September 7, 2016
File No. 80099

Via Electronic Submittal

U.S Environmental Protection Agency, Region 1
Attention: Mr. James DiLorenzo, Task Order Project Officer
5 Post Office Square, Suite 100
Boston, Massachusetts 02109-3919

Re: Transmittal of Evaluation of Potential Asbestos Mobility in the Environment and Impacts to Long-Term Management of Raymark Waste
Raymark Superfund Site – OU4/OU6, Stratford, Connecticut
Task Order No. 0099-RI-CO-01H3

Dear Mr. DiLorenzo:

Enclosed please find the final version of the Evaluation of Potential Asbestos Mobility in the Environment and Impacts to Long-Term Management of Raymark Waste prepared by Nobis for the Raymark Superfund Site.

Please contact me at (978) 703-6013 or hford@nobiseng.com if you have any questions or comments on this transmittal.

Sincerely,

NOBIS ENGINEERING, INC.

Heather M. Ford
Associate/Senior Project Manager

Attachment

c: File No. 80099 (w/attach.)

Nobis Engineering, Inc.
585 Middlesex Street
Lowell, MA 01851
T (978) 683-0891

EVALUATION OF POTENTIAL ASBESTOS MOBILITY IN THE ENVIRONMENT AND IMPACTS TO LONG-TERM MANAGEMENT OF RAYMARK WASTE
RAYMARK INDUSTRIES INC. SUPERFUND SITE – OU3, OU4, AND OU6
September 7, 2016

1.0 INTRODUCTION

Nobis Engineering, Inc. (Nobis) was requested by the U.S. Environmental Protection Agency (EPA) to review information provided in a University of California San Diego (UCSD) news release titled: "*New Study Challenges Assumption of Asbestos' Ability to Move in Soil*"[1] (dated August 19, 2016). The news release indicated that a study led by Dr. Jane Willenbring determined dissolved organic carbon (DOC) attached to asbestos particles caused a change in the electric charge on the particles' surfaces, which allowed the particles to be able to migrate through soil. Dr. Willenbring stated that [for example] "If you have water with organic matter next to the asbestos waste piles, such as a stream, you then have a pathway from the waste pile and possibly to human inhalation."

This memorandum summarizes the review of available information regarding Dr. Willenbring's research and potential implications for proposed remedial responses for long-term management of Raymark Waste at OU4 (low-permeability cap), and at OU3 and OU6 (soil covers).

2.0 TECHNICAL PUBLICATIONS

A quick search of on-line resources did not identify any published scientific articles for asbestos mobility in the subsurface. A check of Researchgate.net identified 67 publications affiliated with Dr. Willenbring.[2] However, there are no publications listed for asbestos mobility as this topic is very new and was only just presented at the 2016 American Chemical Society (ACS) National Conference in Philadelphia on August 22, 2016. Conference proceedings with papers do not appear to be available immediately for on-line viewing at this time, and therefore details regarding the study are unavailable at the moment.

Dr. Willenbring and co-authors likely have submitted multiple papers to various journals, which may take some time to be reviewed, and if approved, published.

In short, the topic is too new to have technical publications available for review for this evaluation.

3.0 2016 ACS NATIONAL CONFERENCE ABSTRACTS

The 2016 ACS National Conference in Philadelphia Technical Program identified several topics related to asbestos mobility including Dr. Willenbring's presentation.[3] Note that Dr. Willenbring is either the author or

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[1] Link to UC San Diego new release: https://scripps.ucsd.edu/news/new-study-challenges-assumption-asbestos-ability-move-soil
[2] Link to Dr. Willenbring's publications: https://www.researchgate.net/profile/Jane_Willenbring
[3] 252nd American Chemical Society National Meeting & Exposition program: https://www.acs.org/content/dam/acsorg/meetings/fall-2016/attendee-resources/philadelphia-onsite-program-noads.pdf

co-author for five papers related to asbestos mobility. Dr. Willenbring was formerly with the University of Pennsylvania (UPenn) prior to joining UCSD. UPenn Center of Excellence in Environmental Toxicology (CEET) has received a $10 million grant from the National Institute for Environmental Health Sciences (NIEHS) to study asbestos-related diseases.[4] Some of the funding was applied to research various topics such as fate and transport, and phytoremediation and biodegradation of asbestos.[5] Findings of the research were presented at the 2016 ACS National Conference. Review of the research topics at the UPenn web page indicates that the research was conducted at the laboratory scale. Abstracts of these papers are provided in this memorandum and key takeaways are provided by Nobis in the notes following each abstract.

