Are Ambient SO$_2$ Levels a Valid Indicator of Projected Acid Gas Filter Life?

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ABSTRACT

The requirement to extend existing lithography equipment working levels and life has required manufacturers and end users to extend their filtration requirements beyond airborne base gases. Due to the effect acid gases can have on optics, masks, reticles, steppers, wafers, and metrology tools, they have become a more important molecular airborne contaminate to remove from inside a fab. SO$_2$ is known to be especially problematic within the cleanroom and exposure tool environment. However, a host of other molecular acids can also be found, some of which are present at considerably higher concentrations; the most prevalent of which are oxides of nitrogen, NO$_x$. Although the removal of NO$_x$ contaminants is currently not considered to be as critical as SO$_2$, its presence can have a significant impact on acid gas sensitive applications. Several of these applications are addressed in this work in order to point out that NO$_x$ contaminants do pose a problem, especially when considering the performance of acid gas chemical filters. More importantly, this preliminary work puts forth the recommendation that in addition to SO$_2$, the concentration of other acid gases should be taken into account when acid gas chemical filter efficiency and life estimates are being made.

Keywords: NO$_x$, oxides of nitrogen, SO$_2$, sulfur dioxide, acid gas filtration, acid gas removal, chemical filtration, Fuel Cells, DAPS, dilution air purification systems, hard disk drives, cleanrooms, exposure tools, contamination control

1. INTRODUCTION

Oxides of nitrogen, NO$_x$, in ambient air are generally a result of emissions from the high temperature combustion processes of automobiles and power plants. NO$_x$ is a generic name given to a group of highly reactive gases that contain nitrogen and oxygen; the major constituents being nitric oxide, NO, and nitrogen dioxide, NO$_2$. Sulfur dioxide, SO$_2$, is a major component of the family of oxides of sulfur, SO$_x$. These gases are primarily emitted when fuel that contains sulfur (e.g. coal and oil) is burned. Fuel combustion accounts for the largest portion of the total SO$_2$ emissions.$^1$
The EPA reports a decreasing trend for national averages of ambient air levels of airborne acidic gases such as NOx and SOx.\textsuperscript{1} In 2002 the national averages were approximately 20 ppb and 6 ppb, respectively. Certain areas of the country with elevated traffic levels, power plants, and refineries, can experience significantly higher levels. Although NOx and SOx levels of 1-5 ppm may seem exorbitantly high, these levels are not uncommon in rush hour traffic. These exceptionally high levels may also be found in many of the major industrial cities around the world. With this in mind, operations that are sensitive to acidic contaminants, such as semiconductor processing and tools, fuel cells, vehicle emissions testing, and hard disk drives (HDD’s), are still required to function within these highly contaminated environments.

Within semiconductor processing fabs, besides SOx and NOx, the molecular acids HCl, H2S, HBr, HF, H3PO4, H2SO4, HNO3, HNO2, and acetic acid are commonly found.\textsuperscript{2-4} Depending on the processes conducted within a given fab, these compounds may arise from either operations within the fab or from the ambient air itself. Typical levels of NOx, SOx, and HCl found within the cleanroom and in ambient air are given in Table 1.\textsuperscript{1, 5-7}

\textbf{Table 1: Acid gas concentrations in typical fab/cleanrooms and ambient air, ppbV.}\textsuperscript{a}

<table>
<thead>
<tr>
<th>Fab/Cleanroom</th>
<th>SO\textsubscript{2}</th>
<th>NO\textsubscript{x}\textsuperscript{b}</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1\textsuperscript{c}</td>
<td>0.04</td>
<td>18.80</td>
<td>0.10</td>
</tr>
<tr>
<td>Site 2\textsuperscript{c}</td>
<td>0.04</td>
<td>5.16</td>
<td>0.03</td>
</tr>
<tr>
<td>Site 3\textsuperscript{c}</td>
<td>0.13</td>
<td>4.31</td>
<td>0.10</td>
</tr>
<tr>
<td>Site 4\textsuperscript{d}</td>
<td>0.01-0.13</td>
<td>0.73-7.30</td>
<td>0.07-1.04</td>
</tr>
<tr>
<td>Site 5\textsuperscript{e}</td>
<td>0.6</td>
<td>27</td>
<td>4.7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Ambient Air</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typical Levels\textsuperscript{f}</td>
</tr>
<tr>
<td>EPA 2002\textsuperscript{g}</td>
</tr>
<tr>
<td>Federal Standards\textsuperscript{h}</td>
</tr>
</tbody>
</table>

