

# Health and Safety Screening of Advanced Materials: A User Interface for Test Design, Selection and Documentation

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**US Army Corps  
of Engineers®**



Funding: Army  
Environmental Quality and  
Technology Research  
program (Dr. Elizabeth  
Ferguson)



# Overview

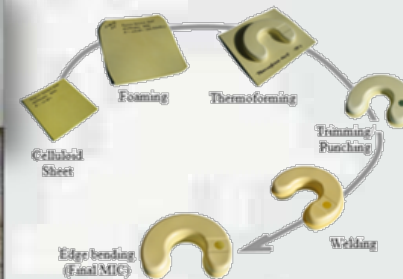
- § Regulation and testing
  - ▶ Definitions & Categorization
  - ▶ Prioritization and Exclusions
- § Case studies
  - ▶ Photocatalytic cement
  - ▶ Foamed celluloid
  - ▶ Printed technologies
    - 2D printed nanosilver circuit
    - 2D printed Temp/humidity sensor
    - 3D printed applications

## The Frank R. Lautenberg Chemical Safety for the 21st Century Act

On June 22, 2016, the Frank R. Lautenberg Chemical Safety for the 21<sup>st</sup> Century Act which amends the [Toxic Substances Control Act \(TSCA\)](#), the Nation's primary chemicals management law was signed into law.

The new law, which received bipartisan support in both the U.S. House of Representatives and the Senate, includes much needed improvements such as:

- Mandatory requirement for EPA to evaluate existing chemicals with clear and enforceable deadlines;
- New risk-based safety standard;
- Increased public transparency for chemical information; and
- Consistent source of funding for EPA to carry out the responsibilities under the new law.



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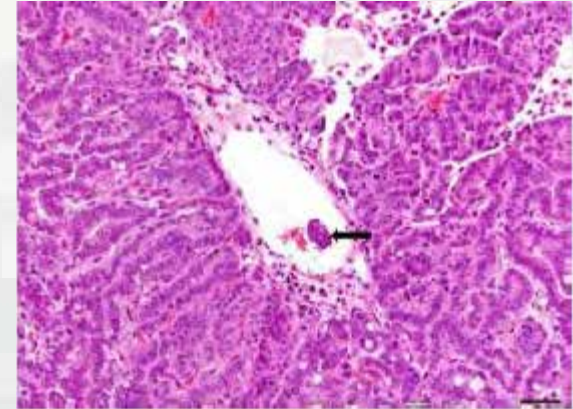
# Are Advanced Materials Sustainable: *For Soldiers? For the Environment?*

§ Typical concerns, include unique:

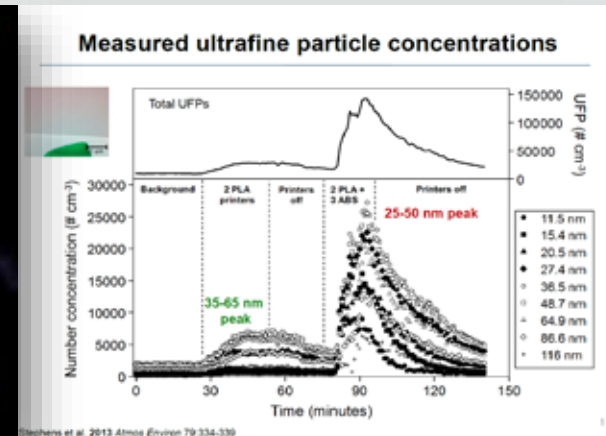
- ▶ Properties
- ▶ Fate, exposure, health effects
- ▶ Uncertainty, regulations, liability

§ Emerging concerns

- ▶ Additive manufacturing / 3D printing
  - Intellectual property, STL files
  - Direct exposure (garage, not industry setting)
  - ASTM F42.06: EHS



Mouse lung with alveolar bronchiolar carcinoma (Sargent, 2013)

