 10 as <15. Knowing what we now know about our detection limit, what we are really saying is this…

“We, in our infinite wisdom, have decided that we need to be 99% sure that the number we measured is not really zero. Since we are not 99% sure, we are not going to tell you the number we got. Instead, we are going to tell you what the number would be if we were 99% sure. That number is 15. So your number is less than 15. But, we’re not going to tell you how much less.”

Now put yourself in the data user’s shoes. If you censor the data and report <15, the data user has no idea what the measured number is. It could be 14.9. It could be zero. The data reporter has no idea how the customer will use this data. Perhaps they just need a ballpark estimate or perhaps this is the key value around which a 50 million dollar pollution control device will be constructed. Does the data reporter know? Should they unilaterally make the decision that nothing less than 99% will do?

The solution is obvious. Don’t censor the data. Rather, report the actual measured result along with the associated false positive risk or detection confidence. Again, from the data user’s standpoint is it better to know nothing with 99% confidence or to know something with 95% confidence? I propose that the latter is the preferred approach.

In the example above, the data should be reported as 10 with a false positive risk of 5%. Using the “false positive” terminology rather than “95% detection confidence” avoids the confusion between: 1) the confidence of the detection decision and 2) the confidence of the result itself. While these are related, they are not the same thing. In the first case, we are stating how confident we are that the result is not zero. In the second case, we are stating how confident we are that the result is actually the number we are reporting. The first is constant, the second may change with concentration.

The data reporter could flag the data as being below their
recommended 99% detection limit of 15 for added documentation. But by reporting the data and its associated false positive risk, all of the information is preserved and passed on to the customer who can make her own decision as to whether 95% is “close enough”. Why should the data reported have the prerogative to decide for the customer what data is good enough? The responsibility of the data reporter should be to give the customer all the information she needs to make her own decisions about the fitness of the data for its intended purpose.

**BIG NOTE:** The single distribution technique described here controls only the false positive risk. The false negative risk (i.e. the risk of deciding a compound is not there when it really is) under this approach is 50%. In other words, if the compound is actually present in the gas stream in amount equal to the detection limit, the measurement process will falsely conclude that it is not present 50% of the time. You might as well flip a coin. This is where that second distribution shown in Figure 2 comes into play. The concepts presented in this paper apply equally well to the dual distribution approach, but the math is a bit trickier.

**Determining the False Positive Risk of Your Data**

We can now move to the issue of how to determine what the false positive risk is for a given result below the detection limit. To do this, we need to know either the blank distribution or the detection limit. Obviously, finding the true blank distribution of the entire measurement process would be best, but unless you are willing to do a series of paired sampling runs (as discussed in Part I), you are not going to have this information. On the other hand, you may have a value for the detection limit from the data reporter. Finally, you may have a detection limit value from the test method used, but that number may be unrealistically low because it is based on only the analytical portion of the test method.

Experience with the method may come into play here. An experienced testing body may have a good idea of what the true detection limit of the method is even without doing the hard work of figuring it out. But at any rate, one should always use a detection limit that they are comfortable with and can defend with data if challenged.

Once you have a detection limit, it can be used to calculate the false positive risk of measurement data if the following assumptions are made:

1. The detection limit represents a 1% false positive risk. This is the most commonly used criteria for detection limit determination. If you have other information that a different false positive rate was used, use that instead of 1%.

2. The detection limit is based on seven replicate blanks. This is a common technique and was recommended by the Office of Air and Radiation on their TTN website prior to the recent changes. Again, if you have other information, use that instead of this assumption.

Use the following 3-step procedure to estimate the false positive risk for measurement data. For this example, we will assume we have a method with a detection limit of 5 and a measurement result of 3. While this may seem like a long explanation, as you will see, it can be implemented in a single spreadsheet cell.

**Step 1: Find the Standard Deviation of the Blank Distribution**

Recall that the blank distribution is formed based on knowledge of the variability of repeated blank measurements. This variability is expressed as the standard deviation. The probabilities from the blank distribution can be easily calculated from multiples of the standard deviation (SD) of the data. For example, the point of 95% confidence (5% false positive) is found at about 2 x SD. The 99% confidence point is found at about 3 x SD.

But we don’t know the standard deviation, right? But we do know the detection limit and we have assumed that it is a 99% confidence limit. Since we now know that the 99% confidence limit is found at 3 x SD, if we take the detection limit and divide it by 3, we will obtain an estimate of the standard deviation. So...

\[ SD = L_d / 3 \]

In our example, \( L_d = 5 \) so...

\[ SD = 5 / 3 = 1.6667 \]

**Step 2: Express the Result in Units of Standard Deviation**

Once the SD is known, the measurement result must be expressed in units of SD so we can calculate the risk. To do this, we simply divide the data by the standard deviation:

\[ \text{Data in units of SD} = \frac{\text{Data}}{\text{SD}} \]

In our example, the data is 3 so...

\[ \text{Data in units of SD} = 3 / 1.6667 = 1.8 \]

**Step 3: Find the Risk**

If you know a bit about statistics, this paragraph may interest you. If not, just skip to next paragraph. Because we are estimating the standard deviation from (presumably) 7 blank replicates, we must use a t-distribution rather than a normal distribution to estimate our risk. In order to use the t-distribution we must know the degrees of freedom of our estimate. Since we are assuming 7 replicates, our degrees of freedom is 7-1=6. Using our standardized data and the degrees of freedom, we can now use a t-table to look up our risk. However, Microsoft Excel has a wonderful function called TDIST that will calculate it for us. I find this much easier than using a statistical lookup table.

www.wpca.info
Microsoft Excel’s TDIST function will use our standardized data to calculate the risk. The TDIST function takes three arguments:

1. The standardized data. In our example, 1.8.
2. The degrees of freedom. This is simply the number of data points used to estimate the SD minus 1. Since we assumed 7 replicates (remember our assumptions from above?) the degrees of freedom for our example is 6.
3. Tails. I’m not going to go into this here. If you are interested in the tails of probability distributions, consult any good statistical textbook. Just use 1.

So our TDIST function looks like this:

=TDIST(1.8,6,1)

If you enter this formula into an Excel spreadsheet, you will get: 0.0610 and maybe some additional digits. This is your false positive risk. To see it more clearly, set the format of the cell to Percentage. The result is now:

6.10%

The false positive risk is about 6%. If you subtract this from one (i.e. 1-0.610), you will get the confidence that this result is not zero (if you are interested in this). For our example it is: 93.9%

So instead of simply reporting the data as <5, we can report it as 3 with a false positive risk of 6%. In a table perhaps it can be shown as: 3(6%). Now there is some information a client can use. The report can certainly flag the data and report the 99% detection limit as 5. This is also useful information for the end user of the data.

