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Status Report on the Preliminary Analysis of HVAC, Gas Distribution, and Fire Safety Equipment Installed in Homes with Chinese Drywall

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This interim technical report is being released as a draft until the full study has been completed, and all of the results are available for interpretation. This CPSC staff report has not been reviewed or approved by, and may not necessarily reflect the views of, the Commission.

Executive Summary

This report is intended to provide a preliminary update on the testing and analysis of residential HVAC (heating ventilation and air conditioning), gas distribution, and fire safety components exposed to emissions from allegedly corrosive imported drywall[1]. The information in this report is preliminary, and no conclusions can yet be drawn with respect to the risk of fire posed by imported drywall. This report provides an update on the test methodology, analytical techniques, and initial results of the CPSC's engineering test program to determine the impact of imported drywall on residential components/systems resulting in potential fire and shock hazards to consumers/occupants.

The CPSC's engineering test program consists of two major phases: (1) *Harvested Component Analysis.* This phase is an analysis of components collected from residences. Depending on the type of component, this includes metallurgical analysis, chemical analysis of corrosion products, and functional performance testing to characterize the nature and extent of damage. (2) *Accelerated Corrosion Testing*. This phase is a qualitative assessment of the reaction of new components to elevated concentrations of emissions which will be used to assess long-term exposure performance of components under controlled laboratory conditions.

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[1] This report uses the terms "Chinese drywall" and "imported drywall" interchangeably but CPSC staff cautions that until completion of its investigation it is premature to consider that all Chinese or imported drywall exhibits the reported health or corrosive characteristics; nor is it correct to assume that all domestic brands are entirely void of any reported health or corrosive characteristics.

A total of 60 residential HVAC, gas distribution, and fire safety components have been harvested by U.S. Consumer Product Safety Commission (CPSC) staff from eight residential locations in Florida and Virginia, which were in the process of remediation[2] by the builder/property owner due to the believed presence of corrosive drywall.

Interagency agreements were established with the National Institute of Standards and Technology (NIST) to conduct metallurgical analyses and perform functional testing of residential HVAC, gas distribution, and fire safety components. The NIST Material Science and Engineering Laboratory (MSEL) was tasked to conduct metallurgical and corrosion analyses of HVAC, gas distribution, and fire safety components to characterize the nature of corrosion and the extent of damage to the components. In addition, NIST's Building and Fire Research Laboratory (BFRL) was tasked to conduct performance evaluations of residential smoke alarms and fire sprinklers to determine if there can be a loss of functionality of these components from exposure to imported drywall emissions.

The NIST-MSEL scientific staff examined sections of natural gas distribution copper pipe and HVAC evaporator coil assemblies from two homes in advance of the broader study of the remaining harvested components provided by CPSC staff. The examination performed by NIST-MSEL consisted of photography, metallurgical cross-

[2] Remediation – the process of removal and replacement of drywall, electrical, HVAC, plumbing, fire safety equipment components, and/or appliances by a builder (or building contractor). The actual scope of components removed and replaced varies from builder to builder.

sectioning, optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Leak tests were also performed on the air conditioning evaporator coils. The objective of these examinations was to determine the extent and nature of the corrosive attack, the chemical composition of the corrosion products, and the potential chemical reactions or environmental species responsible for accelerated corrosion.

A thin layer of a black corrosion product was found on all of the samples provided. Chemical and structural analysis of this layer indicated that this corrosion product was copper sulfide (Cu_2S) and the XRD peaks in the spectrum of this corrosion product corresponded with those of the mineral digenite (Cu_9S_5). Corrosion products were also observed on other types of metals in the AC coils where condensation would frequently wet the metals. The thickness of the corrosion product layer on natural gas distribution pipe was measured and found to be between 5 μm and 10 μm in thickness. This type of corrosion is consistent with copper exposure to reduced sulfur compounds, such as hydrogen sulfide (H_2S).

Evidence of failure was not found on any of the initial samples provided to NIST-MSEL. The nature and extent of corrosion present in these samples is consistent with a general attack form of corrosion that will progress in a uniform manner. However, the unpredictable nature of corrosion attack on metals exposed to reduced sulfur compounds and the exposure duration necessary for initiation of these forms of attack require examination of additional components to draw a conclusion on the probability of this type of corrosion to result in imminent failures that can impact life safety. Additional work is planned to analyze a wider range of components and assess the long-term performance of these components with respect to safety hazards.

The NIST-BFRL developed test protocols to evaluate the potential impact of emissions from imported drywall on the performance of smoke alarms and fire sprinklers. Smoke alarms and fire sprinklers harvested from residences containing imported drywall will be tested with other groups of smoke alarms and fire sprinklers to compare the mean sensitivity and variance in sensitivity to identify where there is a significant change in the detection/operation capability as a result of exposure to emissions from imported drywall, as well as the effects of long-term exposure. Testing of the samples is underway, and updates will be provided to CPSC to guide additional field sample collection.

Introduction

This report documents the status of the U.S. Consumer Product Safety Commission (CPSC) engineering staff assessment of the effects of imported drywall on residential HVAC, gas distribution, and fire safety components. This report is being released in conjunction with a similar technical report on electrical components to investigate the possibility of fire and electric shock safety hazards resulting from emissions from imported drywall. The engineering test program is part of a multi-track program that also includes research into the health effects associated with the emission of gases from imported drywall.

The information in this report is preliminary and no conclusions can yet be drawn with respect to risk of fire posed by corrosive effects that have been associated with imported drywall. The intent of this report is to provide an update on the test methodology, analytical techniques, and initial results of the CPSC's engineering test program to determine the impact of imported drywall emissions on residential components/systems resulting in potential fire and shock hazards to consumers/occupants. The CPSC's engineering test program consists of two major phases: (1) *Harvested Component Analysis.* This phase is an analysis of components collected from residences. Depending on the type of component, this includes metallurgical analysis, chemical analysis of corrosion products, and functional performance testing to characterize the nature and extent of damage. The primary components of interest for this part of the engineering study include:

- **Gas distribution components** including flexible connectors and copper piping. The concern is that potential gas leakage due to pitting[3] could present a fire or explosion hazard.
- **Fire safety components** including smoke alarms and fire sprinklers. For smoke alarms, potential concerns include damage to electronic circuitry and degradation of the sensor. Either condition could result in an inoperable smoke alarm. For fire sprinklers that use metallic fusible elements, potential concerns are that corrosion may adversely affect activation temperatures. Failures of these devices can put consumers at risk.

In addition, HVAC components, including evaporator coil assemblies, are included in this analysis to obtain information on corrosion mechanisms and their effect on other more critical life safety components (gas and fire safety) made of similar metals.

(2) *Accelerated Corrosion Testing*. This phase is a qualitative assessment of the reaction of new components to elevated concentrations of emissions which will be used to asses long-term exposure performance of components under controlled laboratory conditions. Accelerated corrosion testing will be based on emissions identified in

[3] Pitting is a form of extremely localized corrosion that leads to the creation of small holes in the metal.

drywall chamber studies conducted by Lawrence Berkeley National Laboratory, in combination with the results of indoor-air measurements in fifty-one homes conducted by Environmental Health and Engineering. New gas distribution and fire safety components will be exposed to elevated concentrations of selected gases in test chambers at Sandia National Laboratories, for an exposure duration yet to be determined, in order to better understand long-term exposure risks.