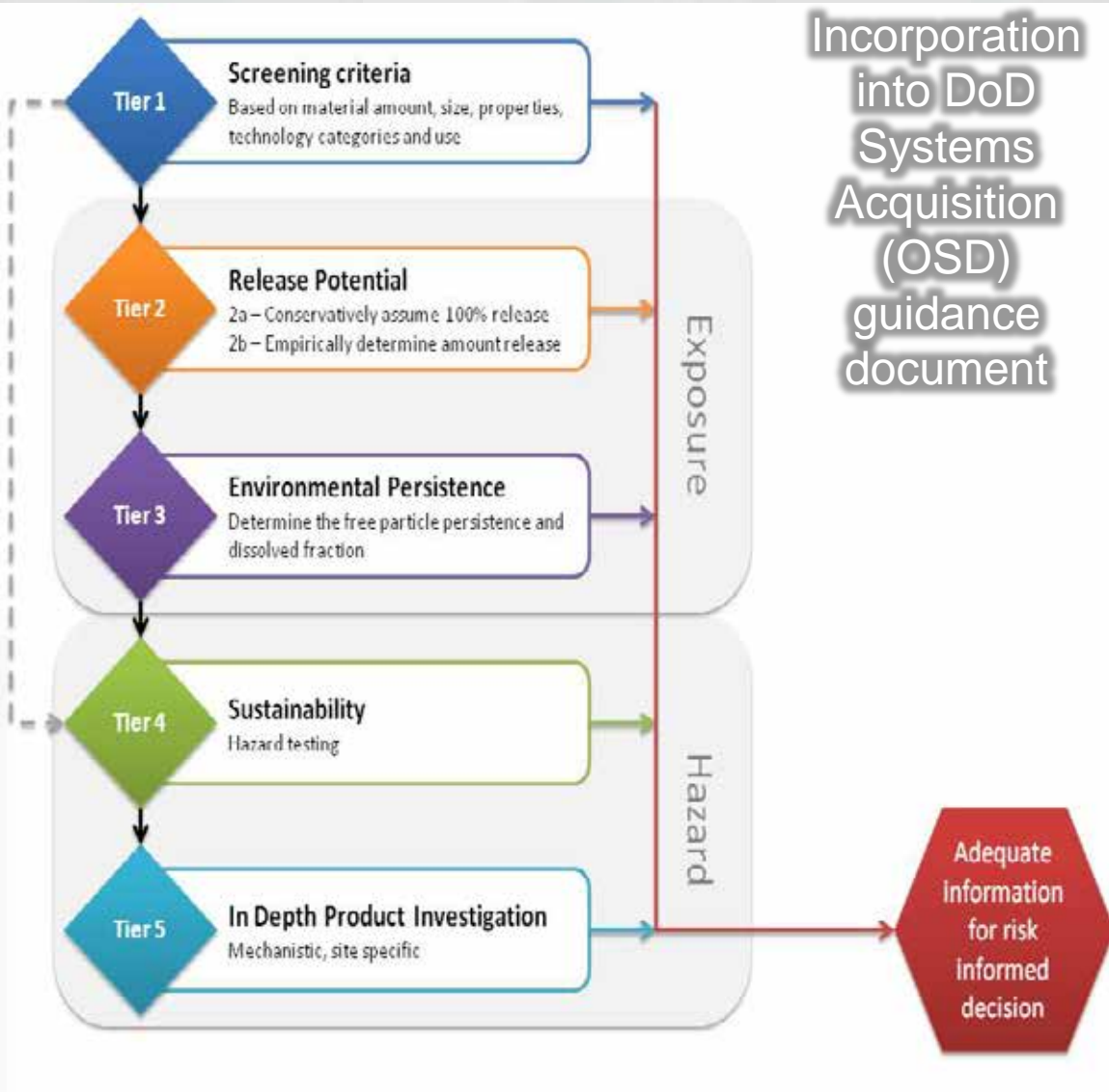
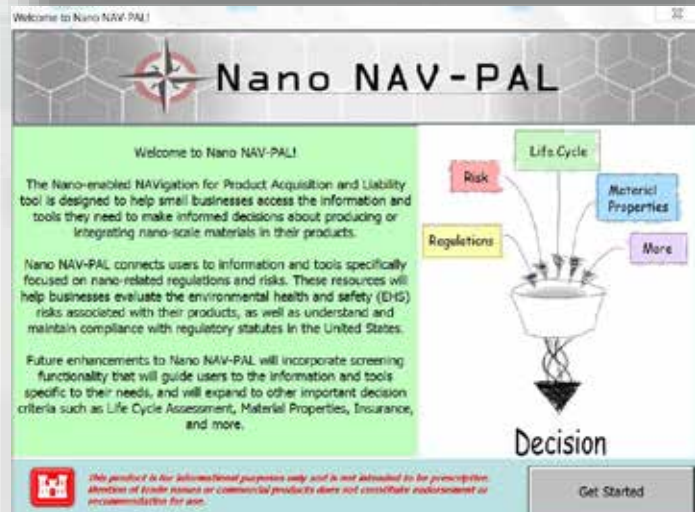


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# NanoEHS Tool Development

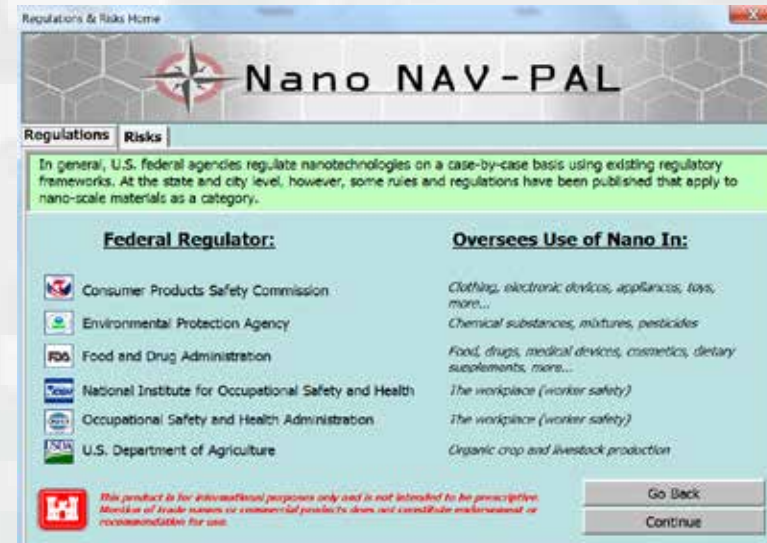


§ Nano-enabled NAVigation for  
Product Acquisition and Liability

§ Tool to help small businesses:

- ▶ enable evaluation of EHS risks of integrating nanomaterials into products
- ▶ Identify resources (tools, databases) for EHS risk assessments

Q19. If an Environmental Health & Occupational Safety (EHOS) screening tool was available to assist nanomaterial producers and integrators, would you or someone within your organization use it?

Regulators & Risks Home

## Nano NAV-PAL

Regulations Risks

In general, U.S. federal agencies regulate nanotechnologies on a case-by-case basis using existing regulatory frameworks. At the state and city level, however, some rules and regulations have been published that apply to nano-scale materials as a category.