Important Takeaways

1. Data below the detection limit is not simply noise -- it contains important information.
2. The traditional technique for expressing data below the detection limit, data censoring, biases the data and destroys information.
3. Data users, not data reporters, should determine how much risk is acceptable in the data given its intended use.
4. Data below the detection limit should not be censored but rather should be reported as measured with an expression of the false positive risk (the risk that the compound of interest is actually not present in the sample).

REFERENCES


Helsel, D.R., “Fabricating Data: How Substituting Values For Nondetects Can Ruin Results, And What Can Be Done About It,” Chemosphere (65), 2434–2439, 2005


1It is worth noting here again that EPA’s Federal Advisory Committee on Detection and Quantitation for Uses in Clean Water Act Programs has essentially recommended the use of this single-distribution approach in their recent draft revisions to the detection limit procedures found at 40 CFR 136 Part B (EPA 2007). This means that, if the recommendation is adopted, EPA’s detection limit approach will be at odds with international standards such as ISO and IUPAC.

For more information, contact Scott Evans, CleanAir Engineering, at sevans@cleanair.com

Additional links:

Impact of Biomass Co-Combustion on SCR DeNOx Operation

By Hans Jensen-Holm, Joakim Reimer Thøgersen, and Nathan White, Haldor Topsøe A/S

Abstract

With increasing requirements for reductions of CO₂ emissions from the power-generating industry, there is a considerable interest in the utilization of biomass and municipal and industrial waste in power plant boilers. Combined with still tighter limits on emission of NOx, the use of biomass fuel represents a challenge to the designers of Selective Catalytic Reduction (SCR) units since the useful life of the SCR catalyst can be significantly reduced.

The mechanisms responsible for the catalyst deactivation are discussed. Alkali-metal aerosols formed during combustion of biomaterial can at worst cause complete deactivation of the catalyst within a few thousand hours of operation. Other
components as e.g. phosphorous can cause severe fouling of the catalyst surface.

The paper describes a number of SCRs implemented to meet these new challenges and includes experience from a variety of plants firing biomass in Europe and the U.S.A. Results from installations in units firing 100% biomass, as well as installations in units with co-combustion of biomass with coal and oil, are presented.

These experiences demonstrate that choosing the right plant configuration and proper catalyst formulation, the negative effect can be limited. Up to 20 weight per cent biomass can be co-combusted with the coals without any noticeable impact on catalyst lifetime. The use of SCR on 100% biomass-fired boilers may be done as a tail-end installation to minimize the amount of poisoning species entering the SCR.

Introduction

An increased production of electricity from renewable energy sources is being promoted and biomass co-firing with coal in existing coal-fired power plants represents an option for combined renewable and fossil energy utilization to reduce CO₂ emissions. Biomass is considered CO₂ neutral with respect to the greenhouse gas balance if the use of fossil fuel in harvesting and transporting the biomass is not considered. Direct co-firing, i.e. firing the coal and biomass in the same boiler, is the simplest and most widely applied technology for co-firing biomass.

Possible biomass sources comprise e.g.:

Wastes and residues
- Wood and bark: forest or tree trimmings, sawdust, demolition wood, crates
- Agricultural residues: straw, olive residue, coconut chips
- Animal wastes: Poultry litter, meat bone meal
- MSW, sewage sludge, paper waste

Peat

Agricultural energy crops: Switchgrass, miscanthus, poplar and willow, bamboo

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>Ash (mg/Nm²)</th>
<th>Soluble Potassium (wt %)</th>
<th>Soluble Sodium (wt %)</th>
<th>Nickel (wt %)</th>
<th>Vanadium (wt %)</th>
<th>Phosphorous (wt %)</th>
<th>Calcium (wt %)</th>
<th>SCR Catalyst Deactivation % PER 10,000 HOURS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous coal</td>
<td>15,000</td>
<td>0.15</td>
<td>0.12</td>
<td>-</td>
<td>-</td>
<td>0.1</td>
<td>0.5</td>
<td>12 (model simulation CF)</td>
</tr>
<tr>
<td>PRB coal</td>
<td>6,000</td>
<td>0.6</td>
<td>1.5</td>
<td>20</td>
<td>20</td>
<td>0.8</td>
<td>22</td>
<td>20</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>100</td>
<td>-</td>
<td>1.5</td>
<td>0.3</td>
<td>0.01</td>
<td>-</td>
<td>1.1</td>
<td>5</td>
</tr>
<tr>
<td>Peat</td>
<td>6,000</td>
<td>0.2</td>
<td>0.2</td>
<td>0.15</td>
<td>0.01</td>
<td>1</td>
<td>1.1</td>
<td>60</td>
</tr>
<tr>
<td>Coal boiler</td>
<td>1,500</td>
<td>-</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>15</td>
<td>15</td>
<td>46</td>
</tr>
<tr>
<td>CFB boiler</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Biomass and coal have fundamentally different fuel properties. Biomass (and low-rank coals) contains larger relative quantities of alkali and alkaline-earth elements (potassium, sodium, calcium, magnesium), phosphorous and chlorine than coal. As all the constituents of the biomass enter the boiler, several technical concerns arise. Higher fuel chlorine contents can lead to greater high-temperature corrosion in boilers. Accelerated fouling and slagging can occur when high potassium containing fuels are utilized.

Also, for the operation of SCR systems, there are technical challenges associated with co-combustion of biomass and coal in boilers designed for coal. The constituents of biomass have the potential to impair the SCR as the SCR catalysts are susceptible to ‘poisoning’ due to condensation of volatile inorganic species on the catalyst surface. Formation of sulphate- or phosphate-based deposits on the catalyst surface or reaction with the catalyst’s active species can significantly reduce catalyst activity, resulting in shorter lifetime. Biomass in the form of wastes may also contribute elements such as arsenic.

Figure 6 shows examples of ‘poisonous’ components in the ash of various fuels and the related SCR catalyst deactivation rates. Figure 7 shows the deactivation trend for various fuel types as activity relative to fresh catalyst activity versus operating time. The activity curves have been calculated.
using a deactivation model developed by Haldor Topsøe that considers ash deposition rate, pore plugging development and chemical impact on active sites.

For biomass firing the SCR catalyst deactivation rate is significantly higher. Typical deactivation rates for installation in a high-dust position are shown in Figure 8.

