Exploratory Procedures with Carbon Nanotube-based Sensors for Propellant Degradation Determinations

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ABSTRACT

Exploratory research is conducted at the US Army Aviation & Missile Research, Development, and Engineering Center (AMRDEC) in order to perform assessments of the degradation of solid propellant used in rocket motors. Efforts are made to discontinue and/or minimize destructive methods and utilize nondestructive techniques to assure the quality and reliability of the weaponry's propulsion system. Collaborative efforts were successfully made between AMRDEC and NASA-Ames for potential add-on configurations to a previously designed sensor that AMRDEC plan to use for preliminary detection of off-gassing. Evaluations were made in order to use the design as the introductory component for the determination of shelf-life degradation rate of rocket motors. Previous and subsequent sensor designs utilize functionalized single-walled carbon nano-tubes (SWCNTs) as the key sensing element. On-going research is conducted to consider key changes that can be implemented (for the existing sensor design) such that a complete wireless sensor system design can be realized. Results should be a cost-saving and timely approach to enhance the Army's ability to develop methodologies for measuring weaponry off-gassing and simultaneously detecting explosives. Expectations are for the resulting sensors to enhance the warfighters' ability to simultaneously detect a greater variety of analytes.

Outlined in this paper are the preliminary results that have been accomplished for this research. The behavior of the SWCNT sensor at storage temperatures is outlined, along with the initial sensor response to propellant related analytes. Preparatory computer-based programming routines and computer controlled instrumentation scenarios have been developed in order to subsequently minimize subjective interpretation of test results and provide a means for obtaining data that is reasonable and repetitively quantitative. Typical laboratory evaluation methods are likewise presented, and program limitations/barriers are outlined.

Keywords: Propellant, rocket motor, off-gassing, automated testing, shelf-life, degradation, weaponry

1. INTRODUCTION

It is common knowledge that (over a period of time) the chemical, electrical, and mechanical properties of missiles and rockets can change, degrade, and eventually result in the units becoming unusable. Throughout the life cycle of military armaments, weaponry health surveillances are implemented in order to evaluate the properties, characteristics, and performance capabilities of the hardware. Reliability, safety, and operational effectiveness of the weaponry are the results from these studies. The functionality of missiles and rockets are often evaluated by being fired or decomposed at routine time-frames after manufacturing and after prolonged storage. The key component addressed by researchers (associated with this paper) is linked to the energetic materials that make up the rocket motor's propellant. Degradations associated with the propellant may include depletion of propellant stabilizer, materials cracking, and material/inert surface de-bonding.

While it is very important to ensure that missiles/rockets are safe and functionally reliable for the warfighter's use, it is extremely expensive to routinely take weaponry apart, dissect them, and destructively determine the degree of degradation in the rocket motor's propellant. The Army Propellant Surveillance Laboratory (Picatinny, New Jersey)

Nanosensors, Biosensors, and Info-Tech Sensors and Systems 2010, edited by Vijay K. Varadan,
Proc. of SPIE Vol. 7646, 764602 · © 2010 SPIE · CCC code: 0277-786X/10/$18 · doi: 10.1117/12.849558

monitors the safety of the world-wide ammunition stockpile. Samples of propellant are taken from ammunition and energetic materials located throughout the world in this ordinary looking facility that assures a safe, reliable and a ready inventory of ammunition.[1] Weaponry stored under varying environmental conditions normally experiences degradation due to both nature aging and aging caused by changes in temperature. "During storage of double-base propellants at elevated temperatures, the stabilizer reacts more and more with the nitrogen oxides (NOx) released by the nitrate esters (nitrocellulose and nitroglycerin) present in the propellant until it has depleted completely. Although the decrease of the primary chemical stabilizer is accompanied by the additional formation of daughter stabilizer reaction products which also possess a residual stabilization capability, the depletion of the primary chemical stabilizer can lead eventually to autocatalytic decomposition of the propellant, self-heating, and cook-off completely."[2]

A host of research teams have destructively examined the effect of aging on composite solid propellant with much of the emphasis being on ignition delay time and other factors.[3,4,5,6] It is extremely costly to utilize destructive testing for determining long-term rocket motor aging and shelf-life. If the cost becomes intolerable, there is always the possibility that shelf-life and aging evaluation programs could be decreased, eliminated, and/or jeopardized by other measures. The negative results from any insufficiency in high quality evaluations could lead to unpredicted missile failures, increased risk to soldiers, and potential loss of advantage on the battlefield.