Federal Regulator:	Oversees Use of Nano In:
Consumer Products Safety Commission	Clothing, electronic devices, appliances, toys, more...
Environmental Protection Agency	Chemical substances, mixtures, pesticides
Food and Drug Administration	Food, drugs, medical devices, cosmetics, dietary supplements, more...
National Institute for Occupational Safety and Health	The workplace (worker safety)
Occupational Safety and Health Administration	The workplace (worker safety)
U.S. Department of Agriculture	Organic crop and livestock production

This product is for informational purposes only and is not intended to be prescriptive. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Go Back Continue



Regulators & Risks Information and Tools

## Nano NAV-PAL

Regulations Risks

Below you will find information and tools that may aid in understanding and characterizing the potential environmental, consumer, and occupational risks of nanotechnologies.

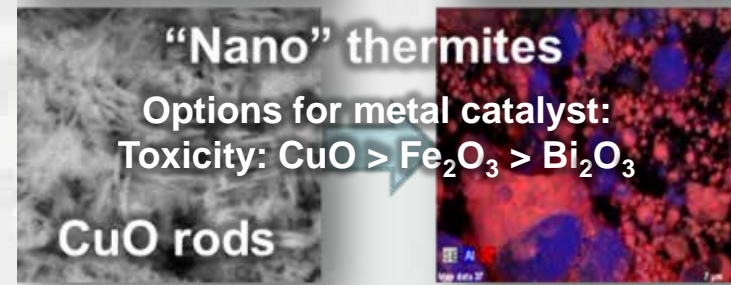
- Environmental Risks
- Consumer Risks
- Occupational Risks
  - Informational Resources**
    - NIOSH Nanotechnology Guidance and Publications
    - NIERCC / OIC Worldwide - Nanotechnology Consensus Workplace Safety Guidelines
    - LifeNanoRisk
    - ISG/TS 12901-2:2014: Nanotechnologies -- Occupational risk management: applied to engineered nanomaterials -- Part 2: Use of the control banding approach
    - CalBRACE
    - SCAFFOLD
    - University of California Center for Environmental Implications of Nanotechnology (UC CEIN) Nanosketch
  - Tools
  - Cross-Cutting EHS Risks

This product is for informational purposes only and is not intended to be prescriptive. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

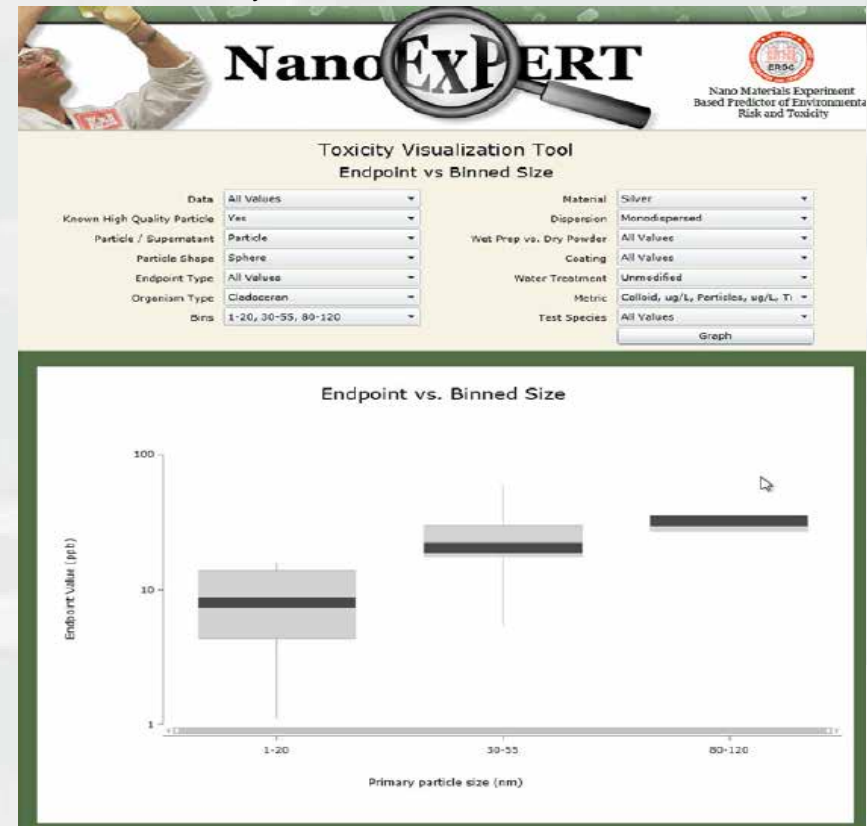
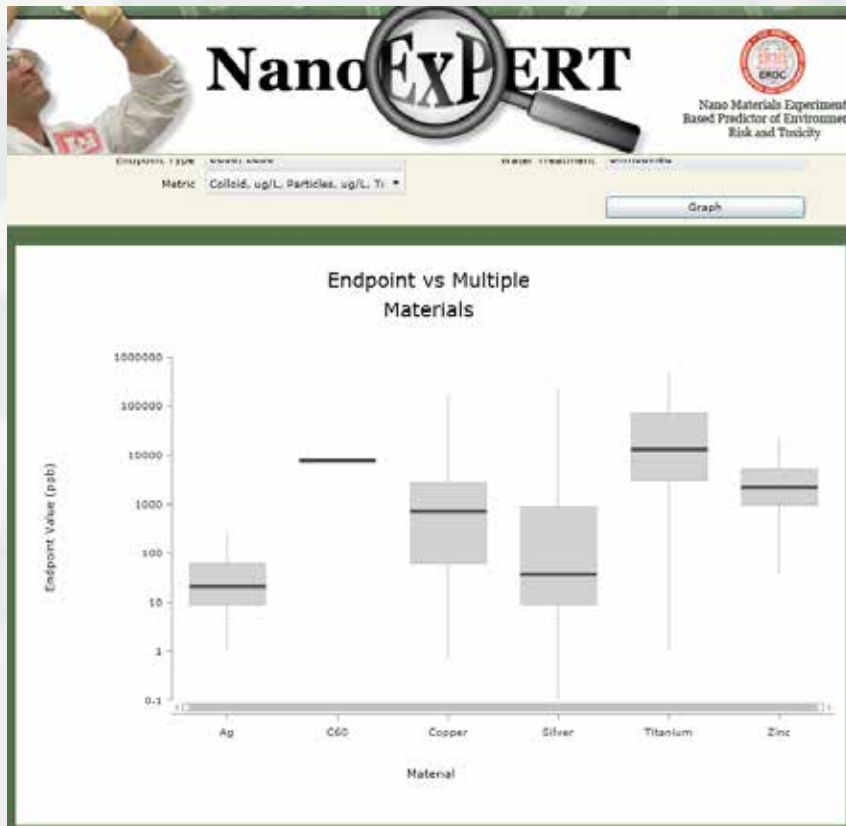
Go Back