**SCR Deactivation Mechanisms**

**Alkali and alkaline-earth metals**

Alkali-metal aerosols formed during combustion of biomaterial are well known to be able to severely impact the performance of SCR catalysts. The sub-micron particles adhere to the surface of the catalyst and are readily transported to the active sites by surface diffusion. Spectroscopic studies suggest that the poisoning mechanism occurs via chemical bonding of the alkali metal to the crucial –V-OH sites, the so-called Brønsted-acid sites which also adsorb and “activate” the ammonia, forming –V-OM (M being K or Na) and thereby blocking the catalytic cycle (see Figure 9). Exposure to alkali-metal aerosols can at worst cause complete loss of activity of the catalyst within a few thousand hours of operation.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Deactivation rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% straw</td>
<td>50% per 1,000 hours</td>
</tr>
<tr>
<td>Wood:</td>
<td></td>
</tr>
<tr>
<td>- Pulverised-fuel boiler</td>
<td>60% per 10,000 hours</td>
</tr>
<tr>
<td>- CFB boiler</td>
<td>45% per 10,000 hours</td>
</tr>
<tr>
<td>- Grate-fired boiler</td>
<td>25% per 10,000 hours</td>
</tr>
<tr>
<td>Peat-fired boiler</td>
<td>30% per 10,000 hours</td>
</tr>
<tr>
<td>Coal-fired boiler</td>
<td>10% per 10,000 hours</td>
</tr>
<tr>
<td>Heavy fuel oil fired boiler</td>
<td>5% per 10,000 hours</td>
</tr>
<tr>
<td>Gas-fired boiler</td>
<td>2% per 10,000 hours</td>
</tr>
</tbody>
</table>

Figure 8: Typical SCR catalyst deactivation rates. Actual deactivation rate depends on specific fuel composition

Cf. Figure 8, exposure to flue gas from straw combustion, results in a very rapid catalyst deactivation. Studies have shown the flue gas to have a high mass concentration (up to more than 2 g/Nm³, depending on type of straw) of submicron particles of 0.15-0.30 µm size (number geo-metric mean diameter). The particles, which are mostly compact agglomerates, consist of almost pure potassium chloride and sulphate with minor amounts of sodium, phosphorous and calcium [2].

In a study by the CHEC group at the Technical University of Denmark in collaboration with Haldor Topsøe, full-length monolith catalyst samples were exposed to aerosols of pure potassium chloride and sulphate in a bench-scale reactor shown in Figure 10 [3]. An aerosol of the salt was then generated by injecting the solution of the salt into the flue gas close to the burner where the temperature was 1000–1150°C. Activities of the catalysts were measured in situ at 350°C typically 2–3 times per day. The catalyst activities as a function of exposure time to the flue gas are shown in Figure 11 on page 10.

Figure 9: Basically, the SCR reaction involves both acid-base and redox catalytic functions. The reaction is initiated by the adsorption of ammonia on Brønsted acid sites (V=O), followed by “activation” of ammonia via reaction with redox sites (V=O). This “activated” form of ammonia then reacts with gaseous or weakly adsorbed NO, producing N₂ and H₂O while releasing V=O. To complete the catalytic cycle, the V=O species is oxidized by either NO or O₂ to regenerate the original V=O species (from [1])

Figure 11 (left) on page 10 shows that after exposure to KCl aerosols at 350°C for 715 hours, the catalyst relative activity was about 69%, which corresponds to a deactivation of about 1.0% per day. There was also a fast decrease of the adsorption capacity for NH₃ on the catalyst. Then the system was cleaned, and without addition of KCl, the catalyst was tested for another 235 hours. During this period, the catalyst activity remained at about 69% and the amount of chemisorbed ammonia also levelled off. This confirms that catalyst deactivation stops when addition of KCl is ceased.

Figure 10: Experimental set-up for catalyst exposure tests (from [3])
The catalyst activity as a function of exposure time to \( \text{K}_2\text{SO}_4 \) is shown in Figure 11 (right). The relative activity decreased to 86% during the first 300 hours, corresponding to a deactivation rate of 1.1% per day. Then the relative activity kept decreasing at a rate of about 0.4% per day; i.e. only 40% of the deactivation rate observed for catalysts exposed to KCl at a similar aerosol load. This difference is ascribed to the difference in aerosol particle size since studies with direct impregnation of catalyst with KCl and \( \text{K}_2\text{SO}_4 \) showed these to have equal poisoning effect. Similar to the KCl-aerosol exposure test, the catalyst capacity for \( \text{NH}_3 \) chemisorption decreased faster than the relative activity. The active sites within the catalyst structure, although not participating in the SCR reaction, react with potassium resulting in a faster decrease in the catalyst capacity for \( \text{NH}_3 \) chemisorption than the observed activity which is impeded by the mass transfer resistances.

SEM-EDX analyses showed that potassium partly deposited on the catalyst outer wall but mainly penetrated into the catalyst wall and the \( \text{NH}_3 \) chemisorption measurements revealed that the Brønsted acid sites had reacted with potassium and were rendered inactive for \( \text{NH}_3 \) adsorption and subsequent reaction with NO. The conclusion was that chemical poisoning of active sites is the dominating deactivation mechanism but physical blocking of the surface may also contribute to the loss of activity.

Figure 11 (right) shows for comparison the deactivation trend of a catalyst exposed to the flue gas from a straw-fired power plant, Masnedø, in Denmark. The deactivation rate is approximately 50% per 1,000 hours, very similar to what was observed in the KCl-aerosol exposure test.

The conclusion is that chemical poisoning of active sites is the dominating deactivation mechanism, but fouling of the surface area may also contribute to the loss of activity in a practical application.
Fouling is a physical blockage of the catalyst pore system by aerosols or other sub-micron ash particles. Figure 13 on page 10 shows how a catalyst exposed to calcium-containing flyash from burning of sub-bituminous Powder River Basin (PRB) coal has developed a dense layer of calcium sulphate which prevents the NOx in the flue gas to reach the active sites in the interior of the catalyst.

**Phosphorous**
Organically bound phosphorous in fuel is released as gas-phase phosphorous during the combustion process. The phosphorous reacts in the gas phase to form polyphosphoric-acid aerosols which during cooling-off condenses in the catalyst pores. Reactions with e.g. calcium and alkali metals form sub-micron particles of pyro- or polyphosphates which deposit on the catalyst surface, causing pore blocking and surface masking with an ensuing loss of catalyst activity.

In some cases, severe deactivation has been reported. Up to 50% deactivation has been observed after 4,000 operation hours when 5% bone residue or sewage sludge has been cofired with bituminous coal [4]. These investigations reveal that phosphor seems to accumulate in the catalyst surface. Figure 14 shows accumulation of phosphorous in the outer 50-100 microns of the wall of a catalyst from a PRB-fired boiler. In this case phosphor penetrates deeper into the catalyst structure than the sub micron calcium-oxide aerosols, which demonstrates that the phosphorous compounds have a high mobility.