Interagency agreements were established with the National Institute of Standards and Technology (NIST) to conduct metallurgical analyses and perform functional testing of residential HVAC, gas distribution, and fire safety components. The NIST Material Science and Engineering Laboratory (MSEL)[4] was tasked to conduct metallurgical and corrosion analyses of HVAC, gas distribution, and fire safety components to characterize the nature of corrosion and the extent of damage to the components. In addition, NIST's Building and Fire Research Laboratory[5] (BFRL) was tasked to conduct performance evaluations of residential fire safety components (smoke alarms and fire sprinklers) to determine if there can be a loss of functionality of these components from exposure to imported drywall.

[4] CPSC Agreement Number CPSC-I-09-0023

[5] CPSC Agreement Number CPSC-I-09-0024

Gas Distribution and Fire Safety Equipment Component Harvesting

The primary objective of the harvesting effort was to obtain samples of gas distribution and fire safety components of interest in order to evaluate any damaging effects from imported drywall. CPSC engineering staff harvested the components of interest from unoccupied homes that were in the process of remediation by homebuilders. HVAC, gas distribution, and fire safety components were harvested in residences located in Florida and Virginia. Table 1 is a summary of the harvested HVAC, gas distribution, and fire safety components.

Table 1. Summary of Harvested HVAC, Gas, and Fire Safety Components

Location	Collection Date	Smoke Alarms	Sprinklers	Copper Pipe (Gas/Water)	HVAC Coils
Chesapeake, VA 1	6/2/09	2	0	4 (water)	0
Nokomis, FL	6/16/09	7	0	0	0
Courtland, VA	7/6/09	2	0	0	0
Chesapeake, VA 2	7/7/09	5	0	7 (gas)	1
Chesapeake, VA 3	7/7/09	5	0	7(gas)	1
Boynton Beach, FL	7/23/09	3	0	0	0
Port Charlotte, FL	8/24/09	4	0	0	0
Fort Meyers, FL	8/25/09	3	0	0	0
West Palm, FL	9/14/09	0	9	0	0
Total		31	9	18	2

Of the components of interest in this phase of the investigation, smoke alarms were most readily available due to their prevalence in dwellings and ease of removal.

The types of smoke alarms harvested were hard-wired with battery back-up and operate on the ionization principle.

Natural gas distribution components were not as easily obtained due to their infrequent use in the areas most affected with imported drywall. Copper gas distribution components were obtained from locations in Chesapeake, VA. (Figure 1)

Figure 1 – Copper Natural Gas Tubing

The HVAC evaporator coils in the dwellings from which components were harvested were either removed from service, had sections missing, or sample collection was not feasible. Two full A-frame evaporator coils were obtained from Chesapeake, VA. (Figure 2)

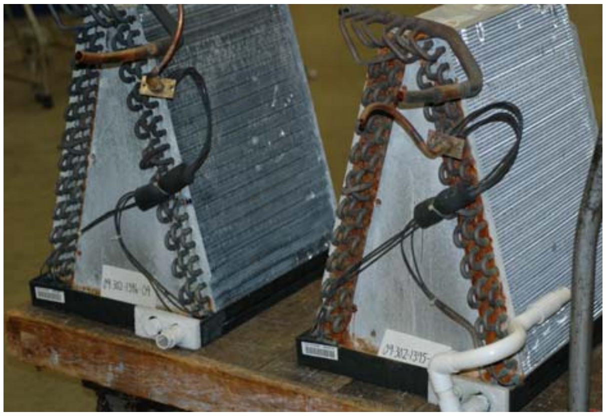


Figure 2 - A-Frame Evaporator Coils

Harvested samples of fire sprinklers were the most difficult component of interest to collect for this phase of the study due to difficulties in locating sites with imported drywall and the process required for removal of the samples. CPSC staff was able to coordinate fire sprinkler sample collection with a condominium complex in West Palm, FL for collection of nine samples. The collection process involved draining the zone of the sprinkler system (Figure 3), removal of the sprinkler head (Figure 4), and collection of trapped water to minimize damage to the residence (Figure 5).

Figure 3 – System Drain

Figure 4 – Head Removal

Figure 5 – Water Capture

Metallurgical and Corrosion Analysis of HVAC and Gas Distribution Components

Harvested samples of HVAC evaporator coils and copper gas distribution components were sent to NIST-MSEL for metallurgical and corrosion analysis. NIST-MSEL prepared an interim report to characterize the nature of corrosion and the extent of corrosion present on these harvested samples from dwellings with imported drywall. The analysis conducted by NIST-MSEL included visual examination, identification of corrosion products by X-ray diffraction, HVAC evaporator coil leak testing/sectioning, and the measurement of the thickness of corrosion products on copper gas distribution components. The NIST-MSEL interim report is contained in Tab A.

Visual Examination and Photography

All samples of natural gas copper tubing exhibited varying degrees of discoloration. This discoloration was due to the presence of a thin layer of a black substance (Figures 6 and 7). The extent of discoloration appeared to vary with the thickness of the layer of this black substance.

Figure 6 – Fireplace Gas Supply

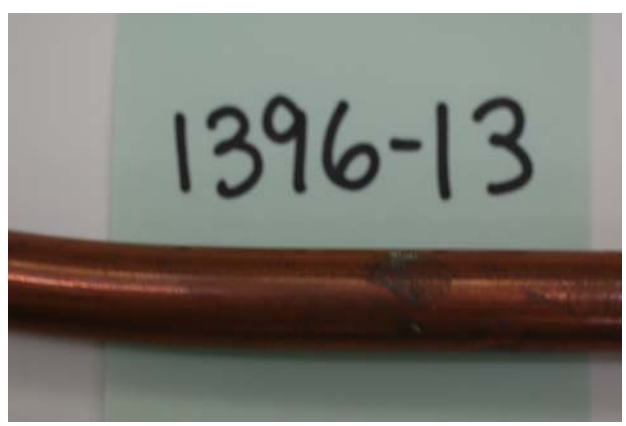


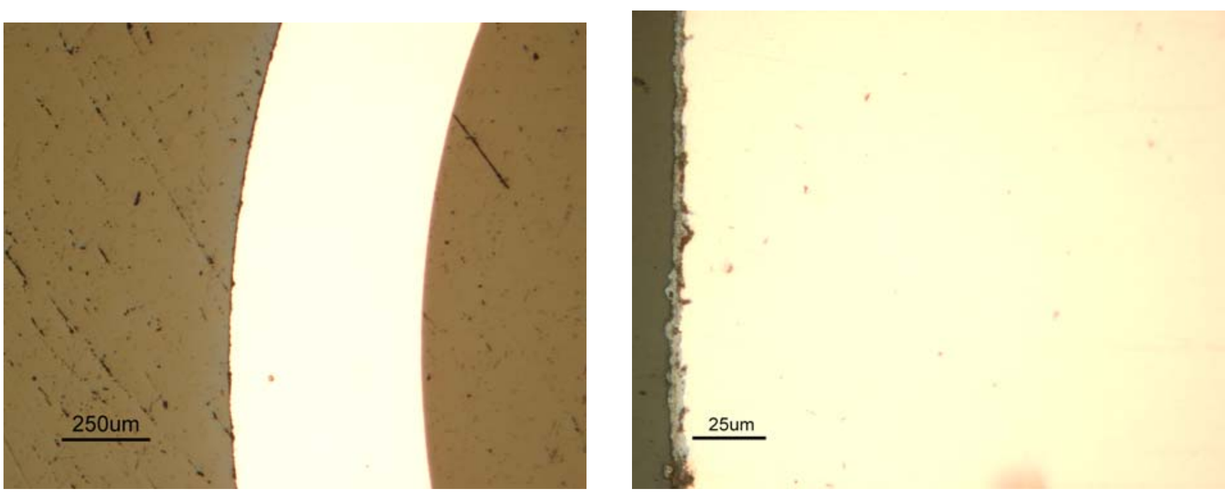
Figure 7 – Attic Gas Supply to Furnace

Identification of the Black Corrosion Product by X-Ray Diffraction

The black substance observed on the surfaces of the copper components was identified by X-ray diffraction. Chemical and structural analysis of this layer indicated that this corrosion product was copper sulfide (Cu_2S), and the XRD peaks in the spectrum from this corrosion product corresponded with those of the mineral digenite (Cu_9S_5).

