

CO₂ Compatibility in 3D

Manufacturing Material Compatibility

Biomaterial Compatibility

Manufacturing Process and Equipment Compatibility





Dimension 1

**Manufacturing
Material
Compatibility**



Material Compatibility Aspects

- All materials are generally compatible with CO₂ Composite Spray and CO₂ Plasma processes with changes (increase or decrease) in surface free energy (SFE) in all cases.
- Metals, ceramics, and glasses of most types are all compatible with Centrifugal Liquid CO₂ immersion and supercritical CO₂ (scCO₂) extraction processes.
- Crystalline polymers such as PTFE, PVDF, PA, PI, PET, PE, EPDM, PEEK, and PP show little, if any, uptake, swelling and distortion during Centrifugal Liquid CO₂ immersion and scCO₂ extraction processes.
- Bioabsorbable polymers such as PGA, PLA, and PDO swell mildly and are compatible with Centrifugal Liquid CO₂ immersion and scCO₂ extraction processes.
- Swelling of amorphous polymers is highly variable and generally less than 15% swell is acceptable without undue degradation of mechanical properties following de-swell.
- Silicone fabricated devices swell significantly during Centrifugal Liquid CO₂ immersion and scCO₂ extraction processes, but show no statistically significant deterioration of mechanical properties following de-swell.
- Fluorocarbons, Nitrile, Butyl Rubber, and Chloroprene are generally not compatible with Centrifugal Liquid CO₂ and scCO₂ processes.

References:

1. "Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents", D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.
2. "Evaluation of the Interactions between Supercritical Carbon Dioxide and Polymeric Materials", S. Sawan et al., Los Alamos National Laboratories, Report No. LA-UR-94-2341, 1994.
3. "Compatibility of Medical-Grade Polymers with Dense CO₂", A. Jimenez et al, J. Supercrit Fluids. 2007 October 1; 42(3): 366-372.



Material Compatibility Chart

CO₂ Treatment Fluids and Conditions

Materials	Spray	Immersion	Immersion	Plasma	Plasma
	(CO ₂ Comp. Spray)	(Centrifugal CO ₂)	(scCO ₂ Extraction)	(Vacuum)	(Atmospheric)
	70 psi, 25°C 2-60 sec.	1200 psi, 25°C 10-120 min.	2500 psi, 35°C 10-120 min.	<500 mT, 40°C 5-60 min.	70 psi, 150°C 2-5 sec.
Solid State					
Metals	Green	Green	Green	Green	Green
Ceramics	Green	Green	Green	Green	Green
Glasses	Green	Green	Green	Green	Green
Thin Metal and Metal Oxide Films	Green	Green	Green	Green	Green
Composites					
Carbon Fiber Reinforced Polymer (CFRP)	Green	Green	Yellow	Green	Green
Glass Fiber Reinforced Polymer (GFRP)	Green	Green	Green	Green	Green
Crystalline Polymers					
Polytetrafluoroethylene (PTFE)	Green	Green	Yellow	Green	Green
Polyvinylidene fluoride (PVDF)	Green	Green	Yellow	Green	Green
Polyamide (PA)	Green	Green	Yellow	Green	Green
Polyimide (PI)	Green	Green	Yellow	Green	Green
Polyethylene terephthalate (PET)	Green	Green	Yellow	Green	Green
Polyethylene (PE)	Green	Green	Yellow	Green	Green
Ethylene propylene diene rubber (EPDM)	Green	Green	Yellow	Green	Green
Polyetheretherketone (PEEK)	Green	Green	Yellow	Green	Green
Polypropylene (PP)	Green	Green	Yellow	Green	Green
Bioadsorbable Polymers					
Poly(glycolic acid) (PGA)	Green	Green	Yellow	Green	Green
Poly(lactic acid) (PLA)	Green	Green	Yellow	Green	Green
Polydioxanone (PDO)	Green	Green	Yellow	Green	Green
Amorphous Polymers					
Polydimethylsiloxane (PDMS)	Green	Yellow	Yellow	Green	Green
Fluorinated PDMS	Green	Yellow	Yellow	Green	Green
Nitrile Polymer (Buna N)	Green	Yellow	Yellow	Green	Green
Fluorocarbon Polymers	Green	Red	Red	Green	Green
Chloroprene Polymers	Green	Red	Red	Green	Green