**Arsenic**
Arsenic (As) is a component present in most of the world’s coal and co-combustion of e.g. waste and sewage sludge can contribute to fuel arsenic content. When the coal is burned, arsenic is released in the furnace as a gaseous oxide, $\text{As}_2\text{O}_3$. $\text{As}_2\text{O}_3$ condenses in the porous catalyst structure and may then block the access to the catalytically active sites. Arsenic in gaseous form can be a main contributor to deactivation of catalysts in SCR DeNOx units on coal-fired boilers.

The susceptibility of the catalyst to poisoning from exposure to arsenic depends strongly on the pore structure of the catalyst. A highly porous catalyst with a diverse pore structure has a high resistance towards arsenic poisoning as the presence of macro-pores ensure access to active sites even when the micro-pores have become plugged by arsenic.
Examples of Experience from Biomass-fired Boilers

DONG Energy, Avedøre Power Station, Denmark

DONG Energy’s Avedøre Power Station Unit 2 is a combined heat and power plant, located in Copenhagen, Denmark. It was commissioned in 2001 and is one of the world’s most efficient power plants with an energy efficiency up to 94%.

Avedøre Unit 2 uses a multi-fuel concept developed by DONG Energy. The unit consists of an 800 MWth main boiler, a 100 MWth straw-fired boiler and 2x135 MWth gas turbines (see Figure 15 on page 11). The ultra-supercritical boiler was originally developed to burn natural gas and heavy fuel oil but was retrofitted in 2002 to fire up to 300,000 tonnes per year of pulverized wood pellets as an additional fuel. The furnace is designed for coal firing and has a tangential firing system with sixteen low-NOx burners. The unit is equipped with dust filter, SCR DeNOx and desulphurisation units.

It was experienced [6] that co-firing of wood pellets and fuel oil resulted in deposits in the convective part of the boiler and in the air-preheater. The deposits consisted of alkali from biomass and sulphur and vanadium from the fuel oil. Such deposits are corrosive and catalyses the formation of SO₃. This resulted in plugging of the air-preheater, in corrosion in the electrostatic precipitator and gas preheater as well as deactivation of the SCR.

An accelerated deactivation was expected as the wood’s relatively high content of potassium and chloride partly vaporizes during combustion, forming a fine aerosol of KCl and K₂SO₄ particles. A catalyst deactivation monitoring program was initiated. Experience during wood-oil co-firing showed that the catalyst deactivated rather fast as shown in Figure 16 on page 11.

It was decided to apply washing of the catalyst. The washing process was required to be fast as it would have to be done frequently due to the rapid deactivation. An in-situ washing process using available untreated water was developed to avoid time consuming removal and re-insertion of the catalyst and the outage was reduced to three days [7]. In the following years, washing was applied several times per year. However, after three years and consumption of 600,000 tonnes of wood pellets, the activity of the catalyst had been reduced by more than 50%. It was concluded that the washes had not been able to effectively counter deactivation of the catalyst and the catalyst was replaced in 2006 after five years of operation.

To reduce the impact of wood co-firing, injection of coal flyash into the furnace was initiated in 2006. The flyash, around six tonnes/hour, is injected through the four “over burner air ports,”
above the third burner level. This solved the above-mentioned problems with deposits, and the sulphuric acid aerosols in the stack were also reduced significantly [5]. Furthermore, the coal flyash to some degree captures wood-ash components that poisons the SCR catalyst such as alkali-metal aerosols, calcium and phosphorous and this has reduced the catalyst deactivation to around 15% per 10,000 hours compared to on average approximately 25% per 10,000 hours before flyash injection as shown in Figure 16 on page 11.

DONG Energy, Studstrup
Power Station, Denmark

DONG Energy’s Studstrup Power Station has two 350 MWe PC boilers – Units 3 and 4 – which were put into operation in 1984 and 1985. The units have since then been modernized regularly and in 2002, a conversion to commercial operation with co-combustion of ground straw was initiated. In each of the two units, four out of 24 burners were modified into ground-straw firing by using the core air pipes of the coal-burners for the air/straw suspension. Up to five tonnes/hour of straw can be fired through each burner. With up to 10% co-firing of straw, the flyash from the units can be utilized in the concrete industry.

Pilot Tests
As deactivation of high-dust SCR catalyst is one the critical issues of straw co-firing, slip-stream reactors were installed on Units 3 and 4. An exposure time of 5,000 hours was achieved in the period 2002-2003. On Unit 4, the average straw share was 11% on a weight basis and 7% on energy basis. Unit 3 was 100% coal-fired and the test reactor on this unit was used as a coal-reference for the deactivation tests.

Three different types of catalysts were investigated. Figure 17 on page 12 shows the relative specific activity as a function of exposure time for a Topsøe catalyst. There is no distinguishable difference in the deactivation trend from exposure to flue gas from coal-firing and from 7% straw co-firing. The observed deactivation was found to be caused by arsenic and formation of surface fouling layers.

Full Scale
In 2007, the two units were retrofitted with SCR DeNOx units with Topsøe DNX® catalyst. Shortly after start-up of the DeNOx plant on Unit 4, a rapid increase in pressure drop was observed and inspection of the reactor revealed severe plugging of the catalyst. Detailed investigation of the plugged catalyst showed that the seminal reason was large ash particles, up to 10 mm in length, primarily originating from the knots of the ground straw, cf. Figure 18 on page 12.

The catalyst was unloaded for washing on site. The cleaning was done by submersion of the catalyst modules into hot water, approximately 50°C, combined with aeration (a...
hot bubble bath”, see Figure 19 on page 12). The washing was by and large successful, however still leaving some 15-20% of the channels plugged. This could be ascribed to the fact that the flyash had partly hardened.

To avoid future incidents, fine-meshed screens were built into the flue gas duct at the exit of the boiler to filter out larger ash particles, see Figure 20 on page 13. The co-firing of straw on Unit 3 had been suspended until sufficient experience had been collected on Unit 4. After five months of satisfactory performance of Unit 4 with no increase in pressure drop across the catalyst, it was decided to equip Unit 3 with similar screens.

**Electrabel, Langerlo Power Station, Belgium**

Electrabel operates two identical 250 MWe coal-fired boilers at their Langerlo Power Station at Genk, Belgium. The two boilers were originally (in the mid 1970ies) constructed as oil-fired boilers but were converted to coal firing in 1985-86. As part of the so-called Langerlo 2000 Environmental Project the two units were retrofitted with flue-gas desulphurisation and SCR DeNOx systems in the late 1990ies.