Measurement of Corrosion Product Layer Thickness

The thickness of the black corrosion product was measured using optical microscopy of sample prepared in cross section. For this analysis, a natural gas supply line was cut perpendicular to the axis of the tube and mounted in epoxy and polished down using standard metallurgical practice exercising care to maintain the edge of the sample with the corrosion products in place. Figures 8a and 8b show optical micrographs of this sample. The measurements indicate that the corrosion product layer varied from 5 to 10 µm thick.



A B

Figure 8a and 8b – Optical micrographs of the wall of a copper natural gas supply line and the corrosion product layer at two magnifications.

Functional Testing of Fire Safety Equipment (Smoke Alarms/Fire Sprinklers)

The NIST-BFRL staff developed test protocols for examining the relative performance of smoke alarms and automatic fire sprinklers to assess the impact of exposure to imported drywall on the functionality of residential fire safety equipment. The NIST-BFRL update is contained in Tab B.

Smoke Alarm Protocol Development

Smoke alarms will be evaluated using the NIST Fire Emulator/Detector Evaluator (FE/DE) (Figure 9).

Figure 9 - NIST Fire Emulator/Detector Evaluator

The FE/DE was developed for the purpose of testing smoke alarms in a controlled environment. The FE/DE is a flow tunnel where fire or nuisance source characteristics can be controlled so that a smoke alarm placed in the FE/DE is exposed to the same stimuli it could experience in its end-use location. Measurements in the FE/DE will be performed for four groups of smoke alarms:

1. Those taken from houses containing imported drywall.
2. Those taken from houses containing domestic drywall. These smoke alarms are to be of the same makes and models as those in the first set. They will have been exposed to the everyday environment in similar dwellings and for a length of time similar to that in Group 1.
3. New smoke alarms of types similar to those above.
4. The smoke alarms from Group 3, subjected to an environment designed to simulate extended tenure in a house with imported drywall. This accelerated corrosion will be performed by Sandia National Laboratories (SNL).

The following comparisons from the results of the planned testing will be made:

- Comparison of the mean sensitivity and the variance in the sensitivity between Group 1 units and Group 2 units to identify whether there was a significant change in detection capability as a result of exposure to the emissions from imported drywall.

- Comparison of the mean sensitivity and the variance in the sensitivity between Group 3 units and Group 4 units to identify the potential of the drywall emissions to compromise the sensing ability of the smoke over a long period of time.

Fire Sprinkler Protocol Development

Fire sprinklers will be tested using a Plunge Test apparatus (Figure 10).

Figure 10 – Plunge Test Apparatus

In this apparatus, a fire sprinkler sample is inserted quickly into a hot air stream at a set velocity. The time to when the fire sprinkler's thermal sensing element activates is recorded to evaluate any effect on the sprinkler's sensitivity. Measurements are to be performed for four groups of sprinkler heads:

1. Those taken from houses containing imported drywall.

2. Those taken from houses containing domestic drywall. These sprinkler heads are to be of the same makes and models as those in the first set. They will have been exposed to the normal environment in similar dwellings for a similar length of time.

3. New sprinkler heads of types similar to those above. Eight units of three models for a total of 24 units. Twelve units will be tested and the other twelve will be sent for accelerated aging (See Group 4).

4. The sprinkler heads from Group 3, subjected to an environment designed to simulate extended tenure in a house with imported drywall. This accelerated aging will be performed by Sandia National Laboratories (SNL).

The intent is to make the following comparisons:

- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and 2 and units from Group 3. This will identify the extent to which either residential exposure affected the actuation time.

- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and units from Group 2. This will identify whether there was a significant change in actuation time as a result of exposure to emissions from imported drywall compared to exposure to "ordinary" household environments.

- Comparison of the mean sensitivity and the variance in the sensitivity between Groups 3 and 4. This will identify the potential of the drywall emissions to affect the actuation time of the sprinkler heads over an extended period of time.
- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and units from Group 4. This will identify the potential for change in actuation time beyond any noted in the comparison of Group 1 and Group 3 units.

Discussion of Preliminary Reports

Discussion of NIST- MSEL Report

The type of corrosion observed by NIST-MSEL is consistent with copper exposure to reduced sulfur compounds, such as hydrogen sulfide (H_2S). Evidence of failure was not found on any of the samples initially evaluated by NIST-MSEL. The nature and extent of corrosion present in these few samples is consistent with a general attack form of corrosion that will progress in a uniform manner. Nevertheless, the unpredictable nature of corrosion attack on metals exposed to reduced sulfur compounds and the exposure duration necessary for initiation of these forms of attack require examination of additional components to draw a conclusion on the probability of this type of corrosion to result in imminent failures that can impact life safety. Additional work is planned to analyze a wider range of components and assess the long-term exposure performance of these components with respect to safety hazards.

Discussion of NIST- BFRL Report

The NIST-BFRL developed test protocols to evaluate the potential impact of imported drywall emissions on the performance of smoke alarms and fire sprinklers. Smoke alarms and fire sprinklers harvested from residences containing imported drywall will be tested with other groups of smoke alarms and fire sprinklers to compare the mean sensitivity and variance in sensitivity to identify whether there is a significant change in performance as a result of exposure to imported drywall emissions, as well as the effects of long-term exposure. Testing of the samples is underway, and updates will be provided to CPSC staff to guide additional field sample collection to complete this analysis.

TAB A – NIST- MSEL Report:

Preliminary Examination of Corrosion Damage to Metallic Materials Removed from Homes Constructed with Imported Wallboard

Interim Report on the Examination of Corrosion Damage in Homes Constructed with Imported Wallboard
I. Examination of Samples Received September 28, 2009

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ABSTRACT

Since many household systems are fabricated out of metallic materials, changes to the household environment that accelerate corrosion rates will increase the frequency of failures in these systems. Recently, it has been reported that homes constructed with imported wallboard have increased failure rates in appliances, air conditioner heat exchanger coils, and visible corrosion on electrical wiring and other metal components. At the request of the Consumer Product Safety Commission (CPSC), the National Institute of Standards and Technology (NIST) became involved through the Interagency Agreement CPSC-1-09-0023 to perform metallurgical analyses on samples and corrosion products removed from homes constructed using imported wallboard. This document reports on the analysis of the first group of samples received by NIST from CPSC.