Compatible under exemplary CO₂ processing conditions

Variable swelling, dissolution, and plasticization effects

Incompatible under exemplary CO₂ processing conditions



Total Mass Loss

Material	%TML scCO ₂ (LCO ₂)
PDMS Vibration Dampeners	3.0 (4.0)
Cotton Tipped Swabs	1.5 (2.0)
Butyl Rubber O-rings	0.3
Fluorosilicone (FS) Connector Insulators	3.5 (7.1)
Polyethylene Film	0.2
Mylar Film	0.1
High Voltage Silicone Insulators	1.6
RTV 630 Silicone Seals	3.4

Supercritical Carbon Dioxide Extraction
240 atm, 305°K, 4 hours

Liquid Carbon Dioxide Extraction
100 atm, 298°K, 4 hours

Extraction of monomers, oligomers, polymers, activators, fillers, plasticizers, and other additives and unreacted by-products.

Reference:

1. "Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents", D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.
2. ASTM E595 – Total Mass Loss (%TML) and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment.



Mechanical Properties

Silicone Rubber MIL-SPEC ZZR-765	Before	After
Hardness (A)	44	48
Tensile Strength (psi)	758	834
Elongation (%)	345	411
Compression (%)	3.4	10.6

Butyl Rubber AMS 3238	Before	After
Hardness (A)	69	63
Tensile Strength (psi)	1440	1204
Elongation (%)	349	330
Compression (%)	12.9	34.9

Supercritical Carbon Dioxide Extraction
240 atm, 305°K, 4 hours

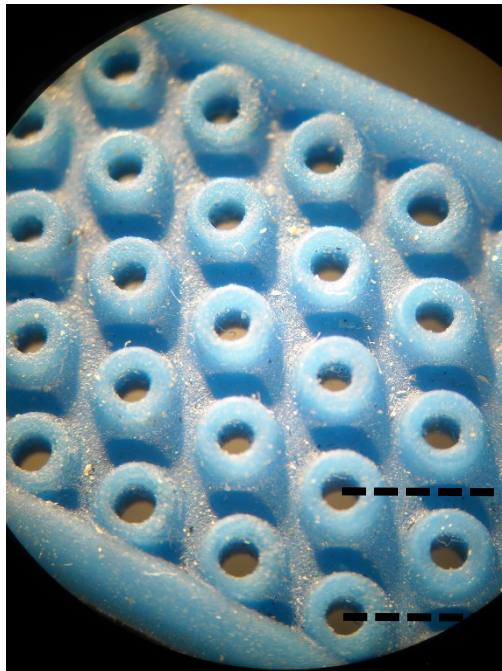
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1. “Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents”, D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.
2. ASTM D2240 - Standard Test Method for Rubber Property - Durometer Hardness.
3. ASTM D412 - Tensile Strength Properties of Rubber and Elastomers.
4. ASTM D575 - Standard Test Methods for Rubber Properties in Compression.



Electrical Resistivity



**Column-to-Column
Electrical Insulation Resistance (EIR)**

Reference:

1. "Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents", D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.



Solvent Selectivity

Property	Before	After	
		Liquid CO ₂	Supercritical CO ₂
Electrical Insulation Resistance (gigaohms) Column-to-Column	3	47	3
Total Mass Loss (%)	-	7.1	3.0