# Nano DON'T!

- § Nano Database Of NO-effect Thresholds
- § <https://nano.el.erdc.dren.mil/>
- § Disseminate to help tech development



Kennedy et al., *Environ Sci Technol*, 2013, 47, 11258-11267



# What is Nano?

## ...Advanced Materials?

*Do we care about SIZE, PROPERTIES, OR BOTH?*

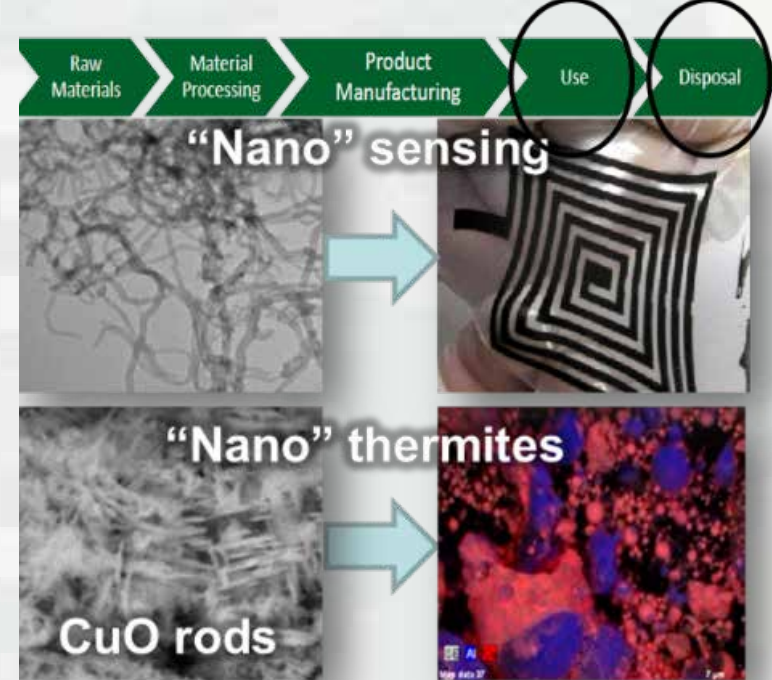
*Size before properties or properties before size?*

**Nanomaterial (Rule for Manufacturers and Processors; EPA TSCA Section 8a)** ...solid (25 °C, 1 ATM); 1 – 100 nm in one dimension and at least 1% particles by mass;  
“...size-dependent property different from properties at sizes greater than 100 nm and is a reason the chemical is manufactured...”

**Advanced Materials (ERDC):** “materials intentionally engineered to exhibit novel or enhanced properties that confer superior performance relative to convention”

*RISK PRIORITIZATION: “Highly uncertain risk profile and the potential to adversely impact environmental health and safety due to (1) direct chemical hazard; (2) components produce hazard; (3) unique release/exposure”*

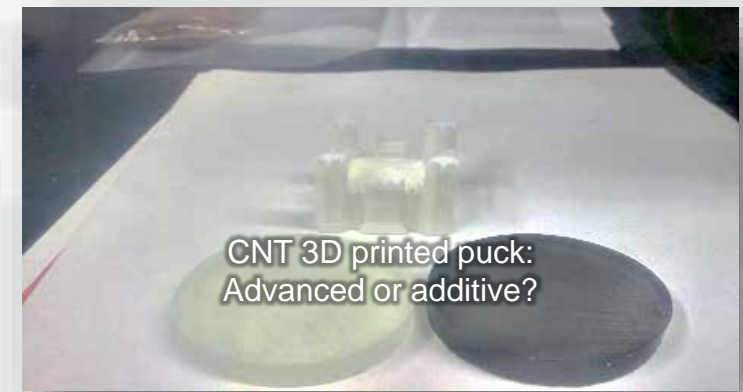
**Additive Manufacturing:** “a layer-by-layer process of producing 3-dimensional objects directly from a digital model, unlike conventional or subtractive manufacturing processes” (GAO, 2015)



*“The fear of acting without “perfect information” → paralysis by analysis...—we need to act on what we know now.”*

—Hansen et al 2014. Nanotechnology risk management, 2nd ed. Elsevier, Amsterdam, pp 9–24

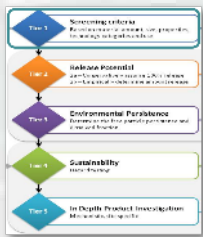
Kennedy et al., *Environ Sci Technol*, 2013, 47, 11258-11267



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# Categorical Exclusions from *Nano-specific* release testing