\textsuperscript{a.} Calculated from anion results.
\textsuperscript{b.} Includes both NO\textsubscript{2} and NO\textsubscript{3} data.
\textsuperscript{c.} Reference 5.
\textsuperscript{d.} Reference 6.
\textsuperscript{e.} This work, see experimental section for method.
\textsuperscript{f.} Reference 7. Reference 1.
\textsuperscript{g.} http://www.arb.ca.gov.
\textsuperscript{h.} NA = not available.

Indeed, NOx is the most prevalent acid gas inside and outside the fab. In support of this, more than 90% of the semiconductor cleanrooms in the USA have been reported to have SO\textsubscript{2} (SO\textsubscript{4}\textsuperscript{2-}) levels of less than 0.1 ppb, whereas only 20% are at this level for NOx (NO\textsubscript{2} and NO\textsubscript{3}).\textsuperscript{2} A large number of cleanrooms are reported to have NOx levels that exceed 1.0 ppb.

In the presence of moisture and UV light, airborne acid gases can generate reactive species that form aerosols, initiate particle nucleation with other contaminants, deposit on surfaces, or react with metals.\textsuperscript{4, 8-15} Within the fab, NOx, SO\textsubscript{x}, and HCl have recently become of a greater concern for 193nm and 157nm exposure tool lenses and reticles. These contaminants are known to form particles and films upon exposure to optics surfaces and basic contaminants such as ammonia; several examples, being ammonia combining with a gas phase chloride species to form the
ammonium chloride salt, and ammonia and SO$_2$ reacting to form ammonium sulfate which has been
found on optics surfaces.$^8$ Although not yet identified as a problem in the clean room or exposure
tools, ammonia is known to react with NO$_x$ emissions when presented with the right conditions to
form ammonium nitrate particulates in the ambient air.$^{14}$

As a result, the desire to extend the working range and life of existing lithography equipment has
required tool manufacturers and end users to extend the focus of their filtration efforts to include
acid gases. This is also true for the manufacturers and end-users of fuel cells, hard disk drives, and
vehicle emissions testing that involve dilution air purification systems (DAPS). The removal of
acidic gases can generally be accomplished in any of these applications using three mechanisms: 1)
physical adsorption; 2) ion-exchange; and 3) chemical adsorption. Chemical adsorption, using
impregnated adsorbents, has been the filtration method of choice for removing acidic gases.
Although often questioned, these materials can generally be applied for the removal of many of the
compounds that make up this class of contaminants.

In applications that require the removal of airborne acid gases, it has been common practice to focus
on a chemical filter’s efficiency and life for the removal of SO$_2$ alone. However, as indicated above,
these applications typically experience acid gases other than SO$_2$ and several that can be present at
concentrations greater than that of SO$_2$. Therefore, by focusing solely on SO$_2$, the true acid gas
ambient concentration is usually significantly underestimated and the life of an acid gas filter
considerably overestimated.

It is the objective of this work to show that impregnated adsorbents used in acid gas filters can
efficiently remove NO$_x$ and SO$_2$ from contaminated airstreams and purge gases. Consequently, they
can effectively protect applications that are sensitive to acid gases. More importantly, it will also be
shown that acid gases which are present at much higher concentrations than SO$_2$, such as NO$_x$,
impact the capacity of an acid gas filter and must be taken into account when estimating, or
evaluating filter efficiency and life.