Liquid Carbon Dioxide Extraction
100 atm, 298°K, 4 hours

Supercritical Carbon Dioxide Extraction
240 atm, 305°K, 4 hours

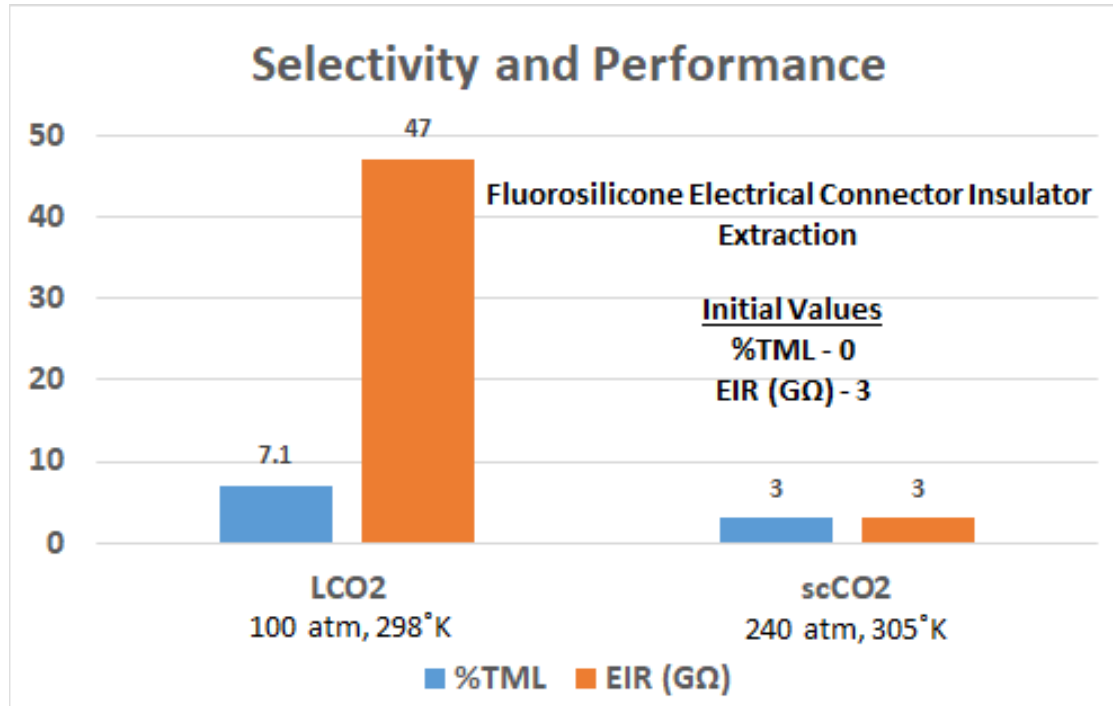
Extraction of monomers, oligomers, polymers, activators, fillers, plasticizers, and other additives and unreacted by-products.

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1. “Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents”, D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.
2. ASTM E595 - Total Mass Loss (TML) and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment.
3. ASTM D257 - Standard Test Methods for DC Resistance or Conductance of Insulating Materials.



Solvent Selectivity



Liquid CO₂ is a better extraction solvent for fluorosilicones, removing both non-volatile and volatile, ionic and non-ionic residues. scCO₂ is highly selective for non-ionic extractables.

Reference:

1. "Dense Phase Carbon Dioxide Cleaning Process: Liquid and Supercritical Carbon Dioxide as Cleaning Solvents", D. Jackson, Hughes Aircraft Co., 10th Annual Aerospace Contamination Control Working Group Meeting, Danvers, MA, May 1987.
2. ASTM E595 - Total Mass Loss (TML) and Collected Volatile Condensable Materials from Outgassing in a Vacuum Environment.
3. ASTM D257 - Standard Test Methods for DC Resistance or Conductance of Insulating Materials.



Cohesion Parameters

Material	δ_T	δ_d	δ_p	δ_h	CO ₂ Solvent Effect
Polyetheretherketone (PEEK) Valve Seat	25.2	20.3	6.3	5.7	No apparent swelling
Carbon Fiber Reinforced Plastic (CFRP) BMS8-276	23.7	20.0	10.0	8.0	No apparent swelling
Poly(glycolic acid) (PGA) Medical Tether	20.5	17.1	8.2	7.9	Slight swelling
Polydimethylsiloxane (PDMS) Insulated Electrical Cable	17.6	17.0	2.0	4.0	Significant swelling
Fluorocarbon Polymer (Viton A) Valve Seat	17.8	14.6	10.0	1.6	Depolymerizes over time
Solvent: Liquid CO ₂	17.9	15.7	6.3	5.7	81 atm, 298°K

References:

1. HSP for Viton A, Internet Reference: <https://pirika.com/NewHP/PirikaE/Packing.html>.
2. Hansen Solubility Parameters, C. Hansen, 2nd Ed, CRC Press, 2007.
3. Launay, Helene et al. "Hansen Solubility Parameters for a Carbon Fiber/Epoxy Composite", Proceedings of the 28th Rise International Symposium on Materials Science, Interface Design of Polymer Matrix Composites – Mechanics, Chemistry, Modelling and Manufacturing, 2007, pp. 221-226.
4. Tang, S. et al., "Hansen Solubility Parameters of Polyglycolic Acid and Interaction Parameters between Polyglycolic Acid and Solvents", European Polymer Journal, Volume 72, November 2015, pp. 83-88.