Researchers at the Army Aviation & Missile Research, Development, and Engineering Center (AMRDEC) have previously investigated several nano-based technologies to solve the problem of sensing extremely small levels of toxic gases associated with both weaponry health monitoring and chemical warfare agent detection. [7] The innovative sensing methods included voltammetry, which is a well established technique for the detection and quantification of substances dissolved in liquids, and surface enhanced Raman scattering (SERS) technique, which enhances Raman scattered light by excitation of surface plasmons on nanoporous metal surfaces (nanospheres). Other methods being investigated to develop novel smart sensors for the detection of chemical agents, home-made explosive devices and propellant degradation are functionalized single-walled carbon nano-tube and nanowire based sensors. [8] For this application the authors are exploring chemical sensory techniques to nondestructively evaluate propellant degradation, motor quality, and thus, weaponry shelf-life. The subsequent plan is to implement miniature chemical sensor systems that can be surface mounted and/or embedded in the weaponry's motor. The Army AMRDEC has collaborated with researchers at NASA-Ames and scientific personnel at the Alabama A&M University (Normal, Alabama) to successfully conduct programs to demonstrate low power, nano-based sensor systems that can detect a wide variety of electro-active chemical analytes at sensitivity ranges as low as parts-per-billion. The most important goal of the project is to advance the proven functionalized single-walled carbon nano-tube (SWCNT) sensor technology and implement miniaturized sensor arrays that can be placed in close proximity to the propellant and wirelessly transmit prognostic/diagnostic information relative to weaponry health.

The AMRDEC research team's accomplishments and current status of exploratory propellant degradation methodologies are outlined in this paper. The initially selected SWCNT sensor technology is described in Section 2. Initial approach for insertion of the SWCNT sensor in the rocket motor's propellant proximity is outlined in Section 3, along with laboratory configurations, and test results. Section 4 has the summary, program developments, and future efforts.

2. SELECTED SWCNT-BASED SENSOR TECHNOLOGY

The primary objective of the AMRDEC research and development project is to develop a miniaturized chemical sensor array package that can be primarily mounted onto a rocket motor to detect and identify multiple analytes associated with propellant off-gassing. The sensor must be ruggedized for military environments and miniaturized for minimal payload additions on rocket motors, as well as on manned and/or unmanned system to detect residue from explosive material. The size, power consumption, and surface temperature dependence of the sensor must be minimized by designing the sensor system in the smallest possible configuration while requiring extremely low power input. Useful lessons learned from attempts to use multi-walled carbon nanotubes (MWCNT) were utilized for developing SWCNT devices. It should likewise be noted that the response of SWCNT devices are more significantly defined than any of the Army AMRDEC configured MWCNT devices.

Research on SWCNT material for propellant off-gassing sensors is extremely rare; thus, the authors' task of finding and utilizing off-gassing detection material and devices becomes quite challenging. Multi-channel SWCNT sensor arrays, originally developed by researchers from the National Aeronautics and Space Administration (NASA) Ames Research Center (ARC), have been used as the baseline sensor for AMRDEC's propellant degradation research.[9,10] The SWCNT sensor array (Fig. 2.0-1), has approximately thirty-two (32) individually functionalized CNT sensor elements for simultaneously sensing of up to thirty-two different analytes or targeted chemical agents (including propellant off-gassing).

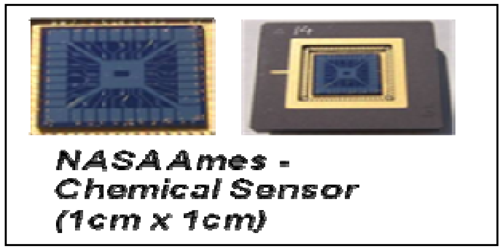

Fig. 2.0-1 Multi-channel sensor array (NASA-AMES)

Some of the details associated with each sensor element (as described in reference 10) are pictorially shown below in Fig. 2.0-2. The carbon nanotubes are depicted in the figure as the randomly shaped particle dispersed across gold electrodes (mainly the dark gray area of the figure). The carbon nanotube-based chemical sensor concept consists of the interdigitated electrode (usually fabricated with gaps using photolithography) with purified SWCNT-based materials for chemical sensing (acting as a chemical-resistor).