2. EXPERIMENTAL

2.1. Fuel Cells:
Fuel cell testing was conducted at Los Alamos National Laboratory (LANL) with and without a
Donaldson Co., Inc. (DCI) Fuel Cell Contamination Control (FC$_3$) filtration unit. A Proton
Exchange Membrane Fuel Cell (PEMFC) was exposed to 1 ppm SO$_2$ and 5 ppm NO$_2$ at the cathode
inlet in two separate experiments. After a specified length of time the exposure to the acid gas
contaminant was turned off. The performance of the PEMFC was evaluated by monitoring the cell
current output throughout the experiment.

2.2. Dilution Air Purification System (DAPS):
The performance of a Donaldson Co., Inc DAPS unit was evaluated at the California Air Resources
Board (CARB). Part of this study was to evaluate the DAPS ability to reduce NO$_x$ and SO$_x$ in the
ambient air to a level that allowed for testing of ultra-low emissions vehicles (ULEV) and super
ultra-low emissions vehicles (SULEV). Ambient air was pulled through the DAPS unit and passed
on to a series of analyzers that include a NO$_x$ analyzer.
2.3. Hard Disk Drive (HDD’s):
Impregnated adsorbent chemical filters from two manufacturers were placed in two separate, but similar HDD’s. The HDD’s were operated within a laboratory environment for an unspecified amount of time. After operation, the chemical filters were exposed to the internal drive and laboratory environment under non-operating conditions for several months. The exposed filters were removed from the HDD’s and analyzed using aqueous extraction followed by ion chromatography (IC). Several unexposed chemical filters were also tested and served as blanks.

A known weight of the impregnated adsorbent was removed from the chemical filter and placed into a clean polypropylene vial. A known volume of DI water was added to the container and agitated for one hour. A portion of this extract was removed and the anions were quantitated using ion chromatography.

2.4. Fabs/Cleanrooms/Tools:
Air sampling for airborne acids, bases, and organics was performed within a cleanroom. Air samples were pulled through adsorbent tubes specifically designed for this purpose. Sampling was performed for a minimum of 24 hours. The acid gas adsorbent tubes were extracted with known volumes of water. The aqueous extracts were analyzed using ion chromatography for anions. The results for the acid gas analysis are given in Table 1 above. We note these results match the measurements made by the real-time monitors in the test locations very well.

Used acid gas filters are generally returned to DCI’s analytical laboratories for characterization and quantitation of the adsorbed acid, base, and organic contaminants. The acid gases adsorbed onto the acid gas adsorbent are identified and quantitated using ion chromatography for anions. Returned filters are also evaluated for their remaining life for each of these contaminant classes. The remaining life is compared against initial filter life estimates and known cleanroom and tool upstream contaminant concentrations. Remaining life breakthrough tests are conducted using a contaminant class surrogate at elevated concentrations. In the case of acid gases, the test surrogate is SO₂. The remaining life for >99% efficiency is calculated from the contaminant concentration, flow rate, and breakthrough curve.

For this study, we have evaluated six returned acid gas removal filters. These have been returned from a variety of field locations from around the world as is listed in the following table.

Table 2: Returned filter location and length of time in use.

<table>
<thead>
<tr>
<th>Location</th>
<th>Filter Type</th>
<th>In Use (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site 1</td>
<td>Exposure Tool</td>
<td>14</td>
</tr>
<tr>
<td>Site 2</td>
<td>Exposure Tool</td>
<td>4</td>
</tr>
<tr>
<td>Site 3</td>
<td>Exposure Tool</td>
<td>4</td>
</tr>
<tr>
<td>Site 4</td>
<td>Exposure Tool</td>
<td>5</td>
</tr>
<tr>
<td>Site 5</td>
<td>Wafer/Reticle Stage-POUa</td>
<td>6</td>
</tr>
<tr>
<td>Site 6</td>
<td>Wafer/Reticle Stage-POUa</td>
<td>14</td>
</tr>
<tr>
<td>Site 7</td>
<td>Wafer/Reticle Stage-POUa</td>
<td>15</td>
</tr>
</tbody>
</table>

a. Point of use filter.
Core samples were taken from each of the returned filters. Both IC analysis for anions and remaining life analyses were performed on each sample.