Surface Free Energy

Surface Free Energy (γ) Changes during Particle-Plasma Ablation^A
mN/m, (γ - estimated)

Metals

Surface	Acetone Cleaned and Oven Dried	CO ₂ Composite Spray ^B	Atmospheric CO ₂ Plasma ^C	Atmospheric Air Plasma ^C
Stainless Steel	48.1	51.1	78.5	76.6
Titanium	43.3	55.8	76.7	78.3

Composites

Surface	IPA Cleaned and Oven Dried	CO ₂ Composite Spray ^B	Atmospheric CO ₂ Plasma ^C	Atmospheric Air Plasma ^C
CFRP UNCOATED	43.9	56.1	76.1	77.2
CFRP PRIMERED	47.6	54.2	75.9	77.9

Polymers

Surface	IPA Cleaned and Oven Dried	CO ₂ Composite Spray ^B	Atmospheric CO ₂ Plasma ^C	Atmospheric Air Plasma ^C
PEEK	50.0	56.5	(>77)	74.8
PEKK	48.4	65.5	77.0	(>77)
HDPE	41.1	32.2	74.4	75.2
LDPE	38.1	33.2	74.6	54.6
PS	46.6	47.5	73.9	76.3
ABS	43.9	53.1	67.6	71.6
PTFE	19.1	15.8	23.2	19.4
PP	40.5	39.1	55.9	46.4
UHMWPE	39.8	37.5	71.0	50.9
PET	36.9	43.6	71.4	70.8
PMMA	32.7	30.2	72.5	(>77)
POM	44.6	55.5	62.1	53.8
Nylon 6,6	54.6	65.6	74.8	79.2
PC	36.8	33.4	73.2	(>77)
PDMS	22.2	20.3	(>77)	(>77)

References:

A. Surface Free Energy (SFE, γ , mN/m²) Test Equipment and Methods:

Kruss DSA-25E

Advance[®] Drop Shape Analysis Software

Sessile Drop Method

Probe Liquids: Methylene Iodide/Deionized Water

ASTM D5946-17

Standard Test Method for

Corona-Treated Polymer Films Using Water Contact Angle Measurements

B. CO₂ Composite Spray Treatment Conditions:

CO₂ Injection Pressure (psi): 1200

CO₂ Injection Rate (lb/s): 0.001

Air Propellant Pressure (psi): 100

Air Propellant Temperature (°C): 20

Scan Rate (inches/s): 2

Treatment Time (seconds): 10

Max. Surface Stress (MPa): >80

C. Atmospheric Plasma Treatment Conditions:

Gas Type: CO₂ or Air

Plasma Type: Blown Ion

Gas Pressure (psi): 70

Power (watts): 480

Scan Rate (inches/sec): 2

Treatment Time (sec): 10

CO₂ Plasma Temperature (°C): 150

Air Plasma Temperature (°C): 232





Dimension 2

Biomaterial Compatibility



Hemotoxicity

Poly(glycolic acid) (PGA) tether

Hemolysis Testing (NIH Direct Contact Method):

Application: Bioabsorbable polymer fiber bundle used for medical applications.

Purpose: To determine the hemolytic properties of materials scoured with liquid CO₂.

Result: Processed samples pass hemolysis testing with a percent hemolysis of 1.4%. These samples are considered non-hemolytic under the test conditions employed.

TEST ARTICLE AND CONTROLS	ABSORBANCE			AVERAGE ABSORBANCE	% HEMOLYSIS
Test Article	0.028	0.028	0.026	0.027	1.4
Positive Control	0.868	0.879	NA	0.874	
Negative Control	0.014	0.16	NA	0.015	

Analysis Performed by: AppTec Laboratory Services

Centrifugal Liquid Carbon Dioxide Extraction
100 atm, 298°K, 1 hour



Cytotoxicity

Poly(glycolic acid) (PGA) tether

Cytotoxicity Testing (ISO 10993-5 Method):

Application: Bioabsorbable polymer fiber bundle used for medical applications.