The samples received by NIST on September 28, 2009 consisted of copper tubing for supplying natural gas and two air conditioner heat exchanger coils. The examinations performed by NIST consisted of photography, metallurgical cross-sectioning, optical microscopy, scanning electron microscopy (SEM), and X-ray diffraction (XRD). Leak tests were also performed on the air conditioner heat exchanger coils. The objective of these examinations was to determine extent and nature of the corrosive attack, the chemical composition of the corrosion product, and the potential chemical reactions or environmental species responsible for accelerated corrosion. A thin black corrosion product was found on samples of the copper tubing. The XRD analysis of this layer indicated that this corrosion product was a copper sulfide phase and the diffraction peaks corresponded with those for the mineral digenite (Cu_9S_5). Corrosion products were also observed on other types of metals in the air conditioner coils where condensation would frequently wet the metals. The thickness of the corrosion product layer on a copper natural gas supply pipe with a wall thickness of 1.2 mm ±0.2 mm was between 5 μm and 10 μm.

These results indicate that a chemical compound that contains reduced sulfur, such as hydrogen sulfide (H_2S), is present in the environment to which these samples were exposed. The literature indicates that these species strongly influence corrosion rates of most metals and alloys even at low concentrations. None of the samples examined were failed components, and no evidence of imminent failure was found on any of the samples examined. All of the corrosion

damage observed to date is consistent with a general attack form of corrosion that will progress in a uniform and relatively predictable manner. No evidence of localized attack was found, but these forms of attack typically require an incubation period before they initiate. Therefore, the number of samples examined to date is too small to draw a conclusion on the relative probability of these forms of corrosion being able to cause or not cause failure. Samples from failed systems or from laboratory tests conducted over a wide range of metallurgical and environmental conditions will be required to assess the probability of these other forms of corrosion causing failure.

Examination of Corrosion Damage to Metallic Materials Removed from Homes Constructed with Imported Wallboard I. Results of the Examination of Samples Received October 1, 2009

D. J. Pitchure and R. E. Ricker

I. INTRODUCTION

Metallic materials in home construction are subject to corrosive attack by the normal internal atmosphere of homes as well as the other environments they encounter during service in the home. The corrosion resistance of the metals in these environments is a major factor in determining the normal deterioration of the performance of household appliances, switches, safety systems, and water, electrical, and gas supply systems. When these systems deteriorate more rapidly than normal, there is a high probability that accelerated corrosion is the cause. Identification of the factors responsible for accelerated corrosion can be done through three ways: (i) identification of the unique characteristics of the homes with accelerated deterioration, (ii) identification of the differences in the environments encountered in the homes with accelerated deterioration, or (iii) identification of failure modes, corrosion product compositions, and responsible chemical reactions.

Of immediate concern is the accelerated deterioration of systems in homes constructed with imported wallboard. Due to the very large number of complaints from the owners of homes constructed with imported wallboard, the Consumer Product Safety Commission (CPSC) has become concerned that this product contains chemical species that alter the internal atmosphere of the home and accelerate corrosion and the deterioration of systems that rely on metals to perform critical functions. As a result, the CPSC has instituted a large multitasked program to look at this product and how it influences the health of occupants, the performance of critical household systems, and the prevalence of this product in homes in the US. As part of this program, the Materials Science and Engineering Laboratory (MSEL) of the National Institute of Standards and Technology (NIST) became involved through the Interagency Agreement CPSC-1-09-0023 to examine metallic samples removed from service in homes constructed using imported wallboard. The objective of these examinations is to identify potential corrosion related failure modes, corrosion product chemistry, and potential chemical reactions. This document reports on the findings of the examinations performed on the first group of samples provided to NIST by CPSC. All findings reported here should be considered preliminary, as more examinations are planned. None of the samples provided to NIST in the first group were failed components. Therefore, none of the conclusions drawn here can address the mechanisms of the reported failures.

II. EXAMINATIONS

A. Sample Selection and Delivery

The samples were selected by CPSC staff and transported and hand delivered to NIST. The samples were received on September 28, 2009 and immediately cataloged for recording and tracking the examinations. All of the samples received were identified with a number assigned to the sample by CPSC. These numbers consisted of eleven digits, starting with: 09-302-####-##. NIST used the last six unique digits of the samples to track them during the examinations. The samples received consisted of a number of lengths of copper tubing used as natural gas supply lines and two air conditioner heat exchanger coils.

B. Visual Examination and Photography

The lengths of copper tubing were discolored to varying degrees. This discoloration, which is illustrated in Figure 1, was found to be due to the presence of a thin adherent layer of a black substance. This is clearly illustrated in Figure 2 where the sample number has been scribed into the sample exposing fresh bare copper. The contrast in this figure is obvious. While this film adhered to the surface, physical contact would result in the transfer of a small quantity of a fine black powder from the film. In some cases, the discoloration was found to be very uniform, but in other cases it was irregular. The extent of discoloration varied with the thickness of the layer.

Figure 1 – Photographs of two representative samples of copper natural gas supply tubing.

Figure 2 – Scribe marks illustrating the contrast between the color of bare copper and a sample of copper natural gas line tubing.

The air conditioner evaporator coils were also examined, Figure 3. From the two coils in this figure it can be seen that all exposed copper surfaces have turned dark. These coils are constructed out of parallel lines of copper tubing placed through thin sheets of aluminum that serve as the heat transfer fins. The copper tubing is linked together by soldered U-bends to the ends of adjacent lengths of copper tubing. The end plates that hold this assembly in place are made out of galvanized steel. Copper manifolds and valves complete the assembly. Figure 4 is a close-up of the end plates and the U-bend region. In this figure, brown and orange corrosion products can be seen on the galvanized end plates, while black and green corrosion products can be seen on the copper tubing. The normal patina that forms on copper in the cyclically wet and dry environment of an air conditioner evaporator coil would be expected to contain copper (I) or copper (II) ions in oxides (black to brownish-red), carbonates (green to blue), sulfates (bright blue), and chlorides (greenish white to blue-green) [1,2]. Again, the black color was found to be due to the presence of a thin layer of a loose black powder.

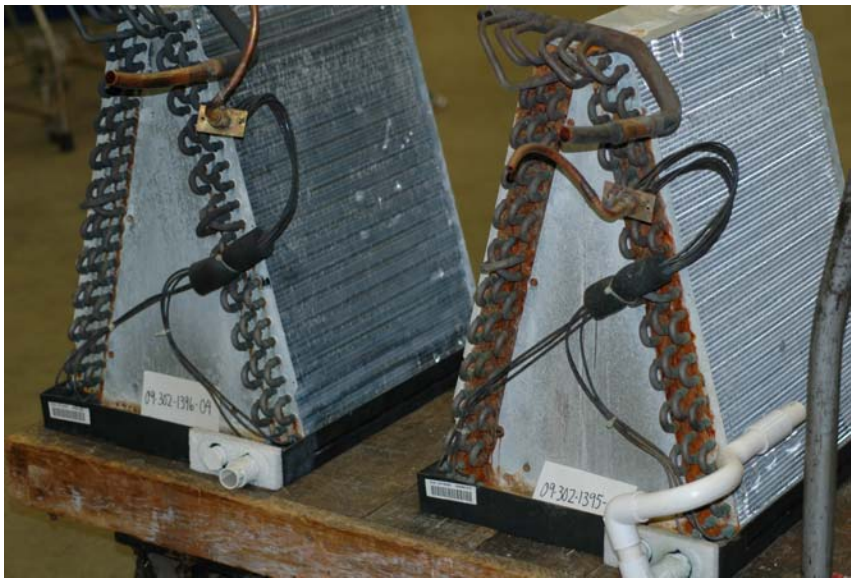

Figure 3 – Photograph of the two air conditioner evaporator coils showing the black discoloration of the copper U-bends and corrosion of the end plate.