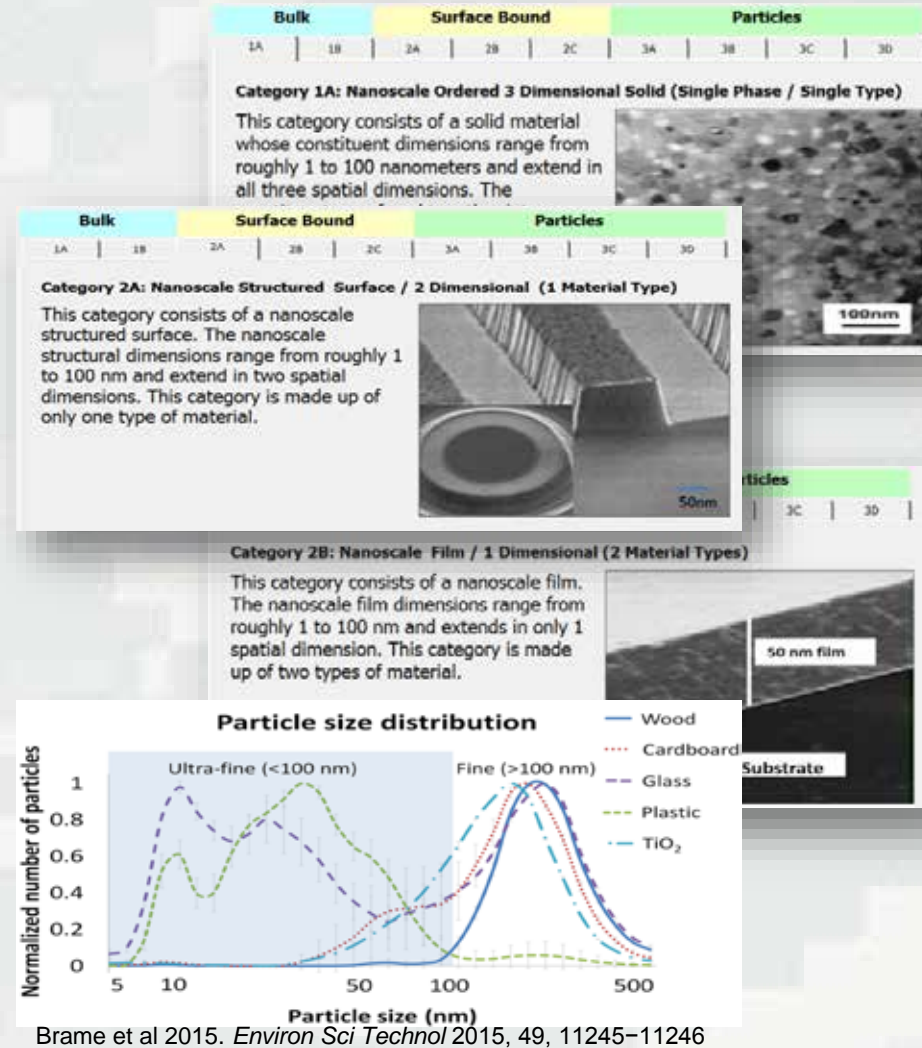
## Intentionally engineered:

- ▶ Nanoparticles that in application are sintered together outside nano-range
- ▶ Nanostructures (“break off”?)
- ▶ Nanofilms are not particles

## Incidentally released

- ▶ Particulates from matrix?

## Low hazard properties?



Brame et al 2015. *Environ Sci Technol* 2015, 49, 11245–11246



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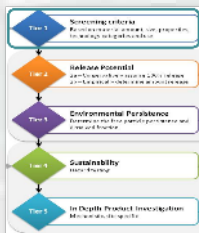
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# Photocatalytic Cement Mortar

## Tier 1: Background, Life Cycle Thinking, Characterization, Categorization

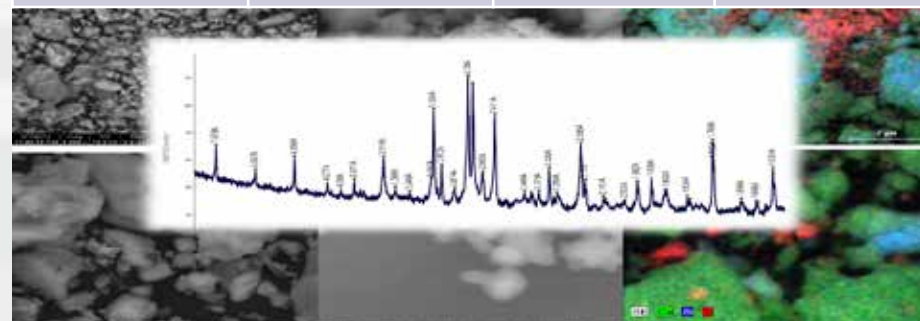


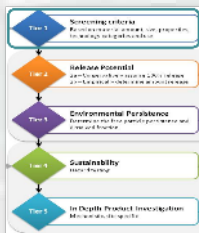
### § Photocatalytic ENM



Size (nm) (SEM)	DLS (nm)	SA (m <sup>2</sup> /g)	VSSA (m <sup>2</sup> /cm <sup>3</sup> )
34 ± 12 (17 - 74)	193 ± 2 (71 - 443)	57 (35 - 65)	241

### § Scenario: Used in seawall; UV, weathering, abrasion





# Dichotomous key: Self cleaning cement

*Provides process for determining material categories, EHS risk prioritization*

## 1. The material is:

- a) Completely dissolved or water soluble (25 °C; 1 atm)...**Terminate classification**
- b) Partially dissolved or water insoluble (25 °C; 1 atm)...go to 3

## 3. The solid phase material(s) / ingredient components:

- a) are intentionally engineered (1) to have novel/enhanced properties, (2) superior performance relative to existing convention or (3) by a novel/advanced process (e.g., 3-D printing)...go to 7
- b) do not individually have intentional novel/enhanced properties and/or is made by conventional methods...go to 4

