

## FINAL REPORT

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### Non-Proprietary Abstract

TDA Research Inc. has developed a device that can be used to cool superheated air to temperatures that are safe to breathe when fighting wildland fires. The device also destroys carbon monoxide. We have called our device the "Wild Fire Rescue Respirator" (WFRR). Wildland firefighters normally wear a heavy jacket, durable trousers, heavy duty boots, gloves, a hardhat, eye protection, and frequently, a bandana type of particulate filter for smoke. A burnover, is the situation where a wildland firefighter is trapped and cannot escape the advancing fire. To survive a burnover, wildland firefighters carry an aluminized "fire shelter." The fire shelter is basically a one-person tent that is designed to reflect radiative heat from the fire as it passes close to (or over) the firefighter. It affords much less protection against direct flames; therefore, the firefighter tries to deploy the shelter in an area relatively devoid of fuel (such as a dirt road).

While the fire shelter protects against radiative heat, if any of the air outside the shelter during a burnover gets inside, there is a serious risk of death because the lungs are far more susceptible to injury by even brief exposures to superheated air compared to exposed skin. Since one can survive brief exposures to air as hot as 300°F as *long as the lungs are protected*, TDA Research Inc. in collaboration with a major personal protective equipment manufacturer, has developed the wildfire rescue respirator, which allows the firefighter inside the shelter to breathe normally while the lungs are protected against superheated air. As an added benefit, our device also destroys carbon monoxide, the partial oxidation product of any carbon containing fuel.

The WRFF is small and lightweight enough to be carried easily with the wildland firefighter's normal equipment and is designed to be used when deploying a fire shelter in the event of the firefighter being trapped in a burnover. The device can be donned while setting up the fire shelter, and then used inside the shelter until it is safe to exit. The firefighter breathes normally through the device and any superheated air that enters the shelter (due to, for example, strong winds blowing up the edges of the shelter) is cooled to ~98°F before entering the lungs. In Phase I, TDA demonstrated that the device would cool air from 300°F to 98°F continuously for more than 30 min. In theory, the unit can be cycled indefinitely. We also demonstrated that we could destroy >2000 ppm of CO entering the device. In Phase II, TDA is working with our industrial partner to optimize the design of the WFRR and determine the best way to package the device.

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## 1. Highlights, Significant Findings

TDA Research, Inc. (TDA) (in collaboration with Mine Safety Appliances Company) has developed a small, cartridge-type device that can be easily worn by wildland firefighters to cool superheated air to temperatures that are safe to breath, with simultaneous removal of CO. We refer to this device as a **Wild Fire Rescue Respirator**, or WFRR. The WFRR would be used while in the fire shelter to provide the user with a source of safe air should the shelter become compromised. In addition, if donned while setting up the shelter, it could protect against superheated air and toxic gases and increase the time available to set up the shelter. Likewise, it could protect against premature exit of the shelter, because late entrance and early exit are common problems encountered in the use of fire shelters (Andersson, 1997). In addition to protection against superheated air, TDA's device incorporates a CO oxidation catalyst that converts CO into non-toxic carbon dioxide (CO<sub>2</sub>) at temperatures between ambient and 350°F to protect the firefighter against CO poisoning in these life-threatening situations.

In Phase I, TDA designed, developed, and tested materials for a wildland firefighter rescue respirator (WFRR) that could be used to protect the firefighter against superheated air and carbon monoxide when forced to deploy a fire shelter during an entrapment. Specifically, we

1. Designed and built a test apparatus to simulate a firefighter breathing superheated air through the WFRR
2. Determined the best material to use for the thermal bed (which turned out to be a cordierite monolith rather than a packed bed of spheres, as we had originally proposed)
3. Tested and verified the performance of a catalytic coating on the cordierite monolith that oxidized CO to CO<sub>2</sub> for protection against this hazard
4. Modeled the transient heat transfer in the monolith for the preliminary design, and

Performed a preliminary prototype unit design based on the data and modeling efforts.

## 2. Translation of Findings

TDA's wild fire rescue respirator represents a new technology for protecting wildland firefighters against the dangers of superheated air during a burnover. Unlike other devices, our WFRR is not a simple thermal capacitor so the time it can be used is NOT limited by the mass of the device. In contrast, our device is a heat exchanger which can be cycled indefinitely. Our commercial partner is Mine Safety Appliances (MSA) a world leader in personal protective equipment design, manufacturing and sales, and we are working with them in Phase II to optimize the design and determine the best packaging methods.

Additional interest has been expressed by several other companies as well (so far only as a result of non-proprietary presentations at conferences) including Elmridge Protection Products, Avon Safety and Scott Safety.

## 3. Outcome, Relevance and Impact

The WFRR uses a regenerative heat exchanger, and in Phase I we found the best material to use for the thermal heat exchanger in the wildfire rescue respirator was a cordierite monolith, a

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material that is readily available and inexpensive. A 1 inch thick by 3.5 inch diameter disk of cordierite monolith is shown in Figure 1. The large arrow shows that the air (both hot and cooled) flows through the channels. This monolith has 400 cells/in<sup>2</sup>. For the experiments in Phase I, we cut appropriately long sections of cordierite monolith (it can be purchased in lengths up to about a foot).

During operation (Figure 2), hot air is pulled (inhaled) through the cool monolith (a bed of spheres or pellets works as well but weighs more and has a higher pressure drop). The monolith cools the air to ~100-110°F. As the air is taken into the firefighter's lungs, it is further cooled to approximately 98°F (body temperature) because of evaporation of water in the firefighter's lungs. Upon exhalation, moist 98°F air then passes back over the thermal bed in the opposite direction and cools the thermal bed (reheating the air) readying it for the next cycle. The hot air exiting the device is somewhat cooler than the ambient (superheated) air. The overall driving force for heat transfer is the heat of vaporization of water at 98°F inside the firefighter's lungs, and (except for the effect of axial conduction) the device is capable of cooling the air for an extended period of time (in theory indefinitely) if there were no heat transfer through the container and no axial conduction down the length of the cordierite monolith.

In addition to protection against superheated air, the WFRR also incorporates a catalyst that will oxidize CO to CO<sub>2</sub> at temperatures of 20°C and higher. A particulate filter can be incorporated for little additional pressure drop or cost. TDA's has developed a low temperature CO oxidation catalyst that is

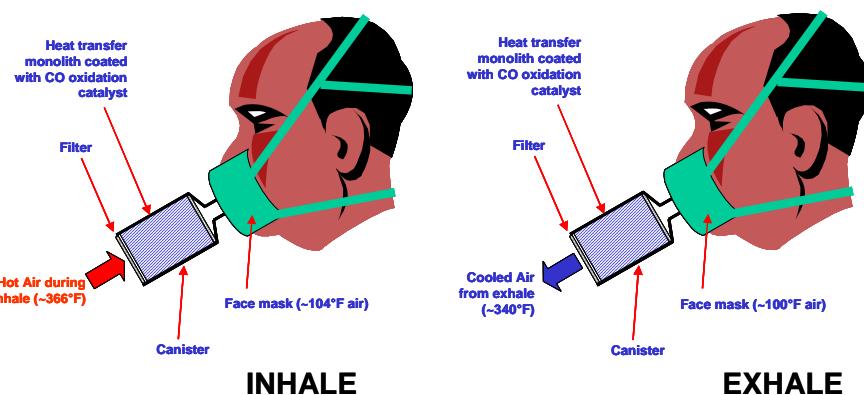


Figure 2. TDA wild fire rescue respirator (WFRR)

based on gold promoted titanium oxide that has been doped with cobalt. This catalyst was originally developed for removing CO from indoor air and has been modified to protect emergency personnel from CO when using escape hoods. The primary difference between the latter application and the application in this proposal is the higher operating temperature, and more importantly, the means by which the catalyst is incorporated into the unit. In the escape hood application, a bed of granules can be used. In the WFRR, the CO oxidation catalyst is best incorporated into the same cordierite monolith that is used as the "thermal bed." Thus, issues related to how to best attach the catalyst to the monolith and how to increase the amount of catalyst used without compromising the performance of the thermal bed become issues with

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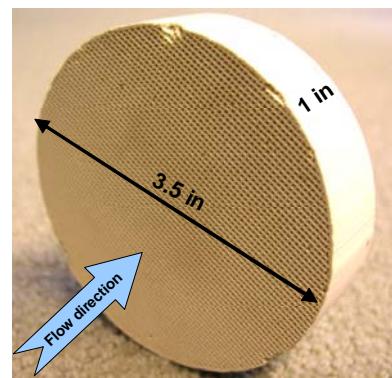


Figure 1. Photograph of cordierite monolith used in Phase I.

the WFRR that are not present in the escape hood application. TDA has received notice that we will be awarded a Phase II project to further develop the CO oxidation catalyst for the escape hood application. As a result, the WFRR project does not need to investigate different catalyst formulations, only how to best incorporate the catalyst into the WFRR.