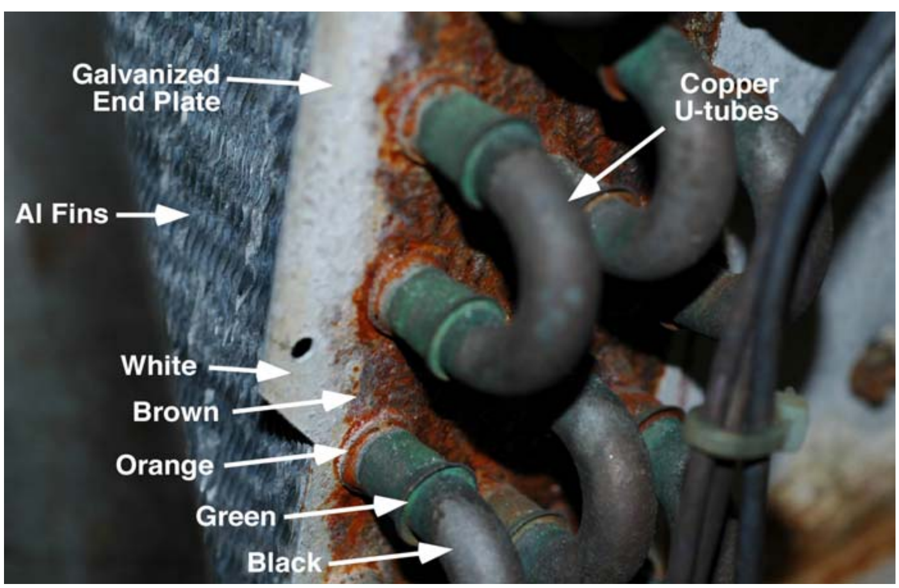

Figure 4 – Close-up photograph of the U-tubes and end plate of an air conditioner evaporator coil showing that there appears to be 5 colors associated with the corrosion products: white, brown, orange, green, and black.

C. Identification of the Black Corrosion Product by X-Ray Diffraction

The black substance observed on the surfaces of the copper components was identified by X-ray diffraction. This was accomplished by scraping the black substance from the surface of one of the sample of copper natural gas line tubing using a razor blade. The powder removed in this manner was accumulated on double stick tape and attached to a glass slide as shown in Figure 5. A powder diffraction pattern was then obtained from this sample of scrapings using Siemens D500 X-ray diffractometer with a Cu K_{α} radiation source operated at 40 kV and 30 mA using a step size of 0.03 degrees, and a dwell time of 5 s.*


Figure 5 – Photographs of the scraped copper natural gas supply line and the slide holding the sample for X-ray diffraction.

Figure 6 shows the results of these measurements in red along with the peak locations in black for copper metal (Figure 6a), copper (I) oxide (Figure 6b) and copper (I) sulfide (Figure 6c) as listed in the International Crystal Structure Database (ICSD). This figure shows that peaks corresponding to all three of these phases are present in the sample of scrapings from the surface of the copper natural gas supply line. Given that the sample was collected by scraping the surface of copper metal with a sharp razor blade, the peaks for copper and copper oxide were expected since copper is a soft metal compared to the steel of the razor blade and will normally form copper oxide when exposed to air. The third phase, copper sulfide (Cu_2S) is not a typical atmospheric corrosion product as the concentration of the reduced sulfur species, such as H_2S, required to form this product is usually very low under normal atmospheric conditions. [1, 3-5] Figure 7 is a summary of the XRD results showing that all but two small peaks, indicated by question marks, are accounted for by these three phases.

* The identification of any commercial product or trade name does not imply endorsement or recommendation by the authors or NIST.

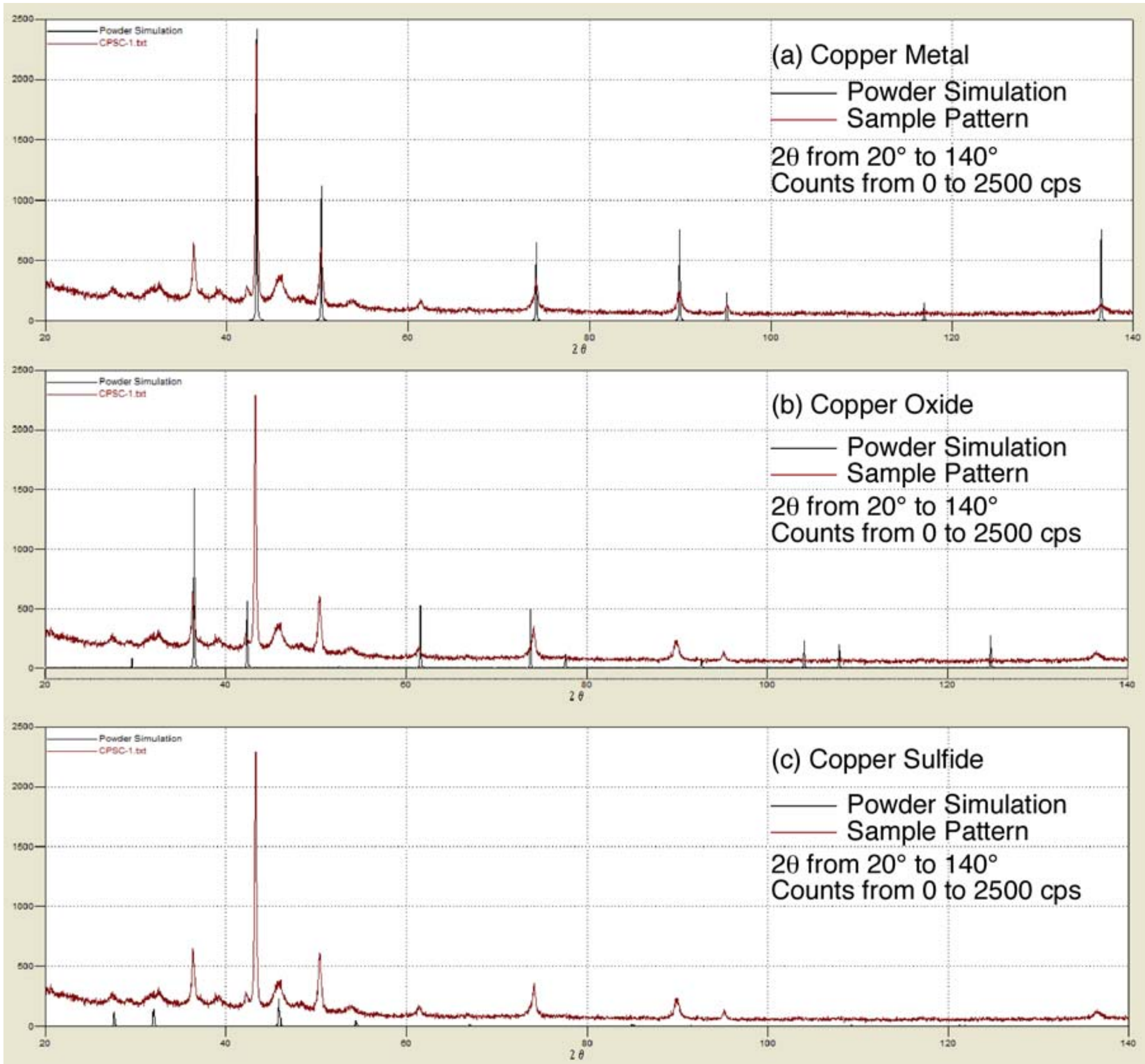

Figure 6 Powder diffraction patterns for the sample of corrosion products scraped off a copper natural gas supply line (red) with, identified in black, the peaks for (a) copper, (b) copper (I) oxide (ICSD #38233), and (c) copper (I) sulfide (ICSD #95395).