## 7. The material is intentionally engineered:

- a) To have novel or enhanced properties (e.g., size, surface area, reactivity, etc.)...go to 9
- b) By a novel process...go to 8

## 9. Advanced material

- a) Is an advancement or improvement of an existing technology/application...go to 10
- b) Is a completely new concept, paradigm...go to 10

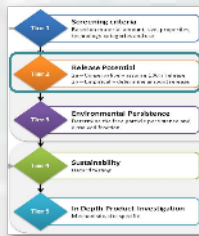
## 10. Advanced material novel/enhanced properties

- a) Come from 1-100 nm size...Nano-enabled technology material...go to 11
- b) There are no nano-scale dimensions



# Cement Mortar

## DURABILITY & Release studies selection



NanoGRID: Guidance for Risk Informed Deployment

Home | Tier 1 | Tier 2 | Tier 3

Initial Screening | Hazard Identification | Testing Identification

Instructions  
Each question is linked to a test that you should consider. Rate 0 if there is no chance the test could be necessary if the product is used as it is intended to be and 5 if the product will definitely need to be tested under that condition. Provide justification in the associated text boxes to ensure transparency in your

0 ← No chance it will be needed → 5 Definitely needed

Aqueous | Ultraviolet | Thermal | Aging | Mechanical | Combustion | Chemical Reactivity | Corrosion | Results

Test	Average Score
Aqueous	2.4
Ultraviolet	3.5
Thermal	1.0
Aging	4.0
Mechanical	3.1
Combustion	0.0
Chem. Reactivity	1.0
Corrosion	1.3

Scenario: Used in seawall; UV, weathering, abrasion

The criteria used to score each test in the prior section are now listed here to be weighted. If you value how a test scores on particular criteria more than others, weight those tests with a higher score than others. If particular criteria are less important to you than others, weight those with a lower score. Weights must be between 0 and 1 and the four weights must sum to 1.

MCDAs: consider more factors

Name of Test	Duration	Magnitude	Cost	Expertise
Submersion	2	1	1	1
Rain Event	2	2	3	2
Sun Light Exposure	5	1	5	3
Scratching	1	5	4	3
Cutting	1	3	5	3
Sandblasting	1	2	5	3
UV & Water	5	5	5	4
UV & Mechanical	5	5	5	4

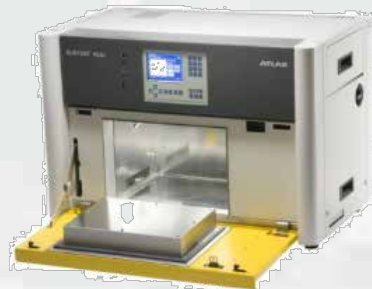
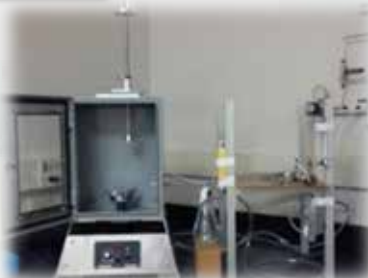
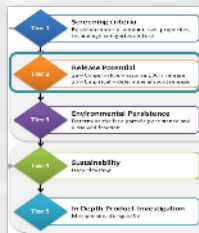
Weight	
Duration	0.2
Magnitude	0.5
Cost	0.15
Expertise	0.15
SUM:	1

Test	Weighted Score
Submersion	1.2
Rain Event	2.1
Sun Light Exposure	2.7
Scratching	2.7
Cutting	3.4
Sandblasting	3.9
UV & Water	4.8
UV & Mechanical	4.8

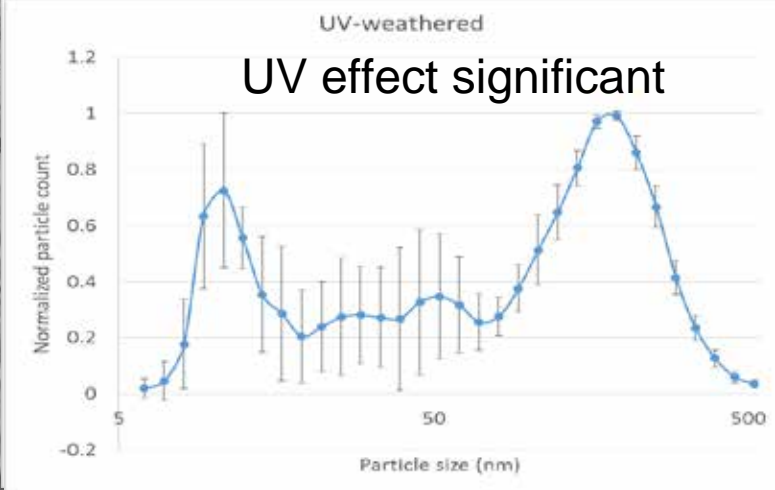
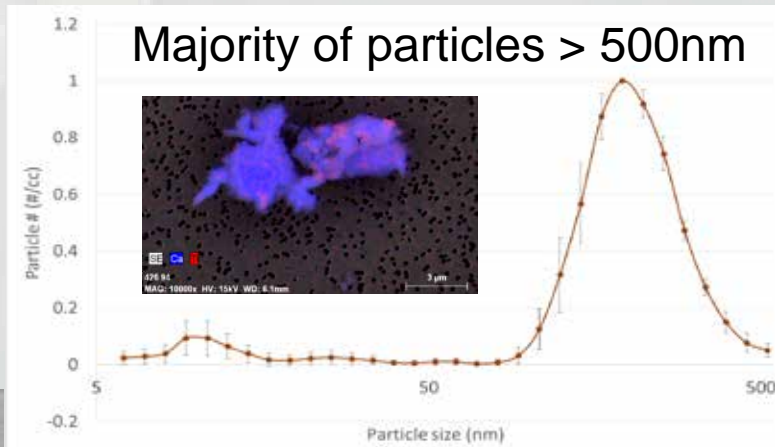


