Improved Respirator Carbons for Ammonia Hazards

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List of Terms & Abbreviations

BET = Brunauer-Emmett-Teller
CBRN = chemical, biological, radiological, and nuclear
CDC = Centers for Disease Control and Prevention
DOE = Department of Energy
EDS = energy-dispersive spectroscopy
EPA = Environmental Protection Agency
FDA = Food and Drug Administration
FESEM = field-emission scanning electron microscope
FTIR = Fourier-Transform Infrared
GHSV = gas-hourly-space velocity (h^{-1})
HEPA = high-efficiency particulate air
ICP-MS = Inductively-Coupled Plasma-Mass Spectrometry
ISS = International Space Station
MPG = Molecular Products Group
NIH = National Institute of Health
NMRD = nonmalignant respiratory diseases
OSHA = Occupational Safety and Health Administration
PM = particulate matter
ppmv = parts-per-million-by-volume
ppmw = parts-per-million-by-weight
RH = relative humidity
SAE = Society of Automotive Engineers
SCCM = standard cubic centimeters per minute
SLPM = standard liters per minute
STEL = short-term exposure limit
TDA = TDA Research, Inc.
TWA = time-weighted average
UK = United Kingdom
US = United States
UV = ultraviolet
XPS = X-ray Photoelectron Spectroscopy
XRD = X-ray diffraction

Abstract

A new ammonia (NH_3) sorbent to protect agricultural workers from both chronic and acute exposure to ammonia was developed that greatly exceeded the performance of the best commercially available ammonia sorbent. In fact, by optimizing each step of the sorbent synthesis process we achieved a 144% improvement over existing commercially available cartridges, with a service life of 17.8 min/g (compared to 7.3 min/g for a 3M ammonia cartridge). The Phase I research also successfully met the criterion specified by the NIOSH standard of protecting the wearer against the penetration of 50 ppmv NH_3 in the inhaled air for ≥50 minutes when challenged with 1000 ppmv NH_3.

More than 700,000 agricultural workers are at risk from exposure to toxic levels of ammonia. Levels often exceed 50 ppmv with lower winter ventilation rates and reach 100-200 ppmv in poorly ventilated buildings or during periodic upsets due to inadequate manure handling. Although disposable ammonia respirator cartridges are commercially available, protecting all agricultural workers with the current technology would be cost-prohibitive. TDA's patented activated carbons that were made from inexpensive and abundant saccharides (e.g. starch and sugar) have increased mesoporosity (pores between 2 nm and 50 nm), which allowed it to be loaded with substantially more additive for ammonia adsorption, and its more open pore structure also enhanced the ammonia uptake kinetics. The ammonia sorbent has the following competitive advantages:

- Decreased breathing resistance, size and weight (because less carbon is required to provide the same protection) for increased wearability and comfort during long shifts
- Extended service lifetime during routine use (e.g., throughout an 8-hour shift)

In Phase I, extensive characterization was carried out to understand the fundamental structure (e.g., poresize analysis) and additive chemistry of both the precursor carbon and the as-manufactured and used sorbents; these analyses greatly assisted us in designing the optimal sorbent. More than 85 bench-scale ammonia breakthrough tests (scaled to the NIOSH standard conditions) were run to demonstrate the sorbent's effectiveness. Performance was benchmarked against the best commercially available ammonia sorbent (Chemsorb 1425).

While we made substantial progress toward our goals during Phase I, further development and testing will be required (in Phase II) to optimize the sorbent's ammonia capacity, scale up production, incorporate it into a prototpye respirator cartridge, and qualify it for industrial use in accordance with the NIOSH standard testing procedure. We are planning eventual field tests by working with our industrial partners to scale-up production and fill prototype cartridges with our sorbent for qualification testing to register it with NIOSH prior to bringing it to market. In summary, a cost-effective, high-capacity ammonia sorbent was developed, that dramatically lowers the amount of sorbent that is needed, thereby lowering the cartridge size, weight and breathing resistance, and making a more comfortable to use mask that people might actually wear. These improvements are crucial to obtain adoption of the new ammonia respirator cartridge by the agricultural community to mitigate the long-term negative health effects of chronic ammonia exposure and help prevent fatalities due to acute inhalation injury.

Executive Summary

In this SBIR project TDA Research, Inc. developed a new ammonia sorbent to protect agricultural workers from both chronic and acute exposure to ammonia (NH_3). According to statistics of the Centers for Disease Control and Prevention (CDC), more than 700,000 agricultural workers are at risk from exposure to toxic levels of ammonia. Levels often exceed 50 ppmv with lower winter ventilation rates and reach 100-200 ppmv in poorly ventilated buildings or during periodic upsets due to inadequate manure handling. This research is addressing this problem by developing a cost-effective, high-capacity ammonia sorbent for use in disposable respirator cartridges to protect agricultural workers. Really, what we are doing is dramatically lowering the amount of sorbent that is needed, thereby lowering the cartridge size, weight and breathing resistance, and making a more comfortable to use mask that people might actually wear. These improvements are crucial to obtain adoption of the new ammonia cartridge by the agricultural community.

Although ammonia respirator cartridges are commercially available, protecting all agricultural workers with the current technology would be cost-prohibitive. Hence, the opportunity exists for the scientific design and development of a new, more effective ammonia sorbent based on TDA's patented activated carbons that are made from inexpensive and abundant saccharides (e.g. starch and sugar). Whereas standard activated carbons are almost completely microporous (pores < 2 nm in diameter), the distinguishing feature of TDA's carbon is its increased mesoporosity (pores between 2 nm and 50 nm), which allows it to be loaded with substantially more additive for ammonia adsorption, and its more open pore structure also enhances the ammonia uptake kinetics.

Significant or Key Findings. By optimizing each step of the sorbent synthesis process using our mesoporous carbon, we were successful in achieving our Phase I goals, including the development of a sorbent that:

- Exceeded the performance of the best commercially available NH_3 sorbent by >50%
- Passed the NIOSH standard testing procedure (STP) for the determination of service life

The ammonia sorbent's increased performance translates into the following competitive advantages compared to the existing technology and practical benefits for the end-users:

- Decreased breathing resistance, size and weight (because less carbon is required to provide the same protection) for increased wearability and comfort during long shifts
- Extended service lifetime during routine use (e.g., throughout an 8-hour shift)

In Phase I, our primary focus centered on creating a superior ammonia sorbent with rapid ammonia uptake kinetics and high capacity by modifying the preparation methods for the activated carbon (the key to obtaining the optimal mesoporous/microporous structure), and improving the chemistry and application methods of the additive that further improves the sorbent. We developed a new impregnation technique (based on existing cost-effective and scalable industrial processes) that capitalized on our carbon's unique pore structure to obtain high loadings of impregnant without compromising its fast uptake kinetics. Extensive characterization was carried out to understand the fundamental structure (e.g., poresize analysis) and additive chemistry of both the precursor carbon and the as-manufactured and used sorbents; these analyses greatly assisted us in designing the optimal sorbent. More than 85 bench-scale ammonia breakthrough tests (scaled to the NIOSH standard conditions) were run to demonstrate the sorbent's effectiveness.

The standard testing protocol required for the registration of air-purifying respirators under NIOSH was followed explicitly to unequivocally demonstrate the efficacy of our new sorbent in a scaled-down test when challenged with 1000 ppmv NH_3 in 64 slpm air at 50% RH. Performance was benchmarked against the best commercially available ammonia sorbent (Chemsorb 1425). The Phase I research successfully met the criterion specified by the NIOSH standard of protecting the wearer against the penetration of 50 ppmv NH_3 in the inhaled air for ≥50 minutes (this is the minimum that must be accomplished; a cartridge that does not meet the NIOSH standard will not be sold). More importantly, we also achieved our own metric of success, attaining a >50% improvement in service life. In fact, we achieved a 144% improvement as measured in minutes of protection per gram of sorbent over existing commercially available cartridges, with a service life of 17.8 min/g (compared to 7.3 min/g for a 3M ammonia cartridge).

Translation of Findings. We will target the most at-risk workers for the greatest potential impact when targeting initial products, and are planning eventual field tests in later research phases by working with our industrial collaborators: 1) Molecular Products, who is enthusiastic about the possibility of incorporating our carbon and sorbent production methods into their existing product line of high performance sorbents, and 2) Avon Protection, who has agreed to work with us to fill prototype industrial cartridges with our sorbent during Phase II for testing and qualification. The cartridge design will also include a built-in HEPA filter for protection against inhalable hazardous particulate matter (PM) that is ubiquitous in agricultural environments. The scientific merits and economic viability of the new ammonia cartridge will be independently evaluated by these industry leaders in personal protection (who have no vested interest in TDA Research) in accordance with the latest standard test protocol (that requires a 1000 ppmv NH_3 challenge at 64 slpm) to demonstrate its efficacy and register it with NIOSH prior to bringing it to market. Both of these companies are interested in serving the large potential market for this product as well as other personal protection applications where our unique carbon could serve as a platform for making sorbents with enhanced performance.

Research Outcomes/Impact. While we made substantial progress toward our goals during Phase I, and our sorbent formulation had a far superior ammonia capacity when compared to existing materials, further development and testing will be required to reduce the sorbent's cost and qualify it in a prototype cartridge for industrial use in accordance with the requirements in the latest version of the NIOSH standard test procedure. There is still significant room to further increase the sorbent's ammonia capacity, by optimizing the carbon structure, the impregnation solution, and the special method by which we apply it to the carbon. We will work with our industrial collaborator, Molecular Products, to reduce the sorbent's cost by scaling up the production of the carbon and minimizing the quantities of waste byproducts from the impregnation process (by developing ways to replenish and recycle the solutions), and streamlining the manufacturing procedure to reduce the amount of labor required.

Our next goals for this project (in Phase II) are to optimize the sorbent's ammonia capacity, scale up production, incorporate it into a commercial respirator cartridge, and qualify it for industrial use in accordance with the NIOSH standard testing procedure for air-purifying respirators [1]. The cartridge will be low cost (essential to adoption by agricultural workers) and it will protect workers against both continuous exposure to low levels of ammonia (~50 ppmv) during an 8 h shift or short-term exposure to high concentrations to allow the worker to safely escape, for example, from an accidental fall into a manure storage pit or exposure to a spill/leak of anhydrous ammonia. Successful commercialization of an ammonia respirator cartridge that contains our new sorbent will enable its widespread use to mitigate the long-term negative health effects of chronic ammonia exposure and more importantly, help prevent fatalities due to acute inhalation injury.

Scientific Report

1.1. Background

1.1.1. Workers at Risk

According to the Centers for Disease Control and Prevention (CDC) more than 700,000 agricultural workers are at risk from exposure to toxic levels of ammonia (NH_3). While the toxicity of anhydrous ammonia used as a nitrogen fertilizer has long been recognized, concerns have recently arisen regarding toxic levels of ammonia arising from the breakdown of urea from livestock urine in poorly-ventilated buildings of the over 257,000 Animal Feeding Operations (AFO) and the over 15,500 Concentrated Animal Feeding Operations (CAFO) in the United States [6]. Ammonia levels in well-ventilated, environmentally regulated buildings can be kept below 10-20 ppmv. However, levels often exceed 50 ppmv with lower winter ventilation rates and reach 100-200 ppmv in poorly ventilated buildings or during periodic upsets due to inadequate manure handling. Firefighters and other first responders are also at risk from ammonia exposure during combustion of nylon, silk, wood, melamine, etc. and from ammonia leaks from industrial refrigeration units. A personal respirator (Figure 1) that contains an effective ammonia sorbent would protect these workers from the deleterious effects of occupational exposure to ammonia.

Figure 1. Example of a general purpose dual-cartridge facemask to provide respiration protection against NH_3 using TDA's product carbon-based sorbent. Retail price of ~$10 for facepiece (center), and cartridges (bottom) for ~$11/pair (Mine Safety Appliances; MSA).

1.1.2. Ammonia Toxicity and NIOSH Standards

Ammonia readily dissolves in water and damages exposed moist tissues of the body, including especially the eyes and mucous-membranes of the nose, throat and lungs. Exposure to ~2500-4500 ppmv NH_3 for ~30 min leads to death by pulmonary edema or asphyxiation caused by NH_3 blockage of oxygen binding to hemoglobin, and at ~5000 ppmv NH_3 is immediately fatal. The U.S. Occupational Safety and Health Administration (OSHA) rates 300 ppmv NH_3 as *Immediately Dangerous to Life and Health* (IDLH). At 150 ppmv, levels that are often reached in agricultural settings, lung tissue can be scarred for life causing chronic respiratory illness. The NIOSH recommended Time-Weighted Average (TWA) over an eight hour working day is 25 ppmv—but many agencies argue that this is too high. The American Industrial Hygiene Association recommends a TWA of 7 ppmv as do NASA toxicologists [7]. The Short-Term Exposure Limit (STEL) for ammonia is 35 ppmv, time-weighted over 15 min [2].

Repeated exposure to ammonia contributes to “farmers’ lung”, which is triggered by ammonia and other airborne agricultural agents [3]. In fact, of the nation’s 1.8 million farmworkers, 13.8% annually reported respiratory symptoms (runny stuffy nose or watery itchy eyes) while 3.1% reported wheezing/whistling in the chest [4]. Respiratory disease workers compensation claimants had an elevated relative risk of 3.27 (95% CI 2.09-4.86) for mortality from nonmalignant respiratory diseases (NMRD) while emphysema mortality was particularly high, with a relative risk of 5.94 (95% CI 2.56-11.70) [5]. These figures are especially alarming because 77% of farm injuries go unreported [6], possibly because many temporarily hired farm workers have undocumented immigration status [7].

Ammonia has also been implicated in chronic bronchitis [8]. For community exposure of children and the elderly, who are often exposed downwind from CAFOs, the ammonia concentration should not exceed 300 ppbv. Although ammonia is not currently regulated as an air pollutant, many groups have been advocating for stricter regulations. Eye damage and temporary blindness have occurred at chronic ammonia exposures as low as 6 ppmv, and permanent blindness at higher levels. Initial eye-tissue damage and necrosis caused by ammonia is often followed by conjunctivitis and secondary eye infections. For these reasons, gas-proof goggles should also be worn with half-facepiece ammonia respirators to protect the eyes.

An added benefit of wearing an ammonia respirator with a built-in HEPA filter is protection from inhalable hazardous particulate matter (PM) that is ubiquitous in agricultural environments. Ammonia is a precursor to secondary ammonium nitrate aerosol, where gaseous ammonia reacts with gaseous nitric acid to form particulate ammonium nitrate [9]. Particles containing sulfuric acid form from the oxidation of gaseous SO_2; these react with other gases, including ammonia. Smaller particles tend to agglomerate into larger ones; photochemistry can take place in some. PM includes primary particles emitted directly from farm sources and the secondary particles generated from atmospheric reactions (and from condensation growth) that tend to be smaller than 1 µm in aerodynamic diameter, making them particularly dangerous in the lungs.

1.1.3. The Need for Improved Activated Carbons for Ammonia Respirators

To protect personnel from dangerous levels of ammonia, manufacturers of respirators had relied upon a phosphoric-acid (H_3PO_4) treated activated carbon produced from coconut-shell sold by Barnebey & Sutcliffe (B-S Carbon 3032). This company has since been acquired by Calgon Carbon, which discontinued B-S Carbon 3032, but sells its own variety of coconut-shell carbon impregnated with phosphoric acid for ammonia adsorption called Ammonasorb II.

However, researchers at NASA [10], for example, reported that Ammonasorb II has 30% lower capacity for ammonia than Chemsorb 1425, the best commercially available sorbent manufactured by Molecular Products, Inc. (which is currently only available in bulk and not inside a respirator cartridge), and 3M's best ammonia sorbent used in respirator cartridges is only slightly better than Ammonasorb II, as verified in our laboratory (Figure 2). This implies that commercial ammonia respirators already suffer from at least a 30% shorter service life—a very significant decrease, and are 30% larger and heavier than they need to be, further obstructing vision and adding to wearer discomfort. This has provided us with the opportunity to develop a replacement ammonia sorbent. Really, what we are doing is dramatically lowering the amount of sorbent that is needed, thereby lowering the cartridge size, weight and breathing resistance (and cost), and making a more comfortable to use mask that people might actually wear. These improvements are crucial to obtain adoption of the new ammonia cartridge by the agricultural community.

1.1.4. Review of State-of-the-Art Sorbents for Ammonia Respirators

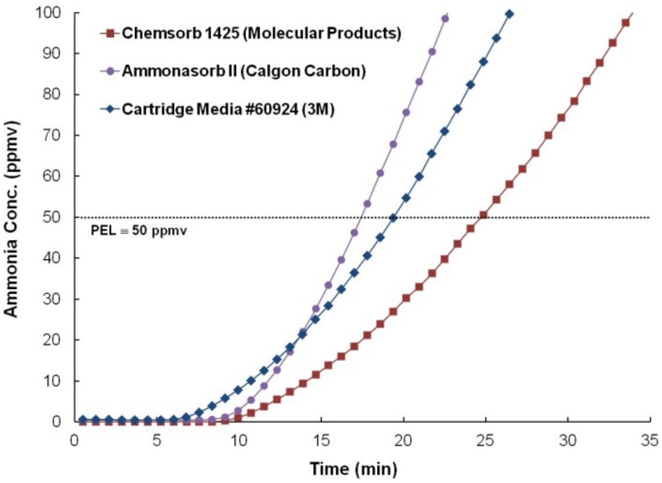


Figure 2. Ammonia breakthrough curves for commercial carbon sorbents. Test parameters scaled to NIOSH standard test protocol (STP): 4.84 cm^3 carbon (bed depth = 1.27 cm) challenged with 1000 ppmv NH_3 in 3.1 slpm air at 50% RH and 24°C.

Activated carbon is commonly used in respirators to remove various contaminants such as organic vapors (e.g., benzene, formaldehyde, etc.) and acid gases (e.g., SO_2, NO_2, HCN, etc.) because of its high internal surface area (>1000 m^2/g) that provides ample sites for these species to adsorb. However, activated carbon by itself is almost completely ineffective for removing ammonia. Significant post-treatment of carbons (by the impregnation of additives) is needed to make them effective for ammonia adsorption. Before it was discontinued by Calgon (a leading carbon manufacturer), Barnebey & Sutcliffe (B-S Carbon 3032) was preferred for use in ammonia respirators. This carbon was produced from pyrolized coconut shell, etched by steam at 900°C to produce slit-shaped micropores (1-2 nm) and materials with very high surface area (>1000 $m^2 \cdot g^{-1}$). Coconut shell has been a preferred source of carbon since its use in gas masks during World War I due to its very high biomass density that allows for compact gas-mask canisters [11]. Etching the carbon with steam produces carbon edge sites terminated principally with hydrogen, ether (C-O-C), phenolic (--OH) and carbonyl/quinine (--C=O) type functional groups [12], which in general are ineffective for binding ammonia. Therefore, carbons are treated with H_3PO_4 to yield an acid content of up to 30 wt.%. Under moist acidic conditions, water condenses in the micropore capillaries and NH_3 is converted into NH_4^+, which reacts to form the stable compound ammonium phosphate, $NH_4H_2PO_4$ (m.p. 190°C). Other leading carbons such as Molecular Products' Chemsorb 1425; Calgon's Ammonasorb II, and Tigg HP are also based on coconut-shell carbons impregnated with H_3PO_4, but Chemsorb 1425 is the best of these by at least 30% [10].

Nucon International offers Ammosorb I-3, which is a coal-based steam-etched carbon further oxidized with nitric acid, which produces a high concentration of carboxylic acid (--COOH) functional groups that can react with basic NH_3 and adsorb NH_4^+, while any remaining nitrates form stable NH_4NO_3 (b.p. 210°C). Heating carboxylic acid groups produces anhydrides and lactones, which can also react with NH_3. According to NASA scientists [10], Dräger X-plore carbons contain ~4 wt.% chloride ion that can react with NH_3 to form very stable NH_4Cl (b.p. 520°C). Zeolites and aluminosilicate clays with strong Lewis acid sites on the surface can bind with the lone pair of electrons of

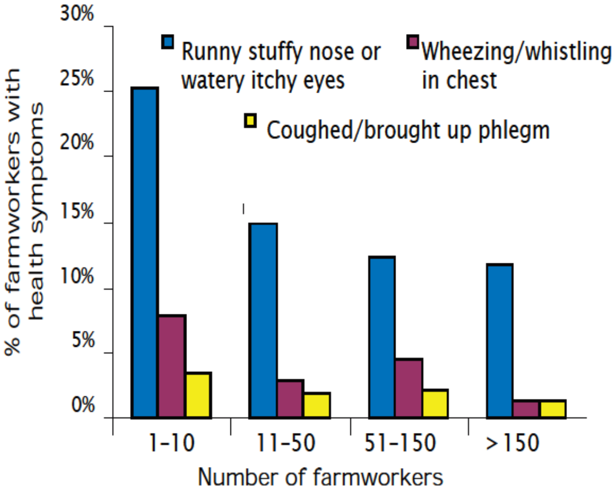


Figure 3. Respiratory symptoms by number of farmworkers employed by farm (DHHS, 2009).

ammonia (**:**NH_3). Zeolites ion-exchanged with transition metals, and especially with $CuCl_2$, are excellent sorbents, the Cu forming stable ammonia coordination complexes [13].

1.1.4.1. Patented Additives for Ammonia Uptake

In general, all manufacturers start with a carbon support, which has no ammonia capacity, and add metal salts, organic and inorganic compounds, and other groups to the carbon that bind to ammonia. Even though it is the additives and not the carbon that removes the ammonia, the pore structure and surface chemistry of the underlying carbon is critical for the ammonia capacity and capture kinetics of the final sorbent. In the patent literature, Dräger [14, 15] and 3M [16] describe the use of various metal additives including Al, Cu, Zn, Ag, Mo, W, V, Cr, Co, Zr, sulfate, and bisulfates ions to capture ammonia [17-20]. The metals Cu, Zn, and Ag form stable coordination compounds with ammonia; the oxides of Mo, W, V and Cr form stable ammonium compounds, and sulfate ions form stable $(NH_4)_2SO_4$ (d. 240°C). Calgon [21] discusses additives containing up to 10 wt.% sulfates and salts of Zn, Cu, Mo, Ag, Cr, Co, Ni, Fe, V, with a preference towards sulfates and Mo, Zn, and Cu.

Additives consisting of organic nitrogen compounds such as pyridine, TEDA (triethylenediamine), TEA (triethyleamine) and DABCO (1,4-diazabicyclo-2,2,2-octane) are often added (especially to CBRN-type cartridges) to aid in the removal of cyanide (HCN), cyanogen chloride (CNCl) and methyl bromide (CH_3Br) [16, 22-24]. They also extend shelf life and may promote metal dispersion by forming chelates, but these compounds have little affinity for ammonia.

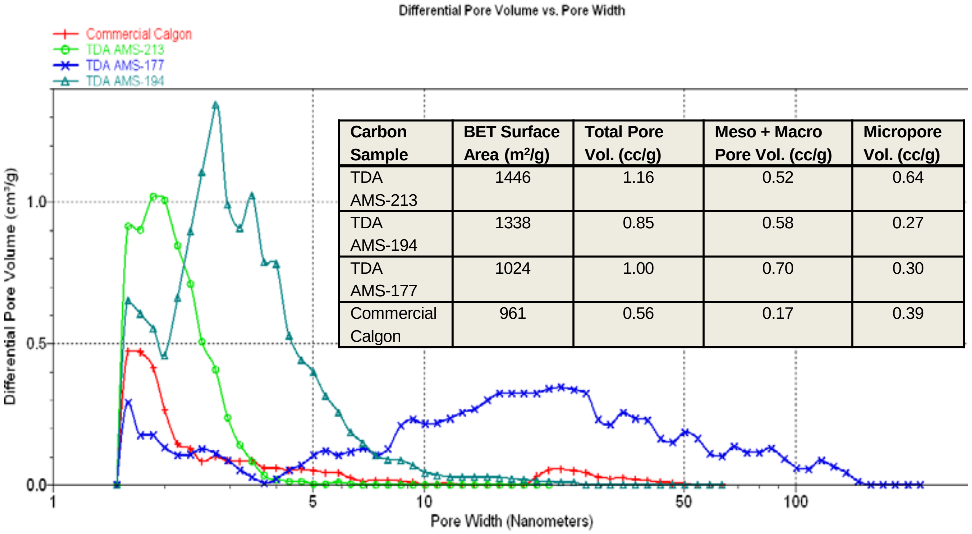
1.1.5. The Need for Superior Carbons

In most cases, the additives that bind NH_3 to unreactive carbon are incorporated into porous supports by manufacturers using the standard incipient-wetness impregnation technique where the additive precursor is dissolved in a solvent (preferably water), and the solution is infused into the pores of the carbon support via capillary action, followed by drying. Impregnation is used because it is a simple, cost-effective way to manufacture large amounts of sorbent at industrial scales. Vacuum and/or heat may also be applied to aid in the process [15]. The solvent is subsequently evaporated, depositing the precursor(s) inside the pores of the carbon.

A problem with steam-etched, coconut-shell-derived carbons is that almost all of the pores are micropores (defined as <2 nm) that are too small to accommodate chelated metal compounds with bulky ligands or large polymolybdate or polytungstate anions. Furthermore, if the pores are too small, the precipitated additives can plug the entrance to the pores, blocking diffusion of ammonia deeper into the pores and making much of the pore volume ineffective. Finally, for many additives that are hygroscopic and bind ammonia as an ammonium ion (NH_4^+), the ion must diffuse through liquid water to reach a binding site. In general, micropores limit the rate of diffusion through liquids and thus the overall rate of ammonium ion uptake. In order to solve these problems, TDA has developed carbon supports that:

- have <u>high surface area</u> (>1200 m^2/g)
- are predominantly <u>mesoporous</u> (Figure 4) with pore diameters ranging from 2 to 50 nm that allow facile impregnation of precursors and faster diffusion of ammonia to adsorption sites (and faster diffusion of NH_4^+ through any liquid water in the pores)
- have <u>high pore volume</u> that accommodates more additive and improves the mass transfer of ammonia by diffusion within the working sorbent (Figure 4)
- have <u>built-in functional surface groups</u> that improve ammonia adsorption capacity and impregnant dispersion (Figure 5 and Figure 6).

TDA's patented carbon and its synthesis technique is designed to make carbons that have all the necessary desired characteristics described above [25-27].



Carbon Sample	BET Surface Area (m^2/g)	Total Pore Vol. (cc/g)	Meso + Macro Pore Vol. (cc/g)	Micropore Vol. (cc/g)
TDA AMS-213	1446	1.16	0.52	0.64
TDA AMS-194	1338	0.85	0.58	0.27
TDA AMS-177	1024	1.00	0.70	0.30
Commercial Calgon	961	0.56	0.17	0.39

Figure 4. Comparison of pore-size distribution of a commercial Calgon carbon (red) to select TDA carbons. Larger pores of TDA carbons enhance liquid-phase diffusion of $NH_4^+$and accommodate the bulkier ammonia-binding additives used in manufacture of ammonia respirators (lower cutoff shown is ~1.4 nm).

1.2. Approach

1.2.1. Innovation – TDA's Patented Mesoporous Carbons

TDA has 20 years of experience in synthesizing mesoporous carbons [27-29] and holds four U.S. patents on processes for their manufacture [25, 26, 30, 31], with additional patents pending. TDA was originally funded by the U.S. DOE to develop carbons for use as ultracapacitors for electrical energy storage, where mesopore volume is a crucial determinant of performance due to the diffusion of ions, as described previously [27]. These carbons all utilize inexpensive (but highly-purified) precursors such as carbohydrates and saccharides, including glucose, sucrose, fructose, lactose and starch [26].

The first step in the manufacturing process is to mix the precursor materials with pore formers such as ammonium phosphate, bicarbonate, and linking agents, and the mixture is then subjected to an activation step where the hydrogen and oxygen are removed from the carbohydrate as water by a combination of chemical dehydration using phosphoric acid and moderate heating (e.g., 200°C). The char is then carbonized and activated at higher temperatures (e.g., 500-900°C) in a rotary kiln. The resulting pore structure of these carbons is distinct from off-the-shelf, commercial coal- and biomass-based carbons with a superior range of mesopore size distribution and mesopore volume. Furthermore, the carbon is not contaminated with lead, arsenic, alkali, etc.

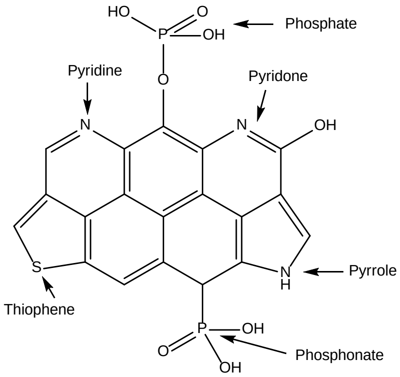


Figure 5. Specialized functional groups of TDA carbons proposed for use in ammonia respirators.

1.2.1.1. Surface Area and Mesoporosity

Mesoporosity is not exclusive to TDA's carbon, but the disproportionate volume of micropores in our carbon is unique; essential for rapid uptake kinetics because it allows ammonia to rapidly diffuse into the sorbent granules to access the internal adsorption sites. Mesoporosity is created during the production process by the addition and decomposition of ammonium compounds such as ammonium phosphates and ammonium bicarbonates. Most of the commercial activated carbons used for the adsorption of small gas molecules nearly exclusively contain micropores that are <2 nm. For example, the pore-size distribution in a leading commercial Calgon carbon is compared to that of TDA's carbons in Figure 4.

Whereas all the carbons in Figure 4 have high surface areas, the Calgon carbon almost exclusively contains micropores, which are too small to accommodate many of the preferred ammonia-binding additives. In contrast, the TDA carbons have significant mesoporosity, which can be tailored, as illustrated by the variation between the different samples in Figure 4. The total pore volumes for the TDA carbons, and more importantly the sum of the macropore + mesopore volume, are significantly higher than those of the Calgon carbon—as much as 4 times higher (see the data in the table inset into Figure 4). The presence of some micropores in TDA's carbon is inevitable, but these can account for an important fraction of the surface area upon which ammonia can adsorb because these pores are accessible through the mesopores.

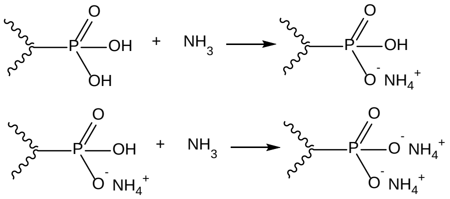


Figure 6. Binding of NH_4^+ to phosphorus functional groups of the proposed carbons for NH_3 removal.

1.2.1.2. Mesoporous Carbon Sorbents with Graphitic Edge Sites Modified with P and N

TDA carbons were produced from the dehydration of glucose (or starch hydrolyzed into glucose) using phosphoric acid, which reacted with glucose to initially form compounds such as glucose-6-phosphate. Upon mild pyrolysis, graphitic sheets formed that were bound together through the edges by polyphosphate cross-linking agents, yielding highly porous carbonaceous materials ("char"). Depending upon treatment conditions, phosphorus binds to graphitic edge sites as mixtures of phosphates and phosphonates (i.e., phosphorus bound directly to carbon as depicted in Figure 5), as evidenced unambiguously by X-ray Photoelectron Spectroscopy (XPS) P-peak-shift analysis (spectra not shown here).

Both phosphate and phosphonate groups are highly acidic (the as-prepared carbons have intrinsic pH of ~3), and react with basic ammonia forming stable ammonium phosphate species (Figure 6), which is only one of several possible ammonia capture mechanisms. Thus, unlike most carbons, which do not appreciably adsorb ammonia by themselves, TDA carbons have significant capacity for ammonia, even without additive treatment (Figure 7). The difference between the shapes of ammonia breakthrough curves for TDA's unmodified carbons AMS203 (advanced mesoporous sorbent) and AMS213 is due to the different pore structures in these carbons; specifically the ratio of mesopores to micropores (AMS203 is more mesporous).

1.2.1.3. Incorporation of Nitrogen to Aid Ammonia-Adsorbing Additive Dispersion

TDA's patented carbon manufacturing process employs ammonium phosphates that serve the primary purpose of creating mesoporosity upon pyrolysis because some of the nitrogen from the decomposing ammonium ions is incorporated into the graphitic edge sites and intercalate between the lattices of graphene sheets. Peak shifts in XPS indicate that N is bound primarily in the form of aromatic pyridinic and pyridonic groups with some pyrrolic species, as shown schematically in Figure 5.

Nitrogen groups do not directly participate in binding either NH_3 or NH_4^+, however, its purpose is to act as a ligand for binding and dispersing the compounds that, in turn, adsorb ammonia and which are used by respirator manufacturers in their proprietary treatments [14, 16]. Pyridine forms stable complexes with copper(II) chloride and zinc (II) chloride (well established since the 1880s), and analogous compounds are likely formed at the pyridinic edge sites, thus allowing dispersion of both $CuCl_2$ and $ZnCl_2$. Highly dispersed chloride ion is also essential for binding ammonium ions as stable NH_4Cl. The phosphorus species also bind Cu and Zn ions as stable phosphates and also aid in metal-ion dispersion.

We discovered early in Phase I that phosphoric acid impregnation treatments were much more effective than either copper or zinc (see Results section that follows). In that case, phosphorous and nitrogen surface groups may have aided in loading the carbon with H_3PO_4 by acting as surfactants that helped wet the internal surfaces and enabled more thorough and even dispersion of H_3PO_4 within the pores.

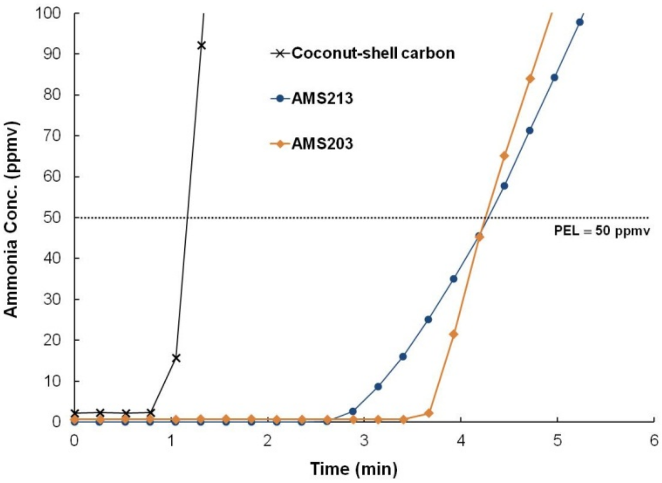


Figure 7. Ammonia breakthrough curves for as-prepared TDA mesoporous carbons vs. coconut-shell microporous carbon. Scaled NIOSH standard test protocol (STP): 4.84 cm^3 carbon (bed depth = 1.27 cm) challenged with 1000 ppmv NH_3 in 3.1 slpm air at 50% RH and 24°C.

1.2.2. Collaboration with Respirator Manufacturers

TDA has initiated a new collaboration with Molecular Products Group (MPG), one of the world's leading suppliers of impregnated activated carbon adsorbents and manufacturer of life critical devices for the treatment of breathable gases. The company traces its roots back to 1924 and the Medical Practitioners United Drug Co. of East London. The company was established in 1973 in Harlow, Essex, UK, when this supplier of high quality calcium chloride to the local pharmacy industry was acquired by Bill McKernan. the company is still growing and has annual revenues of $25M, with 130 employees worldwide, manufacturing products sold to a global customer base with distribution offices in Australia, China and India. Its US headquarters and primary domestic manufacturing facility is located near TDA in Boulder, Colorado.

TDA designed carbons based on MPG's specific needs: a) high surface area carbons with b) mesopores, c) high macro- and mesopore volume and d) ammonia-adsorbing functional groups. These carbons were sent to MPG for post treatment, testing and evaluation. In the Phase II project, TDA will continue working with MPG to further improve our carbons with the objective of commercializing our carbons for ammonia removal (with eventual application to other types of sorbents). Should TDA carbons meet MPG's performance requirements, and depending upon future MPG business needs and priorities, we will begin negotiations for an exclusive supply agreement.

1.2.3. Criteria for Phase I success

The success criteria for Phase I was to develop an activated carbon sorbent with at least 1.5 times the ammonia capacity of the best commercially available sorbent (i.e. MPG's Chemsorb 1425), and that cost less.

1.3. Results

In this Phase I project, we optimized the ammonia uptake capacity of a sorbent for use in ammonia respirators based on TDA's activated carbon. We achieved success by simultaneously combining our carbon's intrinsic properties of both high mesopore volume and phosphorous surface groups with additional impregnation with phosphoric acid (H_3PO_4), the most effective ammonia adsorbing additive for superior uptake. By improving each step of the synthesis process, we succeeded in achieving all of our Phase I goals. We developed and optimized the ammonia sorbent, concentrating on its uptake kinetics and capacity. We evaluated the effectiveness of several concentrations of H_3PO_4 solutions and identified the most effective impregnation procedure. We thoroughly characterized the sorbent's physical and chemical makeup using analytical methods such as ICP, XRD, and nitrogen adsorption isotherms, and demonstrated its performance by running dynamic breakthrough tests in a bench-scale environmental chamber.

Discussion of the results follows in the next Section. While substantial progress was realized towards our goals, none of the parameters were completely optimized for the current sorbent, and even further improvements are expected from Phase II research.

1.3.1. Task 1. Fabrication & Characterization of Mesoporous Carbons Incorporating P & N

We achieved our aims in Task 1 by fabricating mesoporous carbons with different mesopore/micropore ratios and volumes, surface areas, and quantities of phosphorous and nitrogen groups that served as an ideal support for impregnation with the ammonia adsorbing additive phosphoric acid. Several carbons (both as-prepared and modified for ammonia removal) were highly characterized for a scientific understanding of the features optimum for impregnation and ammonia capture.

1.3.1.1. Synthesis of Mesoporous Activated Carbon

The carbon manufacturing process is shown schematically in Figure 8. The general procedure for preparing mesoporous activated carbon using TDA's patented method was to:

Step 1: Blend the ingredients (glucose, dextrose, starch, other carbohydrates; vary phosphoric acid, ammonium compounds) together in an industrial mixer (Figure 9).
Step 2: Pour mixtures into Teflon trays and heat (e.g., 180-300°C), to dehydrate and form char; vary template, temperature and duration to influence the mesopore structure (Table 1).
Step 3: Crush agglomerated solids into granules.
Step 4: Carbonize in a rotary kiln under inert atmosphere (N_2) at high temperature (≥ 500°C) to desorb O and H as H_2O, CO and CO_2 forming micropores and increasing surface area.
Step 5: Granulate the carbons obtained from the rotary kiln to 12×20 mesh particle size for use in respirator cartridges.

By varying proprietary pore-former formulations, and thermal treatment temperatures and

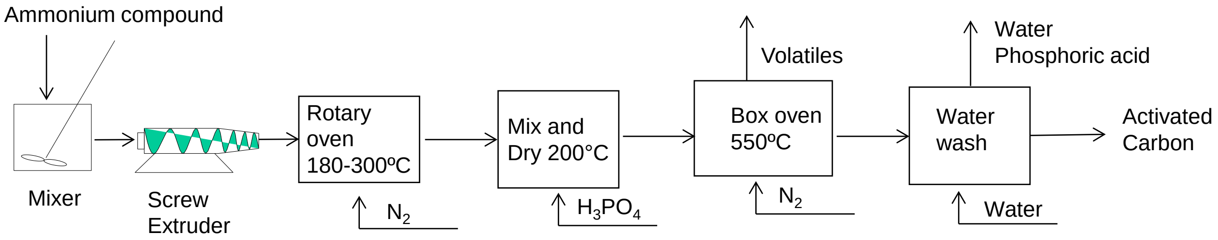


Figure 8. Flow diagram for carbon production process.

durations, the mesopore and micropore volumes (and their ratio) were changed. The first step was to mix the ingredients in our industrial mixer (Hobart, Figure 9) and then extrude 1/16” pellets (Figure 12) using our Bonnot screw extruder (Figure 10). The pellets were charred in a quartz rotary furnace (Figure 11) under flowing nitrogen. The process temperature of this step was key in determining the mesopore size distribution in the final product (Table 1).

Table 1. Carbon charring temperatures.

Sample ID	Char Temp. (°C)
AMS-203	180
AMS-212	300
AMS-213	250

The charred pellets were mixed with phosphoric acid and dried at 200°C, followed by carbonization in our box oven retort (L&L) under flowing nitrogen at 550°C (Figure 13). The product was placed in a stainless steel column that has a fritted disk on the bottom to continuously wash the carbon and remove the residual phosphoric acid (Figure 14). The column was 10.2 cm (4 inches) in diameter and about 90 cm (3 ft) tall, and it could hold up to 10 kg (22 lb) of carbon. After washing, the carbon was dried in an oven at 100°C and was then ready for impregnation with phosphoric acid.

Figure 9. Industrial mixer (Hobart) used to homogenize the ingredients used to make mesoporous carbon.

Figure 10. TDA’s 5 cm (2”) screw extruder (Bonnot).

Figure 11. TDA’s 4” ID quartz rotary kiln used to form char from the extruded pellets under flowing nitrogen at 180-240°C.

Figure 12. Extruded pellets before the thermal processing steps.

Figure 13. Inconel retort oven (L&L) used to activate carbon char impregnated with H_3PO_4 at ≥500°C under inert atmosphere.

Figure 14. Filter column used to wash carbon.

1.3.1.2. Carbon Characterization

Thorough evaluation of the carbons was a prerequisite for optimizing it by further developing the synthesis and impregnation processes. Characterization yielded a good understanding at the fundamental scientific level, and allowed us to further modify the carbon pore structure and chemistry to optimize the sorbent for maximum ammonia uptake properties. The carbons were characterized to determine their surface area, pore-size distribution and pore volume by standard BET (Brunauer-Emmett-Teller) analysis and Density Functional Theory (DFT) methods using nitrogen adsorption/desorption isotherms collected at 77 K (Micromeritics ASAP2020). Quantitative elemental analysis was performed by Inductively-Coupled Plasma-Mass Spectrometry (ICP-MS), Further analysis was also performed by X-ray diffraction (XRD) to determine lattice constants, graphitic island dimensions and stacking widths, and pore-wall dimensions.

X-ray diffraction was performed on each of the samples to estimate the elemental composition and detect phase formation. Elemental composition in preferred samples was further quantified by ICP-AES (Inductively-Coupled Plasma Atomic Emission Spectroscopy). Concentrations of the phosphorous and nitrogen in the carbons were thereby correlated to the preparation conditions. X-ray Photoelectron Spectroscopy (XPS) was used to determine surface elemental composition and high resolution XPS was then used after sputter erosion to determine the chemical states of the elements in the carbons, as identified from XPS peak shifts.

Table 2. Surface areas and pore volumes of TDA carbons (Micromeritics ASAP 2020).

Carbon Formulation	**Lot #**	**BET Surface Area (m^2/g)**	**Total Pore Vol. (cc/g)**	**Mesopore Vol. (cc/g)**	**Micropore Vol. (cc/g)**
AMS-212	ZD710	804	0.40	0.09	0.31
AMS-203	ZD980	981	0.54	0.38	0.16
AMS-213	ZD1165	1136	0.55	0.16	0.39
MP carbon	commerical	1130	0.59	0.13	0.44

Table 3. Surface areas and pore volumes of the carbons treated with phosphoric acid.

Carbon Formulation	**Lot #**	**Treatment**	**BET Surface Area (m^2/g)**	**Total Pore Vol. (cc/g)**	**Mesopore Vol. (cc/g)**	**Micropore Vol. (cc/g)**
AMS-213	583	40.0% H_3PO_4	189	0.090	0.045	0.045
AMS-213	582	32.9% H_3PO_4	386	0.19	0.10	0.09
Chemsorb 1425		30% H_3PO_4	394	0.20	0.07	0.13

Surface Area & Pore Structure Analysis

The surface areas and pore volumes for the samples are shown in Table 2. Carbon types AMS-203, AMS-213 and AMS-212 were made using the same starting materials, but were charred at different temperatures (180°C, 250°C and 300°C, respectively) before being mixed with phosphoric acid and heat treatment at 500°C. We found that this charring step had significant influence on the poresize distributions in the carbons (Figure 15). We found that the both the size and the volume of mesopores changed with temperature (the higher the temperature, the smaller the mesopores and the lower the volume of mesopores). AMS-213 consistently gave the highest BET surface areas and micropore volumes. Compared to our as-manufactured carbons (AMS213 and AMS203), the unmodified base carbon that Molecular Products currently uses to make Chemsorb 1425 has greater micropore volume and smaller micropores (Table 2 and Figure 15). In Table 3 and Figure 16, we compare the surface areas, pore volumes and pore size distributions of the H_3PO_4-treated TDA carbons and Molecular Product's Chemsorb 1425 ammonia sorbent, which is the best performing commercially available ammonia sorbent [10]. Interestingly, we found that the best performing TDA sorbent (based on AMS213 impregnated with 32.9% H_3PO_4 additive solution)had similar surface area and pore size distributions, but greater residual pore volume than Chemsorb 1425 after impregnation,. Treating AMS213 with 40% H_3PO_4 solution eliminated the micropores (Figure 16), suggesting that this additive concentration was above the optimal loading.

X-ray diffraction

X-ray diffraction (XRD) patterns for the as-manufactured mesoporous carbons were collected using a Scintag θ/2θ diffractometer with a Cu target X-ray tube ($\lambda_{K\alpha}$ = 1.540562 Å) operating at

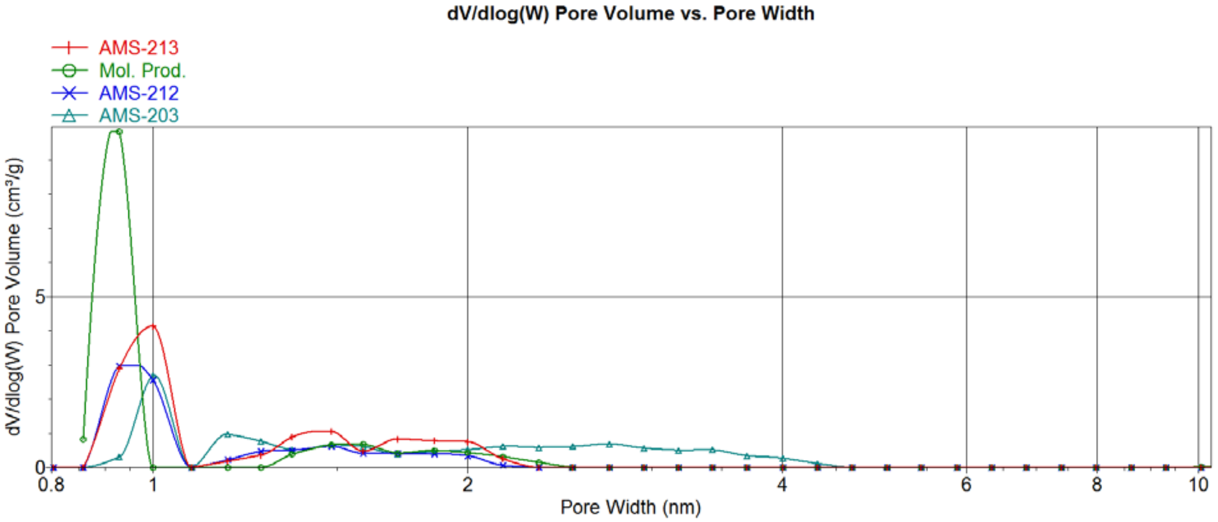


Figure 15. Pore size distribution of TDA carbons and Molecular Product's base carbon.

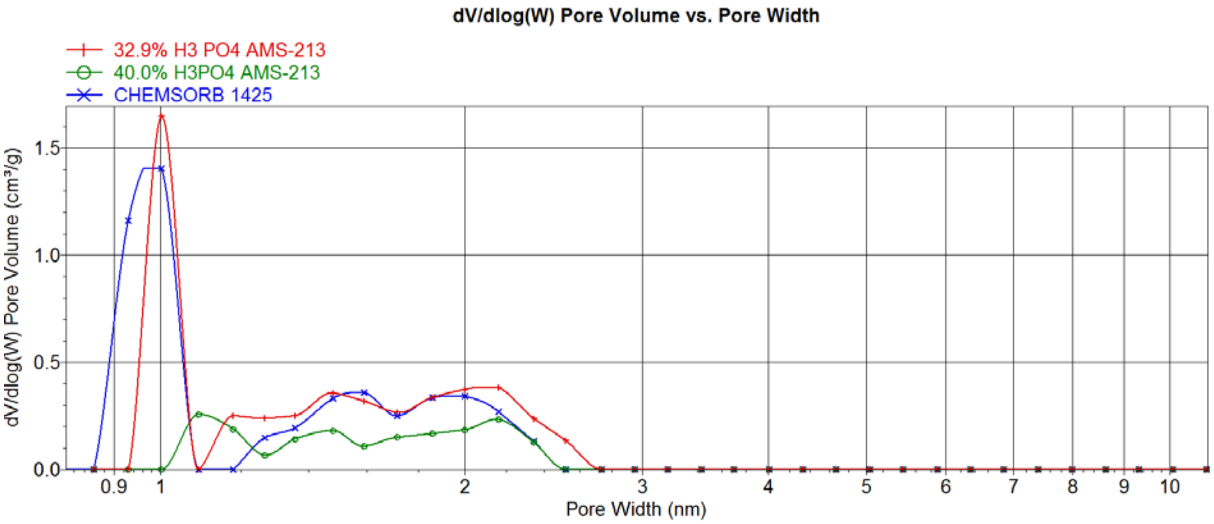


Figure 16. Comparison of pore size distribution of TDA samples and Chemsorb 1425.

45 kV and 40 mA. A XRD pattern for AMS203 is shown in Figure 17. A broad amorphous peak at ~2° (2θ) was evident in the spectrum due to the mesoporous domains, which indicated that the material is mostly amorphous as is typical for mesoporous/microporous activated carbon.

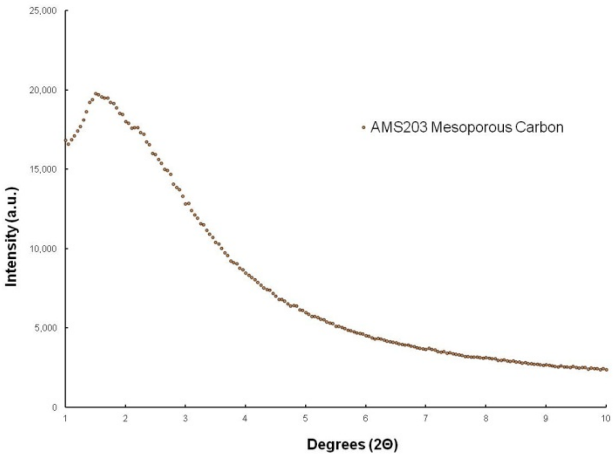


Figure 17. XRD pattern for as-prepared AMS203 mesoporous carbon.

Inductively-coupled-plasma Atomic Emission Spectrometry

ICP-AES was carried out by Huffman-Hazen Laboratories (Golden, Colorado) to quantify the elemental composition of the carbons and optimize the sorbent for ammonia removal. ICP-AES had a lower detection limit of low ppmw concentrations. The carbon samples were ground to -200 mesh particle size and dried at 200°C prior to digesting the samples and running them on the instrument. Table 4 shows the results of elemental analysis performed on the base carbons while the results of analyzing AMS213 treated with $ZnCl_2$ and H3PO4 are provided in Table 5 and Table 6, respectively.

Table 4. Elemental analysis of TDA carbons.

Carbon Formulation	**Carbon (wt%)**	**Hydrogen (wt%)**	**Nitrogen (wt%)**	**Oxygen (wt%)**	**Phosphorus (wt%)**	**Ash (wt%)**
AMS-203	84.70	2.38	1.26	7.26	3.35	0.85
AMS-212	72.02	1.63	3.30	15.59	4.03	4.39
AMS-213	81.17	1.24	2.72	10.25	3.70	0.87
Mol. Prod.	92.99	< 0.5	0.14	2.88	0.03	2.87

Table 5. Elemental analysis of $ZnCl_2$ treated sorbents.

Sorbent	C (wt%)	H (wt%)	N (wt%)	O (wt%)	Cl (wt%)	P (wt%)	Zn (wt%)	Ash (wt%)
3M 6004	72.89	0.99	0.09	2.72	10.8	0.04	10.51	11.17
3M 60924	71.52	0.95	0.10	3.10	10.9	0.04	10.59	12.09
AMS-213 (ZD1168)	73.74	1.43	1.52	8.54	4.3	3.76	4.62	17.63

Table 6. Elemental analysis of phosphoric acid treated sorbents.

Sorbent	C (wt%)	H (wt%)	N (wt%)	O (wt%)	P (wt%)	Ash (wt%)
MP AMS-203	64.61	2.09	1.00	22.42	10.91	5.77
MP AMS-213	60.39	2.06	1.30	24.46	12.93	4.70
Chemsorb 1425	68.67	1.38	0.08	20.19	9.56	4.89

Surface Chemical Analysis

X-ray Photoelectron Spectroscopy (XPS) analysis was carried out on TDA's carbons by Rocky Mountain Laboratories (Golden, Colorado) on a fee basis to obtain semi-quantitative elemental concentrations and to identify the various chemical-binding states of carbon, nitrogen, oxygen, and phosphorus. It should be noted that compositional analysis was semi-quantitative (i.e., ±10 at.%) for standardless XPS because accurate quantification of data could only be achieved through the use of well characterized reference materials of similar composition to the unknown sample. XPS had a nominal detection limit of ~0.1 atom%. Samples were measured at a 90° take-off-angle (TOA) yielding a sampling depth of ~10 nm. The analysis area was ~500 μm in diameter. Analyses were performed with a monochromatic Al kα X-ray source. Energy scales of the spectra were referenced to the C 1s C-C/C-H signal at 284.5 eV.

High-Resolution X-ray Photoelectron Spectroscopy

XPS of elemental composition on the surface of the AMS213 carbon showed that the major elements that could be detected were carbon, nitrogen, oxygen and phosphorus (Table 7).

Table 7. Relative elemental composition of sample surfaces as determined by XPS.

Carbon Sample	C (Atom%)	N (Atom%)	O (Atom%)	P (Atom%)
AMS-213	90	1.0	7.6	1.0

High-Resolution XPS Analysis – Nitrogen. Figure 18 shows a high-resolution XPS of the N 1s region of AMS-213. The deconvoluted peak at 398.4 eV, accounting for 30 atom% of the nitrogen, was assigned to pyridine-like nitrogen at carbon edge sites. A second deconvoluted peak at 401.0 eV occurred at the binding energy of both pyrrolic and pyridonic nitrogen, and accounted for 70 atom% of the nitrogen in the sample

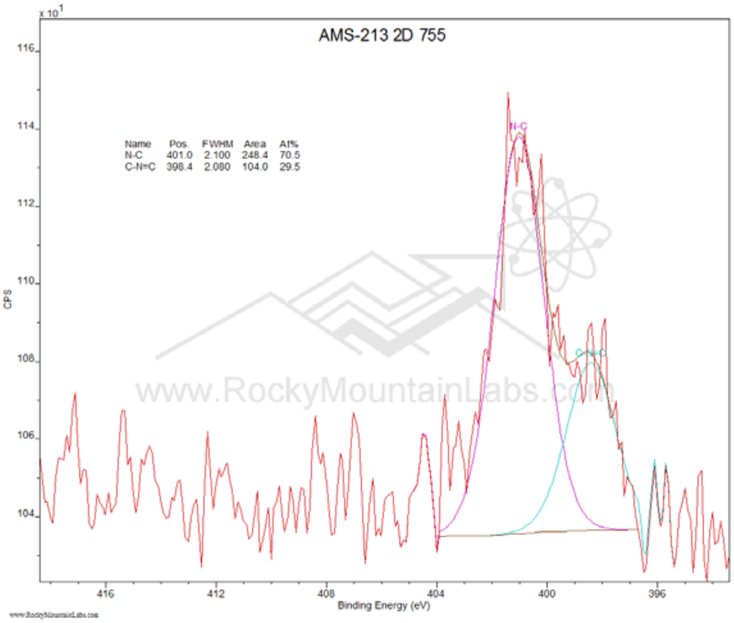


Figure 18. XPS hi-res spectrum of sample AMS-213, N 1s region.

High-Resolution XPS Analysis – Phosphorus. Figure 19 shows high-resolution XPS signals from P $2p_{3/2}$ and P $2p_{1/2}$ orbitals of sample AMS-213. Fitting the P with one specie gave a P $2p_{3/2}$ peak energy of 133.3 eV, which suggested that the P was present as phosphate groups.

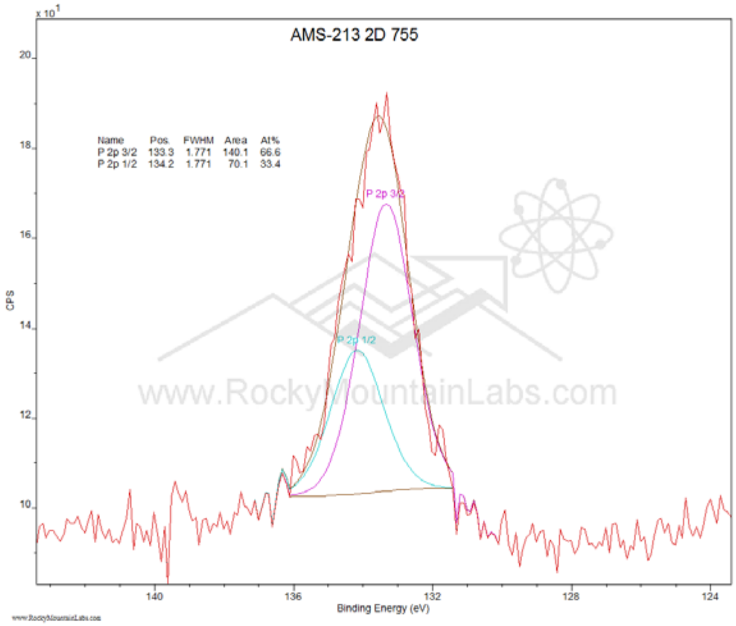


Figure 19. XPS hi-res spectrum of Sample #AMS-213, P 2p region.

High-Resolution XPS Analysis – Oxygen. Figure 20 shows high-resolution XPS of the O 1s region that indicated two chemical types of oxygen were present. The spectrum was consistent

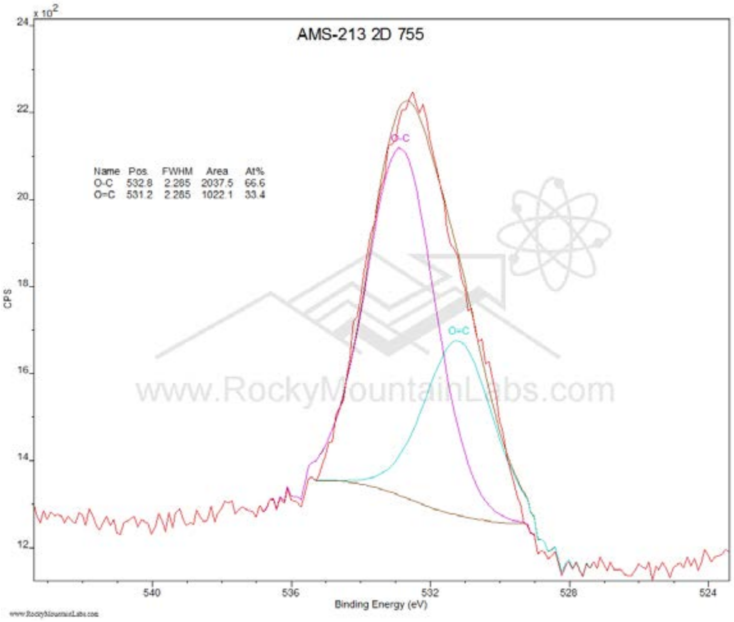


Figure 20. XPS hi-res spectrum of Sample #AMS-213, O 1s region.

with the presence of 33 atom% carbonyl and phosphate groups along with 66% hydroxyl groups.

High-Resolution XPS – Carbon. The carbon on the sample is present mostly as C-C, C-H, C-P (Figure 21). It was not possible to determine the difference between the C-C, C-H and the C-P in XPS. A small amount of the surface C in the sample was oxidized, as indicated by the detection of C-O and C=O, which was consistent with the O analysis.

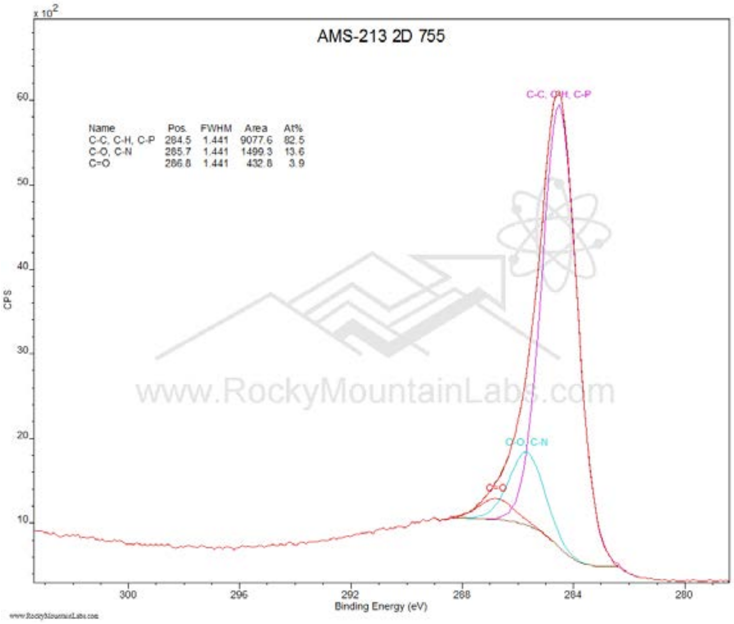


Figure 21. XPS hi-resolution XPS spectrum of Sample #AMS-213, C 1s region.

In Figure 22 we show the likely functional groups that were present on the carbon surface based on the XPS data. The most prominent phosphorus containing functional groups were the phosphate and phosphonate groups. In addition, there were a number of possible nitrogen containing functional groups, such as pyridine, pyridone, pyrrole and bipyridine type groups. XPS did not show evidence of oxidized nitrogen (i.e. nitrate). We speculate that the benefit of functional groups with heteroatoms, especially phosphate, allowed the phosphoric acid that was added to wet the surface of the carbon much better than Molecular Products' current base carbon, which did not have nitrogen or phosphorus functional groups. However, further investigation is warranted to fully elucidate the relationship between the elemental composition and ammonia affinity of TDA's carbons.

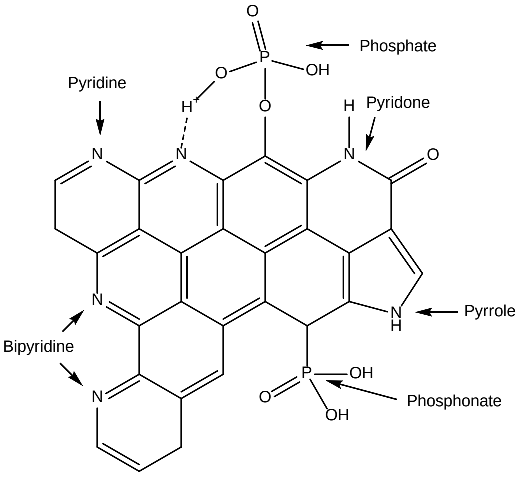


Figure 22. Postulated functionalities on the carbon surface.

1.3.2. Task 2. Ammonia Breakthrough Tests

All of the ammonia breakthrough tests were carried out at conditions that conformed with the NIOSH standard test procedure (STP) to simulate the performance of a full-size cartridge that contained 100 cm^3 of sorbent, but using a smaller sorbent bed with the same aspect ratio and a scaled-down air flow rate [1]. Behavior scales linearly with gas-hourly-space velocity (GHSV = 38,430 h^{-1}) at the same sorbent bed length to diameter (L/D) ratio; therefore, we tested a sorbent bed that contained 4.84 cm^3 of carbon (bed depth = 1.27 cm and L/D = 0.579) [1]. The particle size of all the sorbents tested was in the range of -12+20 mesh (0.85 mm to 1.7 mm; U.S. Standard sieve).

Prior to each ammonia breakthrough run, the sorbent was preconditioned in flowing air in-situ at the test humidity until the humidity reached steady state in the effluent (50% RH ± 3% RH). The sorbent was then challenged with 1000 ppmv NH_3 (± 2%) in 3.1 SLPM (± 50 SCCM) air at 50% RH (± 3% RH) and 25°C (± 2.5°C). All of the breakthrough tests in this report were run at these conditions, unless noted otherwise. After ammonia breakthrough, the endpoint time used to determine the ammonia loading was taken as the OSHA's permissible exposure limit (PEL ≡ 50 ppmv). Some tests were run until the ammonia concentration in the effluent reached >97% of the feed concentration (i.e., >970 ppm) to measure the saturation capacity of the sorbent.

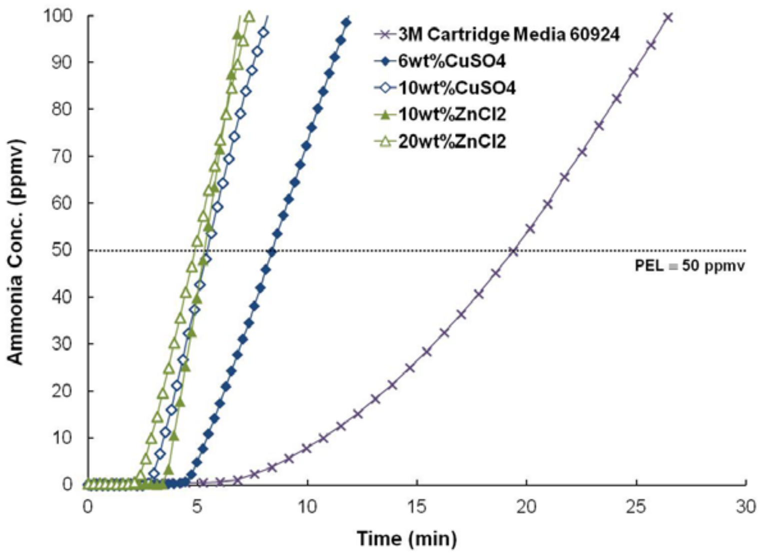


Figure 23. Ammonia breakthrough curves for TDA's mesoporous carbon (AMS213) impregnated with zinc and copper salts, compared to a commercial NH_3 sorbent (3M cartridge media #60924). Scaled NIOSH standard test: 4.84 cm^3 carbon (bed depth = 1.27 cm and L/D = 0.579) challenged with 1000 ppm NH_3 in 3.1 slpm air at 50% RH and 24°C.

1.3.2.1. Impregnation with Cu & Zn Additives

TDA's advanced mesoporous sorbent (AMS) type AMS213 activated carbon was impregnated via incipient wetness with either copper sulfate ($CuSO_4$) or zinc chloride ($ZnCl_2$) in aqueous solutions and dried at 200°C. A loading of 6 wt% Cu (metals basis) was the most effective (Figure 23), with an ammonia breakthrough time of 8.4 min, whereas unmodified AMS213 had a breakthrough time of 4.5 min (see Figure 7, shown previously). With further optimization of the metal salt loading on the carbon the performance could potentially approach that of the ammonia sorbent used in cartridges (3M #60924 media) that had a breakthrough time of 19.4 min (Figure 23), but as described next, we discovered that treating the carbon with phosphoric acid (H_3PO_4) was much more effective for removing ammonia (Figure 25). Therefore, we discontinued the development of an ammonia sorbent based on metal salt additives early in Phase I because they provided only marginal improvement in ammonia capacity over TDA's unmodified carbons.

1.3.2.2. Impregnation with Phosphoric Acid

In a preliminary parametric study, the concentration of aqueous acid solution used to impregnate TDA's AMS213 carbon via incipient wetness was varied from 10-30% (all acid concentrations in this report are in wt%). For these samples, only the exact amount of acid solution that could be adsorbed into the pores was added to the carbon and then it was dried at 200°C for 12 h to remove all residual water (the volatility of H_3PO_4 is negligible at 200°C). The amount of H_3PO_4 loaded into the carbon was between 6.7 and 37.7% (indicated in wt% in the plot legend in Figure 25). These samples had ammonia breakthrough times that were longer than the best copper sulfate impregnated carbon (6 wt% Cu; Figure 23), but were still only about half the performance of either the ammonia cartridge media (3M #60924) or Chemsorb 1425 (Figure 25).

1.3.2.3. Vacuum impregnation with phosphoric acid

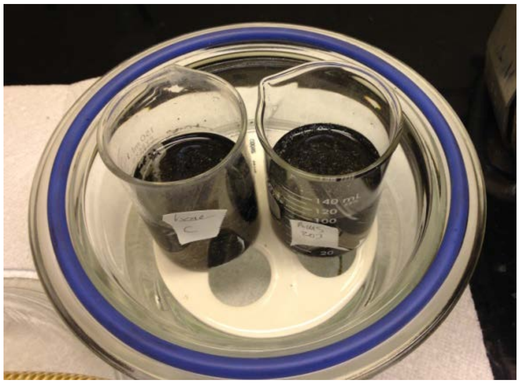


Figure 24. Vacuum-impregnation of TDA's mesoporous carbon with phosphoric acid solution.

AMS213 carbon was then loaded using 20%, 30%, and 40% H_3PO_4 solutions, but instead of simply impregnating the carbon with only enough solution to just fill up the pores, the carbon was immersed in excess H_3PO_4 solution and vacuum was applied to help remove residual gas trapped inside the pores and facilitate the penetration of the H_3PO_4 solution into the carbon (Figure 24). The H_3PO_4 loadings on these carbon samples were also determined after drying them for 12 h at 200°C; loadings of 30.9 wt%, 36.2 wt% and 40.9 wt% H_3PO_4 in the carbon were obtained from the 20%, 30%, and 40% H_3PO_4 solutions, respectively. Vacuum-assisted loading of active agent into the pores of the carbon resulted in much greater ammonia removing capability (Figure 27) that significantly outperformed even the best commercial ammonia sorbent (Chemsorb 1425), which was used as a benchmark.

The performance of the vacuum-impregnated carbon (as indicated by the endpoint, defined as the time to reach an ammonia concentration of 50 ppmv, the OSHA's PEL, at the bed outlet) seemed to peak around a concentration of 30% H_3PO_4 in the impregnating solution (Figure 27). To determine the optimal loading of H_3PO_4 in AMS213 carbon, we fit the test results with a parabolic curve to estimate the concentration of H_3PO_4 solution that would result in the best performance (Figure 26). The apex of the parabolic curve used to fit the data indicated that using a 32.9% H_3PO_4 solution should have resulted in the longest ammonia breakthrough time.

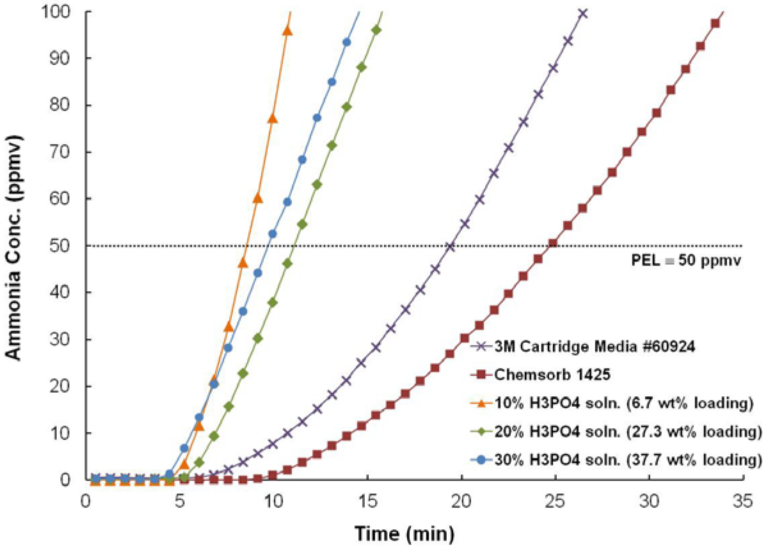


Figure 25. Ammonia breakthrough curves for TDA's mesoporous carbon (AMS213) impregnated with H_3PO_4 compared to ammonia cartridge media (3M #60924) and Chemsorb 1425 (the best commercial ammonia sorbent).

1.3.2.4. Pulsed-vacuum Impregnation with Phosphoric Acid

Based on the curve fit to the ammonia breakthrough test results (Figure 26), AMS213 was loaded with 30.0%, 32.9% and 40% H_3PO_4 solutions to bracket the estimated optimum composition. Furthermore, during impregnation the vacuum was pulsed by periodically returning to atmospheric pressure and re-evacuating multiple times during the 1.5 h soak to help drive air out and force the H_3PO_4 solution even deeper into the pores.

The pulsed-evacuation impregnation method resulted in better performance than continuous evacuation did for the 40% H_3PO_4 solution (Figure 28), possibly due to the additional H_3PO_4 that was loaded into the pulse-evacuated carbon (47.0 wt% vs. 40.9 wt%). However, AMS213 that was pulse-evacuation impregnated with 32.9% H_3PO_4 solution resulted in even greater improvement in the ammonia breakthrough time (Figure 29), even though it was loaded with a slightly lower amount of H_3PO_4 compared to the pulse-impregnated 40% sample (46.3 wt% vs. 47.0 wt%). The sample pulse-impregnated with 30% H_3PO_4 solution performed almost identically to the 40% sample, but it had a significantly lower loading (42.1 wt%).

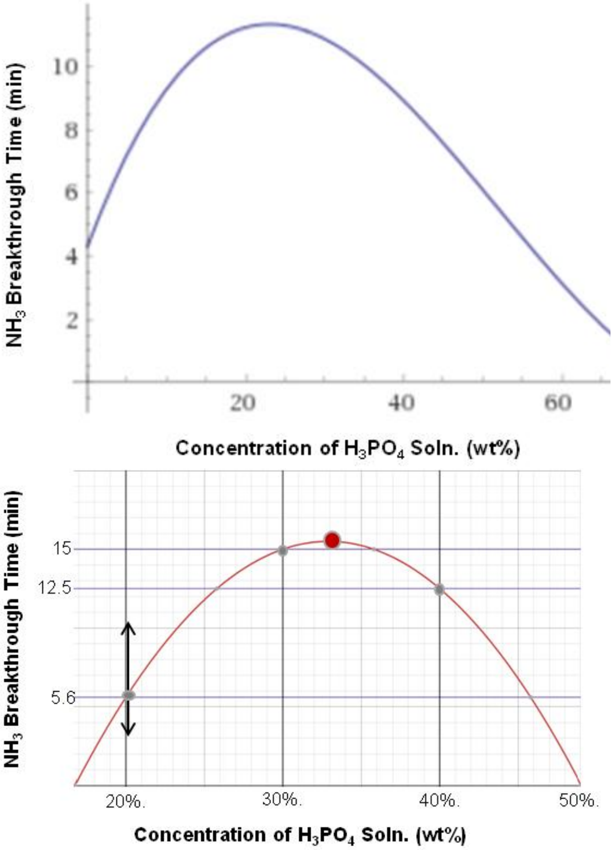


Figure 26. Top: fit of the endpoint times (at 50 ppmv) from ammonia breakthrough tests on TDA's mesoporous carbon (AMS213) that was vacuum impregnated with H_3PO_4 to estimate the most effective composition of impregnant to use. Bottom: Closeup view of the parabolic fit through the optimal region of test data.

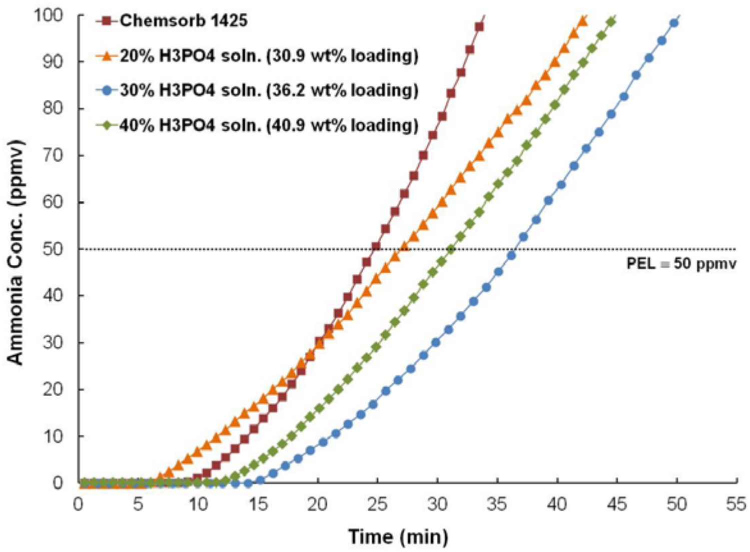


Figure 27. Ammonia breakthrough curves for AMS213 vacuum-impregnated with H_3PO_4, benchmarked against Chemsorb 1425 (the best commercial ammonia sorbent).

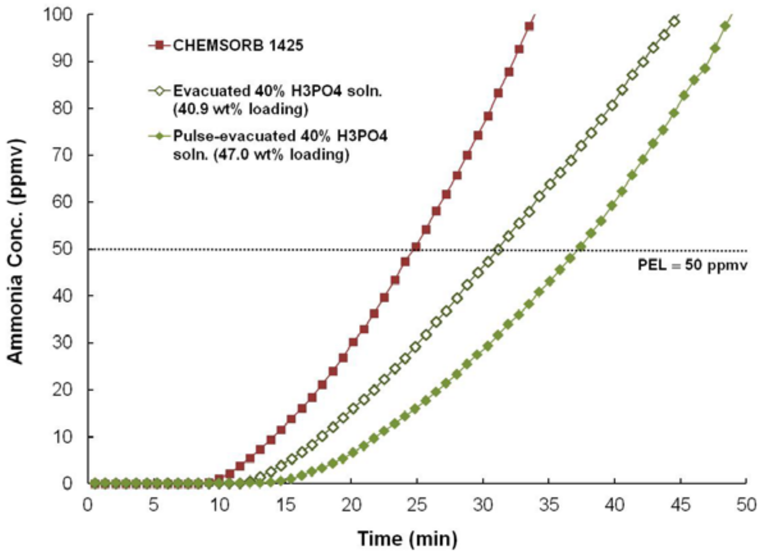


Figure 28. Ammonia breakthrough curves for AMS213 either vacuum- or pulsed-vacuum-impregnated with 40% H_3PO_4 solution. Chemsorb 1425 shown for comparison.

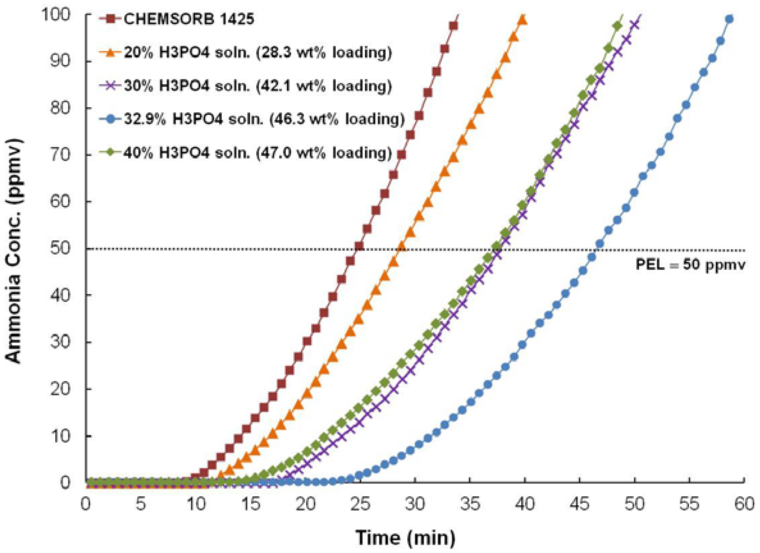


Figure 29. Ammonia breakthrough curves for AMS213 pulsed-vacuum-impregnated with different concentrations of H_3PO_4 . Chemsorb 1425 shown for comparison.

These results suggested that both the H_3PO_4 loading and the method of impregnation affected the distribution of H_3PO_4 within the pores. The sorbents with greater than the optimal loading of phosphoric acid (i.e. > 47 wt%) had slower uptake kinetics as evidenced by shorter breakthrough times, but had greater ammonia saturation capacities due to the additional reactant that resided inside the pores. The sample that was pulse-impregnated with 20% H_3PO_4 solution contained only 28.3 wt%, which appeared to be outside of the optimal range of loadings, as indicated by its shorter breakthrough time (Figure 29).

For comparison, another of TDA's carbon materials (prepared using a modified recipe and

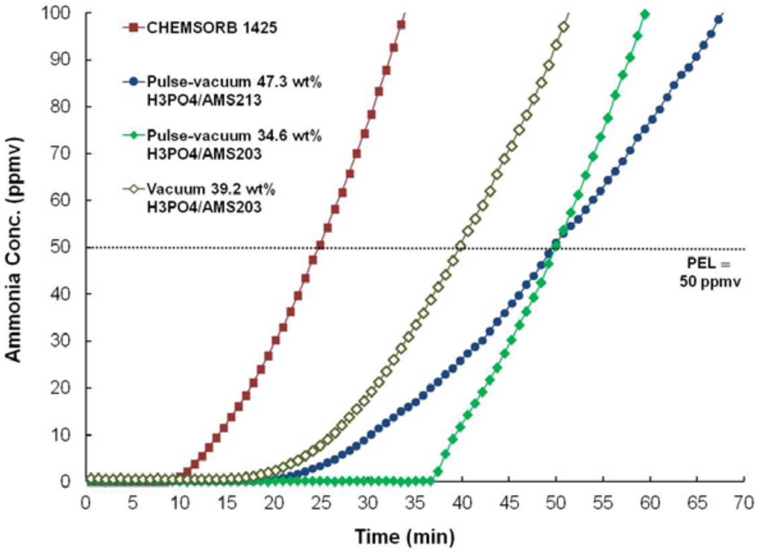


Figure 30. Ammonia breakthrough curves for AMS203 and AMS213 vacuum- or pulsed-vacuum-impregnated with 32.9% H_3PO_4 solution. Chemsorb 1425 shown for comparison.

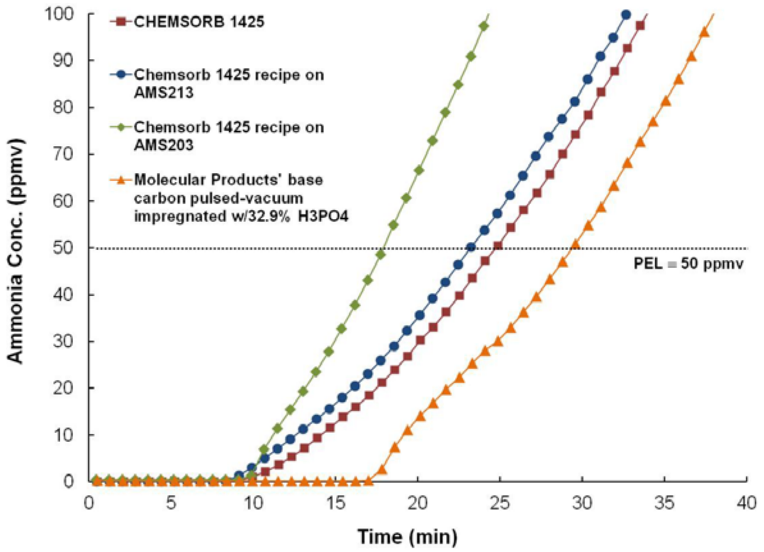


Figure 31. Ammonia breakthrough curves for AMS213 and AMS203 synthesized by Molecular Products H_3PO_4 like Chemsorb 1424. Molecular Products' base carbon treated with 32.9% H_3PO_4 using pulsed-vacuum impregnation by TDA and Chemsorb 1425 shown for comparison.

designated AMS203) that had a different, more mesoporous structure (0.38 vs. 0.16; see Table 2) was impregnated with 32.9% H_3PO_4 solution using either vacuum- or pulsed-vacuum-impregnation. The resultant H_3PO_4 loading on AMS203 was either 39.2 wt% (vacuum) or 34.6 wt% (pulsed-vacuum) and its performance was equivalent to AMS213 that was prepared similarly (with pulsed-vacuum-impregnation). However, it should be noted that the breakthrough curves were shaped differently (Figure 30) because the increased mesoporosity allowed ammonia to more readily diffuse into the pores to reach the adsorption sites during the test.

Interestingly, AMS203 was loaded with significantly less H_3PO_4 than AMS213 under the same impregnation conditions (34.6 wt% vs. 47.3 wt%), but performed just as well, which suggests that further optimization of the loading on AMS203 is warranted. Furthermore, AMS203 that was vacuum-impregnated did not perform as well as the pulsed-vacuum-impregnated sample; replicating the same trend that was observed for the AMS213 samples. This strongly suggests that in addition to the critical role of the carbon's structure, the impregnation method also played an important part in making effective ammonia sorbent.

Samples of AMS213 and AMS203 were both treated by our collaborator, Molecular Products, using the same procedure used to manufacture Chemsorb 1425, which resulted in similar performance for AMS213, but slightly worse performance for AMS203 (Figure 31). For comparison, TDA treated the unmodified microporous activated carbon (based on coconut-shell) that was used to make Chemsorb 1425 with our optimal 32.9% H_3PO_4 solution using pulse-vacuum impregnation, which increased its performance to slightly above Chemsorb 1425. These results showed that the method used to treat TDA's mesoporous carbons was important for optimizing its performance, and that our superior pulsed-vacuum treatment method could also be used to enhance the performance of standard microporous carbon.

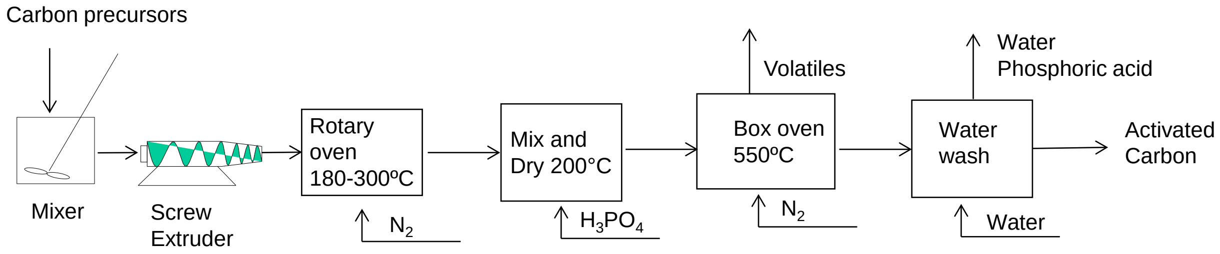


Figure 32. Process used to produce TDA's mesoporous carbon support.

1.3.3. Task 3. Preliminary Techno-Economic Analysis for Mass Production & Scale-up

We carried out a preliminary engineering cost analysis for the best performing ammonia sorbent developed during Phase I. The best performing formulation (AMS-213) was made from cornstarch, dextrose, ammonium bicarbonate and phosphoric acid. Based on the materials costs for AMS-213 and a 23% overall yield (Table 9), we calculated that the cost of the materials that made up the carbon support were approximately $2.16/kg (Pricing source: Alibaba).

The process flow diagram for the AMS-213 carbon is shown in Figure 32. In this process, the ingredients were thoroughly mixed in a mixer, extruded into 1/16" pellets using a screw extruder and charred under nitrogen in a rotary furnace. The charred material was mixed in a 1:1 weight ratio with 85% phosphoric acid, dried at 200°C and then heated to 550°C under an inert atmosphere in a box oven. The activated carbon was then washed with water to remove the excess phosphoric acid and dried.

Table 9. Estimated materials cost for TDA carbon support.

Raw Materials	**kg Required/ kg carbon**	**Unit Cost ($/kg)**	**Cost ($/kg)**
Cornstarch	1.32	0.30	$0.40
Dextrose	0.88	0.60	$0.53
Ammonium Bicarb.	0.22	0.20	$0.04
Phosphoric acid	1.76	0.80	$1.19
Total costs			$2.16

A preliminary economic analysis on the carbon support based on an annual capacity of 500 tons/year is shown in Table 8. The production cost was estimated to be $7.16/kg based on current material prices. A markup of 100% would give a selling price of ~$15/kg, which compares favorably with the current lower performing coconut shell based activated carbon that sells for ~$10/kg.

Table 8. Estimated production costs for carbon support.

Basis 500 tons/year	**Production Costs ($/kg)**
Raw Materials	$ 2.16
Labor	$ 0.80
Utilities, etc.	$ 3.20
Indirect costs	$ 1.00
Total	**$7.16**

In Table 10, we show the materials cost ($/kg) for the ammonia sorbent after it was impregnated with phosphoric acid. Because it had larger pores, the TDA sorbent held 10% more phosphoric acid than Molecular Products coconut shell based carbon. A respirator cartridge holds 100 cm^3 of sorbent and we found that the TDA sorbent was similar in price to the

Table 10. Comparison of materials costs for ammonia sorbents.

Carbon Support	Carbon Support (%)	Phosphoric Acid (%)	Total Cost ($/kg)	Sorbent Cost ($/cartridge)
TDA (AMS-213)	60	40	$9.32	0.37
MP Coconut	70	30	$7.24	0.29

current sorbent. Since the TDA sorbent has a much larger ammonia capacity than the Molecular Products sorbent, it is a much better value.

1.4. Discussion

1.4.1. Phase I Results: Ammonia Sorbent Development and Optimization

Significant progress was made towards our goals in Phase I by iterating between developing the carbon impregnation process and extensively characterizing the sorbents using analytical methods and ammonia breakthrough tests. First, the preparation procedure was optimized by evaluating the effectiveness of different vacuum impregnation methods, then we worked to improve the formulation of the H_3PO_4 impregnant by running parametric studies with different acid compositions, and streamlining the application method by using pulsed-vacuum impregnation. Next, we optimized the sorbent using what we learned from the characterization studies.

1.4.2. Strategy for Sorbent Improvement Going Forward

Extensive characterization studies during Phase I revealed the sorbent's strengths (and its weaknesses), such as high ammonia capacity, but potentially less strength compared to coconut-shell carbon sorbents, as evidenced by some dusting that was observed during breakthrough tests. Physical strength is essential because respirator cartridges can be handled roughly during use and dusting could result in increased breathing resistance through the cartridge. In Phase II, we will address this potential problem by measuring the sorbent’s crush strength (using ASTM D7084-04) and adjusting our manufacturing procedure to increase the carbon’s durability by increasing its resistance to attrition to minimize dusting, without altering its mesoporous structure [32].

There is room to further improve the sorbent’s ammonia capacity and its performance in breakthrough tests by carrying out a parametric study to find the optimum H_3PO_4 loading on AMS203. Whereas the sorbent based on AMS213 seemed to be approaching its maximum performance (e.g., see Figure 29), in Phase I, we only had the opportunity to load AMS203 with 32.9% H_3PO_4 and based on the promising results in Figure 30 that showed sorbent made from AMS203 performed as well or better than AMS213, further investigation of additional impregnant concentrations is warranted to see if its performance can be enhanced further. In addition, only a single protocol was used when impregnating sorbents by pulsed-evacuation (for a duration of 1.5 h with several pulse cycles) and additional enhancement in performance could also potentially be realized by optimizing that process.

1.4.3. Design, Fabrication and Qualification of an Industrial Ammonia Cartridge

While we made substantial progress toward our goals during Phase I and our sorbent formulation had superior ammonia capacity than the best commercially available ammonia sorbent (Chemsorb 1425), our next technical objective for this project is to build a prototype cartridge and test it under representative conditions, as it might be employed by a farm worker in a CAFO environment. The cartridge will be simple to use and low-cost (essential for its everyday use). However, further testing will be required to pass the latest version of the NIOSH standard testing procedure for determining the ammonia service life of air-purifying respirator cartridges and qualify the cartridge for industrial service.

A low-cost, lightweight and conformal cartridge that contains 100 cm^3 of ammonia sorbent is required for industrial use. The cartridge must also include high-efficiency particulate air (HEPA) filter media to protect the worker from aerosols and fine particulates, without unduly restricting the respirable air flow resistance through the cartridge. We will therefore work with another one of our industrial collaborators, Avon Protection, to design and fabricate high-fidelity prototype cartridges filled with 100 cm^3 of the optimal sorbent for testing at both TDA and an independent laboratory for commercial qualification in accordance with the NIOSH standard testing procedure (STP) [1]. To pass the NIOSH STP, a minimum of 3 cartridges must each last for 50 minutes against a challenge of 1000 ppmv NH_3 in 64 SLPM before a penetration concentration of 50 ppmv NH_3 is measured at the outlet.

1.4.4. Scale Up Sorbent Manufacturing

The manufacturing method will also be scaled up to produce multiple kilograms per day of bulk sorbent using TDA's rotary kiln in a continuous process. Scaling up the manufacturing process is required to supply the quantities of sorbent needed to fabricate prototype ammonia cartridges that are needed to carry out the NIOSH qualification tests that are required for industrial use of the cartridge.

We will work to reduce costs by minimizing the quantities of waste byproducts from the sorbent manufacturing process, by developing ways to replenish and recycle the impregnating acid solution, and streamlining the preparation procedure to reduce the amount of time and labor required. TDA has the equipment, personnel and resources available to manufacture large quantities (several tons per month) of sorbent in our high-bay production facility at our Table Mountain laboratory building, but to produce the quantities of sorbent that will eventually be needed for the commercial market (estimated to require >100 tons/yr) we will work with Molecular Products to scale up production at their local manufacturing plant.

1.4.5. Commercialization Plans

Successful commercialization of an ammonia respirator cartridge that contains our new sorbent will enable its widespread use to mitigate the long-term negative health effects of chronic ammonia exposure and more importantly, help prevent fatalities due to acute inhalation injury. Our ammonia sorbent has a significant competitive advantage over the current ammonia cartridges that are commercially available. Most importantly, it will last longer because of the advances in the sorbent's ammonia capacity that we made during this Phase I project. In Phase II, we will continue to optimize both the carbon and the sorbent preparation method. We will also scale up the manufacturing process (by continuing to work with Molecular Products) to produce bulk quantities of sorbent for incorporation into prototype cartridges (manufactured for us by our collaborator, Avon Protection) that will be tested in accordance with the NIOSH STP. In later phases, we will carry out field assessments of the cartridge's performance prior to rolling it out to the commercial market.

TDA staff has extensive experience in sorbent research development and qualification [35-45]. We are currently collaborating with Avon on a project to design, manufacture and qualify a respirator cartridge for firefighters to use during the mop-up phase of a fire (termed "overhaul" operations) and we have worked with Avon previously to manufacture prototype cartridges for a project that boosted the ammonia and nitrogen oxide (NO_x) capacity of the U.S. military's FM-61 cartridge. We have also worked previously with Gentex Corp. to successfully design, fabricate, and pass the tests required for space qualification of a respirator cartridge that is currently used by the crew on-board the International Space Station (ISS) for protection against the chemicals and smoke aerosols produced by a fire or smolder event. Furthermore, due to our experience in the production and sale of disinfectants effective against biological warfare agents, we have gained experience in moving new products through the government registration process (any cartridge used for respiratory protection must pass the appropriate tests and be registered and approved by the NIOSH).

We will initially focus on the industrial market with the greatest potential impact when targeting personal protection products, and the next step is to carry out field tests in later research phases by working with: 1) Molecular Products to scale up carbon sorbent manufacturing; 2) Avon Protection to load cartridges with the sorbent, 3) Battelle (or an equivalent independent certified testing laboratory) to qualify the cartridges in accordance with the NIOSH standard test procedure [1]. The sorbent will be independently evaluated by these collaborators (who have no vested interest in TDA Research) to demonstrate its efficacy, evaluate its economic viability, and register it with NIOSH prior to bringing it to market.

1.5. Disclosure

This report was prepared by Dr. Girish Srinivas, Dr. Stephen N. Paglieri, and Dr. Steven D. Dietz of TDA, who contributed the primary synthetic, development and characterization efforts during the Phase I project. Additional minor effort was contributed by other TDA support personnel, including Jeremy L. Noce and Jeff Martin.

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