Potential Inhalation Hazards in Additive Manufacturing

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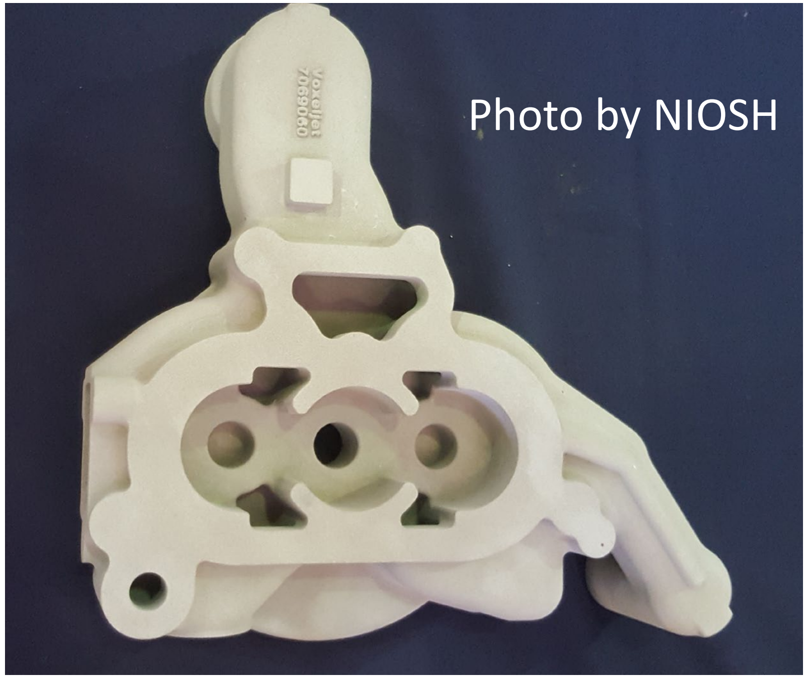
March 16, 2022

Outline

- Overview of additive manufacturing (AM)
- Types of AM processes
    - Principles of operation
    - Feedstocks
    - Inhalation hazards



What is AM?

- Umbrella term
  - Use computer file to control the building of a part
  - Join feedstock material
  - Often using layer-by-layer methodologies

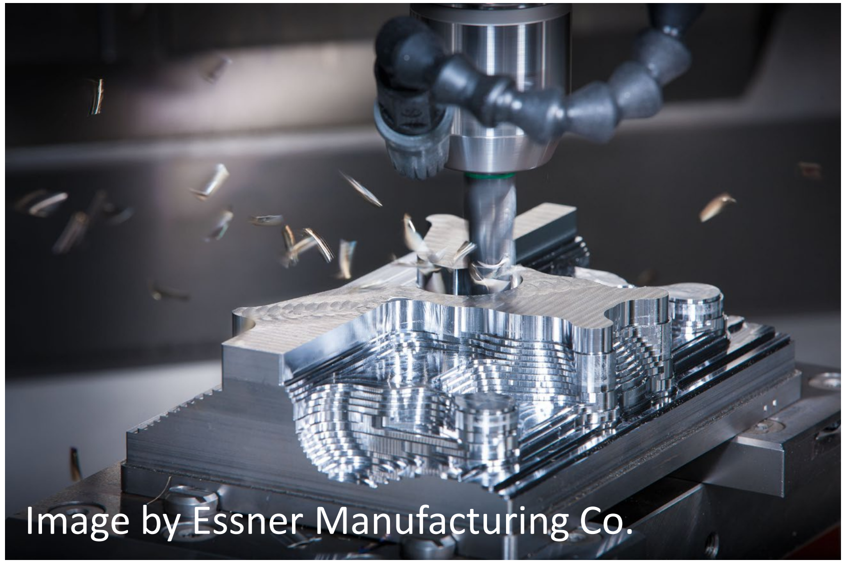
- AM technically different from 3-D printing

Additive manufacturing

- Add only wanted material

Subtractive manufacturing

- Remove all unwanted material



- Construct previously impossible parts
- Reduced waste (maybe)
- Increased supply chain efficiencies
- Less environmental impact

Who is using AM?

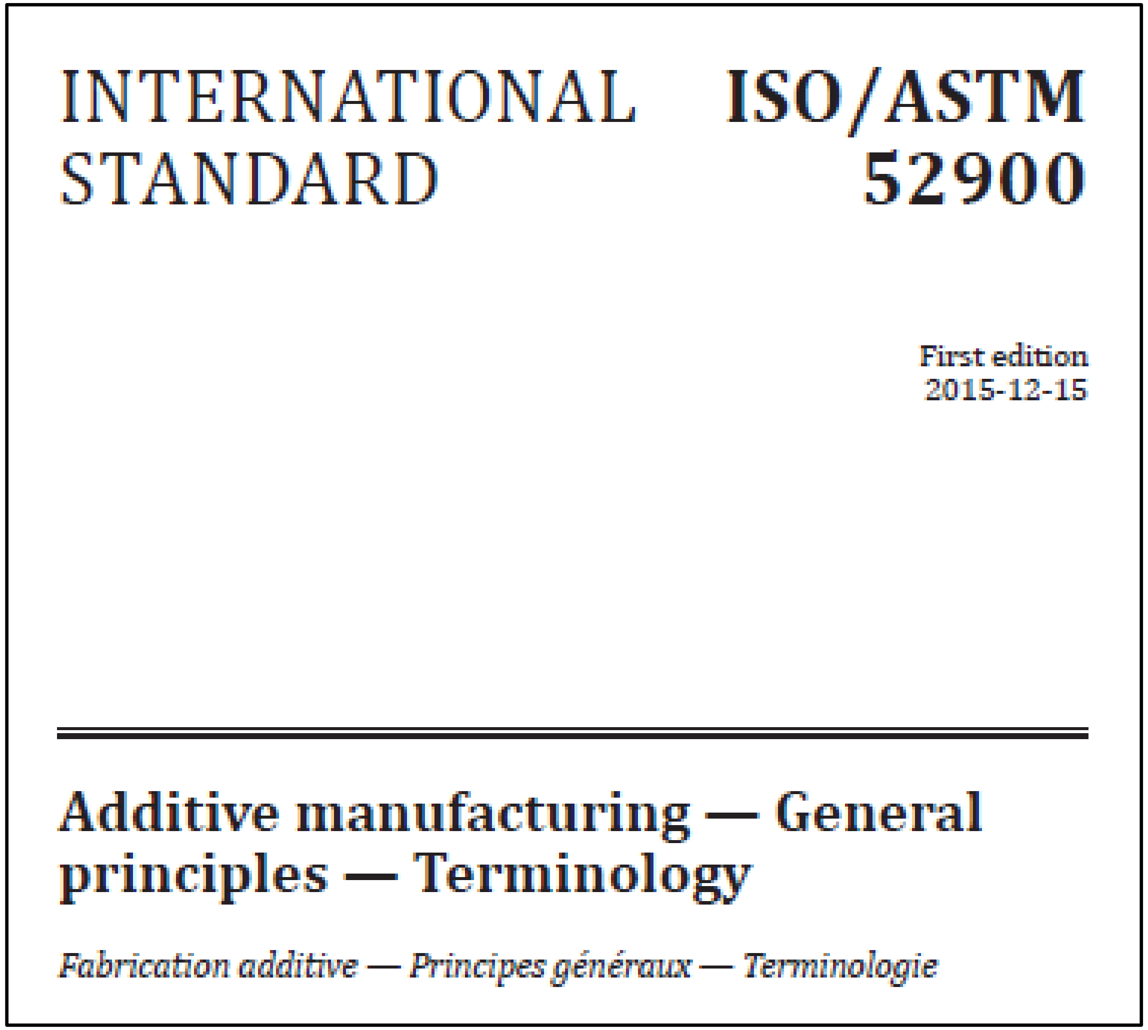
- Top users of AM technologies
  - Automotive (19.5%): tool prototypes and custom parts
  - Medical (15.1%): hearing aids, prosthetic limbs and dental devices
  - Aerospace (12.1%): lightweight parts

- U.S. accounts for approx. 40% of AM systems installed globally

- AM processes that use metals
  - Highest projected market growth

AM Process Categories

- Material extrusion
- Vat photopolymerization
- Material jetting
- Powder bed fusion
- Binder jetting
- Sheet lamination
- Directed energy deposition



INTERNATIONAL STANDARD

ISO/ASTM 52900

First edition
2015-12-15

Additive manufacturing — General principles — Terminology

Fabrication additive — Principes généraux — Terminologie

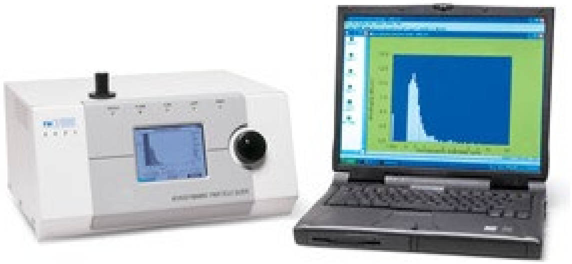
Aerosol emissions characterization

CPC #/cm^3
(10 or 20 nm – 1 µm)

TSI Inc.

TSI Inc.

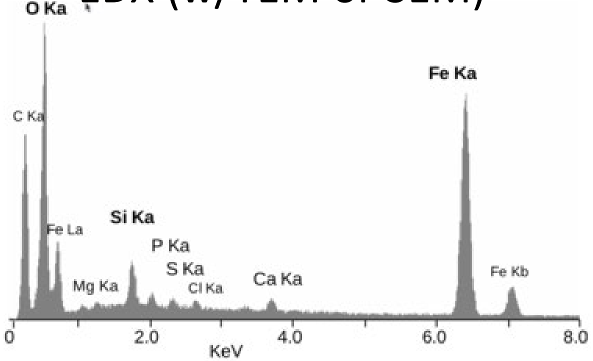
FMPS size and #/cm^3
(5.6 – 560 nm)



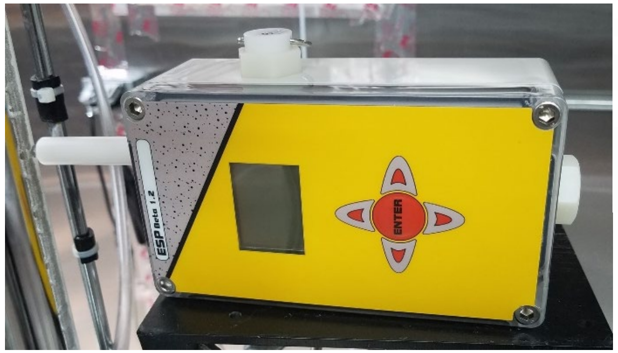
TSI Inc.

APS size and #/cm^3
(0.5 – 20 µm)

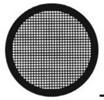
EDX (w/TEM or SEM)



TEM



ESP



Grid

Ted Pella Inc.

Perkin Elmer.