# Cement Mortar

## Tier 2 – Abrasion (after UV/weathering)



Methods: Monday presentation  
Quantifying release of nano- and advanced materials  
 J. Brame, A. Poda, E. Alberts, C. Jackson, A. Kennedy

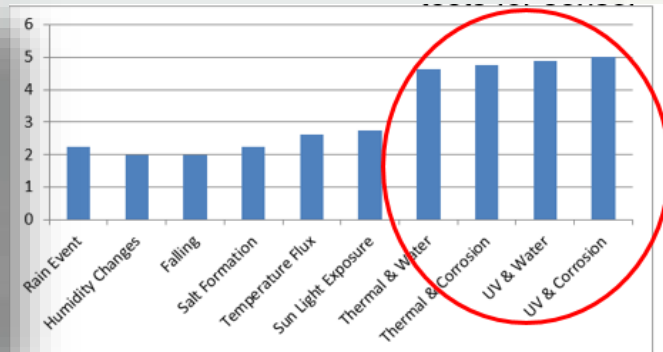


# Safe and Rapid Commercialization of Advanced Materials

## How much of the life cycle is “nano”?



Bulk			Surface Bound			Particles		
1A	1B	2A	2B	2C	3A	3B	3C	3D
<b>Category 3A: Surface bound Nano-object (particles, rods, diamonds etc.) 2 Dimensional Structure (Multi Type)</b> This category consists of a surface bound nano-objects. The nanoscale object dimensions range from roughly 1 to 100 nanometers and extend in two spatial dimensions. This category is made up of multiple types of material.								

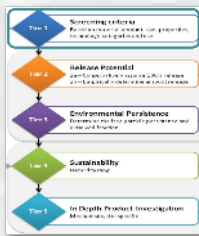


- § LCA environmental impacts are driven by energy and waste incineration (Chappe presentation, look for Tech Connect proceeding)
- § Test scenario: Sensor deployed in environment for 6+ months
- § Exposed to periodic rainfall and UV light exposure (protective casing)
- § Primary testing materials: (1) ink; (2) free printed sensor; (3) encapsulated sensor



# Nanotube sensor

## Tier 1: Background (Life Cycle Thinking)



### § Scenario:

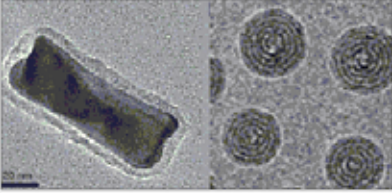
- ▶ Sensor deployed in the environment for 6+ months
- ▶ Not submerged in water but exposed to periodic rainfall
- ▶ UV light exposure

### § Pristine material nano-scale?

- ▶ Yes, conductive properties

### § Product category

- ▶ 3A for printed sensor
- ▶ Ink itself is a fluid suspended nano-object

Bulk		Surface Bound			Particles			
1A	1B	2A	2B	2C	3A	3B	3C	3D
<p><b>Category 3B: Fluid Suspended Nano-object (particles, rods, diamonds etc.) 3 Dimensional Structure (Multi Type)</b></p> <p>This category consists of fluid suspended nano-objects. The nanoscale object dimensions range from roughly 1 to 100 nm and extend in three spatial dimensions. This category is made up of multiple types of material.</p> 								



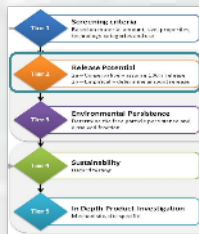
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# Nanotube sensor

## Tier 2 – Release studies selection



NanoGRID: Guidance for Risk Informed Deployment

Home | Tier 1 | **Tier 2** | Tier 3 | Tier 4 | Tier 5

Release | Hazard Identification | Testing Identification

**Instructions**  
Each question on the tabs below is linked to a release test that should be considered. Rate 0 if there is no chance the test could be necessary if the product is used as it is intended to be and 5 if the product will definitely need to be tested under that condition. Provide justification in the associated text boxes to ensure transparency in your responses. If left blank, the most conservative assumption (5) will be entered. Click on the 'Results' tab when you are ready to see which tests you should be most concerned with!

0 ← No chance it will be needed → 5 Definitely needed

Aqueous | Ultraviolet | Thermal | Aging | Mechanical | Combustion | Chemical Reactivity | Corrosion | Results

**Submersion**  
The material will be immersed in water or be submerged during use.  
 0  1  2  3  4  5

**Rain Event**  
The material will be used in an external setting and have the potential to be rained on.  
 0  1  2  3  4  5

**Acid Rain**  
The material will be used in an environment that is subjected to acid rain.  
 0  1  2  3  4  5

**Humidity Changes**  
The material will be used in an environment that is subjected to large changes in humidity.  
 0  1  2  3  4  5

**Washing**  
The material has the potential to be washed or rinsed (i.e. cleaning).  
 0  1  2  3  4  5

Justification Provided:

Help Documentation

RESET TIER 2 QUESTIONS

Save | Generate Report



# Nanotube sensor

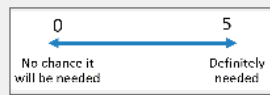
## Tier 2 – Release studies selection

NanoGRID: Guidance for Risk Informed Deployment

Home | Tier 1 | **Tier 2** | Tier 3

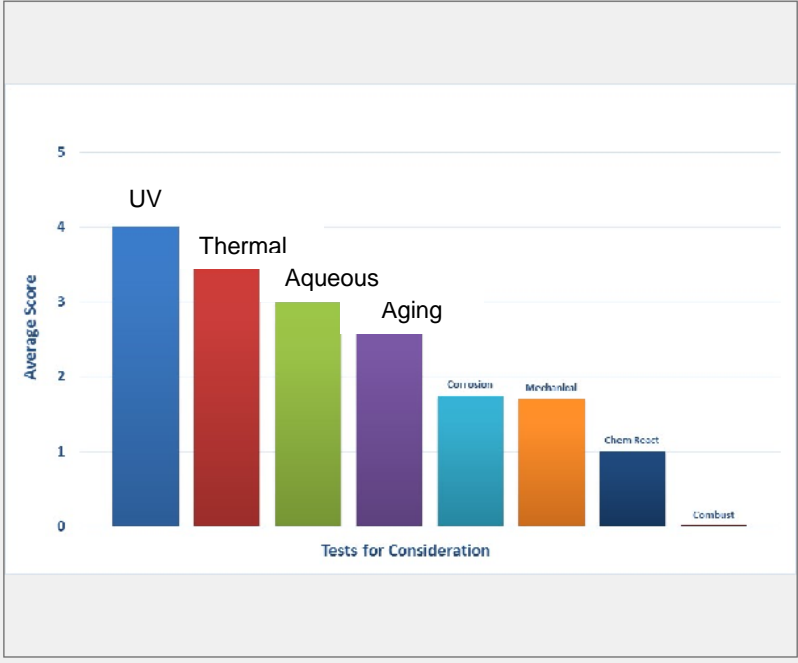
Release | Hazard Identification | **Testing Identification**

**Instructions**  
 Each question on the tabs below is linked to a release test that should be considered. Rate 0 if there is no chance the test could be necessary if the product is used as it is intended to be and 5 if the product will definitely need to be tested under that condition. Provide justification in the associated text boxes to ensure transparency in your responses. If left blank, the most conservative assumption (5) will be entered. Click on the 'Results' tab when you are ready to see which tests you should be most concerned with!



Aqueous | Ultraviolet | Thermal | Aging | Mechanical | Combustion | Chemical Reactivity | Corrosion | **Results**

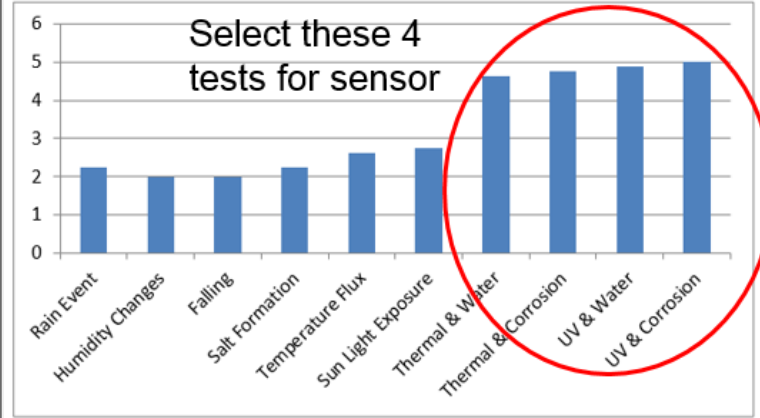
The goal of this graph is to help show you the types of tests that you will want to consider based on the answers to the other tabs in this section. This list is by no means exhaustive to all the tests that could be done, but more or less represents the general tests that one should consider. If you are still having trouble deciding which tests to move forward with, try clicking the button below for a decision tool which incorporates factors such as cost and time.



**Test Selection Tool**

	Weight
Duration	0.125
Magnitude	0.5
Cost	0.25
Expertise	0.125
<b>SUM:</b>	<b>1</b>

Name of Test	Selected
Submersion	N
Rain Event	Y
Humidity Changes	Y
Washing	N
Sun Light Exposure	Y
Light Cycling	N
Temperature Flux	Y
Drying	N
Temperature Elevation	N
Temperature Reduction	N
Matrix Decomposition	N
Scratching	N
Surface Sawing	N
Surface Sanding	N
Cutting	N
Drilling	N
Sandblasting	N
Physical Agitation	N
Compression	N
Falling	Y
Grinding	N
Burning	N
Cleanline Agents	N



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# Number of test materials

## PRIMARY TEST MATERIALS

1. CNT ink
2. Printed CNT sensor (CNTs exposed)
3. Actual humidity sensor product (CNTs encapsulated)

## SECONDARY consideration

- § Silver ink (used to encapsulate the CNTs). Not specifically nano but Ag+ release will be monitored



*"So if this world starts getting you down  
There's room enough for ~~two~~ (3 replicates),  
**UP ON THE ROOF"***

*-- The Drifters*



# Acknowledgments, POCs, questions



## ACKNOWLEDGMENTS

§ U.S. Army Environmental Quality and Installations Research Program, Elizabeth Ferguson, Technical Director



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ERDC Nano: <http://el.erd.c.usace.army.mil/nano/index.html>

ERDC NanoExPERT: <https://nanoexpert.usace.army.mil/>

ERDC Video demos: [http://www.youtube.com/channel/UCe3wh\\_zmg3FATb5bcwnew](http://www.youtube.com/channel/UCe3wh_zmg3FATb5bcwnew)

ERDC Environmental Laboratory: <http://el.erd.c.usace.army.mil/index.cfm>



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# Point of Contact

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§ 601-634-3344



# Brainstorming materials

NanoGRID

NanoNAVPAL

[https://drive.google.com/open?id=0Bw\\_7gDKP9Oj1T21XSjRLRnBkVXM](https://drive.google.com/open?id=0Bw_7gDKP9Oj1T21XSjRLRnBkVXM)