a. **Session TOXI 25 - "*Fate of asbestos in soil: remediation prospects and paradigm*"**, **Jane Willenbring** with Sanjay Mohanty, Ashkan Salamatipour, Cedric Gonneau, Douglas Jerolmack, and Brenda Casper listed as co-authors. This paper is the basis for the August 19, 2016 UC San Diego news release that the Stratford citizen had forwarded to EPA for consideration as part of the Raymark Superfund Site's Public Comment period.

   The verbatim abstract for TOXI 25 follows:

   > **TOXI 25 Abstract: *"****Asbestos, in soil, can undergo physical and chemical changes that alter toxicity and remobilize fibers into the environment. Decreased length of the fibers can increase potential for inhalation. The iron content of the fibers exerts a first-order control on toxicity, through the production of reactive oxygen species. Natural soil environments and geo-engineered soil caps often contain exudates of fungi, bacteria, and plants such as organic acids, siderophone compounds, and dissolved organic matter that alter the surface charge and chemistry of the fibers. We find that siderophore exudates, in particular, increase the removal of both surface and structural iron from Chrysotile asbestos fibers. Other soil conditions such as ionic strength, pH, and dissolved organic carbon vary from soil to soil and may impact the surface charge of the asbestos fibers allowing them to move through soil. In this paper, we document the mobility of asbestos fibers through soil in the presence of dissolved organic matter (fulvic acid). The transformation of the fibers by organic matter leads to charge reversal of asbestos fibers (from positive to negative) that lowers the attachment of asbestos fibers to soil grains. This result challenges the long-standing paradigm that asbestos fibers are immobile in soil and highlights the need to evaluate the long-term effectiveness of current remediation strategies that do not account for possible asbestos alteration and exposure via near- and sub-surface water flow."*[6]

   [**Notes**: This abstract provides more technical details than the UC San Diego new release, and provides insight into possible approaches to address potential asbestos mobility issues. The key information that can be gleaned from the abstract is that natural soil environments and geo-engineered soil caps have microbes and plants that exude organic acids, fulvic acid, and especially siderophone compounds[7] that

[4] http://www.med.upenn.edu/asbestos/
[5] http://www.med.upenn.edu/asbestos/research/
[6] https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16fall&id=2519089
[7] Siderophores are compounds secreted by microorganisms, bacteria, fungi, and grasses with that are chelating agents with a high affinity for iron.

cause surface and structural iron to be removed from asbestos fibers (specifically Chrysotile). In the presence of dissolved organic carbon (fulvic acid), the abstract indicates the surface charge of the asbestos fibers is reversed, reducing asbestos particle attachment to soil grains, thus allowing asbestos fibers mobility.]

b. **Session TOXI 26 – "*Aggregate dynamics and their control on the mobility of asbestos in the environment"***, Douglas Jerolmack with Lei Wu, Carlos Ortiz, and ***Jane Willenbring***. [Note that Drs. Jerolmack and Willenbring are co-authors of each other's papers.]