ICP-MS

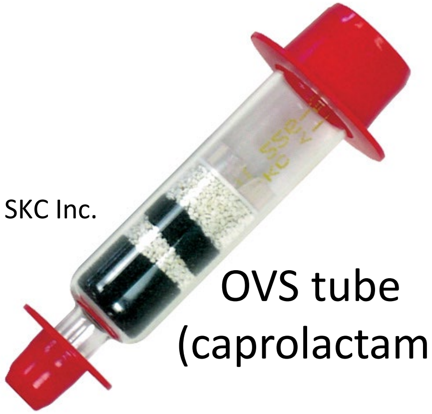
SKC Inc.

Cassette and filter

SEM

VOC emissions characterization

TVOC
(IP <10.6 mV)



SKC Inc.

OVS tube
(caprolactam)

Perkin Elmer

TD tube
(individual VOCs

Agilent Inc.

GC-MS
(identification/quantification
of individual VOCs)

SKC Inc.

Sorbent tube
(acrylates)

SKC Inc.

Impingers
(carbonyls)

Entech

Evacuated canister
(individual VOCs)

Material Extrusion

- Material selectively dispensed by nozzle
    - Includes 3-D printing

- Thermoplastics (filament or pellets)
    - Acrylonitrile butadiene styrene (ABS)
    - Polylactic acid (PLA)
    - Polycarbonate (PC)
    - Etc.

<u>May contain additives</u>

Engineered nanomaterials

Flame retardants

Metals

Ceramics

Material Extrusion

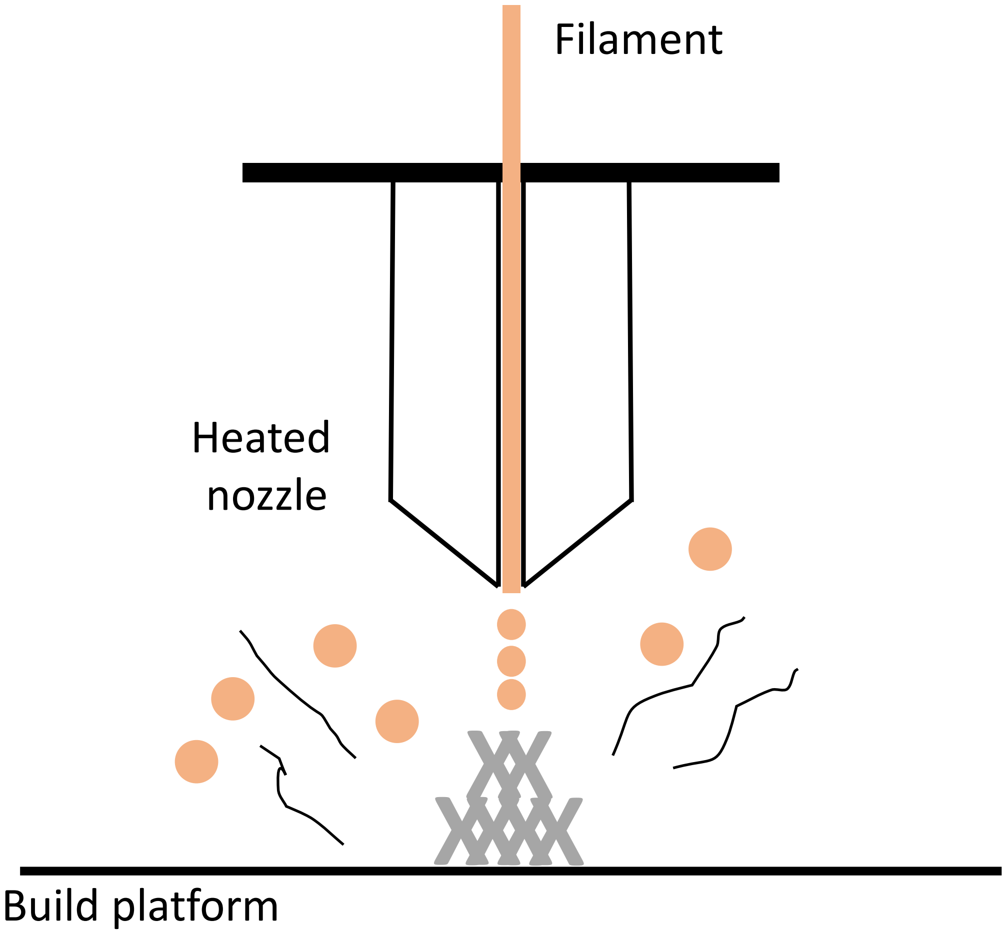
Desktop “3D” printer

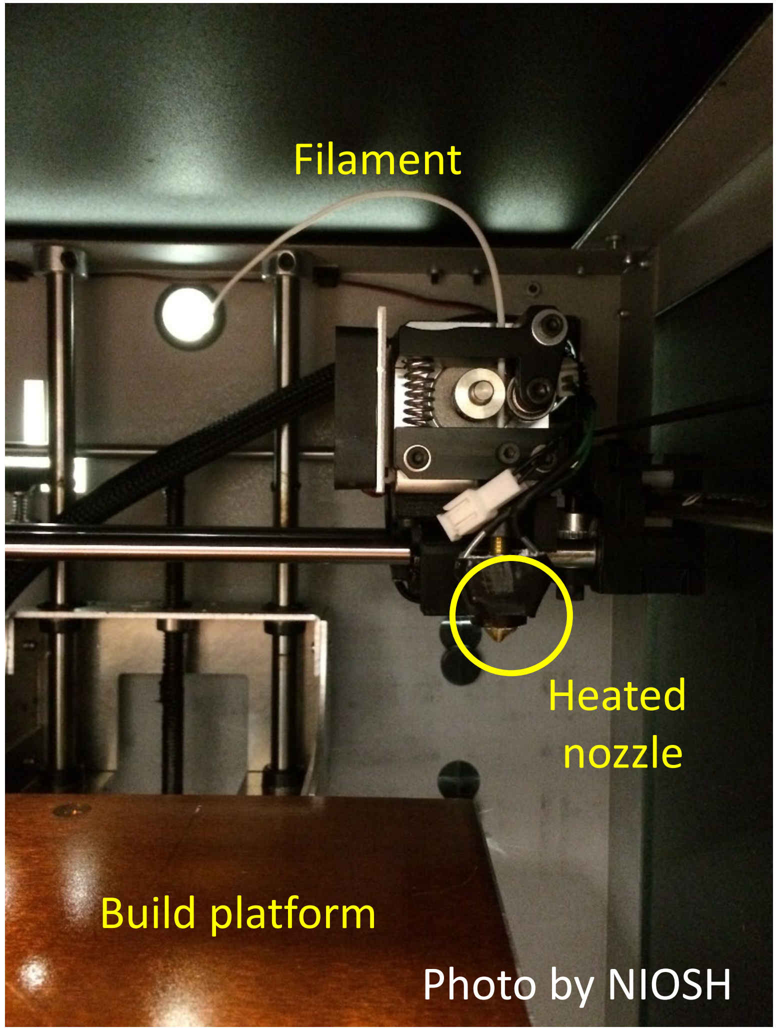
Industrial FDM™ printer

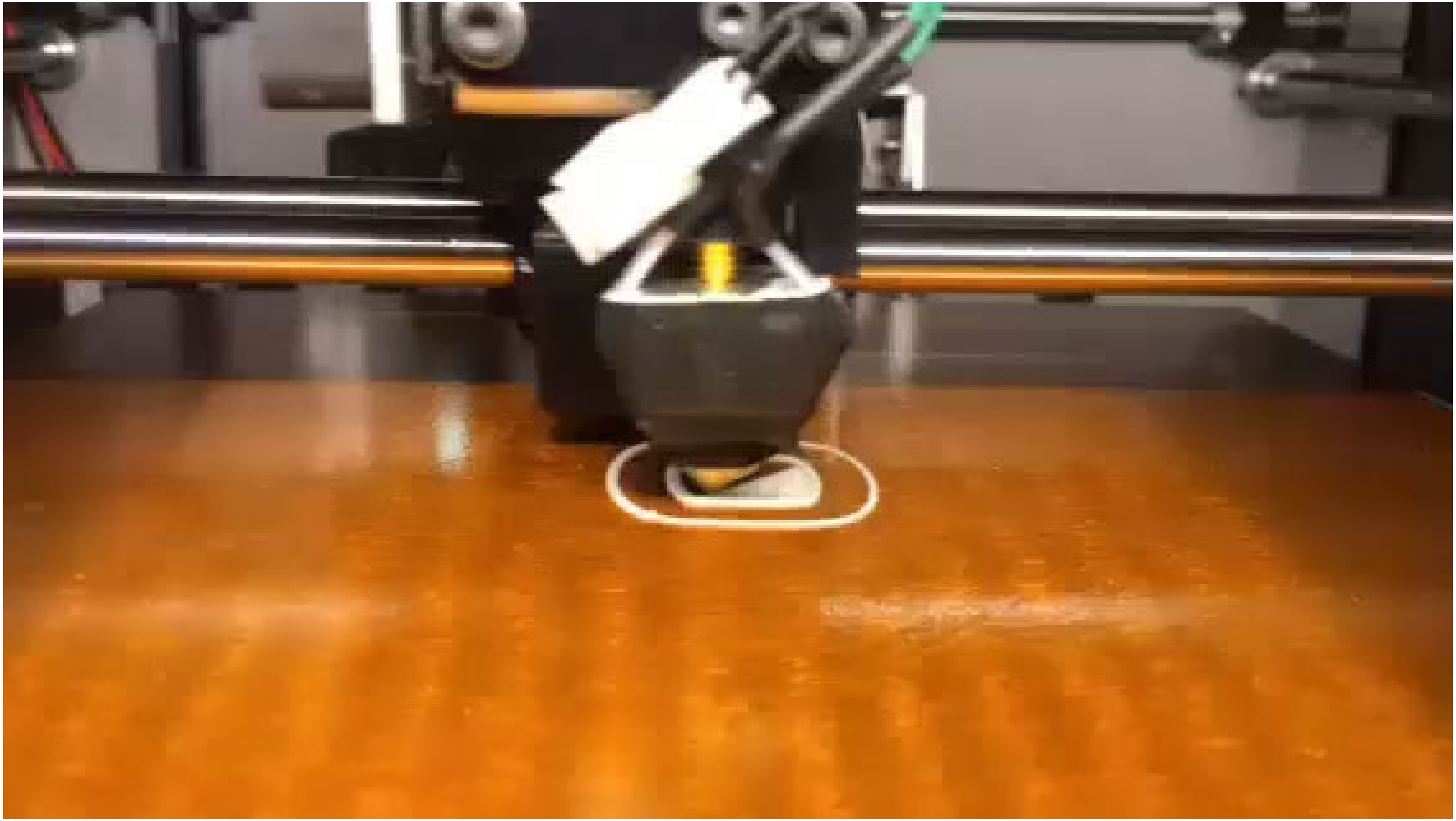
Large format printer

All photos by NIOSH

Material Extrusion



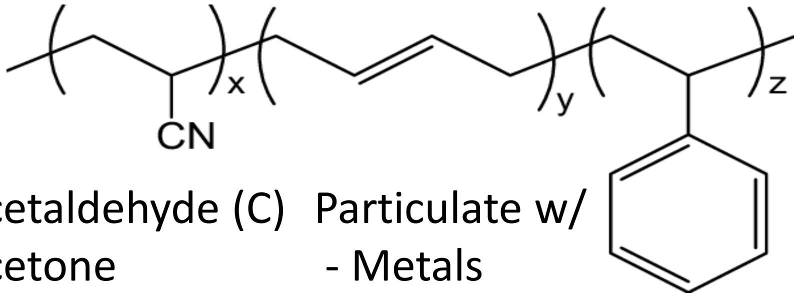




Material Extrusion

- Factors influencing emissions
  - Printer design
  - Print parameters (speed, resolution, raft, etc.)
  - Thermoplastic characteristics (brand, color, infill, **type**)