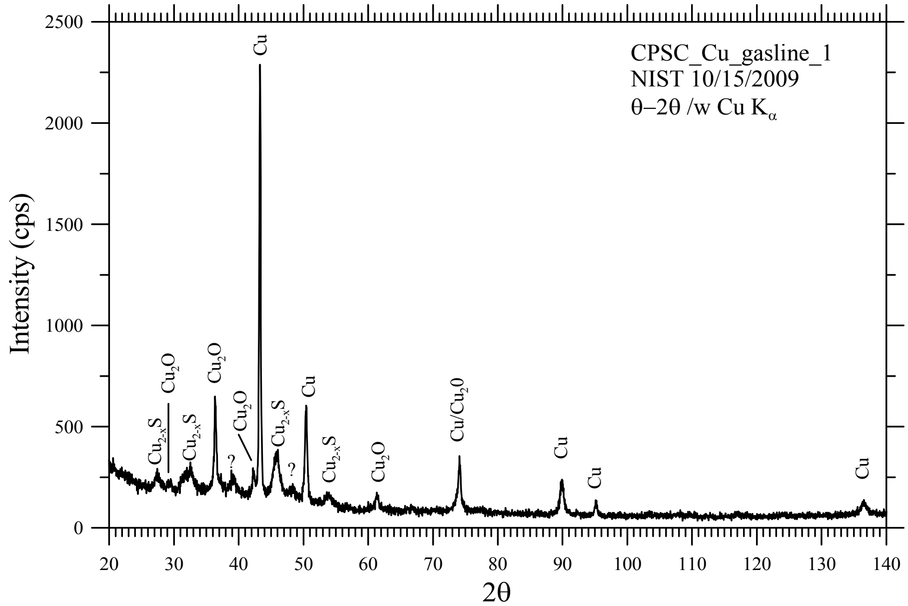

Figure 7 – Summary of peaks found in the corrosion product sample and their identification for showing that only two small peaks were unidentified by the three phases.

D. Air Conditioner Evaporator Coil Leak Testing

Leak testing was performed on the air conditioner heat exchange coils by attaching air tight fittings to the ends of the copper lines and connecting these to a helium gas detector. The inside of the coil was evacuated and helium gas passed over different regions of the coils. No leaks were found by this method. Then, the coils were pressurized with helium and a solution of soapy water was squirted onto different regions of the coils. This method also failed to find any leaks in these coils.

E. Air Conditioner Evaporator Coil Sectioning

To evaluate the possibility of corrosion damage occurring between the aluminum heat transfer fins and the copper tubing inside them, the heat exchanger unit was sliced with a band saw as shown in Figure 8, to expose these internal surfaces for examination of the copper. No evidence of localized attack was found, and the black corrosion product layer was not detected by visual examination.

Figure 8 – Air conditioner evaporator coil after slicing to allow for examination for corrosion damage between the aluminum sheets and the copper tubing.

F. Measurement of Corrosion Product Layer Thickness

The thickness of the black corrosion product was measured using optical microscopy of samples prepared in cross section. For this analysis, samples of natural gas supply lines were cut, mounted in epoxy, and polished using standard metallurgical practice, exercising care to maintain the edge of the sample with the corrosion products in place. Figure 9 shows optical micrographs of this sample where the corrosion product layer varied from 5 µm to 10 µm thick.

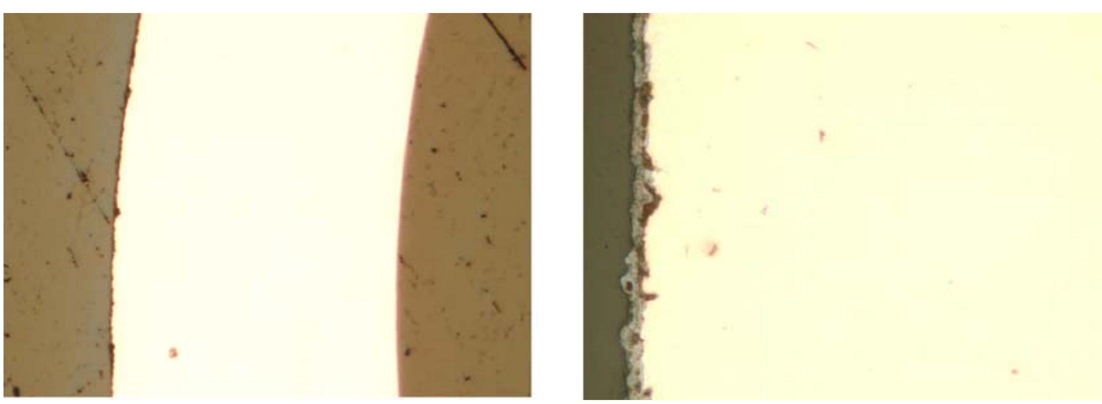

Figure 9 – Optical micrographs of the wall of a copper natural gas supply line and the corrosion product layer at two magnifications (wall ≈ 1.2 mm thick).

III. DISCUSSION AND CONCLUSIONS

The copper metal surfaces of the samples provided for examination were covered with a black film that appears to be a corrosion product. The X-ray powder diffraction results unambiguously identified this substance as a copper sulfide phase. Copper sulfides (Cu_xS_y) can have a wide range of stoichiometry ranging from CuS_2 to Cu_2S with 9 distinctly different phases having been identified over this range depending on the stoichiometry. The powder diffraction pattern was consistent with the digenite phase of copper sulfide that has a stoichiometry of Cu_9S_5 or $Cu_{1.8}S$. The presence of a copper sulfide phase on the surface of the copper indicates that reduced sulfur compounds, such as hydrogen sulfide (H_2S), sulfur (S_8), or mercaptans (thiols), are present in the indoor atmosphere of the homes from which these samples were removed.

Reduced sulfur compounds generally accelerate the corrosion of engineering metals, as sulfur forms stable compounds with most of the parent and alloying elements in these alloys. [3] However, copper and silver are reported to have the greatest sensitivity to this environmental contaminant. [2,6] Rice et al. [2,6] conducted studies on the sensitivity of indoor corrosion rates of different metals to environmental contaminants including hydrogen sulfide. These authors fit the rate of mass increase (*dm/dt*) to the equation

$$\left(\frac{dm}{dt}\right) = A[H_2S]^n \tag{1}$$

where A is a constant, $[H_2S]$ is the concentration or activity of hydrogen sulfide in the atmosphere and n is a measure of the sensitivity of the corrosion rate to changes in the hydrogen sulfide concentration. This parameter, n, is also the slope of a log-log plot as

$$\log\left(\frac{dm}{dt}\right) = \log A + n\log[H_2S] \tag{2}$$

Table I shows the results of Rice et al. [2,6]. This table clearly shows that copper and silver are the most sensitive of these metals to the concentration of hydrogen sulfide.