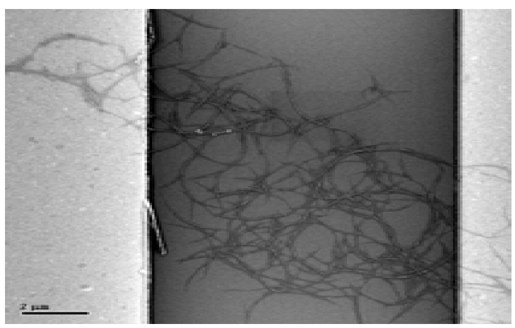

Fig. 2.0-2 Single sensor element with carbon nanotubes across gold electrodes

As can be seen in the previously discussed concept (Fig. 2.0-2), the electrode embraces a defined network of SWCNTs with a density large enough to productively enable electrical contact (between the SWCNTs and electrode) while accomplishing chemical sensing. The overall SWCNT/electrode configuration allows for good gas/vapor adsorption accessibility. The NASA-Ames team acknowledged that the elements can be fabricated via simple processes, at high yield, and resulting units are reliable with reproducible performance. The NASA team provided preliminary results that included conductivity changes when the sensing element was exposed to both NO_2 and explosives; resulting sensitivity was at a range approximated in parts-per-billion (ppb). Impressive selectivity was achieved after NASA researchers coated the surface of the CNTs with polymers. Combining the carbon nanotube-based chemical sensor with MEMS technology, a lab-on-a-chip can be built, which has onboard data processing and potentially wireless communication capabilities. Such a lab-on-a-chip system can be deployed across a wide spectrum of hardware platforms for environmental monitoring, and can be made into a portable handheld device.

2.1 Design Approach [11,12]

In an effort to generate and maximize a design concept that can utilize carbon nanotubes, geometrical configurations for the SWCNT sensor are investigated by the NASA-Ames team. The configuration that allowed for the most acceptable sensitivity and response to chemical analytes is shown in Fig. 2.1-1 (below). As shown in the figure, the schematic diagram (to the left) is the detailed concept for the sensor element. The right side of the figure shows the details of how the carbon nanotubes (CNTs) are aligned on the surface of the substrate; the process is referred to as disperse purified nanotubes in DMF (dimethylformamide). Simple micro-fabrication processes are used in the production of each set of sensor elements. One critical step in the process is what NASA refers to as interdigited micro-scale electrode device fabrication. The process includes solution casting of CNTs across the electrodes.

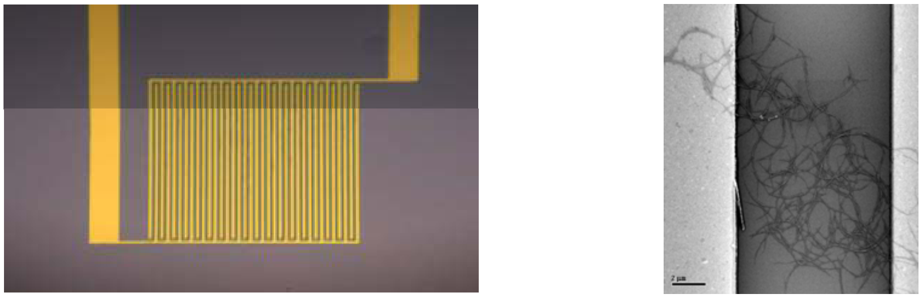

Fig. 2.1-1 Design concept schematic (left) with details (right) of how CNTs are distributed

The design parameters include: response speed, sensitivity, dynamic range, short and long-term stability, resolution, selectivity, operating ambient conditions, operating lifetime, output format, size, weight, and cost. Material selection for each SWCNT sensor element is dependent on both sensor performance characteristics and the analyte being detected.

2.2 Sensor Selectivity

Selectivity is one of the important parameters for the AMRDEC research and development propellant degradation assessment. The selectivity can be achieved by functionalizing each chosen CNT sensor element with material that will only bond with the chosen chemical analyte. Thus, the selectivity is dependent on the sensor material in each element used in the SWCNT sensor array. Electrochemical sensors are not naturally selective and may not normally be able to detect and identify an unknown analyte or mixture of analytes. The chosen method was to build an array of sensors, each with a different material that yields unique responses to a given analyte. Fig. 2.2-1[12] illustrates the use of a sensor array with variation among each sensor element's physical configuration, coating, and doping. The detected and measured concentration of analyte is equated to the relative change of resistance in the sensor element. The NASA-Ames team indicated that the array device "learns" the response pattern in what they refer to as the "training" mode, and unknowns are classified in what NASA refers to as the "identification" mode. The NASA team uses pattern matching (as indicated in the figure) algorithms to convert the data into a unique response pattern. During laboratory assessments, the sensor (including each element) can be "refreshed" using ultra-violet light emitting diode (UV/LED), heating or purging.

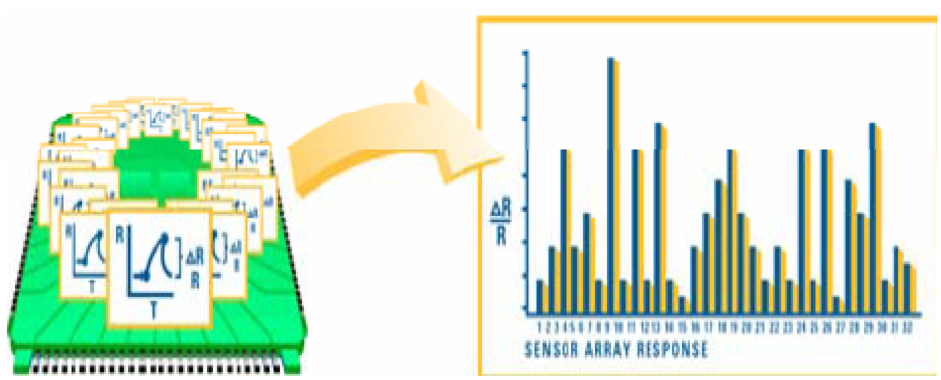

Fig. 2.2-1 Sensor array, change in element output, and pattern matching algorithms

2.3 Sensor Fabrication and Packaging

The SWCNT sensor is fabricated on a one centimeter by one centimeter chip with an array of twelve (12) to ninety-six (96) elements. The fabrication process allows for an increased number of sensing elements to be added to the chip. If there is a need for additional chips (with elements), a four inch wafer can be used to accommodate additional chips. The wafer size can be further increased to 6", 8", or 12" to allow for additional sensing element chips. A sensor array configuration is shown in Fig. 2.3-1. The ultimate goal is to achieve a design that will allow for the size of the SWCNT sensor array and packaging to be readily placed as a system-on-a-chip configuration with readout electronics.

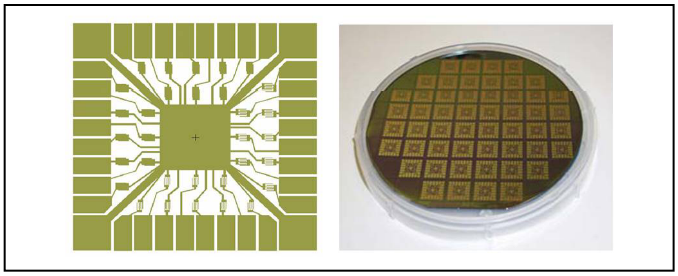

Fig. 2.3-1 Details of sensor elements (left) and chip/wafer (right)

A complete NASA-Ames SWCNT sensor system can be housed as shown in Fig. 2.3-2 (below); however, only individual sensor elements are utilized by/evaluated at the AMRDEC laboratory. The system generally consists of a multichannel chip that can provide high sensitivity/multi-functions. It can be fabricated (via low cost micro-fabrication methods) with built-in integrated signal processing while maintaining low power demands in all operations. Expectations are for the system to be integrated with the additional capability to sense/measure temperature, pressure, and humidity. When comparing data from both NASA and AMRDEC, the response time of the sensor is in seconds and parts-per-million/parts-per-billion (ppm/ppb) detection levels have been achieved.

Fig. 2.3-2 Complete NASA-Ames SWCNT sensor package

2.4 Technical Challenges

Several technical issues requiring further research to form an effective solution to chemical analyte detection utilizing SWCNT sensors are as follows:

1) Models are required to predict sensor selectivity to various material used for functionalizing the CNTs; however modeling can be costly and time consuming.
2) Final determination of sensor behavior at both storage and operational temperature is needed.
3) Reducing the suite of sensor readout and data acquisition electronics to a low power, lightweight design in order to minimize any additional weaponry payload requirements requires additional effort.
4) Developing wireless capabilities for varying weaponry configurations.

5) The sensing elements will be exposed to varying elements (including ingredients associated with the propellant). The potential for damage/wear must be assessed, along with any necessary requirements for the development of protective coatings.

3. INSERTION OF SWCNT SENSOR IN PROXIMITY OF PROPELLANT

3.1 Gas Sensor Calibration

Calibration of the SWCNT is conducted in a test article that is fabricated for propellant aging studies. An aluminum cup with an o-ring cap is shown in Fig. 3.1-1. The cap is fitted with a digital pressure gage (0.0 to 15.0 psi rage with +- 0.1% accuracy) and a valve for delivering gas into the closed chamber. Each sensor is placed into the chamber and held by an electrical clip for calibration. A standardization gas mixture of N_2 and NO_2 (50 ppm NO_2) is used to pressurize the cylinder over a range of gage pressures (from 0.0 psi to 14.0 psi). At each pressure level, the sensor is allowed to stabilize and then resistance measurements are taken to establish the correlation between the sensor resistance and the NO_2 concentration. The results of the calibration of six sensors are shown in Fig. 3.1-2.

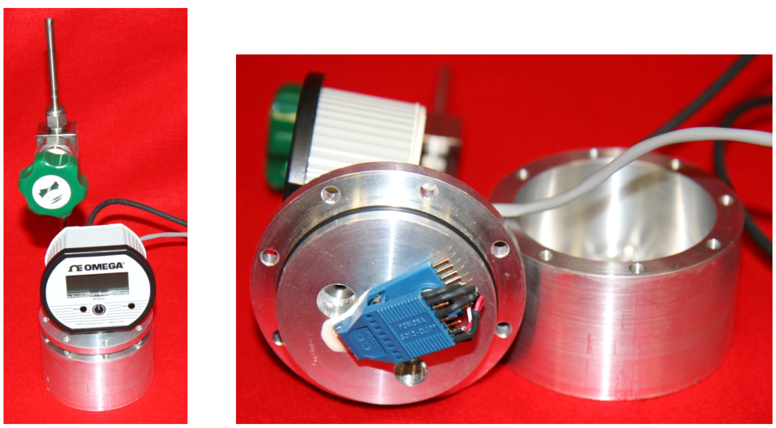

Figure 3.1-1 Calibration and Propellant Aging Test Article

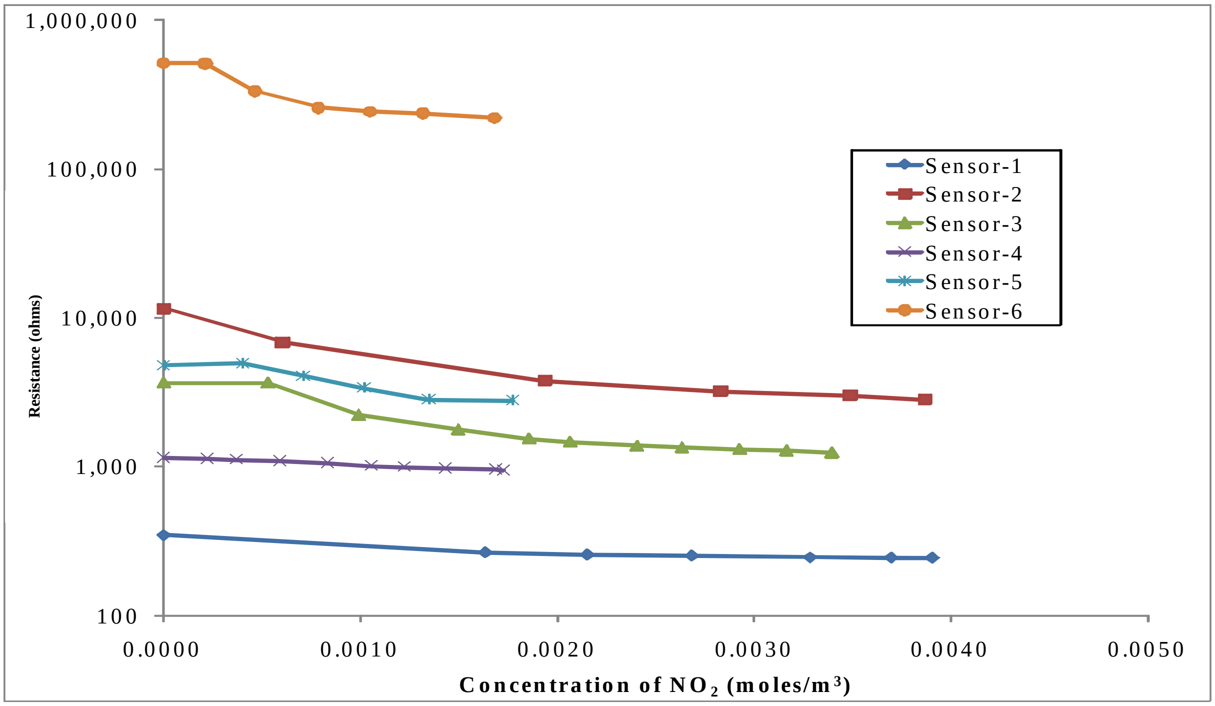

Figure 3.1-2 Sensor Calibration Curves for NO_2 Detection

An examination of Fig. 3.1-2 shows reasonably consistent behavior of the sensors to various levels of NO_2; however, the resistance magnitudes from sensor to sensor are considerable. Although some variability is expected from sensor to sensor, most of what is seen in Fig. 3.1-2 is believed to be related to the resistance between the sensor and the sensor mount. This is very evident in Sensor-6 which is the only sensor that was tested using conductive epoxy to attach the sensor leads. All other sensors are held in the electrical clip. These results emphasize the necessity for consistency between the calibration configuration and the application configuration.

Possibly a more appropriate calibration method is to charge the volume to a low pressure of N_2-NO_2 of known concentration, and then use a diluent gas, such as CO_2, to dilute the mixture to lower levels of NO_2 mole fractions. This would cast the calibration curve into terms of resistance versus ppm of NO_2. This calibration method is planned for all SWCNT sensors, but at the time of writing is not complete.

3.2 Propellant/Sensor Aging Experiment

The propellant/sensor aging experiment consists of placing a known quantity of nitrate ester propellant into the aluminum cup along with a SWCNT sensor. The cup is placed into an oven and artificially aged with elevated temperature to accelerate the propellant decomposition, stabilizer depletion, and gas evolution process. Fig. 3.2-1 shows the cup and propellant sample prior to aging. To establish the starting value of stabilizer prior to aging, a control sample is analyzed for stabilizer content using gas and liquid chromatography.

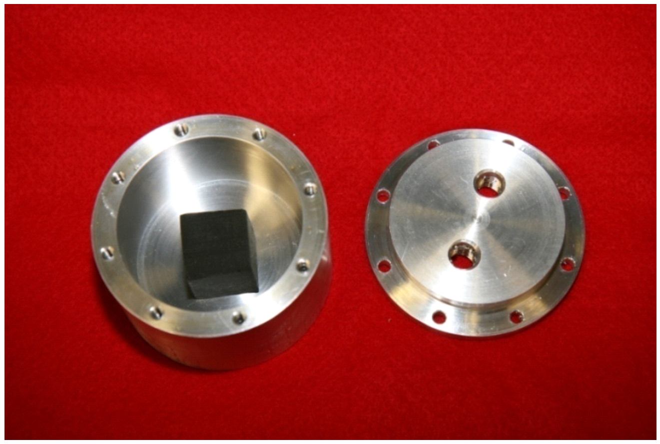

Fig. 3.2-1 Propellant Aging Sample in Aging Cup

The aging cup is placed into the aging oven at 70°C and aged for 42 days. At select intervals, the total pressure and the sensor resistance are recorded. At the end of aging, a gas sample is taken from the cup and analyzed using gas chromotogrphy and the aged propellant is analyzed for remaining stabilizer content. Fig. 3.2-2 shows the sensor calibration curve for the specific configuration used in the aging cup. Fig. 3.2-3 shows the total pressure history and the resistance measurements recorded during the 42 day aging cycle. An initial pressure rise is seen which is consistent with artificially aged articles. The elevated temperature causes an initial out-gassing of the sample which is also recorded by the SWCNT sensor indicating NO_2 as an out-gassing product. As time progresses the total pressure in the cup drops as the SWCNT indicates a decreasing concentration of NO_2. The simplest explanation of this event is that the cup may have a small leak and cannot maintain pressure. This explanation is refuted slightly by the difference in the rate that the NO_2 is decreasing compared to the rate of decrease of the total pressure. A second explanation is that the NO_2 is either reacting with the propellant polymer or is being absorbed/reacting with the epoxy sealant around the sensor wires. However, given the low mole fraction of the NO_2, the total pressure drop cannot be attributed entirely to a loss of NO_2.

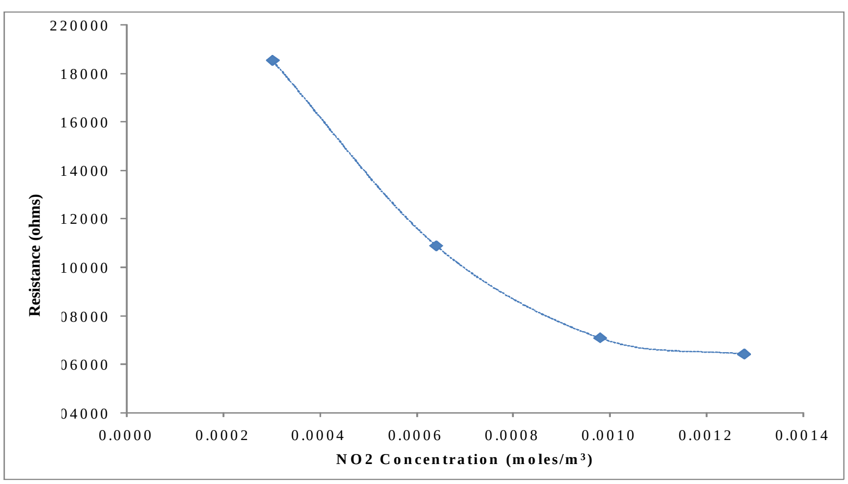

Figure 3.2-2 Calibration Curve for Sensor in Aging Cup Configuration

Table 3.2-1 shows the results of the gas analysis taken from the aging cup. Of note is the higher than expected concentration of NO_2 in the cup. The 0.043 moles/m^3 is at a concentration level that far exceeds the calibration curve. However, for the propellant system in question, the artificial aging corresponds to approximately 14.7 years of natural aging at ambient temperature and thus substantial kinetic decomposition of the propellant should be expected. This is confirmed by the analysis of the remaining propellant which shows a depletion of the N-Methyl-p-Nitroaniline (MNA) stabilizer from a starting mass fraction value of approximately 0.56% down to 0.22%. Extrapolation of the curve in Fig. 3.2-2 does not produce reasonable results and thus dictates that the calibration of the SWCNT must be conducted at much higher concentration values.

Table 3.2-1 Aging Cup Gas Analysis Results

Species	N_2	O_2	CO_2	CO	NO_2
Concentration (moles/m^3)	10.985	0.433	0.673	0.053	0.043
Mole Fraction	0.8876	0.0350	0.0544	0.0043	0.0035

The data shown in Fig. 3.2-3 is the response of the carbon nano-tube sensor in the aging cup due to the accumulation of NO_2 from the propellant decomposition. At specific intervals, the sensor resistance and total gas pressure were recorded. At the completion of the aging cycle, the sensor reading, once converted to mole fraction via the calibration curve (Fig. 3.2-2), is compared to the data in Table 3.2-1 since the data in the table represents the final gas concentration as measured by gas chromatography. However, in the present case, the final gas concentration exceeds the limits of the calibration curve and a meaningful evaluation of the sensor reading cannot be made.

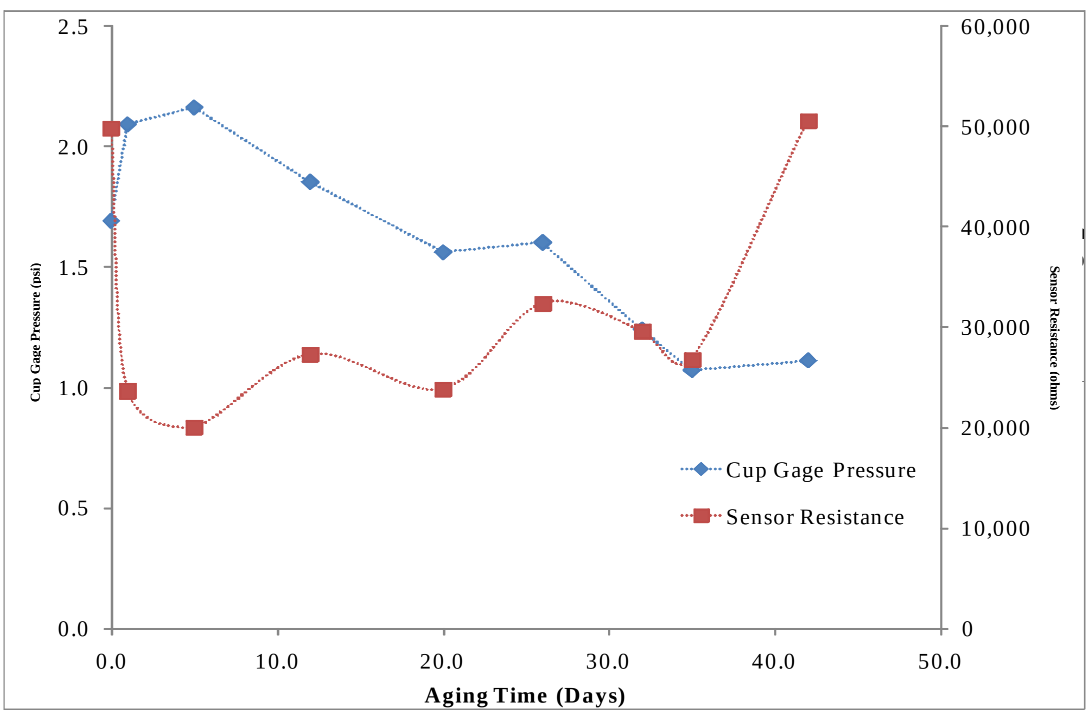

Figure 3.2-3 Pressure and Sensor Data from Propellant Aging Experiment

4. SUMMARY

A synopsis of the AMRDEC research and development project has been presented in this paper in preparation for subsequent integration of sensor array systems onto weaponry's rocket motors. The paper outlines information relative to the development of nano-based chemical sensor array systems for detecting varying level of analytes associated with shelf-life degradation of rocket motors. The carbon nanotube sensors are used to detect and identify multiple analytes from propellant off-gassing and can be used to detect related chemicals. The prototype SWCNT sensor technology, developed by NASA-Ames, is used as a baseline to implement a sensor array detector and is described in this paper. The SWCNT sensor is fabricated (with selected units being integrated with electronics) and laboratory tested. Additional laboratory testing is currently underway. Preliminary results indicate that the SWCNT sensors reacted favorably to small quantities of analytes associated with propellant off-gassing. The data indicates reasonably consistent behavior of the sensors to various levels of NO_2; however, the resistance magnitudes from sensor to sensor are considerable. Although variability is expected from sensor to sensor, it was believed that the variation, as is observed in Fig. 3.1-2, is related to the resistance between the sensor and the sensor mount. Previous evaluation results indicate that the SWCNT sensors are not unacceptably impacted by selected/simulated storage temperatures. The technical challenges, which remain, include modeling sensor behavior, establishing consistency between the calibration/application configuration, miniaturizing the electronics, and assuring that the sensor is ruggedized for long-term mounting/storage in close proximity with the rocket motor propellant. Future efforts will concentrate on field testing the current SWCNT sensor system, integrating wireless technology, reconfiguring the sensor system for mounting to the rocket motor, and equating sensor output to propellant off-gassing/degradation.

ACKNOWLEDGEMENTS

The authors wish to express thanks to the researchers at AMRDEC for their outstanding contributions and the summer students participating in AMRDEC's Science and Engineering Apprentice Program (SEAP) for their significant contributions of evaluating sensor for weaponry prognostic and diagnostic. Acknowledgement is also given to NASA-Ames for their contractor support and initial development of SWCNT-based sensors for missile health applications and chemical agent detection. Special thanks are given to others at the Army AMRDEC's Weapons Development & Integration Directorate for sharing their expertise in the identification of chemical analytes to perform the preliminary assessment of the sensors for weapons health monitoring.

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