The verbatim abstract for TOXI 26 follows:

> **TOXI 26 Abstract:** *"Most colloidal particles including asbestos fibers form aggregates in water, when solution chemistry provides favorable conditions. The size and stability of these aggregates controls their mobility in the environment. To date, the growth of colloidal aggregates has been observed in many model systems under optical and scanning electron microscopy; however, all of these studies used near-spherical particles. The highly elongated nature of asbestos fibers may cause anomalous aggregate growth and morphology, but this has never been examined. Here we studied solution-phase aggregation kinetics of chrysotile asbestos fibers in a liquid cell by in-situ microscopy, in which we track the trajectories of thousands of particles and their associated aggregates over many hours. Experiments reveal that diffusing fibers join by cross linking but that such linking is sometimes reversible. Asbestos aggregates are very sparse and non-compact, with morphologies and growth rates that differ markedly from previous experiments that used near-spherical particles. In order to isolate the control of colloid shape on aggregate dynamics, we also conducted experiments using manufactured spheres and rods made of silica. The growth and structure of aggregates composed of silica rods are remarkably similar to those of asbestos fibers, and both are significantly different from silica spheres, showing that particle shape exerts a primary control that is independent of colloid material properties. Measurements and theory indicate that colloid attachment is stronger for rods compared to spheres, which may be a consequence of enhanced charge heterogeneity on the rod surface due to its elongated shape. We also explored the effects of solution chemistry, finding that the growth of aggregates depends strongly on solution pH but is surprisingly insensitive to salinity. Finally, we conducted flow-cell experiments to examine colloid interactions with porous media, to assess the potential for asbestos fibers to migrate in groundwater. Attachment is reversible and strongly dependent on solution chemistry, while aggregate size also influences transport by straining. Under some conditions, asbestos fibers can be highly mobile in groundwater – contrary to the assumption that mobility is always negligible. Taken together, our work shows how experiment and theory may be used to predict the growth and migration of asbestos aggregates in the environment."*[8]

[**Notes**: The key information provided in this abstract is that: colloidal-sized asbestos particles in water, under the right conditions, can form larger-sized aggregates, which may alter their behavior in porous media transport (i.e., if colloids agglomerate, they may become less mobile); formation of aggregates is highly pH dependent (but there is no information available at this time whether high or low pH favors aggregate

[8] https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16fall&id=2519041

growth). Also, the abstract indicates that colloid attachment (aggregation, agglomeration) is stronger in rod shapes vs. spherical shapes. By definition, a colloid is a particle in the 1 to 1,000 nanometer (or 1 μm) range. In the environmental field, it is understood that colloid-sized particles can migrate through porous media such as saturated subsurface soil. This paper indicates that pH is a strong determinant for colloids to agglomerate, and therefore it may be concluded that under the right pH conditions, colloids could be caused to aggregate, become non-colloidal in size, and their mobility could be reduced.]

c. **Session ENVR 462 – *"Is phytoremediation of asbestos contaminated sites feasible?"*** Cedric Gonneau, Sanjay Mohanty, ***Jane Willenbring***, and Brenda Casper.

The verbatim abstract for ENVR 462 follows:

> **ENVR 462 Abstract: *"***_Asbestos is a colloquial term encompassing several fibrous silicates. Inhalation of the fibers can cause mesothelioma and cancer of the lung. In the US, there are 1312 asbestos contaminated sites including Superfund, Brownfield and naturally occurring asbestos sites. Currently, the EPA protocol for treatment of asbestos contaminated sites is to move it and/or cap it. However, capped piles containing fibers can pose threats to nearby human populations. Indeed, new remediation strategies, such as remediation, should be explored. Three locations with different asbestiform minerals were studied: BoRit, a superfund site with two areas: sediments and stream banks. Nottingham Park, a serpentine site with several mines such as a chromite mine. To determine feasibility of phytoremediaton of asbestos contaminated soils, we evaluated: 1. fertility using Fertility Capability Classification (Texture and 12 modifiers) and determined soils properties (pH, CEC, Phosphorus, total and bioavailable concentrations of heavy metal). 2. toxicity by an ecotoxicological test. We determined percentage of inhibition of seed germination and root growth on three species (one Poaceae, two Brassicaceae). All locations tested differed significantly in the various soil parameters. Among 12 modifiers and 23 soils parameters, limiting factors of fertility were: percentage of gravel, pH, P, K, total concentrations of Ni and Cr. Ni and Cr bioavailability was low. In the ecotoxicological test, all three asbestiform sites had reduced seed germinatioin (5-30% of control). Root growth was reduced 2-50% of control with greatest reduction for Poaceae. Our results showed that it is important to take into account all soil-limiting parameters and not only pollutants. Moreover, utilization of compost will decrease pH and increase soil fertility but could also increase bioavailability of trace elements (Ni or Cr). Indeed, serpentinophytes seem to be a possible method for phytoremediation on asbestiform. Our research proposes and validates a novel approach to the remediation of asbestos-polluted soil."_ [9]