Acrylonitrile butadiene styrene (ABS)



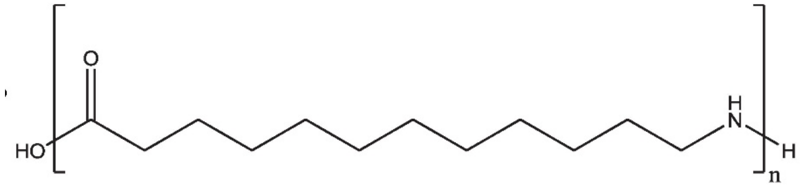
Acetaldehyde (C)
Acetone
Benzene (C)
1-butanol
Formaldehyde (C)

Particulate w/
- Metals
- Bisphenol-A (ED)
- Caprolactam

Styrene
Toluene

C = carcinogen, ED = endocrine disruptor

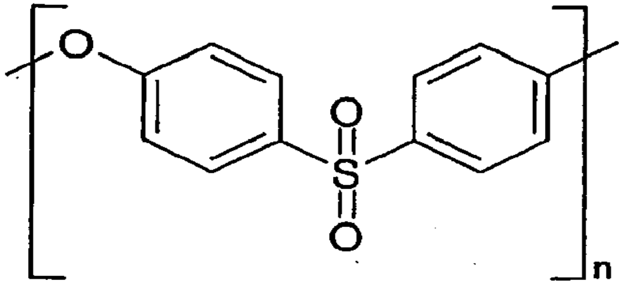
Polyamide (nylon)-12



Acetaldehyde (C)
Acetophenone
Benzaldehyde
Caprolactam
Cyclopentanone
Decanal
Formaldehyde (C)

Lactide
Nonanal
Octanal
Pentanal
Particulate
Styrene
Toluene

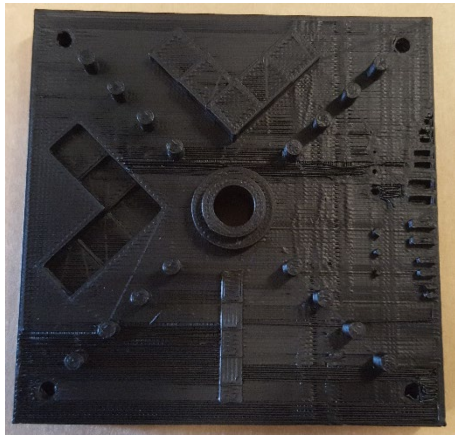
Polyethersulfone (PESU)



Benzene (C)
Chlorobenzene
Dibenzofuran
Phenol
Particulate
SO_2

Material extrusion 3D printers – filament additives

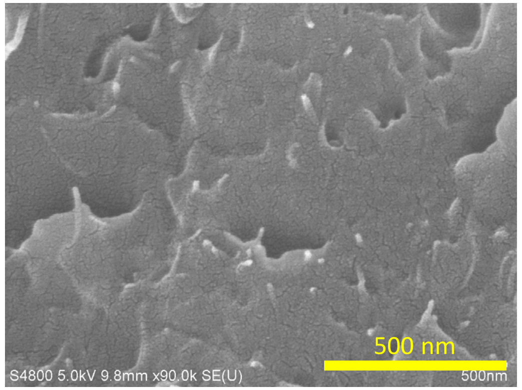
- Desktop 3D printer in 12.85 m^3 chamber
- Three types of filament
  - ABS
  - PLA
  - PC
- Two types
  - Base polymer
  - With carbon nanotubes (CNTs)
- Identical print job (NIST artifact)



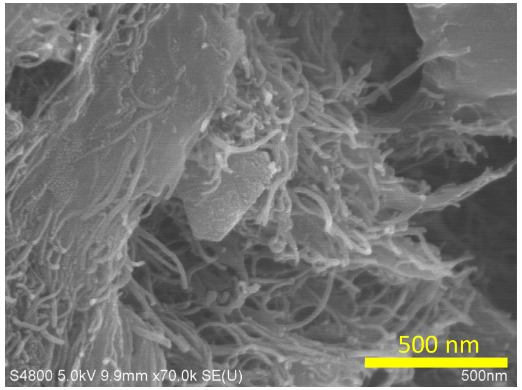
Printed object (10 x 10 cm)

Stefaniak et al. (2018)

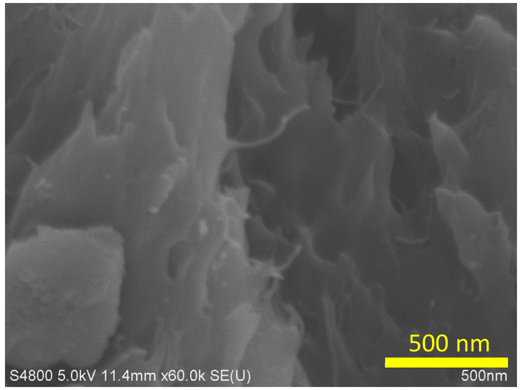
ABS_{CNT}



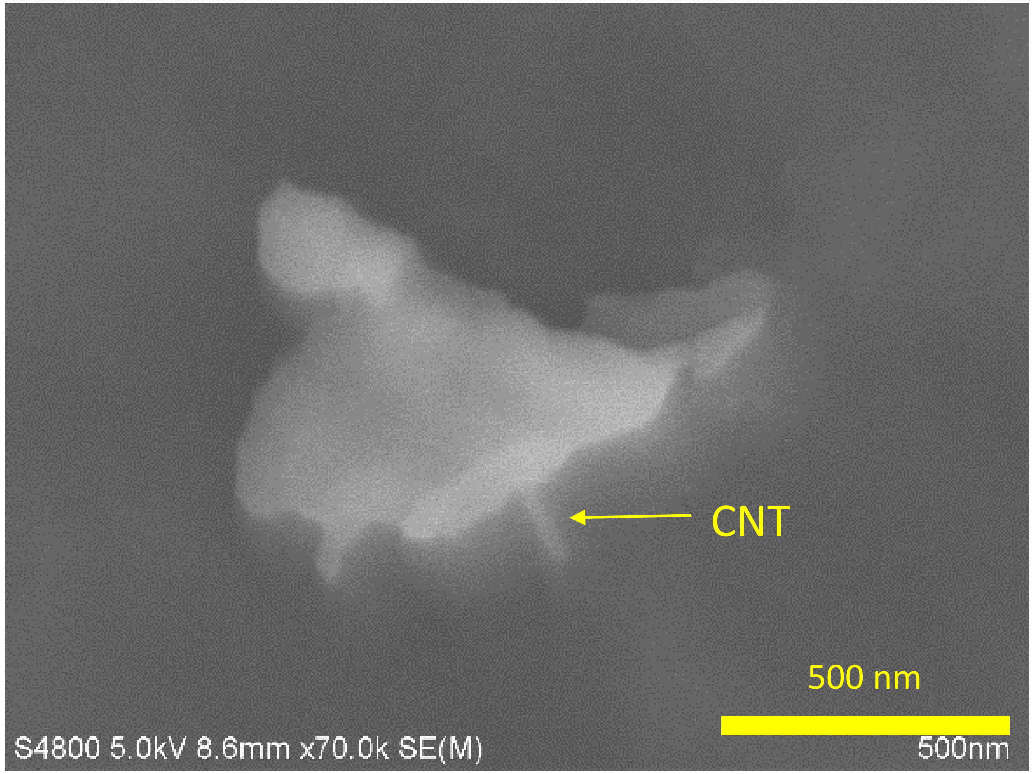
PLA_{CNT}



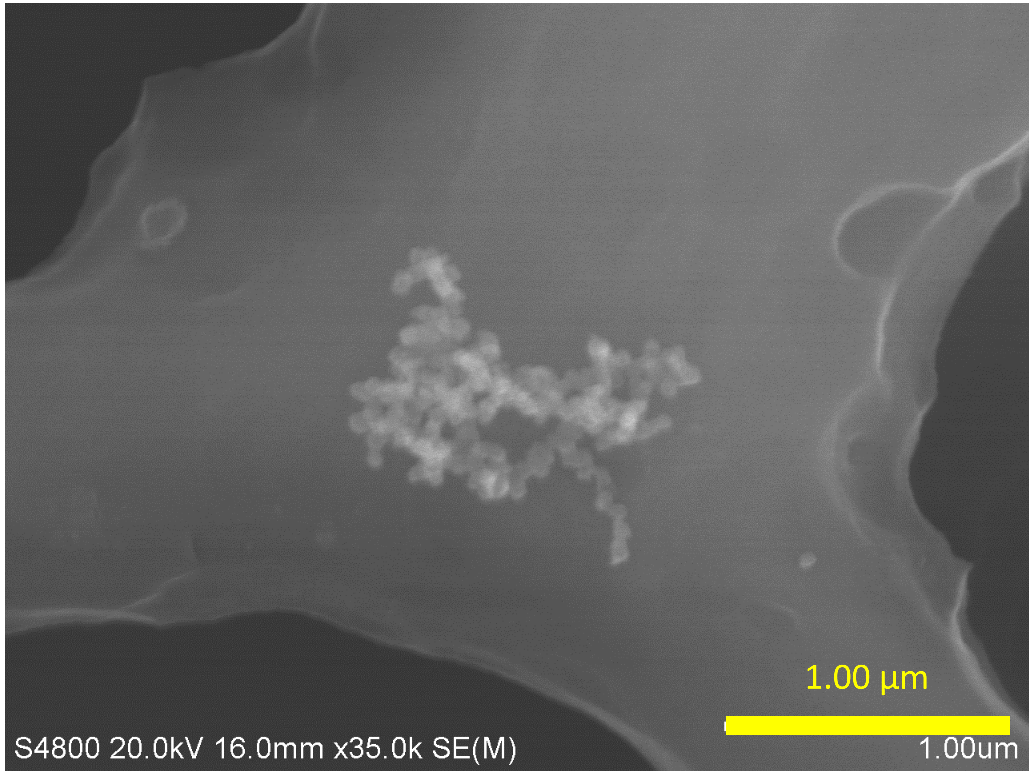
PC_{CNT}



Material extrusion 3D printers – filament additives



Particle emitted while printing with PLA_{CNT}



Particle emitted while printing with base PLA

Stefaniak et al. (submitted)

Vat Photopolymerization

- Liquid photopolymer selectively cured by light
  - Stereolithography (SLA) – laser
  - Digital light processing (DLP) – multi-wavelength light
  - Liquid crystal display (LCD) – UV light