2.5. Filter Performance:
In order to show the effect multiple acid gases can have on the efficiency and life of acid gas adsorbents we have performed three separate breakthrough tests: 1) 50 ppm of SO\textsubscript{2} non-impregnated activated carbon (NIC); 2) 50 ppm SO\textsubscript{2} on impregnated activated carbon (AGR); and 3) 50 ppm NO\textsubscript{2} on impregnated activated carbon (AGR). See reference 16 for a general block diagram of the breakthrough test bench. Contaminants were generated from certified gas standards delivered into the test airstream through mass flow controllers (Aalborg; Orangeburg, NY). The humidity was controlled at 50% RH using a Flow-Temperature-Humidity Controller (Miler-Nelson Research, Inc.; Monterey, CA); Model HCS-401. The temperature and relative humidity of the airstream upstream and downstream of the adsorbent bed were measured using calibrated temperature and humidity sensors (Vaisala; Woburn, MA; Model HMP233). The temperature of the adsorbent bed was controlled at 25ºC using a water-jacketed sample holder and a water bath. Detection of the upstream and downstream SO\textsubscript{2} concentration was achieved using an FTIR detector (Thermo Environmental Instruments; Franklin, MA; Miran Sapphire). The upstream and downstream NO\textsubscript{x} concentration was measured using a Chemiluminescence Detector (Rosemount Analytical; Orrville, OH; 951 NO/NO\textsubscript{x} Analyzer).

3. RESULTS AND DISCUSSION

The ion concentrations given in Table 1 are quite high and since they primarily result from acidic vapors they pose a problem for many sensitive industrial and manufacturing applications. As mentioned above, in the presence of water vapor, SO\textsubscript{2} and NO\textsubscript{x} can lead to the formation of H\textsubscript{2}SO\textsubscript{4} and HNO\textsubscript{3}, respectively. In aqueous solution these acidic gases generate SO\textsubscript{4}\textsuperscript{2-}, NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}, which are detected with excellent sensitivity using ion chromatography (IC) methods. In order to obtain the actual concentration of NO\textsubscript{x} gases in these environments the concentrations of NO\textsubscript{2} and NO\textsubscript{3} must be added together. In nearly all of the ambient air and clean room cases where their concentrations are reported, the concentration of NO\textsubscript{x} generally exceeds that of SO\textsubscript{2}.

In the case studies that follow, we will show that although many sensitive industrial and manufacturing processes are exposed to both of these acidic contaminants, and a host of others, chemical filters are available that are effective at removing them. We will also address the issue of using SO\textsubscript{2} performance alone as a method of rating chemical filter performance and life for the removal of acidic gases. This practice is fraught with problems for the customer and filter supplier due to the prevalence of several problematic acidic gases and the range of chemical filters that are effective at removing them. The results presented here will show that filter performance and life estimates using SO\textsubscript{2} results alone can be misleading and misrepresent the actual quality and performance of a chemical filter.

3.1. Fuel Cells:
It is understood that fuel cells will some day soon power many of our every day conveniences, such as automobiles, buses, cellular phones, and eventually our homes. It was once thought that these power-generating devices did not require chemical filtration. However, Los Alamos Laboratories (LANL), in collaboration with Donaldson Co., Inc. have proven that many common airborne
Contaminants can adversely affect their performance, and, in some cases, quickly kill a proton exchange membrane (PEM) fuel cell.

Figures 1 and 2 show the impact that two ambient air acid gas contaminants, SO₂ and NO₂, which are present at typical ambient air concentrations, can have on the performance of a PEM fuel cell. Both SO₂ and NO₂ significantly impact the performance of a PEM fuel cell. In the case of SO₂, irreversible damage has been done to the fuel cell. With NO₂, fuel cell performance may recover; however, this recovery requires a clean air purge and full recovery depends on the length of exposure time to NO₂.