Table I - The corrosion rate parameter, n, in equations (1) and (2) for different metals exposed to hydrogen sulfide at different concentrations in air specifically formulated to represent a typical indoor air environment and air that is purified to remove all contaminants other than hydrogen sulfide.[Rice, 1982 #4]

Metal	Cu	Ag	Co	Ni	Fe
Representative Indoor Air	0.30	0.55	0.02	0.03	0.05
Purified 70 % RH Air	0.93	0.14	-	-	-

While the results clearly indicate that a reduced sulfur species is present in the indoor atmosphere of the homes that these samples came from, the corrosion product layer observed on these samples was less than 10 µm thick. This layer makes the copper look dark due to the black color and opaque nature of this corrosion product. All of the corrosion damage observed to date is consistent with a general attack form of corrosion that will progress in a uniform and relatively predictable manner. No evidence of any type of localized attack was found, but these forms of attack typically require an incubation period before they initiate. Therefore, the number of samples examined to date is too small to draw a conclusion on these forms of corrosion being able to cause or not cause failure. Samples from failed systems or from laboratory tests conducted over a wide range of metallurgical and environmental conditions will be required to assess the probability of these other forms of corrosion causing failure.

IV. REFERENCES

1. N. de Zoubov, C. Vanleugenhaghe, and M. Pourbaix, Copper, Atlas of Electrochemical Equilibria in Aqueous Solutions, M. Pourbaix ed., NACE International, Houston, TX, 1974, p. 384-92.
2. D. W. Rice, R. J. Cappell, P. B. P. Phipps, and P. Peterson, Indoor Atmospheric Corrosion of Copper, Silver, Nickel, Cobalt, and Iron, Atmospheric Corrosion, W. H. Ailor ed., J. Wiley & Sons, New York, 1982, p. 651-66.
3. K. Barton, Protection Against Atmospheric Corrosion - Theories and Methods, J. Wiley & Sons, New York, 1976.
4. G. Valensi, J. VanMuylder, and M. Pourbaix, Sulphur, Atlas of Electrochemical Equilibria in Aqueous Solutions, M. Pourbaix ed., NACE International, Houston, TX, 1974, p. 545-53
5. T. E. Graedel and N. Schwartz, Air Quality Reference Data for Corrosion Assessment, Mater. Perf., 16(8), 1977, p. 17-25.
6. D. W. Rice, R. J. Cappell, W. Kinsolving, and J. J. Laskowski, Indoor Corrosion of Metals, Journal of the Electrochemical Society, 127(4), 1980, p. 891-901.

TAB B – NIST-BFRL Report:

Activity Report for September 17 through November 17, 2009, "Performance Evaluations of Fire Safety Components Exposed to Emissions from Imported Drywall"

UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
Gaithersburg, Maryland 20899-

November 17, 2009

MEMORANDUM for: Rohit Khanna
Fire Program Area Team Leader
Office of Hazard Identification and Reduction
U.S. Consumer Product Safety Commission

From: Jason D. Averill
Head, Engineered Fire safety Group
Fire Research Division
Building and Fire Research Laboratory

Subj: Activity Report for September 17 through November 17, 2009, "Performance Evaluations of Fire Safety Components Exposed to Emissions from Imported Drywall"

The purpose of this Interagency Agreement is to conduct performance evaluations of fire safety components (smoke detectors and automatic sprinkler heads) exposed to emissions from imported drywall to determine whether there is a loss in functionality of these components.

During this activity period, test protocols were devised for examining the relative performance of smoke detectors and automatic sprinkler heads, options were developed for obtaining test specimens, and initial tests were performed.

<u>Smoke Detectors</u>

Primary testing is to be performed in the Fire Emulator/Detector Evaluator (FE/DE) located at NIST. In this apparatus, two detectors are immersed in a flow of well-characterized smoke. The smoke is generated by an array of twelve cotton wicks, which are ignited to smoldering. The detectors are exposed stepwise to the effluent from an increasing number of these wicks. This results in the detector experiencing approximately eight concentrations of smoke. To increase the precision (i.e., decrease the difference in smoke concentration between successive steps), the test can be repeated with a slightly different air flow. The result is exposure of the detector to a total of about 16 different smoke densities. The electronic response of the sensor unit in the detector is recorded at each concentration, as is the time at which the detector goes into alarm. Extensive experience with the FE/DE has shown that the variance in detector sensitivity, even among detectors from the same manufactured batch, is far greater than the uncertainty in the FE/DE output. Thus, only spot checks of test repeatability will be performed.

Figure 1 shows the FE/DE; Figure 2 is a close-up of the specimen mounting. The assembly holding the 12 cotton wicks is shown in Figure 3, both before and during a test.

Figure 1. The Fire Emulator-Detector Evaluator.

Red arrow: Test Section

Yellow Arrow: Smoke Source Location

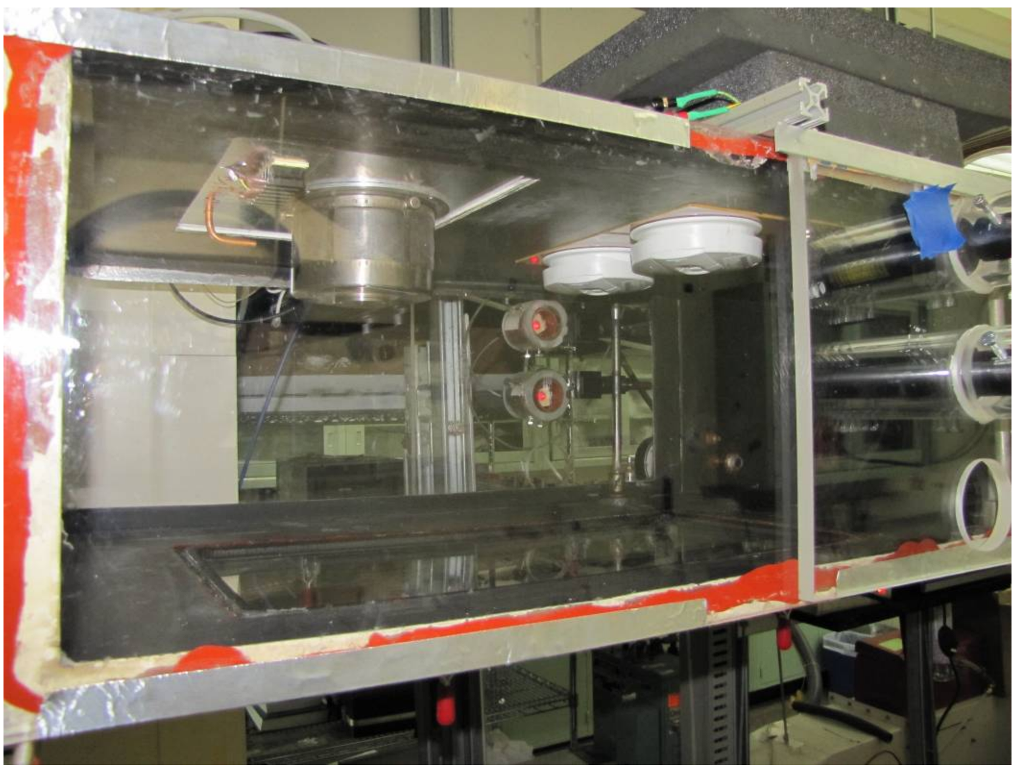

Figure 2. Close-up of the Test Section, Showing Two Ceiling-mounted Detectors and Two Lasers for Smoke Obscuration Measurement.

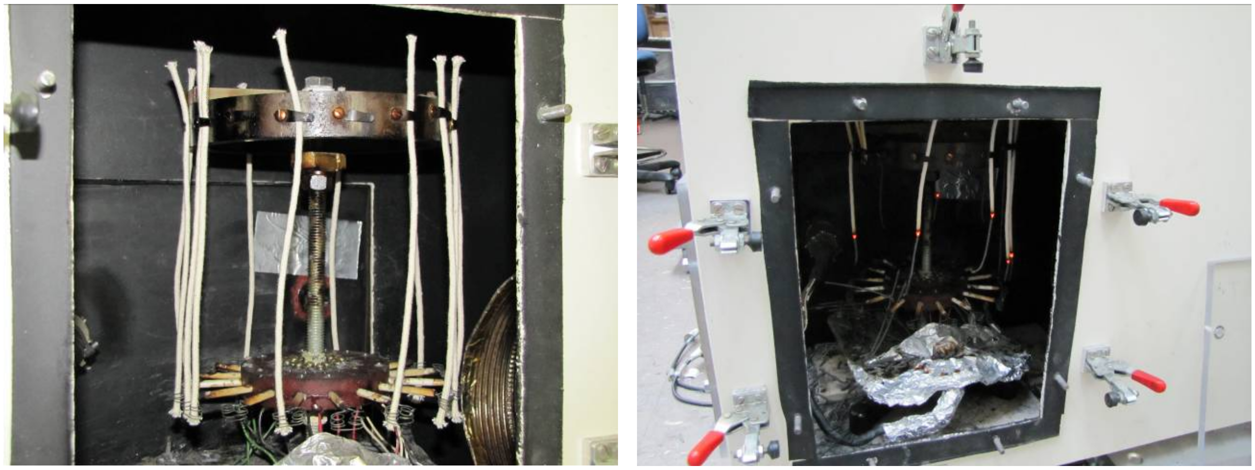

Figure 3. Close up of 12-wick Smoke Source. Left: Prior to a Test; Right: During a Test.

Measurements in the FE/DE are to be performed for four groups of detectors. All detector testing is non-destructive, so each unit can be tested multiple times, as appropriate.

1. Those taken from houses containing imported drywall. At present, three different models of detectors have been provided by the CPSC, consisting of seven units of two models and 15 units of the third. All these detectors are hard-wired with battery back-up and operate on the ionization principle.
2. Those taken from houses containing domestic drywall. These detectors are to be of the same makes and models as those in the first set. They will have been exposed to the everyday environment in similar dwellings and for a length of time similar to that in Group 1. Between seven and 15 of each model have been requested, in order to balance the comparison statistics.
3. New detectors of types similar to those above. Twenty-four units of each of three models have been purchased. Twelve are for immediate testing, and twelve are for future use.
4. The detectors from Group 3, which will have been subjected to an exposure designed to simulate extended tenure in a house with imported drywall. This accelerated aging will be performed by Sandia National Laboratories (SNL). At present, the composition of the aging atmosphere, the duration of the exposure, and the protocol for estimating the time interval being simulated will be provided at a later date, following CPSC staff chamber testing being conducted by Lawrence Berkeley National Laboratory (LBL).

Smoke detectors are expected to have a useful life of about ten years. Conventional practice is to not sell units that are over one year old. The detectors in Groups 1 and 2 are approximately three years old. Thus, it was not possible to locate and purchase new units from the same batches. Furthermore, in the ensuing three years, (a) new (albeit similar) models have replaced the original models and (b) the labeled sensitivities of the new Group 3 models all differ significantly from the original Group 1 and 2 models.

As a result, the intent is to make the following comparisons from the results of the testing:

- Comparison of the mean sensitivity and the variance in the sensitivity between Group 1 units and Group 2 units. This will identify whether there was a significant change in detection capability as a result of exposure to the effluent from the imported drywall.
- Comparison of the mean sensitivity and the variance in the sensitivity between Group 3 units and Group 4 units. This will identify the potential of the drywall effluent to compromise the sensing ability of the detectors over a long period of time.

Because the details of the relationship of the Group 3 detectors to the Group 1 and 2 detectors are not known, it is not possible to determine the likely original performance of the Group 1 and 2 detectors and the extent to which that performance had changed. To partially ameliorate this lack of information, some of the Group 1 and 2 units will be tested according to UL 217 to determine whether the current sensitivity is within the performance range listed on the unit.

Testing of the 65 units (29 + 3 x 12) is underway, and updates will be provided to CPSC to guide additional field sample collection.

Sprinkler Heads

Sprinkler heads are of two types: fusible link and glass bulb. When the fusible link experiences a sufficiently high temperature for a sufficient time interval, the link fuses (melts), and the sprinkler water flow is initiated. The glass bulb is partially filled with liquid. As the temperature of the bulb increases, the liquid expands, compressing the gas in the ullage. When the thermal exposure reaches a critical level, the gas pressure in the bulb is high enough to fracture the glass, initiating the sprinkler water flow.

Each of the sprinkler heads will be tested in the plunge test apparatus. In this apparatus, a (dry) test specimen is inserted abruptly into hot air flowing at a known velocity. The time delay at which the link fuses or the glass fractures is noted. The test is destructive, so multiple tests cannot be performed on any unit. Figure 4 shows the test apparatus.

Figure 4. Plunge-test Apparatus.

Classically, the test is performed at a single standard temperature that is well above the intended actuation temperature of the sprinkler head. This can result in very short actuation times, making it difficult to identify meaningful differences among sprinkler heads, such as for Groups 1 and 2 below. Thus, for this project, preliminary tests of new sprinkler heads similar to those found in imported drywall dwellings will be used to identify a lower flow temperature that will result in longer actuation times. Should sufficient specimens be available, some testing will be conducted at both temperatures.

Measurements are to be performed for four groups of sprinkler heads:

1. Those taken from houses containing imported drywall. Twelve units of each of three models of each type of head (a total of 72 units) have been requested. CPSC staff reports collection of specimens from one condominium complex and more collection underway.
2. Those taken from houses containing domestic drywall. These sprinkler heads are to be of the same makes and models as those in the first set. They will have been exposed to the normal environment in similar dwellings for a similar length of time. Twelve units of each of three models of each type of head have been requested, in order to balance the comparison statistics.
3. New sprinkler heads of types similar to those above. Twenty-four units of each of the three models will be purchased. Twelve of these will be tested and the other twelve will be sent for aging (See Group 4). The models of sprinkler heads do not change often, so it may be possible to obtain the same models as in Groups 1 and 2.
4. The sprinkler heads from Group 3, which will have been subjected to an exposure designed to simulate extended tenure in a house with imported drywall. This accelerated aging will be performed by SNL. At present, the composition of the aging atmosphere, the duration of the exposure, and the protocol for estimating the time interval being simulated will be provided at a later date, following CPSC staff chamber testing being conducted by LBL.

The intent is to make the following comparisons:

- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and 2 and units from Group 3. This will identify the extent to which either residential exposure affected the actuation time.
- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and units from Group 2. This will identify whether there was a significant change in actuation time as a result of exposure to the effluent from the imported drywall, compared to exposure to "ordinary" household environments.
- Comparison of the mean sensitivity and the variance in the sensitivity between Groups 3 and 4. This will identify the potential of the drywall effluent to affect the actuation time of the sprinkler heads over a long period of time.
- Comparison of the mean sensitivity and the variance in the sensitivity between units from Group 1 and units from Group 4. This will identify the potential for change in actuation time beyond any noted in the comparison of the Group 1 and Group 3 units.

We will begin purchasing new units as arriving field specimens clarify the types of in-use units.