- Photopolymer resins
  - Binders
  - Monomers
  - Photoinitiators

<u>May contain additives</u>

Engineered nanomaterials
Flame retardants
Metals
Ceramics

Photo by NIOSH

Vat Photopolymerization


Photo by NIOSH

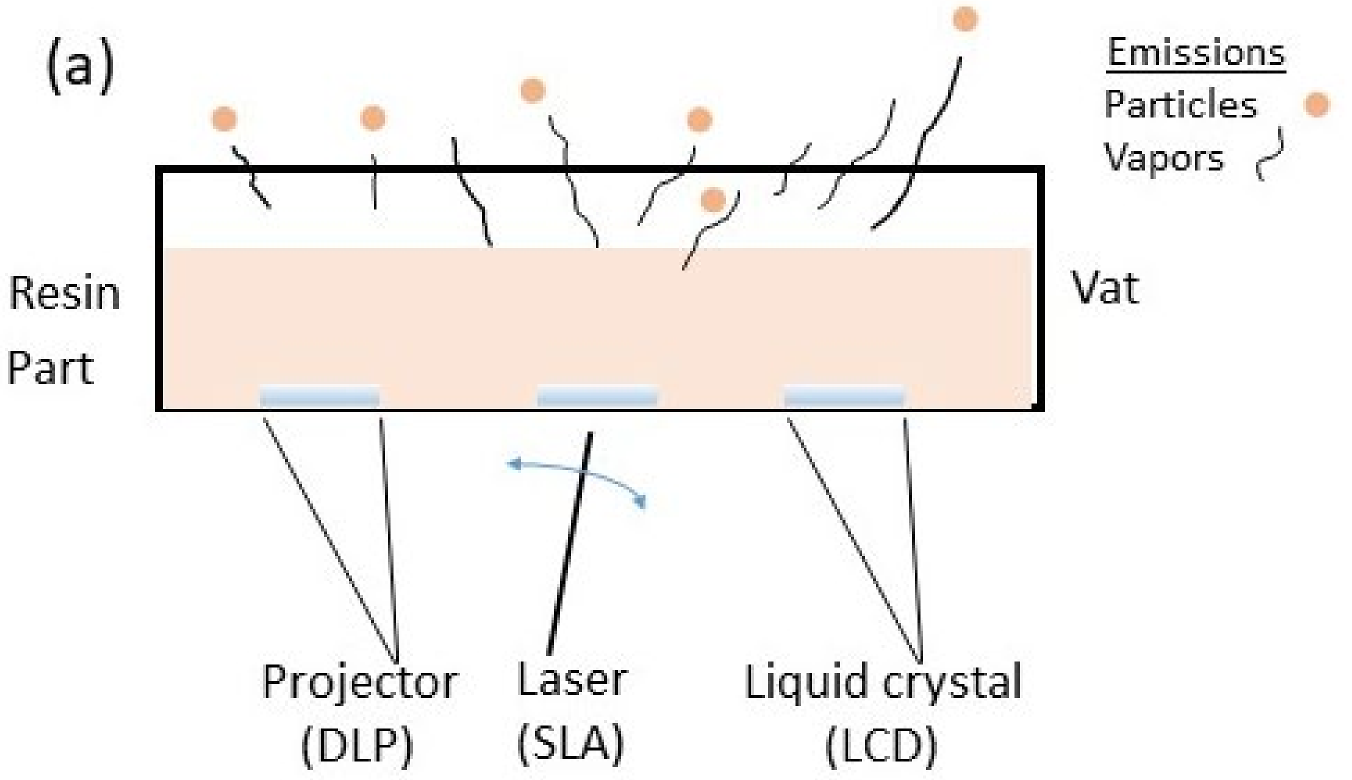
Desktop vat printer

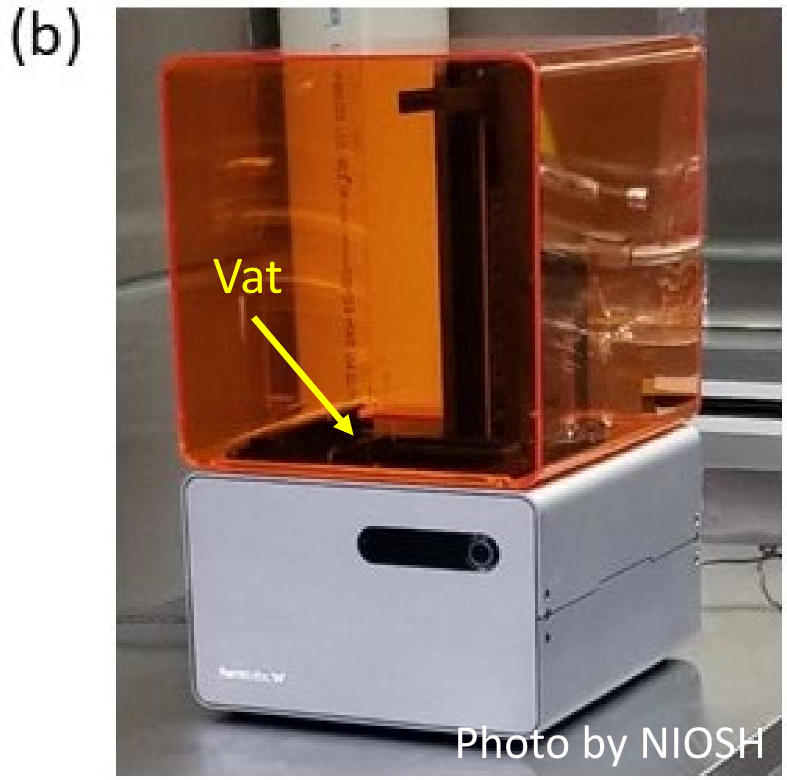
Photo by 3DPrinterOS.com

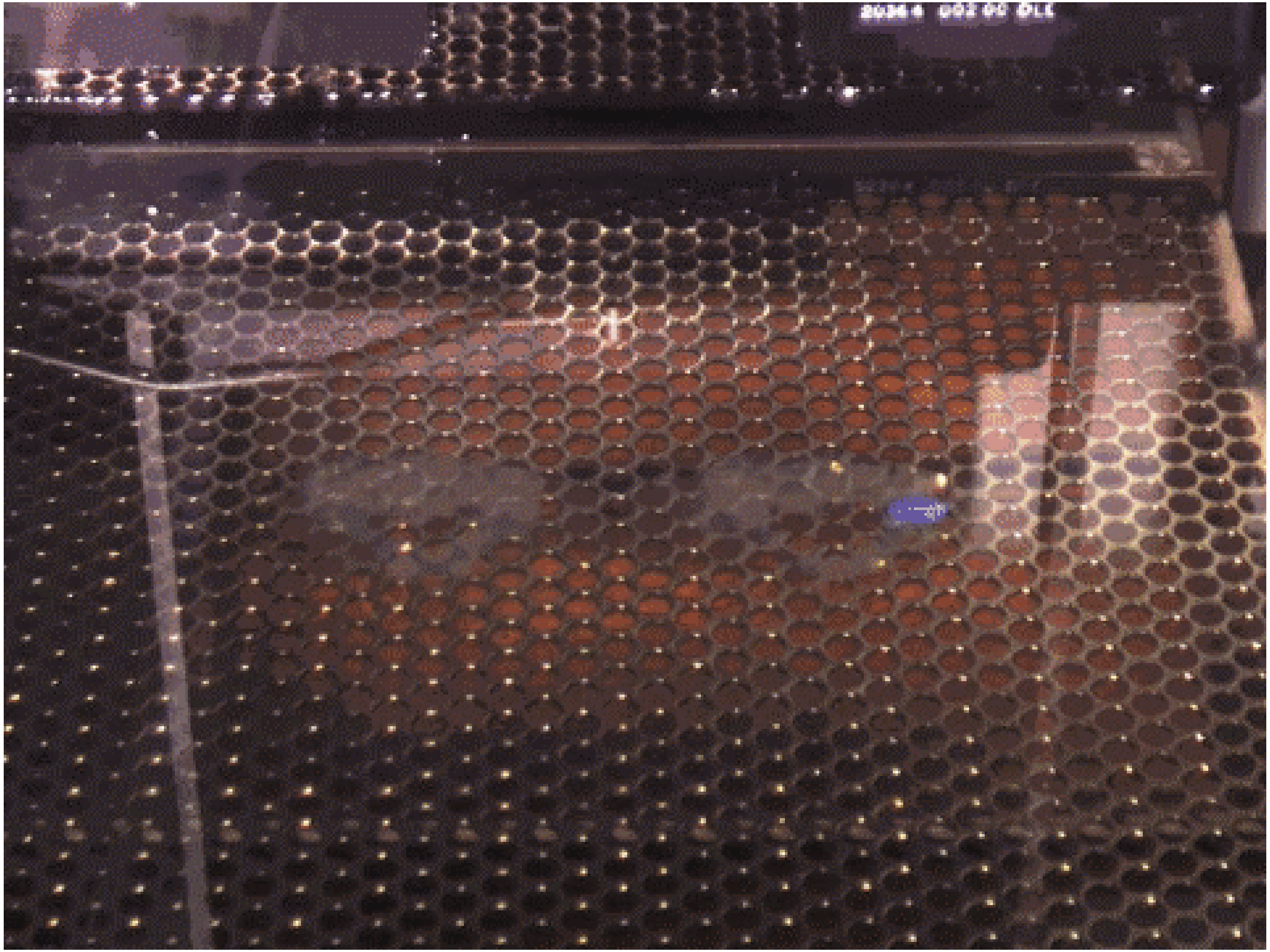
Photo by Morgridge Institute for Research

Industrial vat printers

Vat Photopolymerization







Vat Photopolymerization

- Factors influencing emissions
  - **Printer technology**
  - Resin (color)

Stefaniak et al. J Occup Environ Hyg. (2019)

3-D Printer	Type	# <1 µm/g printed	# 5.6 to 560 nm/g printed	µg TVOC/g printed
Form 1+	SLA	$2.7 \pm 1.6 \times 10^8$	$1.3 \pm 0.2 \times 10^{10}$	277.1±81.5
Pegasus Touch	SLA	$1.3 \pm 0.3 \times 10^8$	$7.6 \pm 0.9 \times 10^9$	160.7±47.4
Nobel 1.0A	SLA	$2.8 \pm 2.6 \times 10^8$	$2.1 \pm 0.9 \times 10^{10}$	321.7±228.7
Titan 1	DLP	$9.2 \pm 3.0 \times 10^8$	$4.0 \pm 1.2 \times 10^{10}$	1280.5±313.3
M-One	DLP	$3.3 \pm 1.5 \times 10^8$	$1.1 \pm 0.3 \times 10^{10}$	1931.2 ±234.4

Vat photopolymerization (VP)

- Freiser et al. (2018) personal exposures to VOCs using passive badges
  - High-speed surgical drilling of temporal bone models
    - Only isopropyl alcohol detected at 590 µg/m^3 (NIOSH REL = 980,000 µg/m^3)
- Yang and Li (2018) monitored TVOC using a PID
  - Printer on but not operating = 123 µg/m^3
  - Printing = 1053 µg/m^3
  - Post-process UV-curing and ethanol cleaning = 1774 µg/m^3 (peak = 6177 µg/m^3)
- Väisänen et al. (2019) monitored VOCs using sorbent tubes with Tenax TA®
  - TVOC (as the sum of individual VOCs)
    - Printing = 427 µg/m^3 (peak)
    - Post-process washing with isopropyl alcohol = 11,000 µg/m^3
- Zisook et al. (2020) monitored VOCs using evacuated canisters
  - During printing only isopropyl alcohol exceeded background

Material Jetting

- Droplets of build material selectively deposited in a pattern

- Photopolymer resins
  - Flexible
  - Many colors

<u>May contain additives</u>

Engineered nanomaterials
Flame retardants
Metals
Ceramics
Etc.

