Comprehensive Environmental Assessment of Engineered Aluminum Nanoparticles in DoD Materiel: Evaluation before Acquisition

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Stages of Acquisition Process Benefiting from Environmental Hazard Assessment

- **A**. Analyze Concept
- **B**. Begin Development
- **C**. Commitment to Rapid Acquisition

**Milestones**
- Concept Decision
- Begin Systems Acquisition
- System Integration
- System Demonstration
- Design Readiness Review
- FRP Decision Review
- Full-Rate Production & Deployment
- Sustainment & Maintenance

**Technologies**
- Pre-Systems Acquisition
- Systems Acquisition
- Sustainment & Maintenance

Technology development and acquisitions process. Adapted from Mike McDevitt, Installations Management Command.
It is estimated that over 85% of the costs of technology occur after systems acquisition.
Comprehensive Environmental Assessment (CEA)

Adapted from Davis, 2007
CEA Process

- **Identify the question(s)**
  - Sources
  - Life cycle stages, fate & transport, matrices, exposure, effects
  - Developed methods and standardized protocols

- **Obtain diverse perspectives**
  - ODUSD Chemical & Material Risk Management
  - NNCO National Nanotechnology Coordination Office
  - ARMY - ARDEC, Army Institute of Public Health, ERDC
  - Navy - NSWC-IHD
  - Air Force - Air Force Laboratory Human Effectiveness Directorate

- **Use collective judgment method**

Adapted from Davis, 2007
ERDC CEA Case Study: Engineered Aluminum Nanoparticles
Applying CEA approach to nanotechnology in the R&D Phase

- Lack of mature industries
- Data lacking or evolving
- Characterization of materials
- Uncertainty is high
- Identify and prioritize knowledge gaps
CEA: **Life Cycle Stages** of nano-Al

![Diagram showing comprehensive environmental assessment with life cycle stages, environmental pathways, fate and transport, exposure and dose, and effects.](image)

- **Life Cycle Stages**: Feedstocks, Manufacture, Distribution, Storage, Use, Disposal
- **Environmental Pathways**: Air, Water, Soil
- **Fate & Transport**: Primary contaminants, Secondary contaminants
- **Exposure - Dose**: Biota, Human populations
- **Effects**: Ecosystems, Human Health
- Analytical methods development and application
Site Visit: ARDEC Picatinny Arsenal Nanotechnology Research Center

- Operates North America’s largest Radiofrequency (RF) Induction Plasma reactor (Tekna Plasma Systems) pilot plant for nano-Al and high performance nonmaterial:
  - Plasma Synthesis
  - 10 micron aluminum powder feedstock
  - Use of nano-aluminum still in the R&D phase
  - Characterization FE-SEM, XRD, XRF, XRD, BET, Thermal analysis
CEA: **Life Cycle Stages – Feedstocks**

- Powder feeder system introduces 10 micron aluminum powder.
- Plasma system combines “top down” and “bottom up” process, solid precursor vaporized and quenched enabling synthesis of nano-Al.
- Feedstock is aluminum oxide passivated in situ with an approximately 5 nm oxide coating.
- Nano-scale powder collected in stainless steel canister inside glove box.
Picatinny Arsenal Nanotechnology Research Center maintains two 300kiloWatt RF Tekna Plasma Systems:

- Metals and metal oxides
- Ceramics

- Cyclone classifier separates product by size, nano-scale powder is collected in a collection chamber under argon

- Synthesis efficiency is 10:1 nanopowder to aggregates, aggregates are stored for research purposes
CEA: Life Cycle Stages – manufacture

- HEPA filtered fan with 100 cfm exhaust hood, hydrogen sensors in enclosure to detect leaks

- Reactor process capacity of 4hrs per day with 4 hours remaining to rapidly characterize product FE-SEM, XRD, XRF, XRD, BET, Thermal Analysis, etc.
**CEA: Life Cycle Stages – distribution and storage**

- Use of nano-aluminum still in the R&D phase
- Stored under inert atmosphere
- Aggregates are stored at the facility (still have research value),
- Current synthesis of 200g batches for rapid characterization
- Stability studies indicate no loss in surface area, however a 20% loss in reactivity due to oxygen diffusion
CEA: **Environmental Pathways** of nano-Al

![Diagram](image)

- **Comprehensive Environmental Assessment**
  - **Life Cycle Stages**
    - Feedstocks
    - Manufacture
    - Distribution
    - Storage
    - Use
    - Disposal
  - **Environmental Pathways**
    - Air
    - Water
    - Soil
    - Primary contaminants
    - Secondary contaminants
  - **Fate & Transport**
  - **Exposure – Dose**
    - Biota
    - Human populations
  - **Effects**
    - Ecosystems
    - Human Health