[**Notes:** This abstract suggests that serpentinophytes can be used for phytoremediation of asbestos. Serpentinophytes are plants with root systems that can penetrate weathered rock and thrive in serpentinic soils, which derive from weathered serpentine rock. Chrysotile asbestos is only one of the six types of asbestos that is a member of the serpentine class. However, the abstract never describes how asbestos could be phytoremediated.]

d. **Session ENVR 463 – "Is bioremediation of asbestos fibers feasible?"** Cedric Gonneau with Sanjay Mohanty, ***Jane Willenbring***, Brenda Casper.

The verbatim abstract for ENVR 462 follows:

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[9] https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16fall&id=2510155

ENVR 463 Abstract: *"The current remediation plan for treating nearly 1300 asbestos-contaminated sites in the U.S. is to cap of the waste pile with uncontaminated soil, but long-term erosion of the capping soil risks re-exposure of the asbestos fibers. We propose an alternative remediation strategy that relies on degradation of asbestos fibers by fungi and plants. In particular, we examine whether plant or fungal exudates can enhance asbestos weathering and change the fiber toxicity by removing iron (a known cause of asbestos toxicity) from asbestos. Chrysotile fibers were suspended in water in the presence of exudates including six organic acids and a siderophore—this particular exudate with a strong affinity to iron. Our results showed that the siderophore increased the removal of iron from asbestos fibers, and addition of organic acids did not affect iron removal. The quantity of iron removed increased with concentration of siderophore. These results indicate that bioremediation technology for asbestos contaminated sites is possible, although further research is needed to quantify the degradation of asbestos fibers in complex subsurface environment."*[10]

[**Notes:** This abstract indicates that siderophore compounds can remove iron from asbestos fibers and lower its toxicity. Also the abstract seems to suggest that with iron removal, the iron-poor asbestos fibers can be degraded. However, there are insufficient details to make any further assessments.]

e. **Session GEOC 41 – "Geochemical triggers for asbestos fibers mobility in groundwater".**
Sanjay Mohanty, Ashkan Salamatipour, Douglas Jerolmack, ***Jane Willenbring***

The verbatim abstract for GEOC 41 follows:

GEOC 41 Abstract: *"The most feasible remediation plan to treat nearly 1300 asbestos-contaminated sites in the U.S. is capping of the contaminated soil by an uncontaminated soil, but this plan relies on the assumption that asbestos fibers should not move through sub-surface soil—a potential exposure route that has not been evaluated to date. We aim to examine whether the typical hydrological and geochemical conditions in the subsurface soil can move asbestos fibers and potentially contaminate groundwater. We injected an asbestos (chrysotile)-fiber suspension through a saturated sand and soil column (a model groundwater system) and examined the fiber mobility under three different geochemical conditions: pH, ionic strength, and dissolved organic carbon (fulvic acid). In the absence of fulvic acid, asbestos fibers were not mobile irrespective of the pH and ionic strength of water. In the presence of fulvic acid, however, nearly 60% of the injected asbestos fibers moved through the column. The enhanced mobility of asbestos fibers in the presence of fulvic acid is attributed to charge reversal of asbestos fibers (from positive to negative) that lowers the attachment of asbestos fibers on sand or soil grains. This result challenges the long-standing assumption that asbestos fibers are immobile in groundwater and highlights the need to evaluate the long-term effectiveness of current remediation strategies that do not account for possible asbestos exposure via groundwater."*[11]

[**Notes:** Presence of fulvic acid caused charge reversal on asbestos fibers, allowing the asbestos fibers to be mobile and move through a laboratory-scale saturated sand and soil column, simulating groundwater

[10] https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16fall&id=2510546
[11] https://ep70.eventpilotadmin.com/web/page.php?page=IntHtml&project=ACS16fall&id=2507074

conditions. This abstract provides similar information about fulvic acid's role in asbestos mobility as the TOXI 25's abstract.]

4.0 SUMMARY OF ACS ABSTRACTS - KEY MECHANISMS THAT MAY AFFECT ASBESTOS MOBILITY

Notes for each of the five abstracts (presented in Section 3.0) related to the fate and transport of asbestos are itemized below for ease of identifying possible approaches to prevent or mitigate unwanted asbestos fiber migration. The papers are based on research results conducted at the laboratory scale under controlled conditions to control for variables. In the field or actual hazardous waste sites, conditions may be different.

TOXI 25 (fate of asbestos in soil):

- Natural soil environments and geo-engineered soil caps have microbes and plants that exude organic acids, and fulvic acid, and especially siderophone compounds, that can cause surface and structural iron to be removed from asbestos fibers (specifically Chrysotile).

- In the presence of dissolved organic carbon (fulvic acid), the surface charge of the asbestos fibers is reversed, reducing their attachment to soil grains, thus allowing asbestos fibers mobility.

TOXI 26 (aggregate dynamics and asbestos mobility):

- Colloidal-sized asbestos particles in water, under the right conditions, can form larger-sized aggregates, which may alter their behavior in porous media transport (i.e., if colloids agglomerate, they can become less mobile);

- Based on lab measurements and theory, rod shaped colloids are more likely to attach than sphere shaped colloids.

- Formation of colloidal aggregates is highly pH dependent (unknown at this time whether low or high pH favors agglomeration, leading to lower mobility in porous formations).

ENVR 462 (phytoremediation of asbestos-contaminated sites):

- There was insufficient information presented in the abstract to assess whether phytoremediation was effective.

ENVR 463 (bioremediation of asbestos fibers):

- Once siderophore (iron-chelating compound exuded by microorganisms, fungi and plants) removes iron from the asbestos fibers, toxicity of asbestos fiber is reduced.
- The abstract suggest the iron-poor asbestos fibers can be degraded, but no specific details are offered.

GEOC 41 (mobilization of asbestos particles):

- In the presence of fulvic acid, mobility of asbestos fibers was enhanced. Nearly 60% of the injected asbestos fibers moved through the test column.

4.1 Combined Results

These five research topics are all related and are overlapping. Using all the outcomes provided in the abstracts, the following maybe surmised:

- The iron-chelating siderophone compounds exuded by soil microbes, fungi and plants can remove surface and structural iron from asbestos fibers, reducing their toxicity (per TOXI 25 and ENVR 463 abstracts).

- Dissolved organic carbon (fulvic acid) appears to be the primary agent for surface charge reversal, allowing asbestos fibers not to remain attached (attracted) to soil particles, resulting in increased mobility (per TOXI 25 and GEOC 41).

- Colloidal-sized asbestos fibers, under the right pH conditions, will aggregate and form larger sized particles, which may affect their behavior in porous media (such as subsurface soil) (per TOXI 26).

- One study suggested iron-poor asbestos fibers can be degraded, but no specific details are offered (per ENVR 463).

5.0 POTENTIAL APPROACHES TO INHIBIT OR PREVENT ASBESTOS MOBILITY

Based on the information provided by the ACS abstracts, the following methods could be used to mitigate potential asbestos migration in subsurface:

- Solidification/stabilization – Various reagents could potentially be mixed with contaminated soil to physically isolate and immobilize the asbestos particles. Potential reagents include cement, pozzolanic material, thermoplastics, polymers, and asphalt. Treatment may be performed in situ or ex situ.

- Chemical fixation – strong acids are used to alter the mineralogy of the asbestos into non-asbestiform crystalline structure.

- High-temperature thermal treatment – Thermally alter the asbestos crystalline structure into non-asbestiform structures.

All of these process options will likely be expensive because of the heterogeneous contaminants present and multiple treatment steps will be required.

6.0 OU4 AND LOW-PERMEABILITY CAPPING OF RAYMARK WASTE

The potential for Raymark waste asbestos mobility is plausible based on the research conducted by Dr. Willenbring and her team. However, the actual reports and associated data are unavailable for more detailed evaluations; further, none of the research has been conducted in the field as a pilot or full scale testing – only laboratory data under controlled conditions. Assuming the observations of the laboratory studies are valid, consolidated Raymark waste (from OU3 and OU6) at OU4 covered by a low-permeability cap could result in asbestos fiber mobility and migration. Excavated Raymark waste from OU3 will contain wetland sediments (organics rich), stream bottom sediments (also organics rich), and general wet soil subject to periodic tidal influx in Ferry Creek. Excavated OU6 Raymark Waste will have less organics and will be less moist than OU3 excavated materials. The combined OU3 and OU6 excavated materials will be generally organics rich and moist. The combination of moisture and organics rich soil and sediment can result in soil and sediment microbes exuding siderophone compounds that remove iron from the asbestos fibers, lowering their toxicity. With organics rich soil and sediment, fulvic acid can be generated that cause the surface charge reversals in asbestos fibers, allowing the fibers to not remain attracted to the soil particles, and become mobile. If the asbestos fibers are released and are colloidal in size and can migrate through the soil pores, and there is groundwater present to convey the particles, then the asbestos could migrate. However, there are so many variables that it is difficult to predict how much of the consolidated asbestos could become mobile or how far they could migrate. Assuming asbestos particles can become mobile and migrate with groundwater, once the colloid-sized fibers enter into different biogeochemical regimes, those conditions may impede or retard further asbestos particle mobility.

7.0 OU3/OU6 AND SOIL COVERS

For unexcavated soil and sediment at OU3 (organics rich and wet) and soil at OU6 (organics rich and has soil moisture), similar to excavated OU3 and OU6 materials described in Section 6.0, the combination of moisture and organics rich soil and sediment can result in soil and sediment microbes exuding siderophone compounds that remove iron from the asbestos fibers, lowering their toxicity. Conditions at OU3 and OU6 at depth would be conducive for fulvic acid generation that can cause the surface charge reversals in asbestos fibers, allowing the fibers to not remain attracted to soil or sediment particles, and become mobile. If the asbestos fibers are released and are colloidal in size and can migrate through the soil pores, and there is a groundwater present to convey the particles, then the asbestos could migrate. However, similar to the OU4 consolidated Raymark waste, there are so many variables that it is difficult to predict how much of the consolidated asbestos could become mobile or how far they could migrate. Once in groundwater, the colloidal asbestos may be able to discharge to Ferry Creek. However, assuming asbestos particles can become mobile and migrate with groundwater, once the colloid-sized fibers enter into different biogeochemical regimes, those conditions may impede or retard further asbestos particle mobility.

8.0 SUMMARY & CONCLUSIONS

The UC San Diego news release highlighted the findings of Dr. Jane Willenbring's research study that indicated potential mobilization of asbestos fibers in soil when subjected to the right conditions. Naturally occurring soil microbes and plants give off exudates that can cause changes to asbestos and promote its mobility and migration. Because the study is so new, no technical publications are currently available to perform a more detailed review. Instead, abstracts for the 2016 ACS National Conference were identified. As it turns out, several other abstracts were found related to the issue of asbestos mobility; all studies were part of a larger research program. These studies were conducted under laboratory conditions to minimize variability so transformation processes and mechanisms can be studies. At this stage, it is unclear how these transformation mechanisms would or could occur under actual field conditions because of how much greater variability and heterogeneity exists in actual conditions vs. controlled laboratory conditions.

Information obtained from the abstracts do suggest that conditions for Raymark waste at OU3, OU4 and OU6 could result in potential asbestos migration. But there is insufficient information available to draw more meaningful conclusions.

Nobis recommends that the full research articles should be reviewed once they are available, and then the conditions for Raymark waste to be consolidated at OU4 or left in place at OU3 and OU6 can be revisited as part of Remedial Design and/or Remedial Action activities.