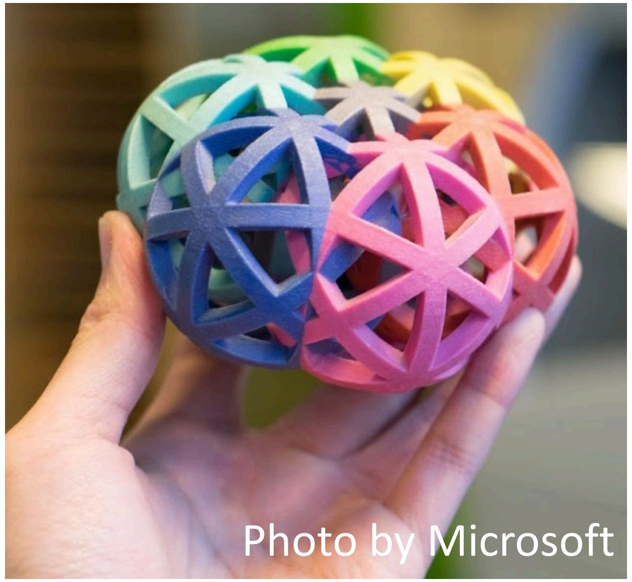


Photo by Microsoft

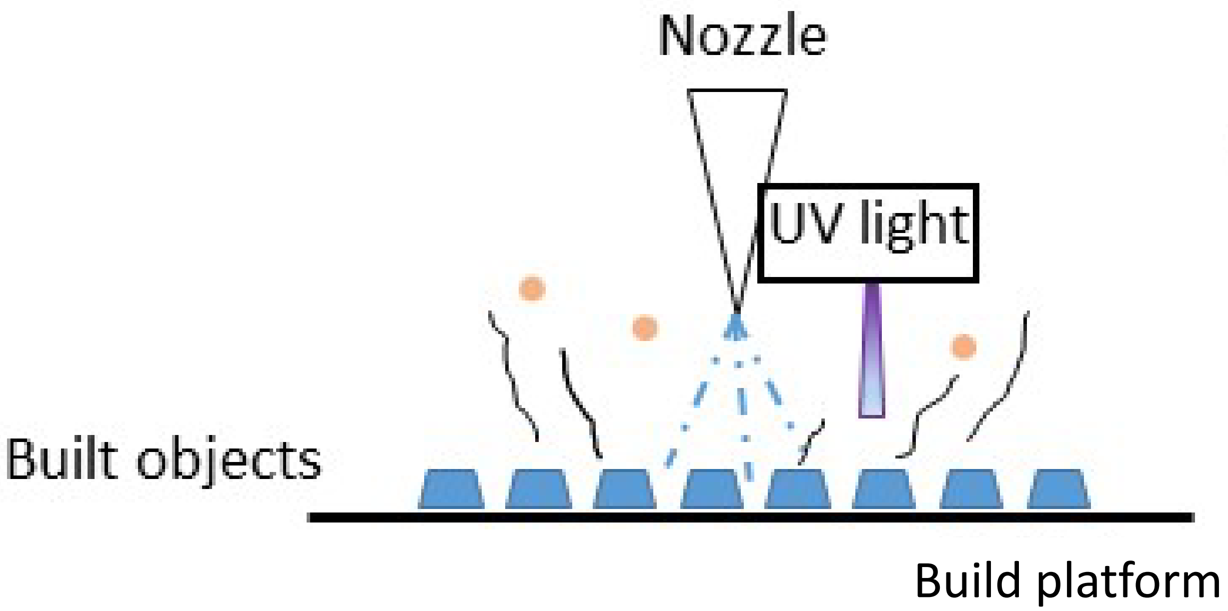
Photo by Computer Aided Technology Store

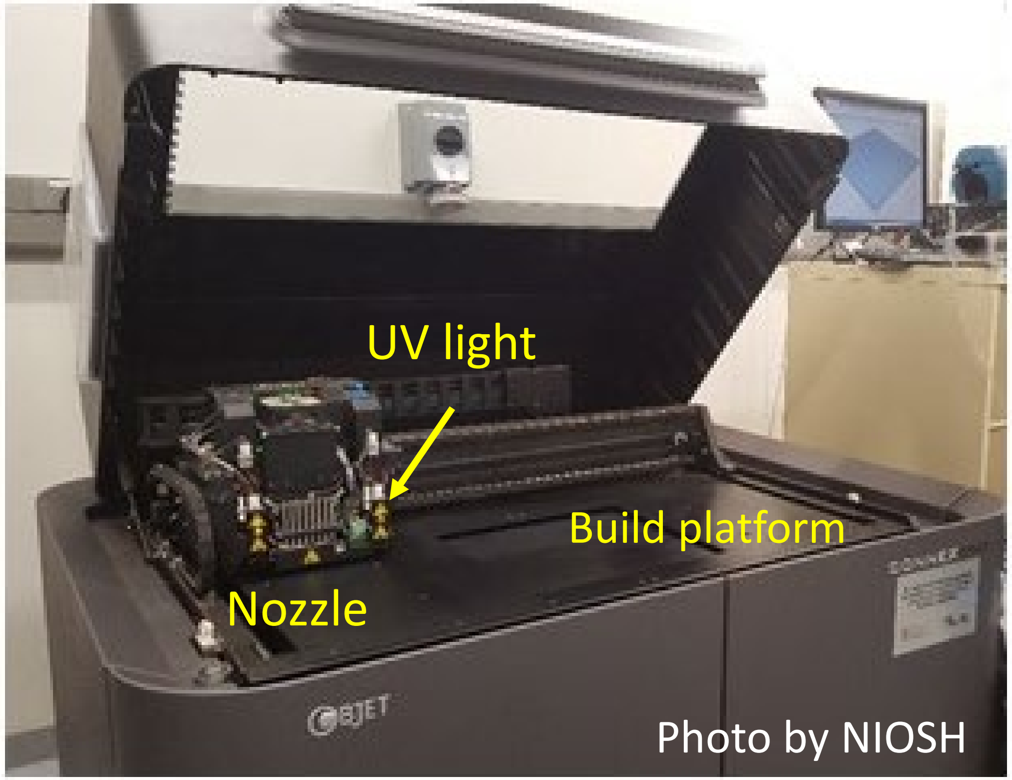
Material Jetting

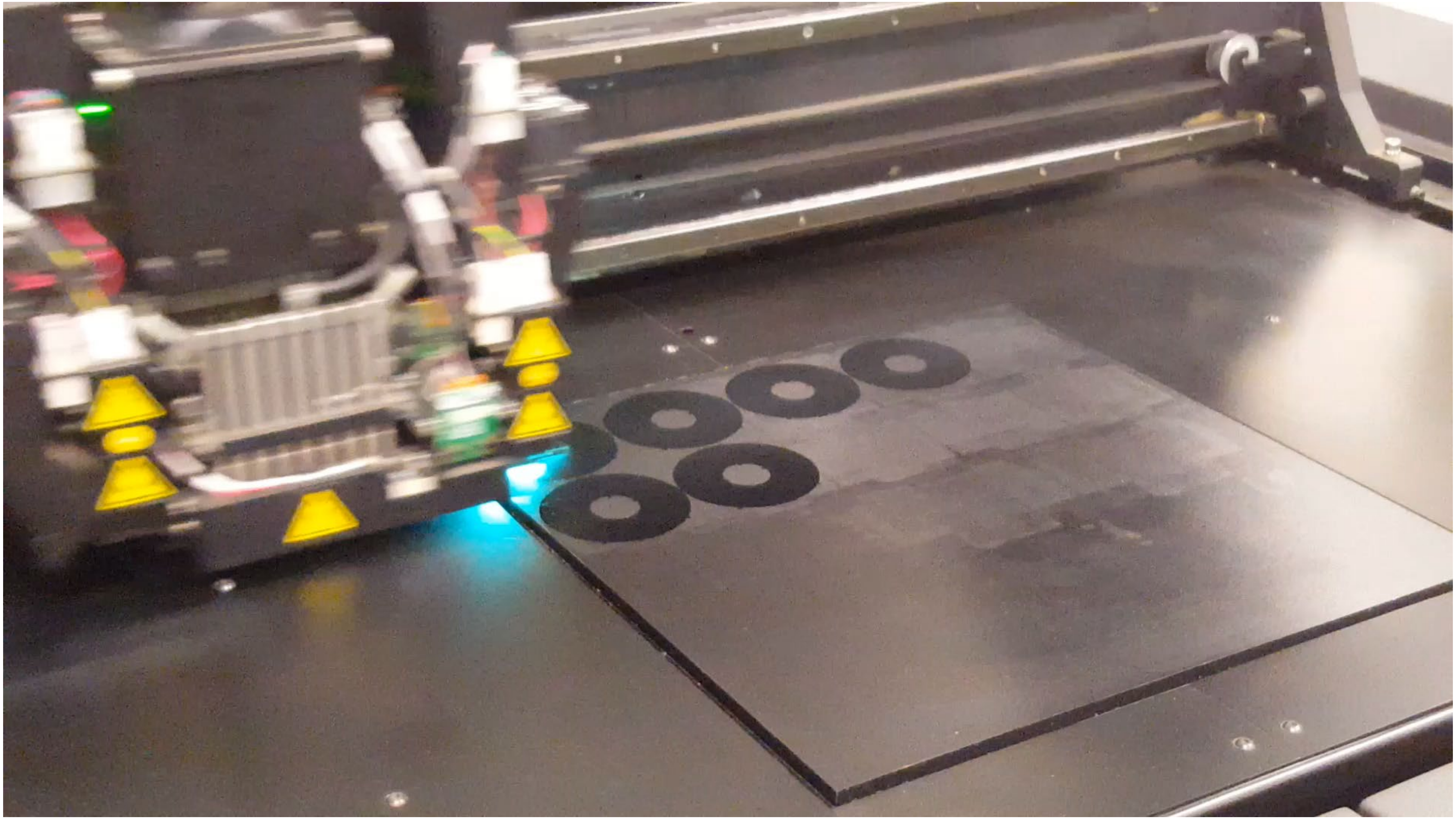
Industrial material jetting printers

All photos by Stratasys

Material Jetting







Material jetting (MJ)

- Ryan & Hubbard (2016) sampled inside a printer enclosure (evacuated canisters)
  - Acetone, n-butanone, 2-butanone, 1,4-dioxane, ethanol, isopropyl alcohol, and toluene

- Stefaniak et al. (2019) monitored TVOCs using a PID and individual VOCs using passive badges
  - TVOC emission rates ERs were 4.5×10^4 µg (lid closed) to 2.5×10^4 µg TVOC/min (lid open) and were not influenced by the lid position
  - Personal exposures to acetaldehyde, acetone, benzene, ethanol, toluene and *m,p*-xylene, or *o*-xylene but were less than 2% of their respective NIOSH REL

Material jetting (cont.)