Since 2003, biomass has been co-fired with the coal and the amount now constitutes 10-20% on mass basis. On average, the fuel blend is composed of 86% coal, 3% olive residue, 4% dried sewage sludge and 7% wood dust from hardboard production. Two thirds of the coal fired is low-alkali South African coal to limit the overall alkali content of the fuel blend. Figure 21 on page 13 shows the fuel and ash analyses. It is seen that the biomass contributes significant amount of phosphorous and alkali metals. Sewage sludge contains high sulphur levels and heavy metals can be in high concentrations. Sewage sludge also has much higher ash content than biomass and to avoid problems with slagging and to maintain ash quality, co-firing rate is generally limited.

At the annual stops, catalyst elements have been taken for chemical analysis and activity tests. Figure 22 shows the catalyst deactivation trend over a period of 55,000 operating hours. It is remarkable that the activity has stabilized at a level around 75% but this is in good accordance with a deactivation model developed at Haldor Topsøe. After an initial
deactivation period, the deactivation almost ceases. The arsenic content in the catalyst increased with operating time until a level of 0.25% by weight at which no further uptake occurred, corresponding to establishment of equilibrium with the flue gas concentration of gaseous arsenic. This level of arsenic has only a marginal influence on the activity of the high-porosity Topsøe catalyst.

Likewise, chemical analyses have shown only a very modest uptake of alkali metals, around 0.2% by weight sodium plus potassium, and less than 0.1% by weight phosphorous has been found. After the initial accumulation, these levels have been constant and do not differ from what can be observed in catalyst on 100% coal-fired units. A slight fouling of the catalyst surface with flyash seems to function as a ‘passivating’ layer in which the alkali metals have low mobility.

<table>
<thead>
<tr>
<th>Service hours</th>
<th>0</th>
<th>3,000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalytic activity</td>
<td>% relative to fresh</td>
<td>Air cleaned</td>
</tr>
<tr>
<td>Potassium, mg/kg</td>
<td>200</td>
<td>12,720</td>
</tr>
<tr>
<td>Sodium, mg/kg</td>
<td>500</td>
<td>1,760</td>
</tr>
<tr>
<td>Phosphorus, wt %</td>
<td>0.33</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Figure 25: Catalyst activity and chemical analysis of catalyst from Sierra Power, U.S.A.

Vattenfall, Combined Heat and Power, Sweden

Uppsala CHP is a 400 MW_e/125 MW_e combined heat and power plant located in Uppsala, Sweden. In 2005, the existing SNCR was retrofitted with an up-flow high-dust SCR unit equipped with Topsoe DNX® catalyst. The pulverized-fuel boiler is 100% biomass fired, burning peat and up to 30% wood dust. The plant is operating 2-3,000 hours per year during winter seasons when there is a demand for heat. Catalyst samples were tested in 2007 and 2008 after the first two seasons. The measured residual activity is shown in Figure 23 on page 14. It is seen that during 5,000 operating hours, the catalyst has lost 37% of its activity corresponding to an exponential deactivation rate of 60% per 10,000 hours. The peat and wood contain 1-2 wt% potassium and around 1 wt% phosphorous in the ash. Chemical analysis of catalyst samples showed only a modest uptake of soluble alkali metals (around 0.1 wt%) whereas 0.5-0.8 wt% iron and 0.2-0.4 wt% magnesium was found. The content of phosphorous had increased gradually from 0.26 wt% after 2,000 hours to 0.66 wt% after 5,000 hours. The phosphorous was found primarily in the outer 200 microns of the catalyst wall at a level up to 1 wt%, cf. Figure 24 on page 14.

Sierra Power, California, U.S.A.

Sierra Power Corporation in Terra Bella, California, U.S.A. operates a small 9 MW grate-fired boiler at a saw mill, fuelled by wood and demolition wood. The plant provides a disposal site for local green waste lumber manufacturers and pallet manufacturers. The plant started up in 1986. In 2008, the plant was retrofitted with SCR DeNOx located downstream a cyclone. A catalyst element was tested after 3,000 operating hours. The element was covered with fine ash and was mechanically cleaned with air before testing. The activity showed 93% activity relative to the fresh catalyst, corresponding to a deactivation rate of 22% per 10,000 hours. This is far lower than the deactivation rate of 60% per 10,000 hours experienced for the pulverized-fuel boiler at Uppsala CHP described above.

Chemical analysis revealed that the catalyst had accumulated more than 1% by weight soluble potassium and also minor amounts of sodium (Figure 25). It was therefore decided to test wash the catalyst in hot water to possibly remove the alkali-metal salts. The washing resulted in more than 60% reduction of the alkali metal content. Surprisingly, however, the catalyst activity dropped from 93% for the air-cleaned catalyst to 79% for the water-washed catalyst.

It is concluded that grate-firing of biomass does not evaporate alkali metals and release the salts as aerosols to the same degree as does pulverized-fuel or CFB firing and thus that this boiler type causes less SCR catalyst deactivation, cf. Figure 8 on page 9. Rather, the alkali-metal salts are found as larger particles with other ash constituents which may deposit on the outer surface of the catalyst. This explains the rather modest decrease in activity for the Sierra Power catalyst in spite of accumulation of more than 1 wt% potassium.
Washing of the catalyst results in dissolution of the salts and transport to the catalyst interior (see Figure 26 on page 15) and bonding to the vanadium active sites. The residual activity of 79% is in fair accordance with the potassium level of around 0.5%, cf. Figure 12 on page 10.

<table>
<thead>
<tr>
<th></th>
<th>Reference coal</th>
<th>Straw</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>47</td>
<td>30-60</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>31</td>
<td>0.4-1.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>6.3</td>
<td>0.3-1.0</td>
</tr>
<tr>
<td>CaO</td>
<td>4.2</td>
<td>7-14</td>
</tr>
<tr>
<td>MgO</td>
<td>1.7</td>
<td>1.7-2.3</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.1</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.9</td>
<td>0.4-1.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.0</td>
<td>14-29</td>
</tr>
</tbody>
</table>

Figure 27: Composition of coal and straw ashes (% by weight)

<table>
<thead>
<tr>
<th></th>
<th>Reference coal</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>LHV</td>
<td>22.8-25.2</td>
<td>15</td>
</tr>
<tr>
<td>Ash content</td>
<td>% by weight</td>
<td>6-18</td>
</tr>
<tr>
<td>K₂O in ash</td>
<td>% by weight</td>
<td>2.0</td>
</tr>
<tr>
<td>K₂O per MJ</td>
<td>g/MJ</td>
<td>0.046 – 0.137</td>
</tr>
</tbody>
</table>

Figure 28: Ash content of potassium on basis of fuel energy content

Vattenfall, Amager Power Station, Denmark

Vattenfall’s Amager Power Station in Copenhagen, Denmark has three units that are all producing electric power to the grid and district heating. Units 1 and 2 were originally identical and taken into service in 1970/1971. Unit 3 was taken into service in 1991. Since 2004, Unit 1 has been out of service and the turbine, the boiler and the environmental control systems are being replaced. Wet flue gas desulphurisation and SCR system including a regenerative gas-gas heat exchanger has been supplied by Alstom [9]. The upgraded Unit 1 will have a firing capacity of 350 MJ/s and be in service again in 2009.