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## 4. Scientific Report

### 4.1 Background and Significance

#### 4.1.1 Respiratory Wildfire Hazards

In 2008 there were 80,094 of unplanned wildfires that burned 5,254,109 acres of land, and there were 7,701 prescribed burns of 1,942,151 acres (NIFC 2008). Prescribed burns are controlled fires that are done in a specific area to consume fuel in order to reduce the chance of a catastrophic uncontrolled fire in the future. The most common wildfire hazards encountered on a day-to-day basis are smoke inhalation and burnovers. During a burnover, the firefighter is trapped by advancing flames, and in addition to the thermal hazard, the smoke contains a large number of hazardous components, including pulmonary irritants (particulates), and toxic compounds generated by combustion such as formaldehyde, acetaldehyde, sulfur dioxide and carbon monoxide. Should a firefighter become trapped in a burnover, skin burns are of secondary importance compared to protecting the airways and lungs from exposure to superheated air and toxic gases (especially carbon monoxide, CO). Currently, only a self-contained breathing apparatus (SCBA), can protect against all contaminates including CO and superheated air, but SCBA are much too heavy (30-50 lb) and cumbersome for the wildland firefighter, who often has to walk long distances to reach the fireline or quickly escape from life-threatening situations. In contrast, TDA's WFRR will weight approximately 200 – 300 grams (~0.5 – 0.75 lb).

##### 4.1.1.1 Superheated Air

The primary defense against heat radiation and superheated air is the fire shelter and it provides some protection from extreme temperatures and toxic gases generated in the event of a burnover (NWCG, 2003). Should the fire shelter become compromised, however, it does little to protect the firefighter from smoke, toxic gases (CO), or superheated air, and the respiratory tract can quickly be damaged. Although it is impossible to predict exact air temperatures in a wildfire due to changes in the fuel and weather conditions, in simulated wildfires, air temperatures have been measured as high as ~1800°F (1000°C) (Butler, 2001). Human beings can tolerate air temperatures of up to 180°F with no respiratory damage if the air is dry (NWCG, 2003), however, the safe temperature drops to 130°F when the air is humid (Andersson, 1997). Both of these temperatures, however, are well below the air temperatures at the flame front during a burnover.

More firefighters are injured or killed from heat-damaged airways or lungs, caused by breathing superheated air, than external burns (NWCG, 2001). For example, during the 1988 Yellowstone fires, 40% of all firefighter medical visits were for respiratory problems due to heat exposure (NIOSH, 2004). Clearly, exposure to air temperatures as high as 1800°F would be rapidly fatal, and this is the reason for using a fire shelter, however, during a test burn in Montana where vehicles, fire shelters and other equipment were instrumented with recording thermocouples, temperatures spikes as high as 284°F were observed inside the fire shelters (Colorado Firecamp, 2006). In a similar test burn in the Los Angeles area, 320°F (160°C) temperature spikes were observed. Brief exposure to air this hot is survivable, provided that the hot air is not inhaled, and while burns to the skin are painful and can be severe, damage to the lungs is much

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more likely to be fatal. For these reasons, safety experts and PPE manufacturers stress that the highest safety priority during a fire entrapment is to protect the lungs and airways against exposure to hot air (NWCG, 2003; Hot Shield, 2006) because once the lungs and airways have been damaged, death from asphyxiation can occur.

#### 4.1.1.2 Carbon Monoxide

Carbon monoxide is produced by the incomplete combustion of carbon containing substances, which is common in fires. CO bonds to the iron in hemoglobin interfering with oxygen transport. At high enough concentrations, organ failure, brain damage and death will occur. Increasing the hazard further, CO is both odorless and colorless and provides no warning of its presence. Worse, lethal concentrations of CO are relatively low ( $\geq 2000$  ppm) and these concentrations are commonly produced in fires (Fierro, 2001).

Wildland firefighters are exposed to CO levels in excess of ceiling/excursion limits during as much as 25% of their time spent fighting fires (NIOSH, 2004) and CO blood concentrations can increase to 150 times normal in 1 minute (IDPG, 2006) — the dense smoke produced in a wildfire has a concentration of CO similar to that in automobile exhaust (Reinhardt, 1999). As a result, the highest levels of CO are most likely to be experienced by wildland firefighters near the fire front, those who are most likely to need to use a fire shelter. At lower concentrations (ca. 21 ppm) CO poisoning produces difficulty with thinking, performing complex tasks, and dizziness, all of which increase the risk of a fatality in a burnover when fast, clear thinking is at a premium (Reinhardt, 1999). Therefore, a small portable device that protects the firefighter from both superheated air and CO poisoning will increase the chances for survival in a burnover.

#### 4.1.2 Existing Respiratory Protection

To date there have been no wildland firefighter respirator standards, however, there is currently one being drafted by the National Fire Protection Agency (NFPA). The goal of the standard (NFPA 2008) will be to specify the "minimum design, performance, testing, and certification requirements for respirators to provide protection from inhalation hazards for personnel conducting wildland fire fighting operations," and apply only "for use in non-IDLH (Immediate Dangerous to Life and Health) wildland environments during wildland fire fighting operations." The new standard will not supersede any other respiratory standards such as the CBRN or NIOSH standards and will be specifically focused on the special environment associated with wildland firefighting. The final standard is scheduled to be released in 2011. The standard borrows from other standards in terms of VOC challenges (e.g. test used  $\text{CCl}_4$  vapors and acid gases (e.g.  $\text{SO}_2$ ) as well as the NIOSH standard for CO but it is expanded to include 6000 ppm challenge as well as the NIOSH 3600 ppm challenge. It does not address superheated air (since other than our WFRR, there have been no simple devices that could afford such protection). The 3600 and 6000 ppm CO levels are part of our Phase II experimental design matrix in Task 3, and in Task 4, we address the VOC and acid gas problem – protection against



Figure 3. Hot Shield® HS-4 respirator (Hot Shield 2008).

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VOC's and acid gases can be simply done using commercially available specialty activated carbons. The main focus of our Phase II proposal is to perfect the performance of the catalyst coated thermal heat exchanger bed so that it can protect the wildland firefighter against superheated air and CO, as there are no lightweight, inexpensive and practical technologies currently available that can protect against these hazards.

With current technology, respiratory protection against superheated air is minimal at best, and protection against CO is essentially nonexistent. Common wildfire hazards, such as burning embers and the particulates in smoke can be dealt with satisfactorily using flame retardant materials (such as Nomex® and CarbonX®) along with particulate filtering masks (Figure 3). Many firefighters simply use a bandana, which removes larger particles in the smoke but provide almost no protection against CO or superheated air. Masks that employ activated carbon a pocket for a disposable activated-carbon particulate shield protect against organic and inorganic vapors but don't completely protect against superheated air (Hot Shield, 2006). In addition, activated carbon does not adsorb CO and is therefore ineffective against this gas.

There is very little in the way of protection against CO for wildland firefighters and currently, the best protection is afforded by personal electronic CO monitors that sound an alarm when CO levels become dangerous. Unfortunately, if the alarm sounds and the firefighter is unable to escape or is confined to a fire shelter, there is no protection whatsoever against CO inhalation. The only practical way to remove CO is catalytic oxidation to CO<sub>2</sub>, which far less toxic. For example, the OSHA TWA (time weighted average for 8 hours of exposure) to CO is 35 ppm, whereas the TWA for CO<sub>2</sub> is 5,000 ppm and the ACGIH STEL (short term exposure limit for 15 minutes) for CO<sub>2</sub> is 30,000 ppm (3%). Fortunately, CO is easy to oxidize given the right catalyst, but unfortunately, the currently available commercial catalyst (Hopcalite) is quickly deactivated by water and therefore cannot be used in high humidity atmospheres. This makes it unreliable for critical applications where high humidity might be encountered along with CO. In contrast, TDA's Au-Co/TiO<sub>2</sub> catalyst that we developed for the CBRN escape hood, is ideally suited to be incorporated into the WRFF because it is unaffected by very high (> 80%) relative humidity, which makes it more reliable in PPE.