- Väisänen (2019) monitored individual VOCs using sorbent tubes w/Tenax TA®
  - Printing and post-printing (washing in water) tasks

- Average TVOC levels (sum of individual VOCs)
  - Printing = 2496 μg/m^3
  - Part washing = 1809 μg/m^3
- Individual VOCs
  - Thirty-one different VOCs quantified in air during printing
    - Isobornyl acrylate (1325 to 2076 μg/m^3)
  - Same VOCs were prominent during post-processing as well as styrene (33 μg/m^3)

Powder Bed Fusion

- Thermal energy selectively fuses regions of a powder bed
  - Selective laser melting/selective laser sintering – laser
  - Electron beam melting – e-beam

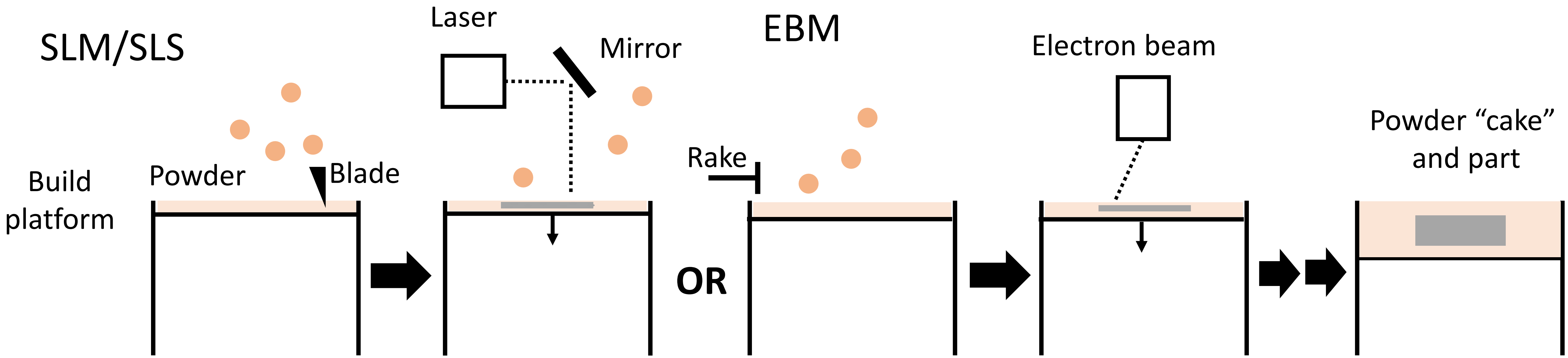
- Feedstock powders
  - Nylon-6
  - Nylon-12
  - Metals (Al, SS)
  - Ceramics
  - Composites

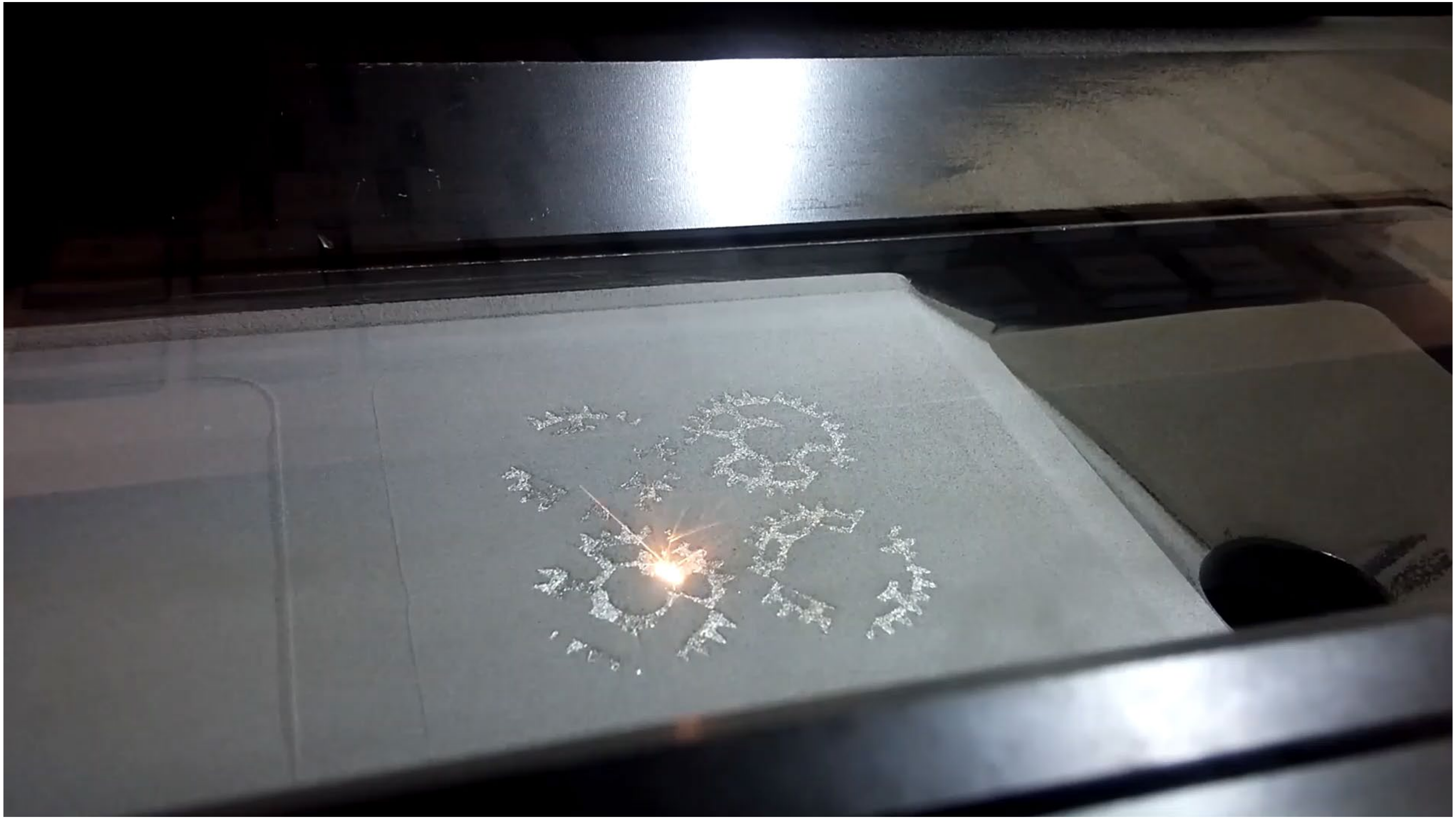
Powder bed fusion

Industrial powder bed fusion printers

All photos by SLM Solutions

Powder Bed Fusion





Video courtesy of Dhruv Bhate

Powder Bed Fusion

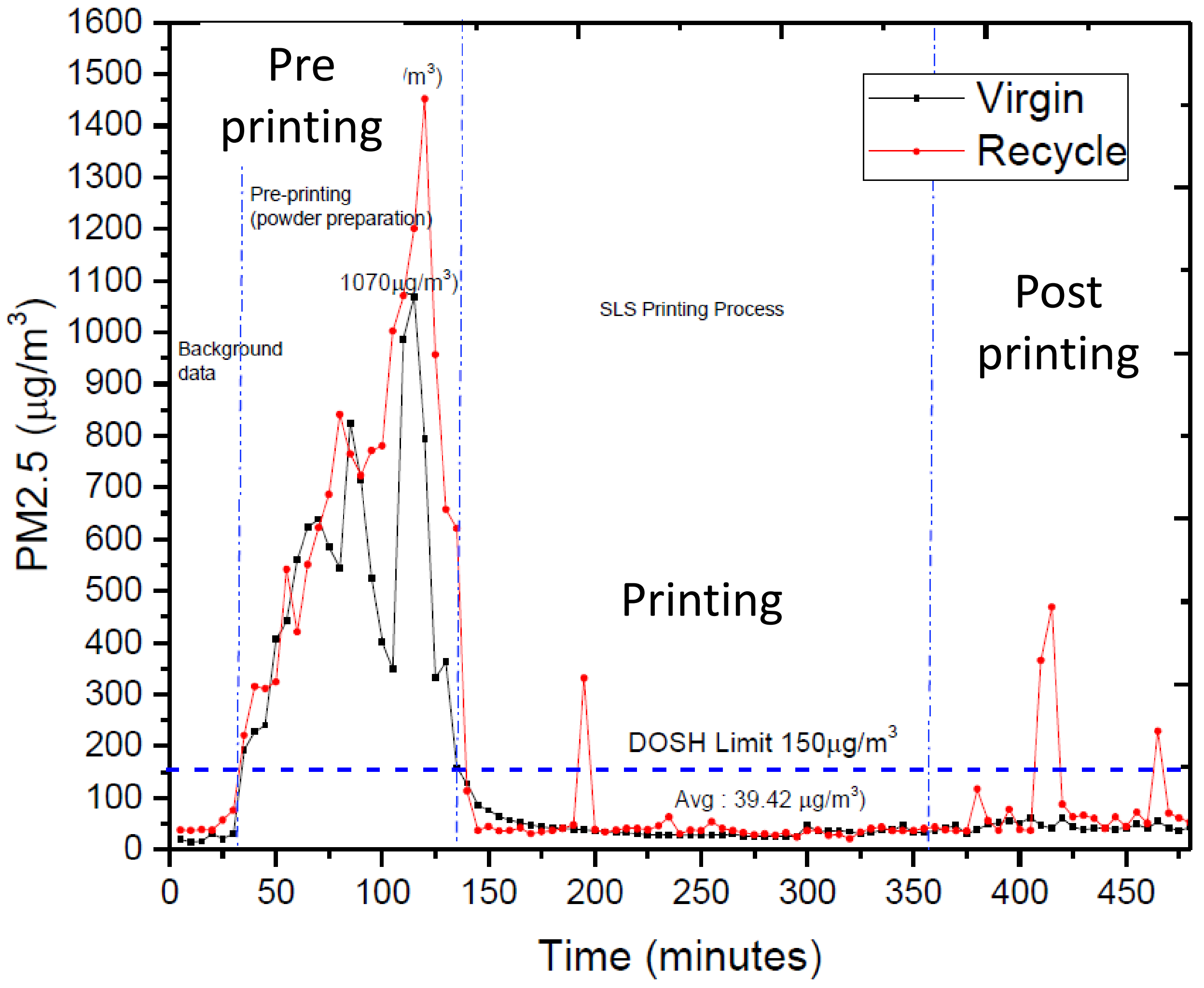
- Factors influencing emissions
  - **Powder (type)**
  - **Task**

Nylon-12[a]	Nylon-12 w/glass[b]
Formaldehyde (C)	Acetaldehyde (C)
Particulate	Acetone
	Formaldehyde (C)

Stainless Steel[c]
- Chromium (A)
- Cobalt (A)
- Nickel (A)