The unit has been designed to be very flexible regarding fuel mix and can burn coal, pelleted straw, wood pellets, or coal-biomass in an arbitrary mixture. Fuel oil can be used as start-up or emergency fuel. The straw has high potassium and low ash contents with the potential of a rapid deactivation of the SCR catalyst, cf. Figure 8 on page 9. Comparing the composition of ashes from coal and from straw it is seen that the potassium content differ one order of magnitude (Figure 27), also on an energy basis (Figure 28).

To enable coal-straw co-firing in any desired ratio, the SCR DeNOx system was chosen as a tail-end installation, located downstream the ESP and wet FGD to minimize the amount of harmful ash constituents reaching the SCR reactor (Figure 29).

Conclusions

Direct co-firing of biomass with fossil fuel is a simple and widely applied technology for combining renewable and fossil energy utilization to reduce CO₂. However, the release of alkali-metal aerosols formed during combustion and phosphorous ash can cause rapid deactivation of SCR catalysts.

The experience from a number of installations of Topsøe’s DNX® catalyst shows that:

- Co-firing of up to 20% biomass can be done without causing extraordinary deactivation of the catalyst compared to 100% coal firing.
- For 100% biomass firing, the deactivation rate can be as high as 60% per 10,000 hours in a pulverized-fuel fired boiler. In a grate-fired boiler, the deactivation rate is lower, 22% per 10,000 hours, presumably because less alkali-metal aerosols are released.
- It is not possible to remove alkali metals bonded to the catalyst’s active sites by simple water washing. On the contrary, alkali-metal salts deposited in the outer surface of the catalyst may be transported to the interior, causing additional deactivation.
- The formation of large-particle ash (LPA) during combustion of biomass must be considered, necessitating installation of LPA screens.

Figure 29: General layout of Vattenfall Amager Power Station Unit 1 (from [9])
The use of SCR on 100% biomass-fired boilers may be done as a tail-end installation to minimize the amount of poisoning species entering the SCR.

Injection of coal flyash in a wood-fuel oil co-fired boiler can reduce problems with deposits in the convective part of the boiler and in the air-preheater and significantly reduce catalyst deactivation rate by capturing poisonous constituent of the wood ash.

REFERENCES

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For more information, contact Nathan White, Haldor Topsøe A/S, at tnw@topsoe.com

Additional links:

Commercial Experience of Ammonia-based Flue Gas Desulfurization Technology
By Amy P. Evans, Director of Technology, Marsulex Environmental Technologies Corporation

Technology Overview
A process for flue gas desulfurization, using ammonia as reagent (AS-FGD) that produces ammonium sulfate (AS) crop fertilizer, was developed by General Electric Environmental Services, Inc. in the early 1990’s and subsequently acquired by Marsulex Environmental Technologies (MET). The field pilot of this technology was successfully executed at Dakota Gasification Company’s (DGC) Synfuels Plant and led to a subsequent full-scale commercial installation of 350 MWe at that site. The commercial DGC FGD system has been in operation and producing saleable fertilizer under DGC DakSul 45® label for over 12 years. Subsequent to the DGC installation, additional commercial AS-FGD plants were installed and are operating today at an oil sand processing facility in Canada (315 MWe) and at a coal (2% sulfur) fired power boiler complex in the People’s Republic of China (2 X 200 MWe).

The AS-FGD process is similar to conventional open spray tower FGD in terms of operational reliability, SO2 scrubbing performance, and absorber equipment/configuration. Principal differences of the AS-FGD compared to conventional include system chemistry, reagent handling, dewatering, elimination or significant reduction of wastewater, elimination of CO2 generation within the absorber, and economic benefits from the sale of the fertilizer by-product.
Commercial Installation: Dakota Gasification Company (DGC)

The Great Plains Synfuels Plant is the only commercial-scale coal gasification plant in the United States that manufactures natural gas for sale. The Synfuels Plant is owned and operated by Dakota Gasification Company (DGC), a wholly owned subsidiary of Basin Electric Power Cooperative (BEPC), based in Bismarck, North Dakota.

The DGC plant began operating in 1984. DGC gasifies lignite (a low-rank form of coal) to produce valuable gases and liquids. The gas path portion of the plant is configured in two 50% trains, with a maximum total capacity of 170 million standard cubic feet per day (MMSCFD) of Synthetic Natural Gas (SNG). Including planned and unplanned outages and rate reductions, the average annual plant loading factor is typically about 90 to 92%. The product SNG is piped into the Northern Border pipeline, which runs to Ventura, Iowa, for distribution in the Midwestern and Eastern United States.

The Synfuels Plant also produces up to 1150 tons per day of anhydrous ammonia, approximately 150 MMSCFD of CO₂, and a variety of other byproducts. The ammonia is primarily sold into the regional agricultural market. The CO₂ is compressed and delivered through a 205-mile pipeline to EnCana Oil & Gas Partnership and Apache Canada Ltd. oil fields near Weyburn, Saskatchewan, Canada, for use in enhanced oil recovery. As an added environmental benefit, virtually all of the injected CO₂ is expected to remain sequestered in the depleted oil fields long after they have been abandoned.

The Synfuels Plant consumes about 18,500 tons of lignite daily. The coal is supplied by the nearby Freedom Mine. The mine is owned and operated by the Coteau Properties Company, a subsidiary of the North American Coal Corporation.

The AS-FGD located at DGC is shown in Figure 30. In the foreground is the storage dome which protects the marketed DakSul 45⁰ ammonium sulfate product from the weather. The beige-colored building to the left of the storage dome is the dewatering building. The beige-colored building to the left of this and in front of the gray concrete stack is the AS-FGD building. Surrounding the AS-FGD is the...
DGC gasification complex.

The process flow diagram for the DGC absorber arrangement is provided in Figure 31 in page 18. Not shown is the wet electrostatic precipitator which was added in 2002 to reduce particulate emissions and opacity.