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#### 4.1.3 TDA Portable Wildfire Rescue Respirator (WFRR)

TDA's portable wildfire rescue respirator (WFRR) protects wildland firefighters against superheated air and carbon monoxide during an entrapment. It can also be worn under a particulate filter type bandana if desired (or a filter could be easily incorporated into the device). Figure 4 shows how TDA's WFRR works. The WFRR is worn the entire time the firefighter is in the shelter. TDA's device uses the thermal heat capacity of a bed of solids to cool incoming superheated air from 350°F to approximately 100°F – the air cools down and the bed heats up. Simultaneously, CO is removed by passing it over an oxidation catalyst that is coated on inside the channels of the cordierite monolith that is used as the thermal bed, where CO is converted into CO<sub>2</sub>.

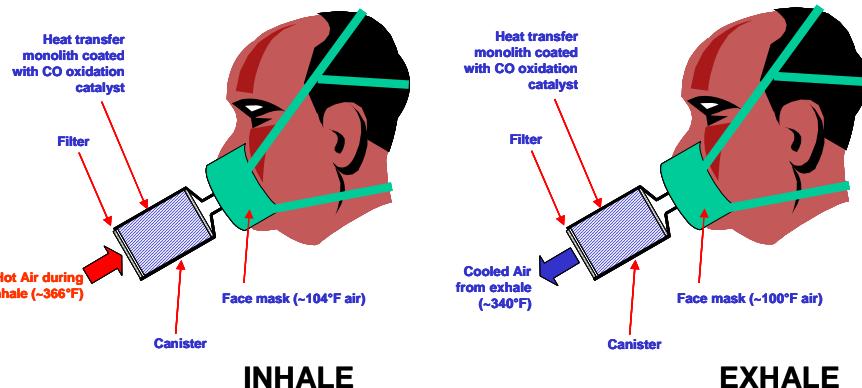


Figure 4. Schematic of TDA's wildfire rescue respirator (WFRR) when inhaling (left) and exhaling (right); all temperatures are from experimental data.

The device works by pushing a thermal wave back and forth through the monolith during breathing. When the firefighter inhales, the monolith absorbs heat from the hot outside air, and when the firefighter exhales, the air from the lungs absorbs heat from the monolith, cooling it for the next cycle. As air is inhaled, it cools from ~300°F to about 100-110°F and is then further cooled to approximately 98°F (body temperature) by the evaporation of water in the firefighter's lungs. When the firefighter exhales, 98°F air from the lungs passes back through the monolith in the opposite direction, which cools the bed (reheating the air exiting the device) for the next cycle. The air exiting the device is somewhat cooler than the ambient (superheated) air. The overall driving force for heat transfer is the heat of vaporization of water at 98°F inside the firefighter's lungs, which means that the internal temperature of the respirator is always about 100°F, no matter what the external temperature is (up to 366°F was tested in the lab).

While a more modest temperature near 250°F is more likely to be encountered during actual use of the WRFF, we chose to perform several high temperature tests in Phase I to mimic the results obtained during a test burn in Montana where vehicles, fire shelters and other equipment were instrumented with recording thermocouples, and temperatures spikes as high as 284°F were recorded (Colorado Firecamp, 2006). Also, in a similar test burn in the Los Angeles area, 320°F temperature spikes were observed in fire shelters. Thus, even in a properly deployed shelter, air temperatures close to 300°F are possible inside the shelter. Therefore, we also performed some tests with an inlet temperature of 366°F.

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It is important to point out that TDA's wildfire rescue respirator is not a simple thermal capacitor. TDA's WFRR is actually a non-steady state heat exchanger. This distinction may appear merely semantic but it is not. The difference is very important. In a thermal capacitor, the solids are continuously heated until they reach the inlet air temperature (in this case the superheated air temperature, ~350°F). Therefore, once the entire device heats up, it no longer functions. In contrast, TDA's WFRR is a heat exchanger, heat from the fire is temporarily stored in the thermal bed during inhalation (in Phase I we found that the best material was a cordierite monolith), and then rejected (pushed back out) during exhalation. Thus, if axial conduction could be completely eliminated (along with no heat leaks elsewhere), TDA's WFRR could (theoretically) cycle indefinitely.

## 4.2 Phase I Results and Discussion

### 4.2.1 Objectives of the Phase I Project

The overall goal of the project is to design, develop, and test a device that can be used by wildland firefighters to protect them against the hazards of superheated air and carbon monoxide when using a fire shelter during a burnover. The device needs to be lightweight, reliable, rugged, simple to operate and have a long shelf life. In order to develop this device we identified several goals for the Phase I project. All of the goals of the Phase I project were successfully met, which were:

1. Build a test apparatus to simulate the firefighter's breathing through the WFRR
2. Determine the best material to use in the thermal bed heat exchanger
3. Test the effectiveness of incorporating TDA's CO oxidation catalyst into the WFRR
4. Model WFRR and transient heat transfer, and
5. Design preliminary prototype unit

### 4.2.2 Summary of the Phase I Results

Because of the 25 page limitation for the Phase II proposal, we are presenting highlights of the Phase I results, a full Phase I final report will be submitted later. In Phase I, TDA designed, developed, and tested materials for a wildland firefighter rescue respirator (WFRR) that could be used to protect the firefighter against superheated air and carbon monoxide when forced to deploy a fire shelter during an entrapment. Specifically, we designed and built a test apparatus to simulate a firefighter breathing air at temperatures between 250°F and 350°F at 80% relative humidity through the WFRR. We tested both glass and aluminum spheres of two different sizes and a cordierite monolith as thermal bed (heat exchanger) materials and found that the choice of material had less of an effect than the length of the bed. Furthermore, we found that the cordierite monolith had the lowest weight and pressure drop of all of the materials tested, and furthermore, there was no chance of bed settling that could result in channeling as can happen with packed beds if the material shifts. In all cases, the exit (breathing) air temperature was between 100°F and 110°F for 30 minutes, which is an acceptable temperatures for this amount of time.

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We then examined several configurations for incorporating CO oxidation catalysts into the WFRR. In one test we coated a one inch thick porous glass honeycomb material with our previously developed  $\text{Au}/\text{Co}_3\text{O}_4\text{-TiO}_2$  CO oxidation catalyst and placed it on the hot air side of the WFRR. In this configuration, the CO concentration was reduced from 3600 ppm to about 600 ppm. Since this is far too much CO breakthrough, we then coated a 1.5 inch long piece of cordierite monolith with the  $\text{Au}/\text{Co}_3\text{O}_4\text{-TiO}_2$  catalyst (no glass honeycomb) and the CO concentration was reduced to 160 ppm. We then tested a 3.5 inch long cordierite monolith that was coated with catalyst and the CO concentration was reduced to about 20 ppm. In the experiments with the catalyst coated cordierite monolith, the monolith serves both as the

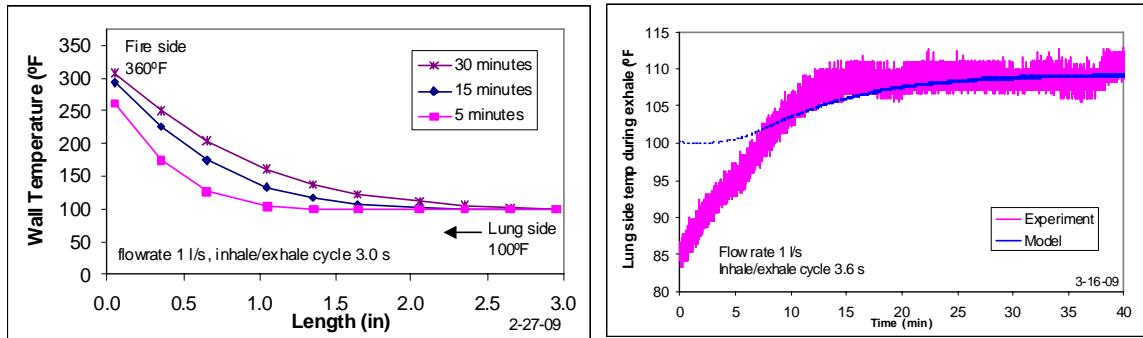


Figure 5. Results of numerical modeling the cordierite monolith using SINDA/FLUINT – temperature vs. length and time (left) a the predicted lung side temperature compared with experimental data for a 400 cells/in<sup>2</sup>, 3.5 inches in diameter x 2 inch long cordierite monolith.

thermal bed to reduce the inlet air temperature from 350°F to ~100°F suitable for breathing, and as a support for the  $\text{Au}/\text{Co}_3\text{O}_4\text{-TiO}_2$  catalyst used for CO oxidation. These experiments clearly demonstrated that our WFRR device could cool superheated air to breathable temperatures while simultaneously decreasing the concentration of CO in the heated air to safe levels and that the length of the monolith for cooling needs to be about 2 – 2.5 inch long. We then modeled the performance of the WFRR using a finite element fluid flow/transient heat transfer program (SINDA/FLUINT) and found that the model and experimental results were in excellent agreement, showing that the wildfire rescue respirator performed as expected (Figure 5). Finally, we have performed a very preliminary design of the wildfire rescue respirator to approximately determine the size, weight and cost of the device.