A = allergen, C = carcinogen

Damanhuri et al. (2019)



[a] Damanhuri et al. IOP Conf Series. (2019)
[b] Vaisenan et al. J Occup Environ Hyg. (2018)
[c] Graff et al. J Indust Ecol. (2017)

Binder Jetting

- Liquid bonding agent selectively deposited on powder

- Feedstock powders
  - Polymers
  - Metals
  - Ceramics
  - Composites

- Joiners
  - Binders
  - Activators

Photo by the American Ceramic Society

Binder jetting

Photo by 3D Printing Media Network

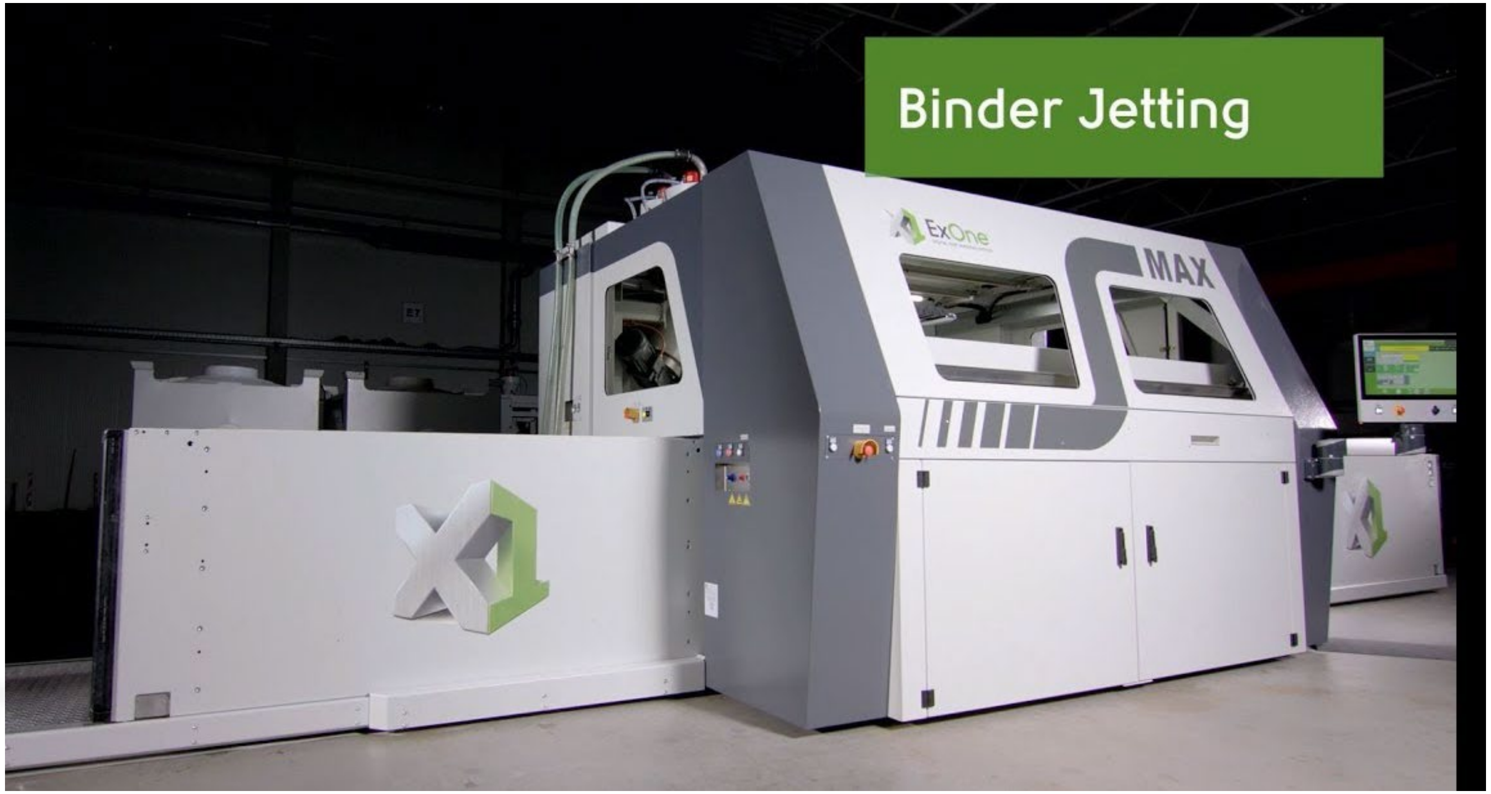


Photo by ExOne

Industrial binder jetting printers

Binder Jetting

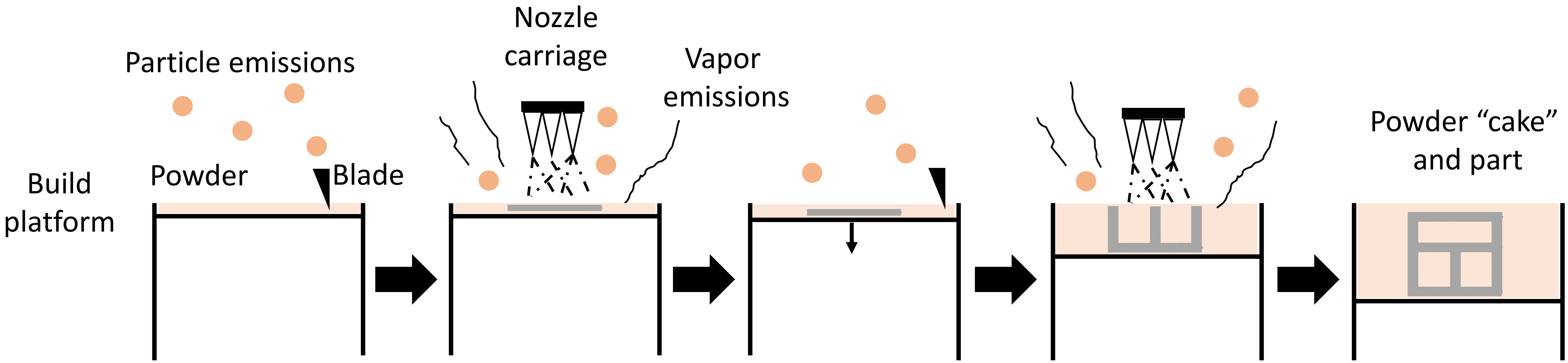


Photo by Afshar-Mohajer et al. Build Environ. (2015)

Binder jetting (BJ)

- Afshar-Mohajer et al. (2015) – TVOCs using a photoionization detector (PID)
- Standby mode (0 to 60 min)
  - Large increase
- Printing (60 to 180 min)
  - Small increase
- After-printing (180 to 240 min)
  - Little decay followed by burst

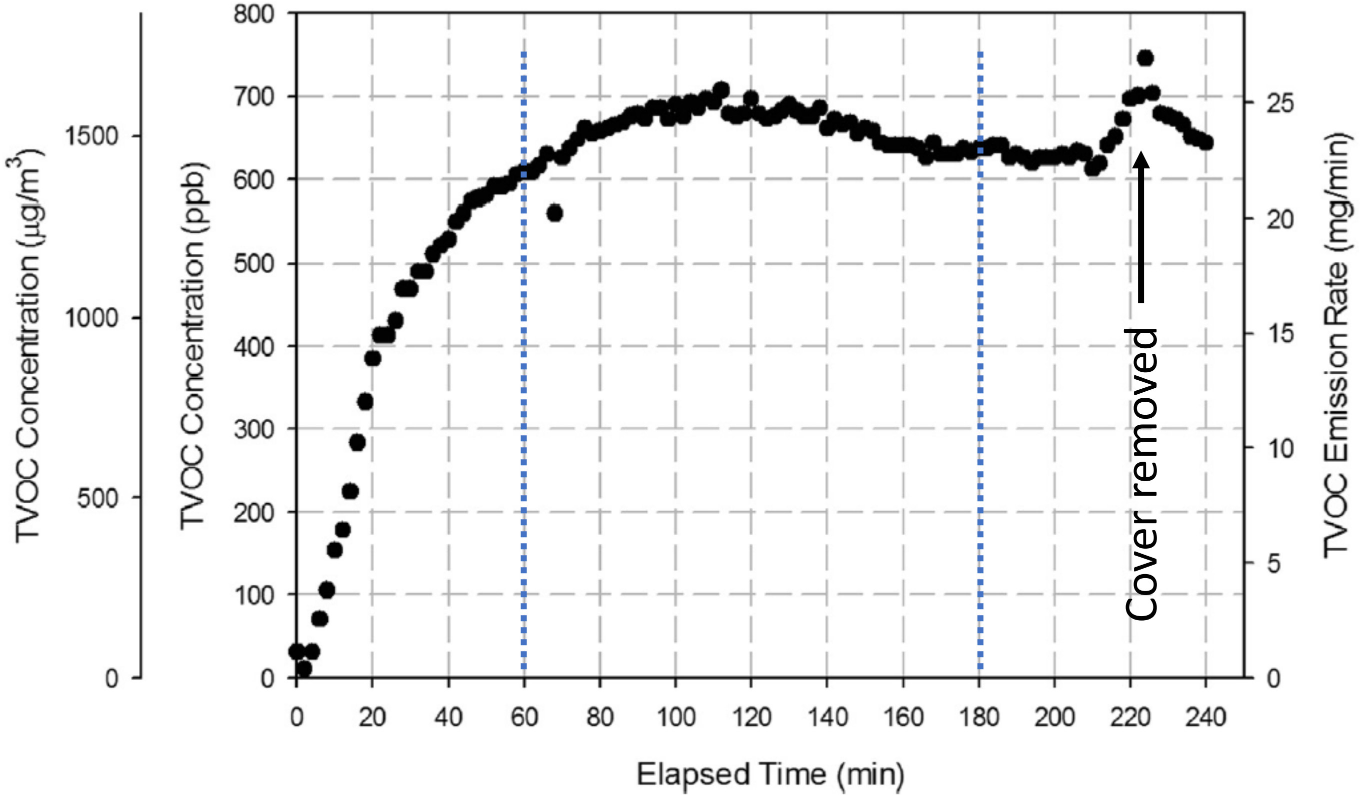


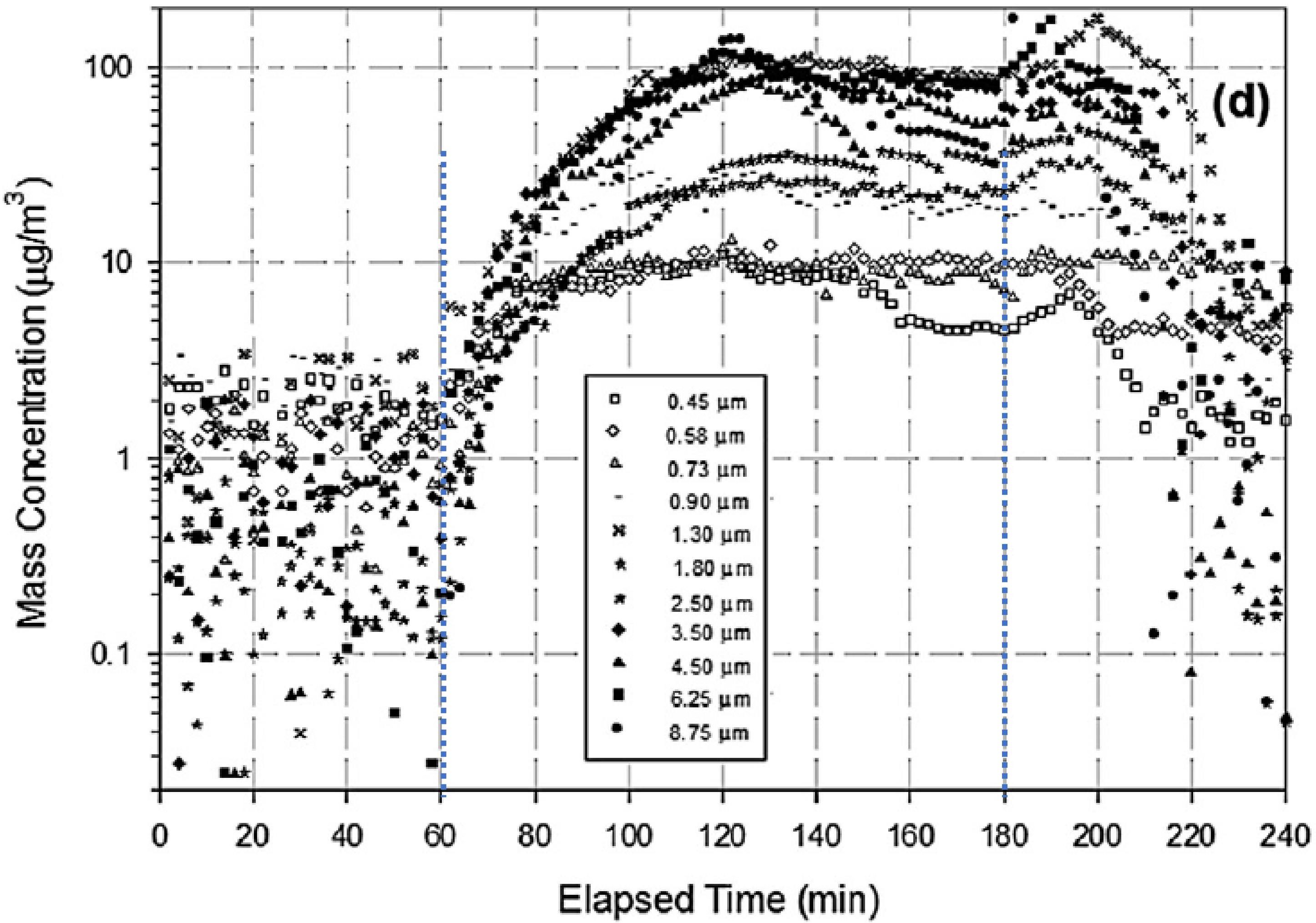
Fig. 7. Concentration and emission rate of TVOC as a function of time.

Binder solution in storage tank emitted VOCs even when the printer was off

Binder Jetting

- Factors influencing emissions
  - **Printer design**

(c)



Afshar-Mohajer et al. Build Environ. (2015)

Sheet lamination

- Sheets of material are bonded to form a part
- Feedstock sheets
  - Papers
  - Polymers
  - Ceramics (tape)
  - Metals (tape, films, or ribbons)
- Two basic types of printers
  - Form-then-bond
  - Bond-then-form

Photo by Loughborough University

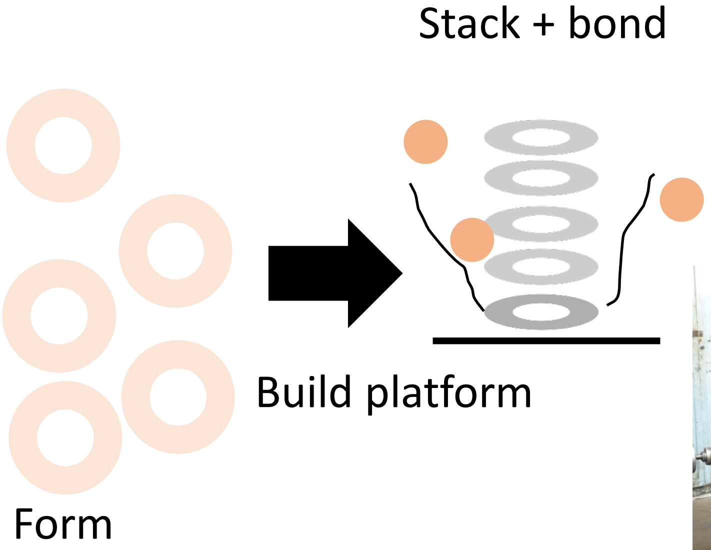
Sheet lamination

Industrial sheet lamination printer

Photo by Impossible Objects

Sheet lamination

Form-then-bond



Bond-then-form

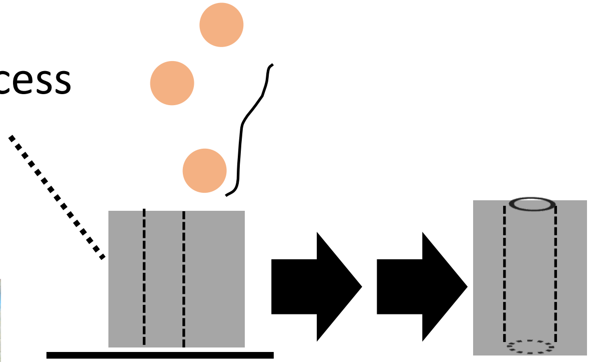


Photo by Microsoft

Directed energy deposition

- Focused thermal energy fuses materials via melting as they are deposited
  - Laser
  - E-beam
  - Plasma
  - Electric arc
- Feedstock materials
  - Wire
  - Powder
- Similar to robotic welding

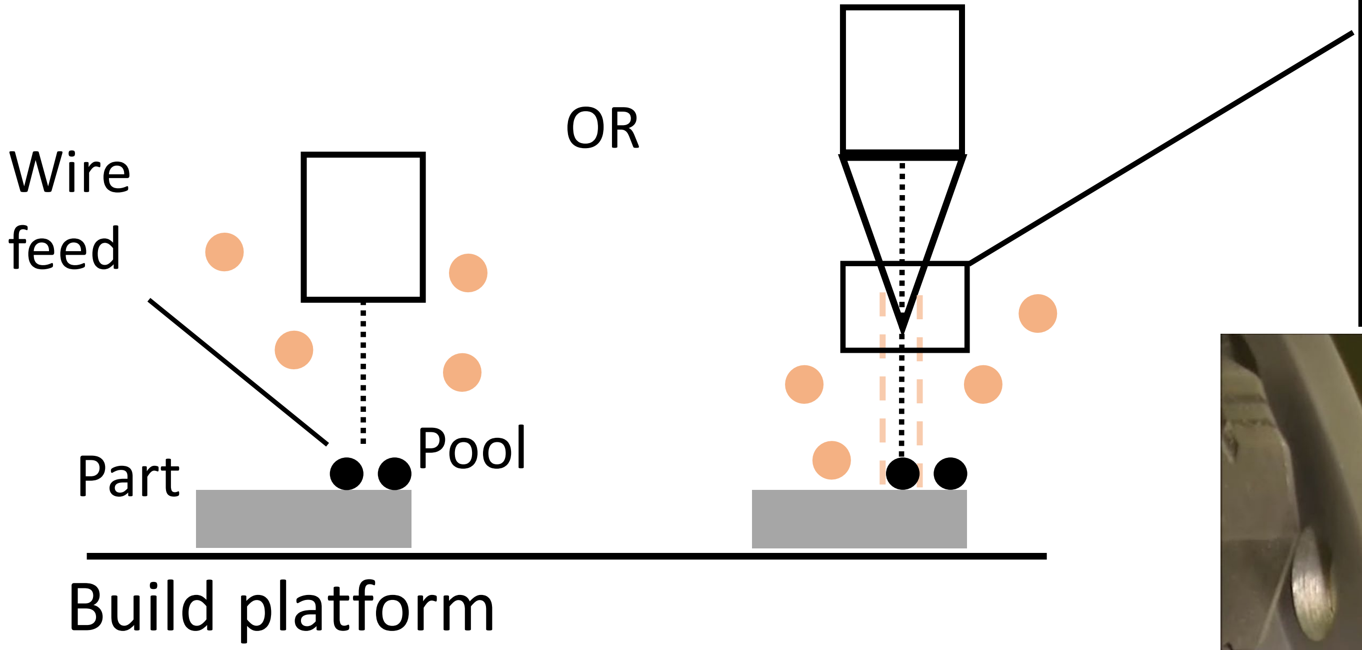
Photo by Optomec inc.

Directed energy deposition

Photo by Optomec Inc.

Industrial directed energy deposition printer

Directed energy deposition



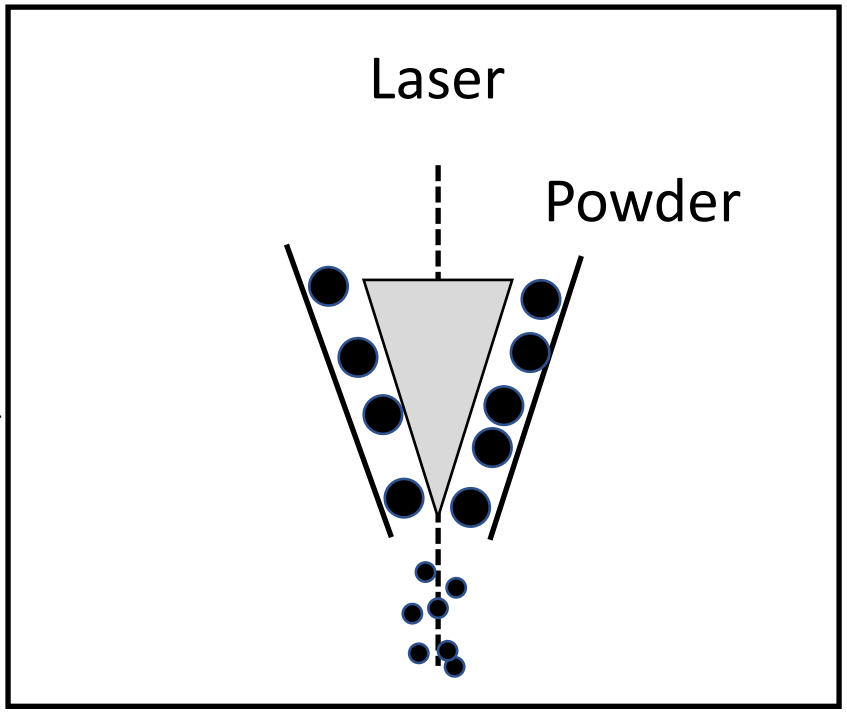


Photo by 3Dprintingindustry.com

Summary

- AM processes
  - Seven broad categories

- Expected to continue rapid growth

- Understanding inhalation exposures
  - Complex (complementary and confirmatory approach)

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For more information, contact CDC
1-800-CDC-INFO (232-4636)
TTY: 1-888-232-6348 www.cdc.gov