The AS Flue Gas Desulfurization unit at the Great Plains Synfuels plant removes 93% of the SO$_2$ from the flue gas leaving the plant’s three Riley boilers producing a marketable Ammonium Sulfate fertilizer. The AS-FGD unit consists of a prescrubber and absorber where the SO$_2$ is recovered through Absorption, Neutralization, Oxidation, and Crystallization processes. After the AS-FGD, a Dewatering and Compaction unit further refines the ammonium sulfate crystals to the saleable product.

The prescrubber humidifies and cools the incoming flue gas (location 1) while crystallizing the ammonium sulfate. For later installations, the design was simplified by eliminating the prescrubber such that the absorber combines both crystallization and absorption functions. The SO$_2$ in the humidified flue gas is absorbed in the absorber forming bisulfite anions (HSO$_3^-$) in solution. The SO$_2$ free flue gas passes through an electrostatic precipitator (not shown in Figure 31 on page 18) to remove particulates before discharge to the atmosphere. The SO$_2$ now in solution is recovered as ammonium sulfate ((NH$_4$)$_2$SO$_4$).

Oxidation air is blown into the solution to oxidize the bisulfite anions to bisulfate anions (HSO$_4^-$). The dissociation of the bisulfite and bisulfate anions acidifies the absorber solution leaving sulfite (SO$_3^{2-}$) and sulfate (SO$_4^{2-}$) anions. Vaporized ammonia is mixed with the oxidation air to neutralize the absorber solution forming ammonium cations (NH$_4^+$). Part of the absorber solution is pumped back to the prescrubber, where the incoming flue gas evaporates some of the water causing the ammonium and sulfate ions to precipitate out as ammonium sulfate crystals. The scrubbed flue gas is routed to the atmosphere through a 400 foot tall chimney.

The prescrubber solution containing the ammonium sulfate crystals is pumped to the Dewatering and Compaction unit. Then the slurry is dewatered by hydroclones, centrifuges, and dried in the raw product dryer. The ammonium sulfate is dried in the final product dryer with a co-current flow of air. After drying, the product is cooled in the cooler with a countercurrent flow of air.

A 50,000-ton capacity dome stores the fertilizer on-site until it is shipped by rail or truck.

The original design parameters for the DGC AS-FGD are provided in Figure 32 above.

Pertinent performance guarantees and comparative tested performance values for DGC are provided in Figure 33 below.

**Fertilizer Product**
The AS-FGD can be designed to meet the requirements outlined in Figure 34 on page 20. There are several influences
on the quality of the AS fertilizer product as it relates to the characteristics in Figure 34. For appearance, the color of the crystal is naturally white, but can be influenced by impurities such as flyash and unburned carbon particles that enter the AS-FGD system in the flue gas. The more efficient the particulate control device upstream of the AS-FGD, the fewer such impurities enter the AS-FGD and discolor the product. Other sources of impurities can be in the makeup water to the system and from corrosion products within the system. A quality source of clean makeup water should be used for the AS-FGD system. Corrosion is mitigated by using the proper corrosion-resistant materials of construction.

The nitrogen assay reflects on the purity of the AS product. The lower the quantity of impurities that enter the system via the makeup water and flue gas, the higher the N assay. If needed, a filter/purge stream can be designed into the system to remove impurities and improve the AS product purity. The desired moisture content of the AS product can be achieved by a properly designed drying and cooling system and by protecting the AS product from the weather.

**AS-FGD System Description**

The AS-FGD system design at DGC uses proven wet flue gas desulfurization components with an open spray tower to achieve the same high reliability/availability as the more...
traditional limestone-based FGD. The ammonium sulfate fertilizer is a valuable by-product which is salable. Additionally, the process greatly minimizes, if not eliminates, wastewater discharge.

The AS-FGD absorber system is similar in some regards to the limestone/gypsum FGD process, as illustrated in Figure 35 on page 20, as many components are common between these two processes. Similar components include the absorber vessel, recycle pumps, and spray nozzles. The ancillary systems, which differ significantly, are reagent handling and dewatering. Limestone-based FGD usually requires a reagent slurry preparation system, consisting of a limestone storage silo, weigh feeder, wet ball mill with all required accessory equipment, cyclone classifier, ball mill product sump with agitator, ball mill product pumps, limestone slurry tank and limestone slurry feed pumps. In comparison, the AS-FGD ammonia feed system essentially consists of (an) ammonia storage tank(s), ammonia feed pumps and a vaporizer (in the event of anhydrous ammonia supply). The ammonia reagent used for the AS-FGD process can be either anhydrous (<0.1-wt% moisture) or in the aqueous form. The AS-FGD process generally employs centrifuges for dewatering, in lieu of belt or rotary drum filters, based on their ability to produce a low moisture cake and smaller plot area requirement. In some applications, addition of an external crystallization system may be required.

One benefit of the AS scrubbing system is no or minimal liquid purge is discharged to waste water treatment. The chlorides in the process are controlled by directing a small purge water stream to the ammonium sulfate product drier, which results in the recovery of more product and serves to strengthen the product.

A basic process comparison of the AS-FGD and conventional limestone/gypsum FGD is shown as Figure 35 on page 20.

**Economics**
The favorable economics of the AS-FGD technology resides in the ability of the user to fire potentially lower cost, higher sulfur coals and/or other fuels while generating a high-value ammonium sulfate fertilizer product. The economic model of the AS-FGD favors higher sulfur fuels because the sulfur serves as a feedstock in the AS production.

The process chemistry is based on the following basic reactions:

\[
\begin{align*}
SO_2 + 2NH_3 + H_2O & \rightarrow (NH_4)_2SO_3 \\
(NH_4)_2SO_3 + \frac{1}{2}O_2 & \rightarrow (NH_4)_2SO_4
\end{align*}
\]

One mass unit of ammonia is consumed for every four mass units of ammonium sulfate fertilizer generated. Market prices for bulk ammonium sulfate and ammonia generally track with each other (Figure 36), with the price of natural gas being one factor common to both. The approximate 4:1 ratio of AS produced per unit of ammonia, applied to the market prices for both commodities, and the amount of sulfur (as SO\(_2\)) absorbed generally determines the gross value of the AS produced over time. At the 4:1 ratio, ammonium sulfate production has historically maintained a substantial premium over the cost of purchased ammonia reagent resulting in a revenue stream for the owner.

**Economic Evaluation Factors**
The gross differential between by-product fertilizer value and cost of ammonia reagent forms the basis for evaluation of the application of AS-FGD. If one assumes 100 tons AS/year are produced per equivalent megawatt of boiler size, per % sulfur in the fuel, a 600 MW plant at 85% generation would produce 50,000 tons of AS per % fuel sulfur in a year. Given representative market prices of $450/ton for ammonia and $200/ton for AS, the production ratio (1 part ammonia > 4 parts AS) would relate to a gross positive differential of $87.50 US/ton of AS produced. Additional economic factors include: availability and the site-specific delivered price of ammonia; infrastructure and cost to receive, handle and store the ammonia reagent; ability to fire higher sulfur fuels; savings in FGD wastewater handling/treatment; and the regional marketplace sell price for the AS produced. Fertilizer production and marketing can be handled by the owner or outsourced to others.