#### 4.2.3 Phase I Results.

##### 4.2.3.1 Results for Task 1: Build a test apparatus

Figure 6 shows the Phase I apparatus. The test cell that holds the thermal bed materials is a cylinder that is about 3.5 inches in diameter that is capped with a hemispherical "bell" at each end. In a real wildfire, there is an "infinite" reservoir of superheated air outside of the wildfire rescue respirator. To simulate this situation, and to avoid having to deal with transient heating and humidification of the air streams, the apparatus was designed so that 60 liter/min of hot air was continuously flowing as was 60 liter/min stream of humidified "lung" air at 98°F. Breathing by the firefighter was then simulated by switching back and forth between hot air and lung air as

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shown in Figure 7 using a series of simultaneously activated pneumatic 3-way valves. The timing for switching the air actuated valves, as well as logging the temperatures was done using a desktop PC running the process control program "Control EG." This program uses proportional-integral-derivative (PID) logic to control all of the temperatures (heating tapes) in the system. Temperature data were recorded by Control EG and then exported and worked up using Microsoft Excel.

During inhalation, two computer-controlled, air-actuated 3-way valves direct hot air (250-350°F) through the test cell, through the thermal bed, and past the "lung side" thermocouple where the air is cooled to about 100°F (Figure 7). Following the inhalation step, the valves were again switched, and "lung air" at 98.6 °F air and 80% R.H. flowed through the thermal bed in the opposite direction, re-cooling the thermal bed. The amount of time required by the valves to switch from inhaling to exhaling (and back) was 0.3 seconds. The heating air and lung air flowed for 1.5 seconds to give a total flow time of 1.8 liter/sec. One inhalation/exhalation cycle took 3.6 seconds which corresponds to 16.67 breaths/minute. Overall, each air flow rate was 1.0 liters/second (60 liters/minute) with a breath volume of 1.8 liters/breath.

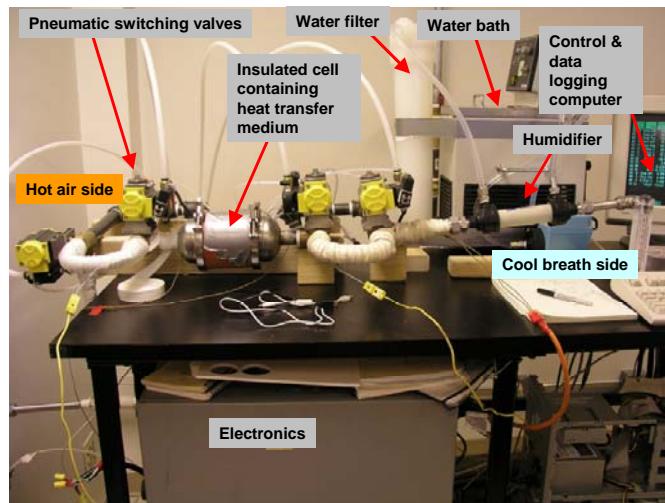


Figure 6. Photograph of Phase I test apparatus (left) and close up of inlet air heating system (right).

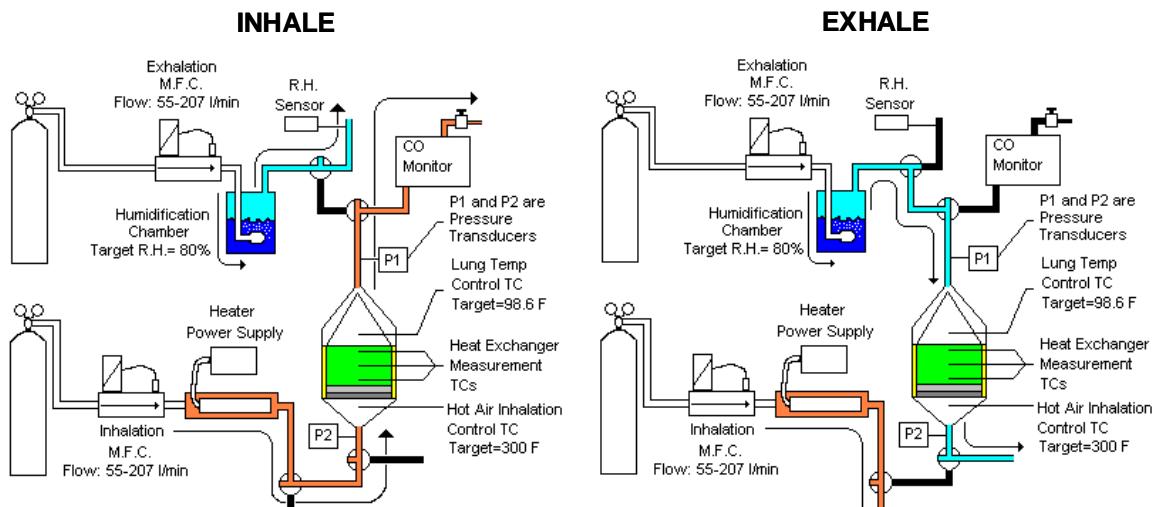


Figure 7. Flow path through test cell during inhalation (left) and exhalation (right) steps.

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Our industrial collaborator, Mine Safety Appliance (MSA) has determined that humans who experience external skin temperatures in excess of 250°F will develop severe problems regardless of the temperature of the air that they are breathing. Therefore, we chose a hot air inlet temperature of 250°F as our benchmark case. We also tested the wildfire rescue respirator using an inlet air temperature of 350°F to measure its performance under the most extreme conditions that are likely to be encountered by a wildland firefighter.

The glass Spheres (1 mm and 5 mm diameter) were purchased from Ceroglass, and the 1 mm and 5 mm aluminum spheres were purchased from Pellets, LLC and AirSoft respectively. The monolith was purchased from Applied Ceramics. The monolith was made from cordierite ( $Mg_2Al_4Si_5O_{18}$ ) and had 400 cells/in<sup>2</sup> (CPSI) where the channel walls were 0.007 in thick. The thermal beds were held in place in the test cell (see Figure 6) with closed cell silicone foam. The foam closed the air gap between the thermal bed and the metal test cell to minimize heat losses to the room. The lung side air was humidified using a Perma Pure, LLC module that had warm water circulating on outside and air on the inside of hollow membrane fibers.

As discussed above, carbon monoxide is formed in fires, and therefore, we tested the wildfire rescue respirator with a CO oxidation catalyst incorporated into the thermal bed. For Phase I, we chose an inlet CO concentration of 3600 ppm because this is the standard for the NIOSH CBRN certification test. The 3600 ppm of CO was introduced into the hot air side by simply adding 216 cm<sup>3</sup>/min of 100% carbon monoxide into the primary heated air flow. A Fuji ZRH Infrared Gas Analyzer (Fuji Electric Co., LTD) was used to measure the levels of CO and CO<sub>2</sub> in the gas that reached the lung side of the apparatus after it had been cooled by the thermal bed.

#### 4.2.3.2 Results for Phase I, Task 2: Determine the best material to use in the thermal bed

##### 4.2.3.2.1 Materials Tested

The performance of the material used in the bed depends on the relative rates of heat transfer to the solids compared with the rate of conduction of heat into the solids, the ability of the solids to store energy and the conduction of heat down the length of the bed (axial conduction). Most solids have comparable heat capacities (Table 1) but can vary substantially in thermal conductivity. We examined borosilicate glass (e.g. Pyrex) and aluminum spheres because these materials have similar densities and heat capacities but extremely different thermal conductivities, as well as a cordierite monolith which has the advantage of being in one piece. This avoids the possibility of bed channeling, greatly simplifies and reduces the cost of manufacturing, and produces minimum pressure drop.

##### 4.2.3.2.2 Thermal Bed Results Using Glass and Aluminum Spheres

**Statistical Experimental Design.** The function of the thermal bed material is to temporarily store the sensible heat from cooling the hot fire side air from 250-350°F down to ~100°F, and then to be able to reject that heat when the firefighter breathes out 98°F. Both the heat capacity

Table 1. Properties of thermal bed materials

Material	Density (lb/ft <sup>3</sup> )	Specific Heat (Btu/lb °F)	Thermal conductivity (Btu/ft hr °F)
Aluminum (6060-T6)	168	0.23	110
Pyrex glass	139	0.2	0.63
Cordierite	162	0.35	1.73

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of the solids in the thermal bed and their thermal conductivities are potentially important properties – heat capacity determines how much energy can be stored, and the thermal conductivity is important in determining the response time of the device. The results of a statistically designed experiment are shown in Table 2.

Table 2. Results of the  $2^3$  full factorial experiment for evaluating different thermal bed materials.

Run No	Material	Size	Bed Length	Lung (°F)	Hot (°F)
1	Glass	1 mm	2 inch	$99.8 \pm 1.0$	$253.6 \pm 2.3$
2	Aluminum	1 mm	2 inch	$98.9 \pm 0.9$	$252.6 \pm 3.4$
3	Glass	5 mm	2 inch	$101.4 \pm 1.0$	$265.9 \pm 4.4$
4	Aluminum	5 mm	2 inch	$103.6 \pm 0.6$	$257.9 \pm 5.7$
5	Glass	1 mm	3 inch	$98.7 \pm 0.8$	$251.0 \pm 2.2$
6	Aluminum	1 mm	3 inch	$99.9 \pm 0.9$	$254.5 \pm 3.8$
7	Glass	5 mm	3 inch	$99.3 \pm 0.7$	$254.6 \pm 2.5$
8	Aluminum	5 mm	3 inch	$100.8 \pm 0.7$	$259.5 \pm 6.8$

In Phase I, we conducted a statistically designed experiment to measure the relative the importance thermal conductivity, surface area of the bed material, and bed length on the ability of the WFRR to perform multiple cooling cycles without degradation in performance. Each of the three variables was examined at two levels (a high and a low level) using the  $2^3$  full factorial experimental design (Table 2), which enabled us to generate a quantitative response model for the thermal bed's performance in terms of these variables that is given by  $T_{inhaled}(\text{°F}) = \mu + 0.5[\beta_1(\text{material}) + \beta_2(\text{size}) + \beta_3(\text{length}) + \beta_{12}(\text{material})(\text{size}) + \beta_{13}(\text{material})(\text{length}) + \beta_{23}(\text{size})(\text{length}) + \beta_{123}(\text{mat})(\text{size})(\text{length})]$ . In this empirical linear model equation,  $\mu$  is the overall average of the response of interest ("lung temperature") for all of the runs, and the  $\beta_i$  terms give the magnitude of the effect of each variable on the response in question (steady state lung side temperature). For example, the magnitude of  $\beta_1$  indicates the effect of the thermal conductivity of the solid (Al is high and glass is low)  $\beta_2$  the effect of the bead size, which determines the heat transfer surface area and  $\beta_3$  the effect of the length of the bed, which is important if there is any significant axial heat conduction. The value of  $\beta_i$  will be positive if the high level of that variable increased the inhaled air temperature and negative if it made the temperature decrease. Similarly, the larger the value of  $\beta_i$ , the more influence that variable has on the inhaled air temperature. The cross terms (e.g.  $\beta_{12}$ ) indicate the effect of interactions, in this example variable 1 (material) and bead size (variable 2). The three way interaction term  $\beta_{123}$ , is generally used as a measure of experimental error since 3-variable interactions are uncommon. A detailed discussion of experimental design is given in Box et al. 1978.

Figure 8 shows the data from a run that was typical of the other seven runs, when testing the cordierite monolith. In all cases it turned out that when the inlet temperature of the hot air was about 250°F, the inhaled air (lung temperature) was about 100°F and that this was the case regardless of whether aluminum or glass spheres were used as the thermal bed as shown in Table 2.

The fact that it does not matter much if glass or aluminum is used, nor is the size of the spheres very important is consistent with the behavior observed in packed beds of particles in general (Smith 1981).

This phenomenon is commonly observed in fixed catalyst beds and is a result of the poor thermal contact between the particles – the particles (in our case spheres) are just touching so that heat conduction between the spheres is poor. As a result, the thermal conductivity of the bed is essentially that of the gas in the interstitial spaces (Smith 1981).

This effect is illustrated rather dramatically in Figure 9 that shows the effective thermal conductivities of four types of packed beds: silver (Ag) with vacuum between the particles, Ag with He gas,  $\text{Al}_2\text{O}_3$  with vacuum, and  $\text{Al}_2\text{O}_3$  with He. Because there is only point-to-point particle contact, heat conduction between the particles is poor. Thus for the vacuum cases, radiation is the dominant mode of heat transfer between the particles. This explains why the effective thermal conductivity of a bed of Ag particles ( $k = 400 \text{ W/m}^* \text{K}$  for solid silver) has an effective thermal conductivity that is 1700 times lower ( $0.23 \text{ W/m}^* \text{K}$ ). At the same time, a packed bed of alumina has an effective thermal conductivity of  $k = 0.06 \text{ W/m}^* \text{K}$ , which while lower than the silver bed, is quite a bit smaller than the thermal conductivity of bulk  $\text{Al}_2\text{O}_3$  ( $8 \text{ W/m}^* \text{K}$ ). When the void space is filled with He gas (which has one of the highest thermal conductivities of all gases ( $k = 0.15 \text{ W/m}^* \text{K}$ )) the effective thermal conductivity of the bed is about the same as the thermal conductivity of the gas regardless of whether Ag ( $k = 400 \text{ W/m}^* \text{K}$ ) or  $\text{Al}_2\text{O}_3$  ( $k = 8 \text{ W/m}^* \text{K}$ ) are used. Nevertheless, while we expected that the difference between aluminum and glass spheres as the thermal bed material would not make a large

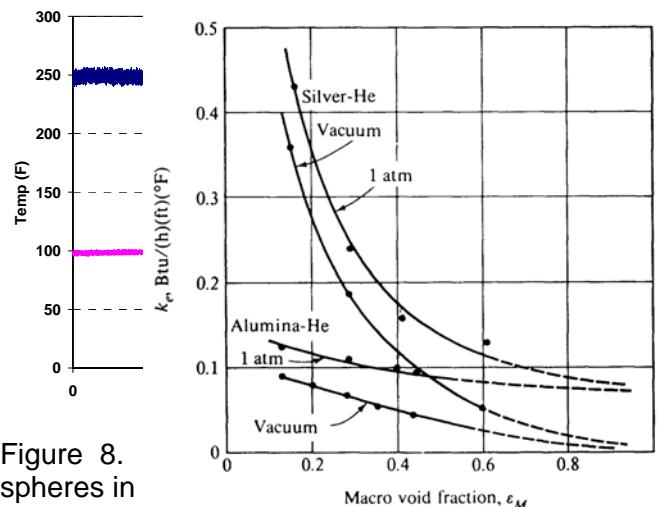


Figure 8. spheres in

Figure 9. Comparison of effective thermal conductivity of packed beds in vacuum and helium (Smith 1981).

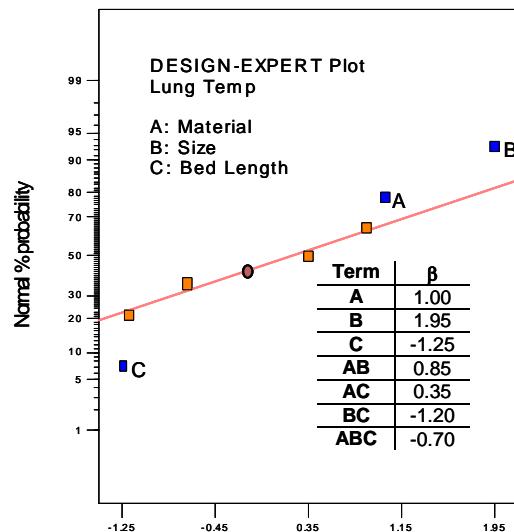


Figure 10. Normal probability plot showing that all three factors affect the lung temperature.

Figure 10. Normal probability plot showing that all three factors affect the lung temperature.

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difference, it can still make a small difference, and therefore we needed to determine its effect verify experimentally because even temperature increases as small as 20°F could render the wildfire rescue respirator unusable for breathing.

Figure 10 is a normal probability plot of the responses along with the values calculated for the  $\beta$ 's (called the effects in the graph) that go into the response equation given above. In a normal probability plot, the  $\beta$  terms that can be plotted on a straight line are statistically random at the level of accuracy of the experiments. Thus,  $\beta$  values that are significantly off of the line are real effects. Obviously, there is a considerable amount of subjectivity when the effects are small (which of course indicates that they are also relatively unimportant in controlling the response being measured), but in some cases, the controlling variables are considerably "off the line." Nevertheless, the magnitude of the  $\beta$  values shown in Figure 10 indicate that the bed length and size of the spheres (which affect heat transfer) were slightly more important than the type of material used, but that the inhaled air temperature was rather insensitive to all three, indicating that the bed was over designed in Phase I. Therefore it might be possible to reduce its size (which would reduce the bulk of the final product) when we optimize for length and monolith diameter in Phase II.

#### 4.2.3.2.3 Thermal Bed Results Using Cordierite Monolith

Because of the insensitivity of the inhaled air temperature to the type of configuration of the material in the thermal bed, we decided to test a cordierite monolith as the thermal bed material. Cordierite is used as a low pressure drop catalyst support in automobile catalytic converters and is a synthetic, high temperature material with the formula  $Mg_2Al_4Si_5O_{18}$ . The advantages of the cordierite monolith compared with a packed bed of beads, spheres or other particles are: 1) lower weight, 2) lower pressure drop, 3) no possibility of channeling that can occur with packed beds when they settle as the WFRR is moved about, and 4) far greater simplicity for manufacturing, which lowers cost. Figure 1 above, shows the honeycomb structure of the cordierite monolith. Gas flows through the cells down the length of the monolith and heat is transferred from the gas to the walls of the solid. Because the cells are small (we used 400 cells/in<sup>2</sup> cordierite monolith) the gas flow is laminar, which provides the greatest heat transfer with the lowest possible pressure drop (in contrast, heat transfer coefficients are much higher for turbulent flow, but so are the pressure drops). The heat capacity of the cordierite then stores the energy, which heats up the solid. During exhalation, the firefighter's breath (98°F, ~80% RH) removes this heat and cools the cordierite monolith back down for the next inhalation of hot air.

Table 3 is a summary of the tests done with the cordierite monolith at the thermal bed material. Note that in two of the tests we used an inlet hot air temperature of 350°F, to determine how well the cordierite monolith could cool a firefighter's breath under the most harsh circumstances where the firefighter would have a reasonable chance of survival while in a fire shelter. In all of the cases where the barometric pressure was 12.2 psia (Golden, CO

Table 3. Cordierite monolith test results

Cordierite	Lung (°F)	Hot (°F)
2 in monolith (Denver)	103.8	350
2 in monolith (sea level)	115.5	350
1 in monolith (Denver)	100.7	250
1.5 in monolith (sea level)	110	250

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elevation), the cooled air temperature "breathed in" was between 100 and 104°F when the inlet temperature was 250°F. When the pressure was increased to 14.7 psia to simulate operation of the WFRR at sea level and the inlet temperature was increased to 350°F (conditions that simulate the worst possible situation), the outlet (cooled air) temperature increased to about 110-115°F, which will be uncomfortable, but is still tolerable, certainly when the issue is survival. The temperature increase that accompanies the pressure increase is due to the density of air increasing by about 20% at the higher pressure. The other properties that are important in heat transfer such as the heat capacity, thermal conductivity and viscosity change by less than 1% much upon going from 12.2 to 14.7 psia (for a given temperature). Figure 11 shows typical results for 2 inch cordierite monolith with a 350°F inlet air temperature at 12.2 psia (left), and the effect of increasing the pressure from 12.2 to 14.7 psia with a 1.5 inch monolith (right).

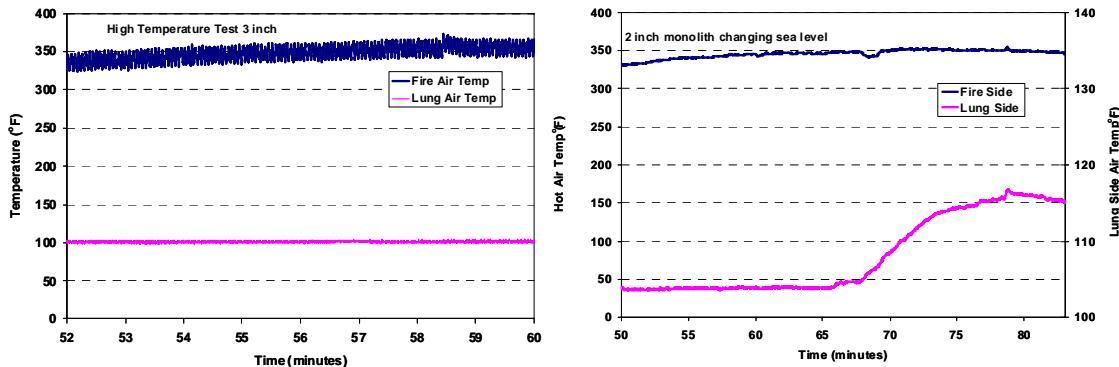


Figure 11. Hot (350°F) inlet air test with cordierite monolith (left) and effect of increasing the barometric pressure to sea level (right).

#### 4.2.3.2.4 Control Experiment without a Thermal Bed

Whether a bed of glass and aluminum spheres, or a cordierite monolith is used, hot air at 250°F is cooled to about 100°F regardless of the material used, and as discussed above, this is largely due to the fact that the heat transfer characteristics of the bed are more affected by the air properties than the properties of the solids. To ensure that our results were accurate, we ran an experiment without any thermal bed material present (empty container shown in Figure 6). These results are shown in Figure 12 where an inlet hot air temperature of about 225°F produces air that is only "cooled" to about 180°F. This small amount of cooling is due to heat losses in the system (because

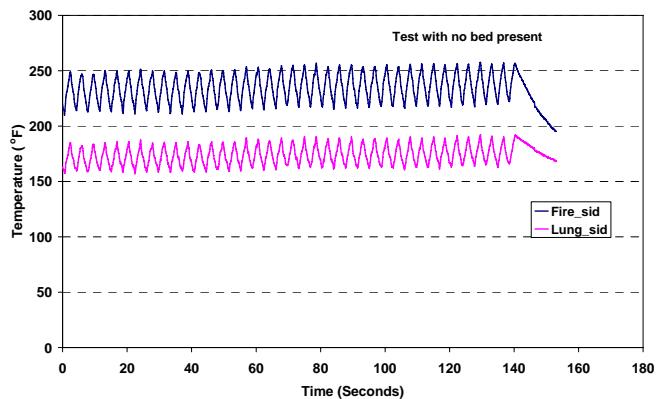


Figure 12. Results for test with no thermal bed in place showing "lung side" air temperature between 160 and 180°F.

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it cannot be perfectly insulated). Nevertheless, the results shown in Figure 12 indicate that the results we obtained that are shown in Figure 8, Figure 11, Table 2 and Table 3 are real and that cooling of the firefighter's breath is possible using our device.

#### 4.2.3.2.5 CO Oxidation Catalyst Test Results using a Coated Monoliths

As mentioned in the background, significant amounts of CO are produced in fires, and even if one can cool the superheated air to temperatures that are safe to breath if high concentrations of CO are present, there is a serious danger of the firefighter being poisoned. To remove CO, we have incorporated a unique catalyst that was developed over several years at TDA for low temperature CO oxidation. The catalyst is based on gold-promoted, cobalt oxide ( $\text{Co}_3\text{O}_4$ ) doped titania ( $\text{TiO}_2$ )

Massive gold (which for catalysis means crystallites larger than about 10 nm) is catalytically inactive because of the element's high atomic number, which causes contraction of the 6s valence electrons (the so-called lanthanide contraction), which makes the 6s and 5d levels unavailable for chemical bonding at ordinary temperatures (Bond et al. 2006). In contrast, nanometer sized Au crystallites are catalytically active when supported on various transition metal oxides (TMO's), and experimental evidence indicates that as the size of Au crystallites decreases to about 5-10 nanometers (or smaller), a transition from metallic to nonmetallic character occurs, and Au begins to exhibit catalytic activity (Bond et al. 2006). Au/TMO catalysts have now been shown to be active for CO oxidation at temperatures as low as -70°C, as well as room temperature propylene epoxidation, gas phase synthesis of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) from  $\text{H}_2$  and  $\text{O}_2$ , cyclohexane oxidation to cyclohexanone, and a wide variety of other industrially useful partial oxidations (Bond et al 2006; Corti et al. 2005).

TDA has been working in Au catalysts for more than a decade and is currently developing a Au/ $\text{Co}_3\text{O}_4$ - $\text{TiO}_2$  catalyst for oxidizing CO to  $\text{CO}_2$  at 0°C for use in CBRN escape hood respirator cartridges. We were recently awarded a NIOSH Phase II SBIR to continue this work, and our industrial partner is Mine Safety Appliances. Rather than develop a separate CO oxidation catalyst for the WRFF, we are using the same catalyst *formulation* in the WRFF that is being developed for the CBRN application. In the CBRN application however, the catalyst is present as a bed of granules, and in the WRFF, a thin washcoat of catalyst inside the channels of the cordierite monolith is used to maximize air/catalyst contact, and to minimize pressure drop and the amount of catalyst needed. A much smaller amount of catalyst can be used in the WRFF application because the temperatures are near 250°F, where these catalysts are extremely active (they were designed to function at temperatures as low as 32°F).

The preparation of Au/ $\text{Co}_3\text{O}_4$ - $\text{TiO}_2$  catalyst deposited on the cordierite monolith is done in three separate stages: 1) preparation of 10%Co on  $\text{TiO}_2$ , 2) adding 1% gold to the Co/ $\text{TiO}_2$  to produce the Au/ $\text{Co}_3\text{O}_4$ - $\text{TiO}_2$  and 3) wash coating the catalyst inside the channels of the cordierite monolith. Once the Au/ $\text{Co}_3\text{O}_4$ - $\text{TiO}_2$  catalyst powder is made it is mixed with a binder and dip-coated inside the cordierite channels followed by a final calcining step. The last calcining step decomposes binder leaving the catalyst particles attached to the cordierite walls of the monolith.

Figure 13 shows the results of CO oxidation tests using catalyst coated cordierite monoliths. The 2 inch long cordierite monolith contains approximately 2 grams of Au/ $\text{Co}_3\text{O}_4$ - $\text{TiO}_2$  catalyst

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and the 3.5 inch monolith contains about 3.5 grams. At a flow rate of 64 standard liters/min (slpm) the space velocity with respect to the amount of catalyst present in the monolith is 288,000 cm<sup>3</sup> of heated air per gram of catalyst per hour. For comparison, a typical industrial catalytic process operate at space velocities of 2000 to 10,000 h<sup>-1</sup>. Thus, our catalyst is extremely active. In the test with the 2 inch monolith, the concentration of CO exiting the monolith was reduced from 3600 ppm to about 160 ppm (95.6% conversion) in spite of having a residence time of only 333 *milliseconds*. Increasing the length of the monolith to 3.5 inches increases the residence time to 583 ms. Under these conditions, the outlet CO concentration is reduced to 20 ppm, which is below the OSHA PEL of 35 ppm (Figure 13). Also, the data shown in Figure 13 are for a breather test, and for an inlet temperature of 250°F, the outlet breathed air temperature is only about 100°F. Thus, while 2 inches of monolith is sufficient for cooling the air to acceptable temperatures, the added length is needed to insure adequate CO destruction. Pressure fluctuations in the gas cell of the IR analyzer are responsible for the noise in the CO signals because, pressure increases and decreases that accompany valve switching increase and decrease the CO concentration slightly with the effect being more pronounced at lower CO concentrations where one is closer to the limit of detection of the instrument. Nevertheless, in spite of the exothermic nature of CO oxidation reaction, the breathed air temperature only increases by about 3°F, and because the adiabatic temperature rise from the oxidation of 3600 ppm of CO would otherwise be about 60.8°F, the fact that we observed  $\Delta T = 3^{\circ}\text{F}$ , indicates that the unit is properly designed to accommodate the thermal load from both the external superheated air and the extra heat from CO oxidation. These results also show that the catalyst formulation used in the earlier CBRN application is satisfactory for the WFRR application, easily oxidizing CO to CO<sub>2</sub> at WFRR temperatures. Optimizing the method of bonding the catalyst to the cordierite monolith is one of the tasks in Phase II.

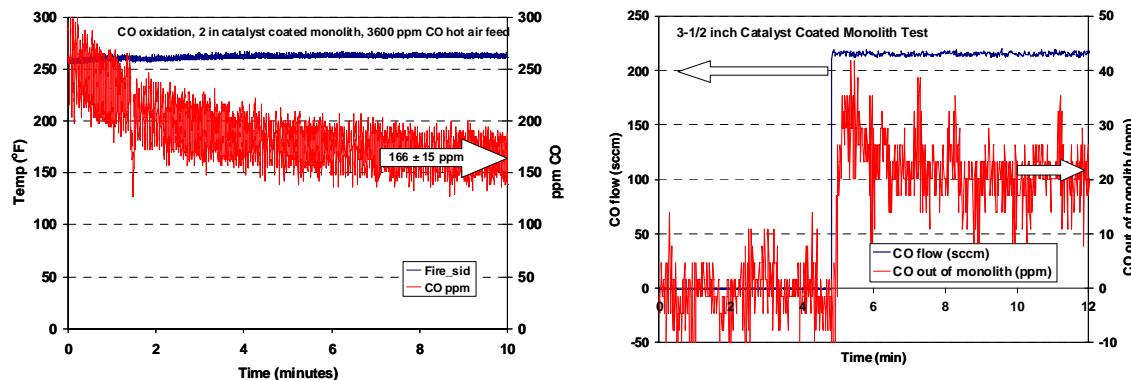


Figure 13. Reduction of CO concentration from 3600 ppm to 160 ppm using a 2 inch long cordierite monolith (left) and to ~20 ppm using a 3.5 inch long monolith coated with TDA's 1%Au/5%Co<sub>3</sub>O<sub>4</sub>/TiO<sub>2</sub> catalyst (right). Both were breathing tests.

#### 4.2.3.3 Results for Phase I, Task 3: Model WFRR and transient heat transfer

The transient thermal storage behavior of the cordierite monolith heat exchanger is important to understand for optimizing the design of the WFRR, therefore, we modeled the heat exchanger component of the firefighter mask using SINDA/FLUINT, a comprehensive finite-difference,

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lumped parameter (circuit or network analogy) computer program that is used to analyze simultaneous heat transfer and fluid flow in complex systems. Using the Sinda/Fluint model we can predict performance of the WFRR over a wide range of system properties and designs, and determine the lightest and smallest design to remove the required heat load. In particular, the model we run to determine the length of the heat exchanger required to cool the air.

The monolith used in the experimental studies was 3.5" in diameter and contained 400 cells/in<sup>2</sup>. Inhaled and exhaled air pass down through the same square heat exchanger channels but flow in reverse directions. The SINDA/FLUINT simulation was built to predict the convective heat transfer between the inhaled and exhaled air and the monolith walls, including heat conduction through the walls in the flow direction. Axial conduction is not significant (which is good in our application) because cordierite is a poor thermal conductor. For computational efficiency, one flow channel was modeled using its fraction of the total flow. Thirty thermal nodes were used in the axial flow direction. The monolith wall was modeled by a single cell, because there is no gradient across the wall perpendicular to the flow direction, because the convective heat transfer coefficient (16 BTU/ft<sup>2</sup> hr °F) is much smaller than the wall conduction heat transfer coefficient (1200 BTU/ft<sup>2</sup> hr °F). Radiation and convective heat loss to the environment was neglected. We used the air properties included in the software. The slightly increased heat capacity due to humidity in the air was accounted for by increasing the mass flow rate appropriately. The effect of CO<sub>2</sub> exhaled was also calculated to be very small and was neglected. We calculated the inhaled air temperature exiting the monolith and entering the lungs as a function of key parameters. The geometry and material properties of the monolith and the input conditions are given in Table 4.

Figure 14 shows the temperature gradient in the 3" monolith after 5, 15, and 30 minutes. Across the first part of the monolith, there was a steep gradient where the heat from the fireside air enters the unit. After flowing across the first two inches of the monolith, the temperature was decreased from 360°F to 111°F after 30 minutes of use. There was very little further temperature decrease achieved in the last inch of length. The outlet gas temperatures for different monolith lengths is shown in the left panel of Figure 14) and the full transient profile of the outlet temperature for the 2 inch monolith is shown in the right panel of Figure 14.

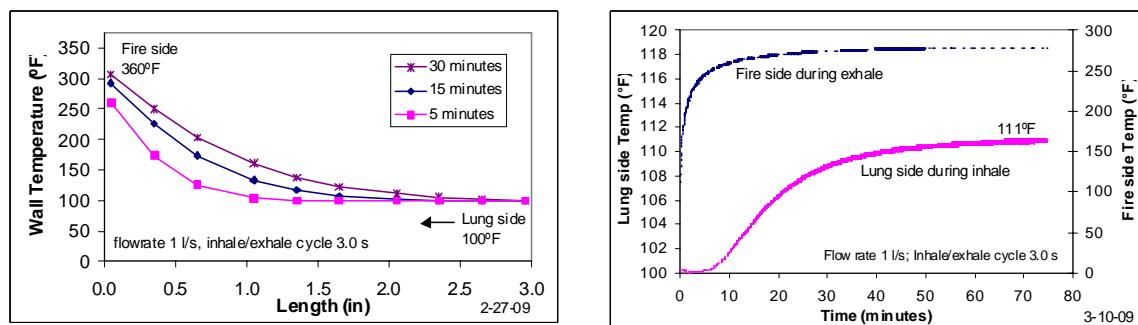


Figure 14. Axial temperature profile (left) and time to maximum lung side temperature for 2 inch cordierite monolith (right) predicted by SINDA/FLUINT modeling.

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Figure 15 shows both the experimental data compared with the SINDA/FLUINT model predictions for the lung side outlet gas during inhalation. The model is in excellent agreement with the experimental data predicting that the hot air is cooled from 250°F to approximately 107°F, indicating that the SINDA/FLUINT model can be used as a predictive tool when used in Phase II when optimizing the WFRR.

#### 4.2.3.4 Results for Phase I, Task 4: Preliminary prototype unit design

Our preliminary design of a WFRR was based on the following assumptions: 1) metabolic rate of 1,000 Btu/h, 2) altitude from sea level to 10,000 ft, 3) dew point = < 90°F (36 Torr water vapor pressure, 4) maximum allowable pressure drop of less than 1 inch water, 5) inlet air temperature of 350°F, 6) breathed air temperature no higher than 113°F, and 7) air flow during inhalation or exhalation equal to 2.5 ACFM average, 5.0 ACFM peak. The heat transfer calculations assumed 1) fully developed *laminar* flow for heat transfer coefficients and pressure drop and 2) there was no axial conduction in the heat exchanger (this was found to be a reasonable assumption based on both our laboratory tests and modeling results).

Figure 16 shows the bed weights (in grams) and pressure drops (27.7 in H<sub>2</sub>O = 1 psi). For any given length of bed, the cordierite monolith is the lightest material that we tested. For example, a 3 inch long cordierite monolith weighs 221 grams and has a  $\Delta P = 0.09$  in H<sub>2</sub>O, whereas a 3 inch bed of 1 mm glass spheres weighs 726 grams and gives a  $\Delta P = 1.47$  in H<sub>2</sub>O. Even a 2 inch bed of 1 mm aluminum spheres weighs 476 grams and produces a pressure drop of 0.997 in H<sub>2</sub>O. Because the cordierite monolith beats any of the other materials in both weight and pressure drop, is not susceptible to channeling, is the most mechanically durable material, and the easiest to assemble. Therefore, the cordierite monolith is the material of choice for the WFRR.

Table 4. Parameters used in SINDA/FLUINT modeling.

##### Material and thermal properties

Specific heat	0.35 cal/g°C
Thermal Conductivity	3.0 W/m-K
Density	1.77 g/cc
Nusselt number (for square channel)	4 (dimensionless)

##### Monolith geometry

Cells per square in	400/in <sup>2</sup>
Internal cell height,	0.043 in
Internal cell width	0.043 in
Cell wall thickness	0.007 in
Overall monolith diameter	3.5 in

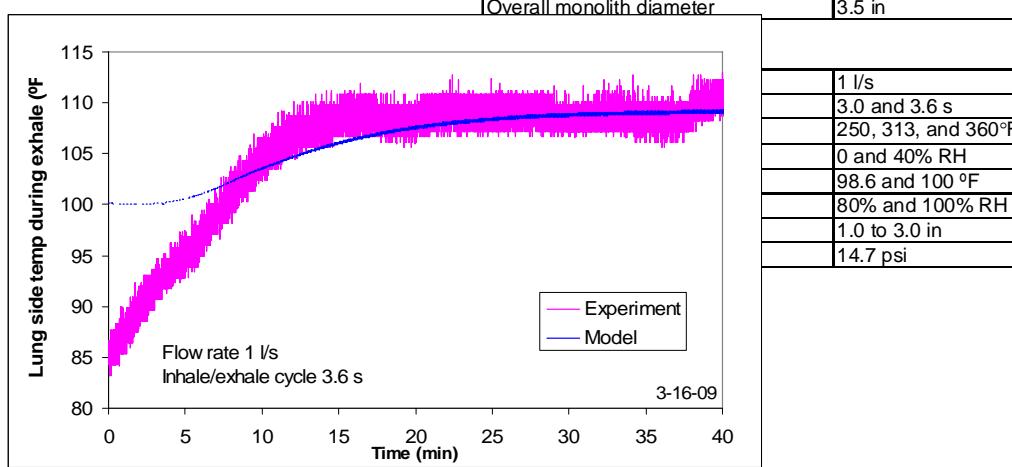


Figure 15. Comparison of SINDA/FLUINT model with experimental results.

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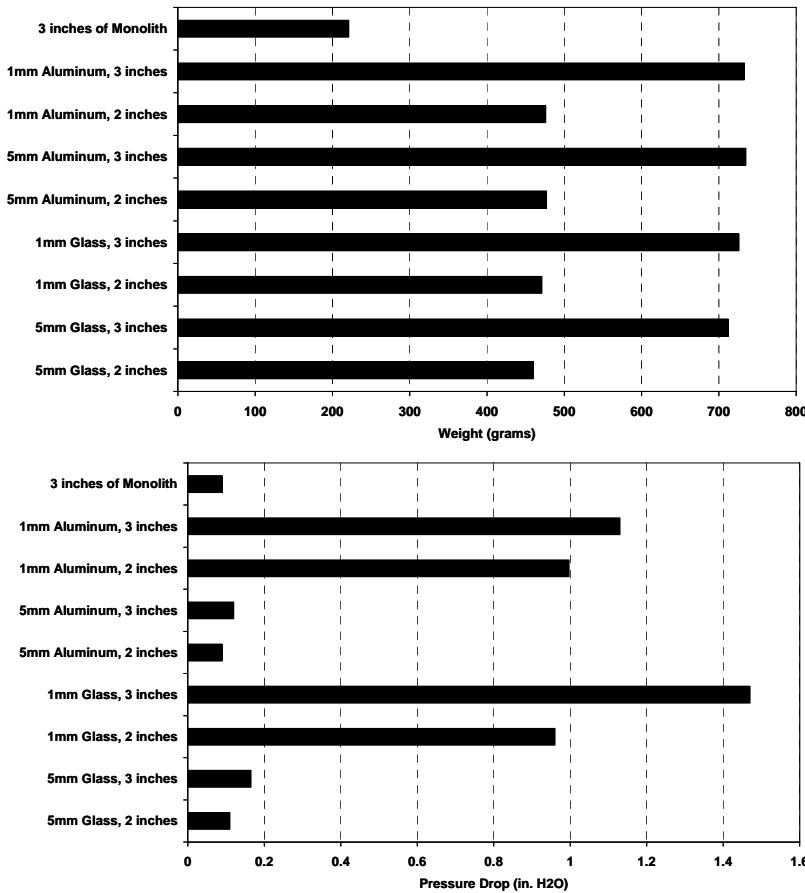


Figure 16. Weight and pressure drop for different bed materials and lengths.

#### 4.2.4 Phase I Summary and Conclusions

In Phase I, TDA designed, developed, and tested materials for a wildland firefighter rescue respirator (WFRR) that could be used to protect the firefighter against superheated air and carbon monoxide when forced to deploy a fire shelter during an entrapment. Specifically, we designed and built a test apparatus to simulate a firefighter breathing superheated air through the WFRR, determined the best material to use for the thermal bed (which turned out to be a 400 CPSI cordierite monolith, tested and verified the performance of a catalytic coating that oxidizes CO to CO<sub>2</sub> for protection against this hazard, modeled the transient heat transfer in the monolith for the preliminary design using SINDA/FLUINT, and finally, performed a preliminary prototype unit design based on the data and modeling efforts.

### 5. Publications and Conferences

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- July 2009, Non-proprietary presentation presented to NFPA committee for wildland firefighting
- March 2010, Upcoming Extramural Funding presentation to NIOSH (NPPTL)

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