- Analytical methods development and application
CEA: Environmental Pathways of nano-Al

Technology development and use for nanoaluminum

- **Research and Development**
  - **Material Feedstock**
    - Al powder
    - Al solutions
  - **Production**
    - Material
    - Byproducts
    - Waste/emissions
  - **Distribution**
    - Storage
    - Spills
    - Shipping
  - **Deployment**
    - Ignition
    - Propellants
    - Additives
  - **End of Use**
    - Demilitarization
    - Recycling
    - Disposal

- **Pathways**
  - **Air**
    - Inhalation
    - Deposition
  - **Water**
    - Ingestion
    - Contact
  - **Soil**
    - Ingestion
    - Contact

- **Receptors**
  - **Human**
    - Soldier
    - Worker
    - Public
  - **Eco-Terrestrial**
    - Wildlife
    - Birds
    - Plants
  - **Eco-Aquatic**
    - Wildlife
    - Fish
    - Plants
### CEA: Fate and Transport of nano-Al

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**Analytical methods development and application**
CEA: Fate and Transport of nano-Al

- Particle size dictates oxidation potential
- Nano-Al/ Al$_2$O$_3$ interacts with soil, water, and strongly with humic acids
- Highly agglomerates affects mobility in soil
- Surface charge changes with leachate alters mobility
- Micron-sized Al$_2$O$_3$ has greater sorption than nano-Al$_2$O$_3$
CEA: **Exposure-Dose of nano-Al**
CEA: Exposure-Dose
% content of nano-Al

Plot of extinction values for Al triangular prisms (Faber et al. 2008)
CEA: Exposure-Dose of nano-Al

Most likely routes of nano-Al/Al₂O₃ exposure: Inhalation > Dermal > Internal (oral, ip, iv)

- ARDEC-NIOSH collaborative framework "Nano-powder Synthesis & Associated Safety Precautions at ARDEC"

TWA and other occupational exposure values?

R&D laboratory evaluations of occupational exposures?
CEA: Effects of nano-Al
CEA: Problems with Effects of nano-Al

- Nano-Al/Al₂O₃ is highly agglomerated
- Is aged nano-Al the same as nano-Al₂O₃?

Increased Oxidation

Nano-Al

Nano-Al₂O₃

Nano-Al
CEA: Effects of nano-Al

Ecosystems:
- Less toxic to daphnids and algae than other NPs
- More toxic to juvenile zebrafish than adults
- Causes atherothrombotic events in zebrafish
- Produces differential effects on benthic organisms
- Mildly toxic to bacteria
- Mildly phytotoxic (root growth inhibition) due to ROS
- Soil nematodes and earthworm reproduction negatively affected
CEA: Effects of nano-Al

Human Health:

1. Inhalation –
   Negatively affects alveolar macrophages function

2. Dermal –
   Dermal contact may increase proinflammation, dermatitis

3. Internal –
   Neurotoxicity (blood brain barrier disruption) and
   Increased genotoxicity
**Preliminary Conclusions**

- Potential sources and releases of nano-Al to the environment that will likely occur through air, water, or soil exposures through the production, use, and disposal of nano-Al propellants, igniters, and additives.

- However, these preliminary findings are the result of an assessment from the R&D community.

- Data collection is still required to gain a better understanding of the future deployment and handling of nano-Al as a military technology.
Data Gaps / Moving Forward

- **Life Cycle:** Further collaboration required within the R&D community such as ARDEC, NSWC-IHD, and AFRL to discuss life cycle phases.

- **Environmental Pathways:** This is a potential laboratory and field research project (modeling and hyperspectral imaging analysis for nano-Al/energetic combustion analyses)

- **Exposure:** Exposure to biota and humans is perhaps the biggest area of uncertainty in this entire nano-Al CEA.

- **Environmental Fate:** Once nano-Al has moved beyond the R&D phase, field testing will be imperative to study nano-Al/Al2O3 propellants and energetics in the field.

- **Effects:** Data needs to reflect of actual particle sizes, i.e., nanoparticle agglomerates vs. monodispersed nanoparticles.
Questions?
References


Faber, Benjamin J., Schatz, George C., and Camden, Jon P. Electrodynamics Calculations of SMSERS Active Junctions and New UV Active Subtrates. Nanoscape Vol. 5: 41-51


Critical review and advising from Dr. Mike Davis, Senior Science Advisor, U.S. EPA and Dr. Thomas Seager, Professor, University of Arizona