From these results, one can envision every time they enter a major city, or pass a refinery, in their “filterless” fuel cell powered car, it slows down, or even worse, it completely stops. The type, and concentration, of the airborne contaminants will dictate whether or not this will require major repairs or an extended clean air purge. However, since an acid gas filter can effectively remove both SO₂ and NO₂, it can successfully protect the PEM fuel cell against these contaminants, thereby alleviating these concerns. It can also be imagined that an AGR filter that only takes into account SO₂, or NOₓ, concentrations may end up under-performing or being under-sized.

This exact scenario was essentially duplicated at the research facility of a major fuel cell manufacturer. Degradation in fuel cell performance was observed every morning and evening at rush hour. This was attributed to elevated levels of SOₓ from vehicle exhaust. Chemical filters provided by Donaldson Co. Inc. were integrated and successfully alleviated the problem. However, an estimate of the expected filter life for the chemical filter design based solely on the SO₂ concentration was significantly over predicted. In other words, the AGR chemical filter solved the problem, but didn’t last as long as would have been predicted based on the SO₂ concentration alone. It was later confirmed that SOₓ and NOₓ were both actually present in significant concentrations. A modified chemical filter design resulted in a far superior filter that is still in use today, more than one year later.

3.2. Dilution Air Purification Systems (DAPS):

The measurement and evaluation of vehicle emissions is being impacted by the production of ultra-low emission vehicles (ULEV) and super ultra-low emissions vehicles (SULEV). The contaminants emitted from these vehicles can be significantly lower than that of the ambient air in the test facility. Since the test systems typically require dilution air in order to prevent condensation, the air is typically taken from the ambient air and mixed with the vehicle exhaust. Purified air must be provided for an accurate background for the analyzers. As a result the removal of acidic and VOC contaminants is required.

NOₓ and SOₓ levels in the ambient air can range from <0.1 ppm to upwards of 5.0 ppm. In emissions testing of spark-ignition engines SO₂ levels are not critical; however, they are a problem for the testing of emissions from diesel engines. For accurate emissions testing, the concentration level for both of these contaminants should be less than 0.1 ppm.

At a CARB test facility, a DCI, DAPS prototype is under evaluation. Although this system is proving to be quite effective at establishing the required levels, the presence of both NOₓ and SO₂ in the ambient air influences the performance of the acid gas filter and the filter life estimate. The current tests are being run on spark-ignition engines; therefore, SOₓ levels are not being monitored.
However, our experience is that the DAPS test system will meet the desired SOx removal specifications for both spark-ignition and diesel powered engines. At CARB, NOx levels are being monitored upstream and downstream of the DAPS unit; however, the performance against the major components of NOx is not differentiated. Initial testing indicates the acid gas removal media is approximately 60% efficient against NOx. It is our experience that NO is not efficiently adsorbed on the filter, but NO2 is readily adsorbed with excellent efficiency. Since, the major constituent of ambient air is NO2, the acid gas removal media is removing the majority of the NO2 and the majority of the downstream contaminant that is being detected is NO.

3.3. Hard Disk Drives (HDD’s):

Hard disk drives are expected to perform in environments that can contain airborne molecular contaminants at relatively high concentrations. In order to function in these environments and protect the head-disk interface from corrosion from acid gases and stiction caused by organics, integrated chemical filters are generally used. These filters are expected to perform three functions for the life of the HDD: 1) clean-up the internal drive environment; 2) protect the internal drive environment from the external environment; and 3) provide moderate control of the drive’s internal humidity.17

Since HDD’s must function in a broad range of environments such as offices, the aggressive atmosphere of a factory, or in a laboratory, the chemical filter can be exposed to NOx, SO2, and other acid gases, at a total concentration that approaches 1.0 ppm.17-19 Although HDD and chemical filter manufacturers are one of the few industries that evaluate their products with a series of acid gases, filter designs are still usually based on the performance against SO2.

The following table presents IC results for used and unused HDD chemical filters. The anion levels have been converted to the respective acid gas. We have assumed that the quantity of each anion found on the used filter that is in excess of that found on the blanks can be attributed to adsorption of acid gases.

Table 3: Comparison of acid gas exposure in a hard disk drive for two different acid gas chemical filters.a, b

<table>
<thead>
<tr>
<th>Filter Type</th>
<th>SO2</th>
<th>NOx c</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Filter A</td>
<td>98</td>
<td>131</td>
<td>ND</td>
</tr>
<tr>
<td>Filter B</td>
<td>10</td>
<td>178</td>
<td>2</td>
</tr>
</tbody>
</table>

a. Values are reported in µg/gram of adsorbent. b. Acid gas values are calculated from the measured anion level assuming all anions in excess of the blank can be attributed to acid gas adsorption. c. Sum of nitrite and nitrate levels. ND = level found on used filter was similar to the blank.

On both acid gas filters, the amount of NOx found exceeds that of SO2. These higher levels of NOx on the AGR filters suggest the concentration of NOx in the HDD environment is significantly higher than that of SO2 and HCl. Therefore, when considering the life of HDD AGR chemical filters NOx should be taken into account since it influences the filter’s active capacity.
3.4. Fabs/Cleanrooms/Tools:
It has been reported that cleanroom air in fabs is not as clean as set forth by roadmap limits.\textsuperscript{2} Of the molecular acids found in the cleanroom air, NO\textsubscript{x} compounds are found to be the most prevalent, but have been determined to be less detrimental to semiconductor processing than SO\textsubscript{x} compounds. This high level of NO\textsubscript{x} in the cleanroom has been attributed to chemical filters supposedly being less effective at removing NO\textsubscript{x} than SO\textsubscript{2}.\textsuperscript{2} Although, this is known to be true for NO\textsubscript{x}, it is not the case for NO\textsubscript{2}.\textsuperscript{19} We note, that since NO is converted into NO\textsubscript{2} in the atmosphere through photochemical oxidation it is more important for a chemical filter to be effective at removing the major constituent of NO\textsubscript{x}, NO\textsubscript{2}.

DCI provides chemical filters for Full fab Filtration, cleanrooms, processing tools, and point-of-use applications. The performance of these chemical filters for removing acidic, basic and organic airborne contaminants has been previously reported.\textsuperscript{16, 21, 22} As part of their total filtration program, analysis of the actual filter environment and of the returned filters is performed for all three sets of contaminants. The returned chemical filters are subsequently analyzed for remaining life and a qualitative and quantitative analysis of the adsorbed contaminants.

Analysis of the returned filters can provide quantitative information at contaminant levels of less than 0.001 ppb for organics, 0.01 ppb for NO\textsubscript{x}, and 0.90 ppb for SO\textsubscript{2}. These minimum detectable levels are for an acid gas filter that has been in the field for a minimum of six months. The significantly higher level for SO\textsubscript{2} is attributed to the elevated SO\textsubscript{4}\textsuperscript{2-} levels that naturally occur in the activated carbon used for impregnation. We note with adsorbents other than this version of activated carbon, the minimum detectable for SO\textsubscript{2} approaches that for NO\textsubscript{x}. Besides providing a time-weighted average of the range of contaminants in the cleanroom, tool, and on the filter, this approach helps to establish future design criteria and better filter performance estimates.

Acid gas removal chemical filters were returned to DCI from seven locations. The acid gas levels found on these filters from the IC analyses are given in the following table.

Table 4: Acid gas levels measured on returned AGR filters.\textsuperscript{a, b}

<table>
<thead>
<tr>
<th>Filter Location</th>
<th>Filter Type</th>
<th>SO\textsubscript{2}</th>
<th>NO\textsubscript{x}\textsuperscript{c}</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site-1 Exposure</td>
<td>Exposure Tool</td>
<td>599</td>
<td>7904</td>
<td>ND</td>
</tr>
<tr>
<td>Site-2 Exposure</td>
<td>Tool</td>
<td>438</td>
<td>2172</td>
<td>67</td>
</tr>
<tr>
<td>Site-3 Exposure</td>
<td>Tool</td>
<td>157</td>
<td>1752</td>
<td>27</td>
</tr>
<tr>
<td>Site-4 Exposure</td>
<td>Tool</td>
<td>1564</td>
<td>5903</td>
<td>137</td>
</tr>
<tr>
<td>Site-5 Wafer/</td>
<td>Wafer/Reticle Stage-</td>
<td>208</td>
<td>112</td>
<td>39</td>
</tr>
<tr>
<td>Site-6 Wafer/</td>
<td>Reticle Stage-POU</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Site-7 Wafer/</td>
<td>Wafer/Reticle Stage-</td>
<td>199</td>
<td>280</td>
<td>131</td>
</tr>
<tr>
<td>Site-7 Wafer/</td>
<td>Reticle Stage-POU</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Values are reported in µg/gram of adsorbent. \textsuperscript{b} Acid gas values are calculated from the measured anion level assuming all anions in excess of the blank can be attributed to acid gas adsorption. \textsuperscript{c} Sum of nitrite and nitrate levels. ND = level found on the used filter was similar to that of the blank.
In all cases, except Site-5, the level of anions that can be attributed to NO\textsubscript{x} gases is significantly higher than for SO\textsubscript{2} and HCl. These NO\textsubscript{x} levels can probably be attributed primarily to NO\textsubscript{2}. With such large amounts of these acidic contaminants on the AGR chemical filter, it must be very effective at removing both NO\textsubscript{x} and SO\textsubscript{2}. The higher level of NO\textsubscript{x} found on the filters is attributable to the elevated concentration of NO\textsubscript{x} in the environment, relative to SO\textsubscript{2} and HCl. When considering the life of these AGR chemical filters for the removal of acid gases, it is critical that NO\textsubscript{x} be taken into account since in these field applications it has consumed the majority of the filter’s useable capacity.

3.5. Filter Performance:
The relative efficiency of the AGR chemical filters for SO\textsubscript{2} and NO\textsubscript{x} are compared with NIC activated carbon in the breakthrough curves given in Figure 3. These elevated concentration (accelerated) breakthrough tests reveal that AGR chemical filters are capable of providing acid gas removal efficiency’s, for SO\textsubscript{2} and NO\textsubscript{x}, of essentially 100%. It has previously been reported that chemical filters do not work well for the removal of NO\textsubscript{x}.\textsuperscript{2} These data reveal that the AGR chemical filter used in this work is very effective at removing NO\textsubscript{2}. Although, our preliminary results indicate that it is not effective at removing NO. Counter to some thoughts within the filtration industry that NIC carbons can be effective at removing acid gases, our results indicate this is not the case at the test concentrations used here.

Since the acid gases, NO\textsubscript{2} and SO\textsubscript{2}, are efficiently adsorbed by the AGR media and not removed by NIC carbon, the impregnant in the AGR media must play an important role in the removal of both of these acid gases. Based on the chemical composition and charge of the anions found on used filters, it is fair to assume SO\textsubscript{2} (SO\textsubscript{4}\textsuperscript{2-}) requires twice as much impregnant/catalyst as does NO\textsubscript{x} (NO\textsubscript{2}\textsuperscript{-} and NO\textsubscript{3}\textsuperscript{-}), which may explain the difference in the breakthrough curves. We note in the NO\textsubscript{2} breakthrough test we observed that some of the NO\textsubscript{2} was catalytically converted to NO. This phenomenon has been previously reported.\textsuperscript{20}
3.6. Acid Gas Chemical Filter Life Estimates:

Table 5 provides the life estimates to reach 99% removal efficiency, based on a known challenge concentration of SO₂ (typically 5 ppb), for the AGR chemical filters used at the seven locations provided in Table 2. These estimates are compared with the field life (In Use) and remaining life results.

Table 5: Acid gas chemical filter life estimates.

<table>
<thead>
<tr>
<th>Filter Location</th>
<th>Filter Type</th>
<th>Life Estimate&lt;sup&gt;a&lt;/sup&gt; (years)</th>
<th>In Use&lt;sup&gt;b&lt;/sup&gt; (years)</th>
<th>Tested Remaining Life&lt;sup&gt;c&lt;/sup&gt; (years)</th>
<th>Actual Remaining Life&lt;sup&gt;d&lt;/sup&gt; (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Site-1</td>
<td>Exposure Tool</td>
<td>5.0</td>
<td>1.2</td>
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a. AGR filter life estimate for acid gases based on a typical application acid gas challenge concentration of 5 ppb SO₂. b. Length of time the AGR filter has been in use. c. Returned filter remaining life estimate based on accelerated breakthrough test results. d. “Actual” AGR filter remaining life estimate that takes into account the real filter usage by elevated acid gas concentrations found in the field.

The field challenge concentration for acid gases is typically provided to the filter manufacturer by the customer and is generally specified as 5 ppb SO₂. AGR filter life estimates for the application are based on the typical field challenge concentration, field experience, and accelerated laboratory performance data. Accordingly, the AGR filter life estimates turn out to be extreme, suggesting the chemical filter has been over-designed for acid gases. However, after performing remaining life testing on returned filters it is evident the acid gas exposure these filters have experienced in the field is significantly greater than originally was specified. Adjusting filter life estimates for the “real” filter usage, after remaining life testing, at these elevated acid gas concentrations provide a more realistic estimate of the expected field life of an AGR filter.

As we have indicated above, AGR filters will effectively remove many other acid gases besides SO₂. Furthermore, some of these acid gases are present at concentrations higher than that of SO₂. As a result, the AGR filter usage for acid gases in the field will always be increased relative to estimates based solely on SO₂. This exact set of circumstances has been found in nearly every field application where AGR filters have been installed. Therefore, it is recommended that the industry attempt to base AGR chemical filter life estimates on a combination of acid gases, and as a minimum SO₂ and NOₓ.
4. SUMMARY

The most abundant acid gases in ambient air and in cleanrooms are found to be oxides of nitrogen, NOx. However, within the cleanroom and exposure tool, the impact of NOx gases has yet to be addressed to any significant extent. To bring this subject to the forefront, we have revealed that NOx contaminants can impair the performance of several other applications known to also be sensitive to acid gases. Accordingly, since NOx gases are generally found in such large quantities relative to other acid gas contaminants, they may indirectly affect semiconductor processing by significantly impacting the efficiency and life of acid gas filters. Despite the prevalence of NOx contaminants in the environment, most acid gas filter efficiency and life estimates are based solely on their performance against sulfur dioxide, SO2. This preliminary work has attempted to present a seminal case for addressing both NOx and SO2 acid gases when acid gas chemical filter performance estimates are being considered.

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The authors thank Los Alamos National Laboratories for their valued contributions to this work. We also recognize the efforts of Karen McDonald and Eivind Stenersen of Donaldson Co., Inc. in ensuring the ongoing success of the projects outlined in this work.

REFERENCES


Figure 1: PEM fuel cell current output when exposed to 1.0 ppm of SO$_2$ injected at the cathode inlet with and without an acid gas chemical filter (DCI chemical filter, data courtesy of Los Alamos National Laboratories).
Figure 2: PEM fuel cell current output when exposed to 5.0 ppm of NO₂ injected at the cathode inlet with and without an acid gas chemical filter (DCI chemical filter, data courtesy of Los Alamos National Laboratories).
Figure 3: Breakthrough curves for SO$_2$ and NO$_2$ on NIC (non-impregnated) and AGR (acid gas removal) adsorbents. Tests were performed at 50 ppm contaminant, 50% RH, and 25°C.