**Ammonia as a FGD Reagent**
Ammonia, being a highly reactive reagent, is very effective in the scrubbing of SO\(_2\) from flue gas. A performance
advantage of ammonia, as compared to limestone, is that due to ammonia’s water soluble chemistry, scrubbing to a set efficiency while firing higher sulfur fuels would require a lower L/G. This relationship over a range of fuel % sulfur content for a constant liquid-to-gas ratio (L/G) is illustrated in Figure 37.

![Figure 37: Impact of Fuel %S on SO₂ Removal for Ammonia versus Limestone](image)

**Process Description**

After particulate removal, hot flue gas flows to the AS-FGD absorber, where it is counter-currently contacted with saturated ammonium sulfate slurry. The flue gas is cooled close to adiabatic saturation temperature and ammonium sulfate is crystallized by the evaporation of water from the slurry. Thus, the absorber acts as an evaporator-crystallizer in which the heat of the flue gas is used for the production of ammonium sulfate crystals. The absorber slurry is recirculated from the reaction tank in the bottom of the absorber vessel to individual spray levels by dedicated recycle pumps. SO₂ is removed from the flue gas by contact with absorber slurry recirculated through these spray levels. The cleaned gas passes through a two-stage horizontal mist eliminator for removal of droplets and exits through a stack to atmosphere.

As SO₂ is absorbed from the flue gas, the pH of the process liquor will tend to decrease. Ammonia (anhydrous, wet-gaseous or aqueous) is introduced to maintain the pH of the absorber slurry at the desired value. The ammonia reacts with absorbed SO₂, oxygen and water to form ammonium sulfate. By properly applying proprietary and patented design aspects and maintaining proper absorber operation, ammonia slip in the absorber outlet flue gas will be maintained at less than 10 ppmv.

The liquid level in the absorber tank controls the automatic addition of make-up water. The make-up water is added via washing the horizontal mist eliminator with fresh water. In this manner, the mist eliminator is regularly washed and deposits are returned to the process.

A portion of the absorber slurry containing ammonium sulfate crystals is automatically withdrawn for dewatering and separation of the AS product. This slurry bleed is first dewatered in a hydroclone and then in a centrifuge to produce ammonium sulfate cake with low moisture. All liquor recovered from the dewatering process is returned to the absorber. The centrifuge cake is dried and cooled to produce a sugar-like crystal ammonium sulfate product that can be applied directly as a fertilizer. Alternately, depending on the regional or national fertilizer market, the centrifuge cake can be processed in a drying and compaction system that generates a hard granular AS product. The crystal and granular products generated from the AS-FGD process are shown in Figure 38. Granular AS can be blended with other fertilizers to achieve a custom-designed mixture which is optimal for the crops to be grown. In either case, the dried AS product is easily handled, transported and stored in weather-protected storage facilities.

![Figure 38: Examples of Granular (Left) and Standard Crystal Ammonium Sulfate Product](image)

**Chemistry**

Similar to the chemistry using a limestone reagent, the major steps of the AS-FGD chemistry are absorption and oxidation. As previously mentioned, the basic chemical reactions which occur in the AS absorber are as follows:

\[
\begin{align*}
\text{SO}_2 + 2\text{NH}_3 + \text{H}_2\text{O} & \leftrightarrow (\text{NH}_4)_2\text{SO}_3 \\
(\text{NH}_4)_2\text{SO}_3 + \frac{1}{2}\text{O}_2 & \leftrightarrow (\text{NH}_4)_2\text{SO}_4
\end{align*}
\]
The actual chemical mechanism is more complex and involves sulfite-bisulfite and sulfate-bisulfate reactions:

\[ \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SO}_3 \] (3)
\[ \text{H}_2\text{SO}_3 + (\text{NH}_4)\text{SO}_4 \rightleftharpoons \text{NH}_4\text{HSO}_4 + \text{NH}_4\text{HSO}_3 \] (4)
\[ \text{H}_2\text{SO}_3 + (\text{NH}_4)\text{SO}_3 \rightleftharpoons 2\text{NH}_4\text{HSO}_3 \] (5)

SO\(_2\) in the flue gas first comes into contact with spray droplets of aqueous slurry. In reaction (3), SO\(_2\) from the flue gas dissolves in the water to form sulfurous acid. In reactions (4) and (5), the sulfurous acid reacts further with dissolved ammonium sulfate and sulfite salts in the solution to form intermediate acidic species. The formation of the sulfurous acid, including the acidic species, lowers the pH of the slurry.

\[ \text{H}_2\text{SO}_3 + \text{NH}_3 \rightleftharpoons \text{NH}_4\text{HSO}_3 \] (6)
\[ \text{NH}_4\text{HSO}_3 + \text{NH}_3 \rightleftharpoons (\text{NH}_4)_2\text{SO}_3 \] (7)
\[ \text{NH}_4\text{HSO}_4 + \text{NH}_3 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 \] (8)

The ammonia added to the process in reactions (6) to (8) neutralizes the acidic species to ammonium sulfite and ammonium sulfate. This neutralization serves to restore the pH to its desired value.

\[ (\text{NH}_4)_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons (\text{NH}_4)_2\text{SO}_4 \] (9)

Oxidation air injected into the absorber tank in reaction (9) oxidizes the remaining ammonium sulfite to ammonium sulfate.

\[ (\text{NH}_4)_2\text{SO}_4 \text{ (aqueous)} + \text{heat of evaporation} \rightarrow (\text{NH}_4)_2\text{SO}_4 \text{ (solid)} \] (10)

The resulting ammonium sulfate solution is saturated and ammonium sulfate crystals, in reaction (10), precipitate from the solution due to chemical reaction and water evaporation into the flue gas. The heat of evaporation is supplied by the residual heat in the flue gas.

Conclusions
The AS-FGD commercial plant at DGC has been in successful operation at DGC for well over a decade. Although the absorber portion is similar to conventional open spray tower FGDs in terms of equipment and operability, the AS-FGD differs in terms of chemistry, reagent preparation, dewatering and the site-specific economic model.

The Author wishes to thank Claudia Miller and Steve Pouliot of DGC for their contributions to the paper cited as Reference 3 from which much of the DGC-specific related materials were drawn from for this article.

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Additional links: