

Airborne Molecular Contamination: Formation, Impact, Measurement and Removal of Nitrous Acid (HNO_2)

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ABSTRACT

Airborne molecular contamination (AMC) is a significant contributor to the loss of yield in semiconductor processes.¹⁻⁴ The impact of weak acids has only been considered for process technologies of 22 nm and below.⁵⁻⁸ One such weak acid is nitrous acid (HNO_2 or HONO), which has no demonstrated direct impact on processes or equipment, but has nevertheless been a target for removal by AMC filtration. HNO_2 is commonly formed on all surfaces in all environments from NO_2 gas, one of the main oxides of nitrogen formed from combustion processes and ambient air photochemistry. This study investigated the behavior of the NO_x/HNO_x system around typical AMC filter adsorbents. We find that NO gas passes through AMC filters unchanged, whereas NO_2 is converted mostly to NO , but also to HNO_2 at the low ppb level, increasing AMC load downstream of filters. Various adsorbents can capture HNO_2 , but filter lifetimes are short due to the release of the volatile compound over time. The recommendation is to critically evaluate the impact of HNO_2 on processes and equipment and adjust AMC filtration needs accordingly.

INTRODUCTION

Controlling Airborne Molecular Contamination (AMC) has become an indispensable part for high yield operations in semiconductor processing. What started decades ago with concerns about a few base compounds, such as ammonia¹, expanded to controlling most measurable gas-phase contaminants classified as acids, bases, and organic compounds, plus some unclassified compounds like hydrogen sulfide, ozone etc., down to parts per trillion (ppt, 10^{-12} mole fraction) levels in order to achieve semiconductor features below 22 nm, and to prevent critical dimensions from being degraded, coatings from delaminating, or metal surfaces from corroding.⁵⁻⁸

Acidic gases have been a concern since the inception of 193 nm technology. Initially focused on strong acids that cause corrosion on equipment or hazing of optics through the formation of salts (reactions with ammonia, for example),²⁻⁴ more recent concerns are about the weaker acidic compounds, such as formic and acetic acids, which can cause process degradation by affecting resist⁸ and other coatings.

Although no strict definition exists, weak acids are considered to be those with a pK_a of 3.2 or higher (acid strength, lower number indicates stronger acid), which includes formic, acetic and other organic acids, but also nitrous acid (HNO_2 , $\text{pK}_a = 3.3$) and hydrofluoric acid (HF , $\text{pK}_a = 3.2$). In contrast to its strongly acidic counterpart nitric acid (HNO_3 , $\text{pK}_a = -2$), however, HNO_2 is not a stable compound and its formation can easily be reversed into its components. As a result, HNO_2 is rarely considered in atmospheric chemistry cycles and very few dedicated studies exist.^{9,10} In contrast to a variety of other nitrogen compounds like NO_x , HNO_2 is also not usually found in significant amounts in the combustion process of nitrogen containing fuels.¹¹

NOMENCLATURE

A common misnomer used in the semiconductor industry is “ NO_x ”. The atmospheric science community has referred to the mix of NO and NO_2 gases as NO_x for decades, and the authors propose to continue the exclusive use of that acronym for this purpose. The scientific community also uses the acronym NO_y to refer to the mix of other reactive nitrogen oxides, such as PAN (peroxy acyl nitrate), N_2O_3 , N_2O_5 etc., all commonly found in the atmosphere.

However, there is no such acronym in atmospheric chemistry to describe the sum of acidic species HNO_2 and HNO_3 , which is what the semiconductor industry incorrectly calls “ NO_x ”. Common use also suppresses the minus signs in ionic forms, leading to further confusion between HNO_2 in water (NO_2^- , nitrite) and the gas NO_2 . Here are the most common forms of oxidized nitrogen gases:

NO: nitrogen oxide; **NO_2 :** nitrogen dioxide

NO_x : $\Sigma \text{NO} + \text{NO}_2$

NO_y : $\Sigma \text{NO}, \text{NO}_2$, PAN, reactive oxides (“odd nitrogen”)

HNO_2 : nitrous acid, a weak acid without known impact

Nitrite: NO_2^- , the ionic form of HNO_2 in water

HNO_3 : nitric acid, a strongly corrosive acid

Nitrate: NO_3^- , the ionic form of HNO_3 in water

HNO_x : $\Sigma \text{HNO}_2 + \text{HNO}_3$ (suggested acronym)

Virtual NO_x^- : HNO_2 artifact formed in water solutions¹⁵

If any acronym is needed, instead of explicitly stating the individual acids, the authors propose to adopt HNO_x to indicate the acidic character and avoid confusion with NO_x .

SOURCES AND REACTIONS FOR HNO_2

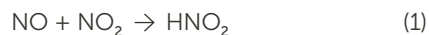
A. Atmospheric HNO_2

Atmospheric HNO_2 forms primarily through heterogeneous reactions on surfaces (e.g., particles), as witnessed by highest concentrations found during nighttime, when available airborne particle surfaces are highest.^{11, 13} The compound is also destroyed on surfaces (equilibrium) and through photolysis, reactions induced by light, explaining its distinct diurnal cycle when local sources are absent.⁹ In the gas phase, HNO_2 is an unstable, short-lived intermediate between the stable forms of NO_x and HNO_3 . Concentrations of actual gas-phase HNO_2 in the atmosphere are usually at the ppt level and up to 1 ppb, hence, not of concern to semiconductor processing at this time.

B. Formation of HNO_2 on surfaces

Typical concentrations of HNO_2 that are found by this laboratory in various semiconductor environments, such as air handlers, cleanrooms, scanner, and track tools, are a few parts per billion (ppb, 10^{-9} mole fraction), mostly much below 10. However, much of the found HNO_2 can be a result of an artifact described in the next section.

What complicates the evaluation of the impact of HNO_2 is its instability. It is mainly formed from NO and NO_2 , two reactive gases from combustion processes (car exhausts, heating systems, industrial emissions, etc.). The primary formation of HNO_2 on surfaces mentioned above explains why high surface adsorbents, such as activated carbons, may be effective in triggering the conversion of NO_2 to HNO_2 . Such highly porous surfaces are found in AMC chemical filters, and they can accelerate that formation to be much faster than through these more common, but slow, gas-phase reactions:



Any formation of HNO_2 , however, is easily reversible and yields the originating gas NO_2 or NO and $\bullet\text{OH}$ radicals. High surface carbon filters, however, cannot be avoided for most applications, because they are needed to remove organic AMC from the airstreams, something that is not easily or cheaply done with non-carbon based adsorbents. This formation pathway is currently the main concern in the industry, as it makes AMC filters appear to be “outgassing” HNO_2 when applied to environments with significant NO_x challenge.

C. Formation of HNO_2 in air samplers

Another issue that exacerbates evaluating the impact of HNO_2 is its measurement. HNO_2 is unstable in air, but also forms and decomposes in aqueous solution. The compound is not available or stable in pressurized gas tanks.

The industry and associated laboratories most commonly use impingers/bubblers, devices that contain deionized water through which the air of interest is drawn with the use of a pump to dissolve all soluble contaminants (usually acids and bases) in that water for later analysis by ion chromatography¹⁴ (Figure 1).



Figure 1. Typical deployment of a wet impinger/bubbler for the determination of acids and bases.

The authors reported before about the formation artifact of HNO_2 in water impingers/bubblers.¹⁵ The effect was named *Virtual NO_x^-* (note the minus sign indicating the ionic form), because the resulting HNO_2 that forms in the aqueous solution is artificial, creating a 'virtual' and inflated signal for actual nitrite concentration. This effect is based on the conversion of NO and mostly NO_2 to HNO_2 (as nitrite, NO_2^-) in water, along the lines of Eq. 1, which happens faster in water than in the gas-phase.

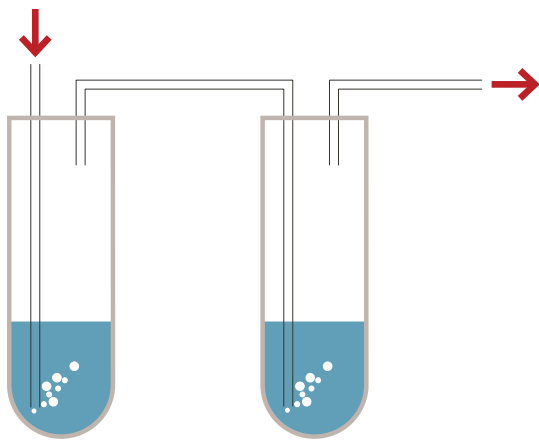


Figure 2. Concept of wet impingers configured for serial operation.

The authors found that about 1% of NO_x in ambient air is converted to HNO_2 in impingers. Given that typical atmospheric concentrations of NO_x are in the 30-50 ppb

range, and was found to be as high as 1000 ppb in the vicinity of combustion sources, the amount of HNO_2 measured in impinger samples can quickly approach several ppb, in turn triggering alarms for the level of acidic AMC. The cited application note mentions a potential workaround for the artifact, but it involves duplicate equipment and is typically not done by laboratories (Figure 2).

Taken together, atmospheric HNO_2 is negligible in most cases. The amounts of HNO_2 produced in impinger/bubbler sampling can significantly contribute to reported values, but the HNO_2 formed by high surface adsorbents may be the biggest contributor to the measured HNO_2 (or dissolved nitrite) concentration in semiconductor environments.

IMPACT OF HNO_2 ON PROCESS AND EQUIPMENT

Based on a lack of understanding the chemistry and instability of the compound, the main concern about HNO_2 in semiconductor environments appears to be perceptual, as that any presence of nominally "acidic" compounds is generally undesired. However, there are many organic acids that should trigger similar concerns, but are typically ignored, such as lactic acid, which often is detected in semiconductor environment air samples.

Whereas strong acids can significantly impact process steps and equipment at the ppb level, however, there is no published or direct impact of HNO_2 on any semiconductor process step or equipment and in many cases, its existence at single digit ppb levels in semiconductor samples has been largely ignored for years by equipment and chipmakers.

The only issue the authors are aware of is that HNO_2 may possibly facilitate corrosion of bare metals by hydrogen sulfide (H_2S), but it is the H_2S causing the corrosion, not the HNO_2 , the latter only attacking a protective coating to let the H_2S penetrate to the metal.¹⁷ Note that HNO_2 is only thought to facilitate, but not cause that impact. Removing the actual, corrosive contaminant (H_2S), which is easily achieved with AMC filters, will alleviate that problem and HNO_2 remains a compound without known, direct impact.

REMOVAL OF HNO₂ AND OTHER AMC

Generally, HNO₂ can be removed from air streams like strong acids, by adsorbing it with a base, and forming a salt:



In the most common case, a basic carbonate (MCO₃, with M being a metal) can be used either as a pure granulate or, to improve capture efficiency and capacity, as a coating on a porous carrier, such as carbon, zeolite, or others. Carbonates are inorganic compounds, fairly unreactive, aside from their basicity, and do not volatilize, but they are weakly basic, hence, acid/base reaction is limited, so is the stability of the resulting salt. Hydroxides such as NaOH or KOH can also be used and have much higher basicity (and toxicity!), but they react with atmospheric carbon dioxide (CO₂) to form the weaker carbonates Na₂CO₃ or K₂CO₃.

Another approach is to use a cationic ion exchanger, usually granular polymers that have their surface modified to carry organic amines. The basicity of these can be strong, resulting in a stronger bond of weak acids such as HNO₂.

All other approaches to capturing acids are combinations of these two basic principles and may involve fabrics or membranes or other carriers and chemicals. All of these approaches also work for strong acids, such as hydrochloric acid (HCl) and sulfuric acid (H₂SO₄).

Whereas it is possible to prevent the formation of HNO₂ by using non-carbonaceous adsorbents for dedicated applications of acid removal, the typical semiconductor environment requires to control all AMC, acids, bases, and especially organic compounds. The only cost effective solution to removing organic AMC is through the use of activated carbon adsorbents.

There are other adsorbents for the removal of organics, such as ion exchange solutions and modified zeolites or the use of catalytic destruction, often aided by ultraviolet light, that all have been demonstrated to work well for the removal of specific compounds, but none of these work well for the wide range of C₃ to C₂₆ contaminants that are typically monitored and of concern to cause process issues.

And all such solutions are either very expensive compared to activated carbons, or require the use of electro-pneumatic systems (UV catalysts) that need power, maintenance, repairs, and can have downtimes, something semiconductor applications do not tolerate.

Most importantly, though, capturing or avoiding the formation of HNO₂ in air handler systems, FFU cleanroom protection or even at the tool level does not eliminate the problem. NO₂ gas is converted to NO to some extent on AMC filters, but much of it penetrates the filters and makes it into the cleanroom and into the process tools, due to its volatility and high concentrations in the atmosphere. We reported that a few percent of the ambient NO_x gets converted to HNO₂.

Any additional AMC filter or surface downstream of the initial filtration step will again form HNO₂ from the remaining NO₂. This problem will propagate all the way inside process tools, where more HNO₂ can be formed on the wafer itself, or any other hard surface, because surface-to-air volume ratios are higher indoors than in the atmosphere.¹⁸ The issue can be minimized with AMC filters, but not completely eliminated, because complete filtration of ambient NO₂ would require massive amounts and frequent change of adsorbents.

MEASUREMENT OF HNO₂ FOR THIS STUDY

HNO₂ can be measured with no-contact, long-range optical methods such as DOAS,⁹ but their setup and operation is involved and unsuitable for small-scale measurements that require close proximity to the test site (e.g., AMC filter outlets). Denuder systems are another solution, and similar in functionality to impingers/bubblers, but more involved.⁹ IMS online monitors can detect acidic AMC, but it is unknown if they specifically react to the presence of HNO₂.¹⁹ Chemiluminescence monitors are likely to detect the compound, but their converter system will convert it to NO, hence, they cannot detect the difference between NO₂ and HNO₂.⁹

Contrary to what was speculated to be a workaround,¹⁵ using dry adsorbent sample trap media (a base-coated solid state pad or adsorbent) was found to produce nearly as much Virtual NO_x⁻ as wet impingers, hence, did not provide any advantage for this study.

Based on the formation of Virtual NO_x^- mentioned above, this study employed dual, serial impingers (Figure 2), where the air enters the first and exits the second impinger. The first impinger captures all actual HNO_2 in the inlet air, plus the Virtual NO_x^- produced in the impinger from ambient NO_x . The second impinger only produces Virtual NO_x^- , absent of actual HNO_2 , which is soluble enough to be entirely scrubbed in the first device. The numerical difference between the impingers yields the actual HNO_2 . The conversion of NO_x to HNO_2 is only 1-3% of the NO_2 concentration, hence, the second impinger is exposed to nearly as much (99-97%) of the NO_2 that the first impinger experiences, and Virtual NO_x^- production is about the same in both.

For the setup of testing different adsorbents for the removal of HNO_2 from air streams, we employed several different test concepts.

- Deep beds: Many tests were carried out in deep bed stations, where a tubular device was filled with the adsorbent, much akin to a gas purifier. However, flow rate was adjusted to mimic the flow across an AMC filter in real world applications. This method is best for comparing many different adsorbents.
- Patch tests: The next larger setup employed 50 mm diameter patches of AMC filter material, where the adsorbent is sandwiched between layers of fibrous scrim and loft, as it is used in AMC filters.
- AMC filters: To validate real world performance, we carry out full size AMC filter tests, as they are deployed in semiconductor environments.

RESULTS FOR HNO_2 REMOVAL AND PRODUCTION ON AMC FILTER ADSORBENTS

A. Measurement and Removal of HNO_3

Nitric acid (HNO_3) is well captured by impingers and dissolves as nitrate (NO_3^-). It is stable in solution and strongly corrosive to equipment and materials. Easy to calibrate and handle, measurement detection limits are a few ppt.

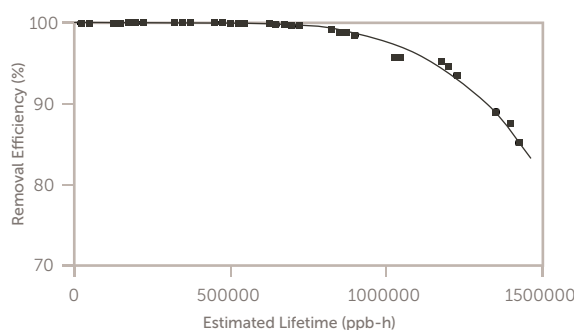


Figure 3. Lifetime curve for HNO_3 removal on activated carbon-based media. After initial 100% capture efficiency, HNO_3 slowly breaks through.

HNO_3 is a strong acid ($\text{pK}_a = -2$) and is efficiently removed with carbonaceous AMC filters, exhibiting long lifetimes/high capacities. Lifetime estimates here are expressed in ppb-h (parts per billion - hours), a product of the challenge concentration and time (Figure 3). This metric enables easy calculation of filter lifetime in hours by dividing the ppb-h metric by the measured, average concentration.

B. Measurement and Removal of HNO_2

Nitrous acid is a weak acid ($\text{pK}_a = 3.3$) and often in equilibrium with NO_x or HNO_3 . As described, the low acidity affects how it is formed and detected and can create artifacts, artificially inflating actual HNO_2 air concentrations. In addition, HNO_2 can form on surfaces, including wafers, which is not detected by air samples.

Removal of HNO_2 undergoes a similar process as HNO_3 , with the added complication that additional HNO_2 is formed from NO_x in air, which is ubiquitous and significant. Combustion processes in urban environments frequently cause a background signal of 30-100 ppb of NO_x , usually a third of which is NO_2 . Closer to combustion sources, NO is more prevalent (it is the original nitrogen oxide formed in the process), further away from combustion sources, NO gets increasingly oxidized to NO_2 . The latter is mostly responsible for the heterogeneous formation of HNO_2 . This adds to the overall acid load and diminishes the adsorbent lifetime by exhausting the capacity faster.

C. Conversion of NO₂ on Carbonaceous Adsorbents

The conversion of NO_x can be demonstrated on common carbon adsorbents. Whereas NO passes through the filter almost unchanged (Figure 4), NO₂ does not, but is rather retained and slowly breaks through to about 20% of the original challenge (Figure 5), while the other 80% of the NO₂ is converted to NO (Figure 6).

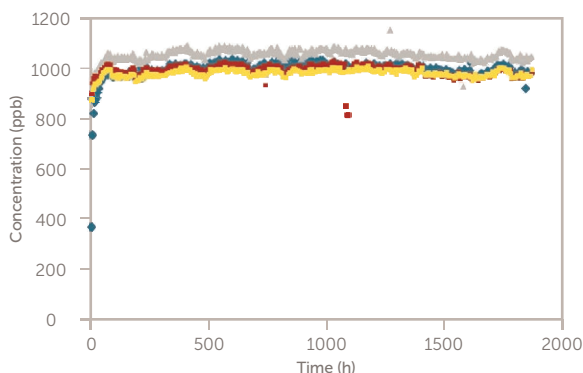


Figure 4. NO gas passes through various carbon-based carbon adsorbents virtually unchanged. Challenge concentration was about 1 ppm (=1000 ppb), which is found unchanged downstream of the adsorbent.

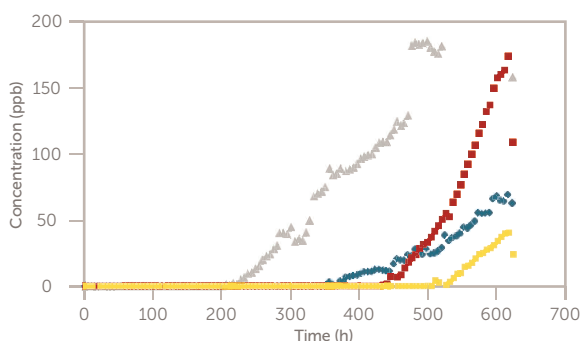


Figure 5. A challenge of 1 ppm NO₂ on various carbon adsorbents with increasing base character shows initial retention (while also being converted to NO), then a gradual and accelerating breakthrough until it levels off.

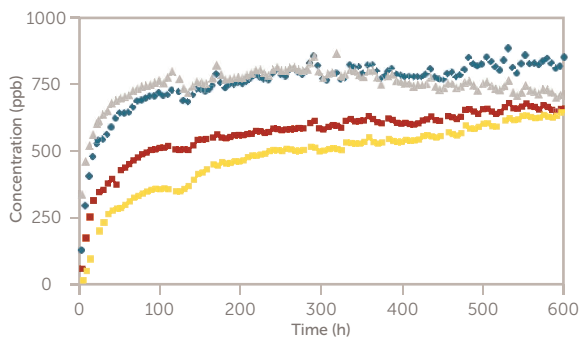


Figure 6. Conversion of NO₂ to NO. These are downstream concentrations of NO when the same adsorbents of Figure 5 were challenged with 1 ppm of NO₂. The early, gradual increase suggests an accelerating conversion, likely assisted by the increasingly acidic character of the adsorbent.

D. Formation of HNO_x on Carbonaceous Adsorbents

In the process of NO_x conversion, HNO₂ is formed from both NO and NO₂, whereas HNO₃ is only formed from NO₂, but was not detected downstream of NO.

Formation of HNO₂ from NO was low, about 1% of the NO challenge. Formation from NO₂, however, was very significant, but delayed, as the formed HNO₂ is adsorbed until the adsorbent capacity is exhausted (Figure 7). We found that about 5-10% of the NO₂ gets converted to HNO₂, substantially more than we found happening in water impingers reported above.

NO₂ conversion to HNO₃ was also found, but only about 1% of the NO₂ challenge was detected as HNO₃. HNO₃ is a strong acid and is retained well by carbonaceous adsorbents.

Based on these results, the best AMC filtration solution requires the use of a strong base coating or material to maximize HNO_x capacity and lifetime. The strength of the base coatings, however, is often restricted by material processing limitations. We also found that coating an activated carbon with more than 15% chemical reduces or eliminates its capacity for organic AMC.

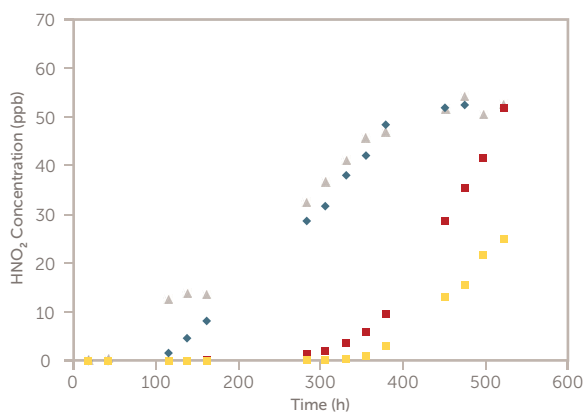


Figure 7. Formation and breakthrough of HNO₂ on various carbon-based adsorbents over time. Increasing base strengths (▲<◆<■<□) on the adsorbent delays breakthrough and increases capacity, as expected.

E. Alternative Adsorbents

As mentioned, the use of ion exchange adsorbents with basic character allows to capture acidic compounds without releasing them over time. We also did not find any NO_2 conversion on cation exchangers. There are, however, four concerns about cationic ion exchange resins.

First and most important is their very strong release of amines (causing T-topping) and associated fish-like odor. Second, if all of the NO_2 gets passed through the AMC filter stage unchanged, it is available, and makes it more likely, to form HNO_2 on any surface, all the way to the wafer. Third, these adsorbents are 5-10 times more expensive than carbon-based adsorbents. Lastly, this type of adsorbent is limited in applications and unable to capture organic or base AMC.

If deployed in conjunction with carbon-based adsorbents to capture organic AMC or to alleviate the amine odor, the problem of NO_x conversion and HNO_x formation returns. If the ion exchange is deployed in a separate, downstream layer, it may delay the carbonaceous HNO_2 formation, but at high cost, and the amine odor will be released into the environment unchecked.

Non-carbon based adsorbents carrying some form of permanganate (usually KMnO_4 or NaMnO_4) are available to convert (but not remove) NO_2 , but were also found to produce HNO_2 at similar levels compared to carbonaceous adsorbents, albeit with a more shallow release curve. In addition, permanganate does not capture organic or base AMC, hence, has very limited applicability. Being a strong oxidant, it may also trigger unwanted conversions of organic AMC to volatile species that do not have long lifetimes on filters. Similar limitations apply to using titanium oxides (TiO_2), which were reported to destroy NO_2 and HNO_2 .²⁰

Other types of adsorbents without carbon content are molecular sieves (zeolites) or similar minerals, also organic ion exchangers without acidic or basic character, where pore size can be tailored to capture specific AMC types, but none of these are broad-band adsorbents and they remove only a few, targeted compounds.

The potential exists to use porous, non-carbon adsorbents coated with a base material to capture acids. Some tests were carried out in this laboratory, but we found that capture efficiency and capacity are much reduced compared to carbon-based adsorbents.

Finally, we want to note that some tests indicated the formation of formic acid at the ppt level on increasingly acidic media (either loaded carbonaceous adsorbents or cationic ion exchangers) in the presence of carbon or perhaps carbon dioxide. This has not been studied yet, but to fully understand the behavior of acidic AMC around adsorptive media warrants further investigation.

CONCLUSIONS

HNO_2 is not a stable acid or AMC, it is formed and destroyed in-situ on surfaces. It is difficult to accurately detect and quantify due to measurement artifacts. HNO_2 formation happens in the presence of NO_2 gas, a combustion product in the atmosphere, whereas formation from NO gas is negligible.

There is no known, direct impact of HNO_2 on any semiconductor process or equipment. The concern about HNO_2 in semiconductor environments appears to be largely perceptual based on its nominally acidic character.

There are cost-effective solutions to delay the formation and release of HNO_2 , but lifetime/capacity of such AMC filter solutions is limited. Some solutions to prevent its formation exist, but they are either expensive, or outgas amines, and most do not capture any other AMC type.

Good AMC filter solutions require a balance of chemical performance (removal efficiency, capacity), physical performance (pressure drop, size, weight,...), operational concerns (toxicity, smell, outgassing), and cost. Most importantly, AMC filter solutions need to work for all environments and target a broad range of AMC types, preventing the sole use of specialized solutions. Characterizing the AMC spectrum through competent analysis and customizing the filtration solutions to address all above concerns is important.

To minimize cost, effort, and risk in broad-band AMC protection, the recommendation is to critically evaluate, quantify, and publish any actual impact of HNO_2 or reduce emphasis on its capture, if no impact is found.

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