Purpose: To determine the cytotoxicological properties of materials scoured with liquid CO₂.

Result: Processed samples pass cytotoxicity testing and are considered Non-Toxic under the test conditions employed.

TEST ARTICLE AND CONTROLS	CYTOTOXICITY SCORES	
	Score/Replicate	
	24 HOURS	48 HOURS
Test Article	1/1	1/1
Positive Control – CdCl ₂	4/4	4/4
Int. Control - Black Rubber	2/2	2/2
Neg. Control – Vial Caps	0/0	0/0
Cell Control – L-929	0/0	0/0

Centrifugal Liquid
Carbon Dioxide
Extraction
100 atm, 298°K, 1
hour

Analysis Performed by: AppTec Laboratory Services



Endotoxicity

Poly(glycolic acid) (PGA) tether

Endotoxicity Testing (Gel Clot Method):

Application: Bioabsorbable polymer fiber bundle used for medical applications.

Purpose: To determine the endotoxological properties of materials scoured with liquid CO₂.

Result: Endotoxins were not detected in the processed samples.

TEST ARTICLE AND CONTROLS	RESULTS	
	<u>REPLICATE 1</u>	<u>REPLICATE 2</u>
Test Article Extract	Negative	Negative
Positive Product Control	Positive	Positive
Positive Endotoxin Control	Positive	Positive
Negative Water Control	Negative	Negative

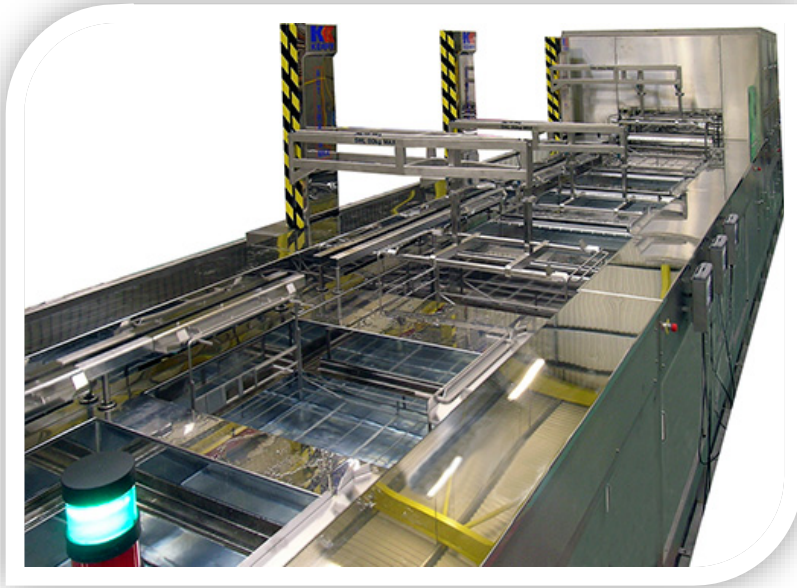
Centrifugal Liquid
Carbon Dioxide
Extraction
100 atm, 298°K, 1
hour

Analysis Performed by: Northview Laboratories, Inc.

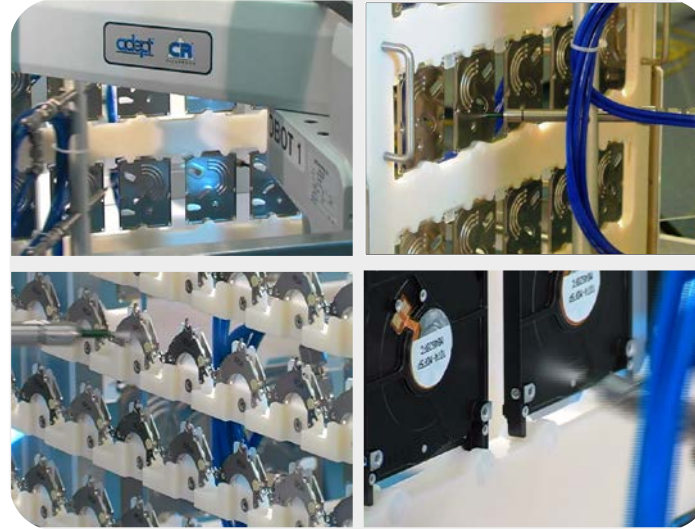
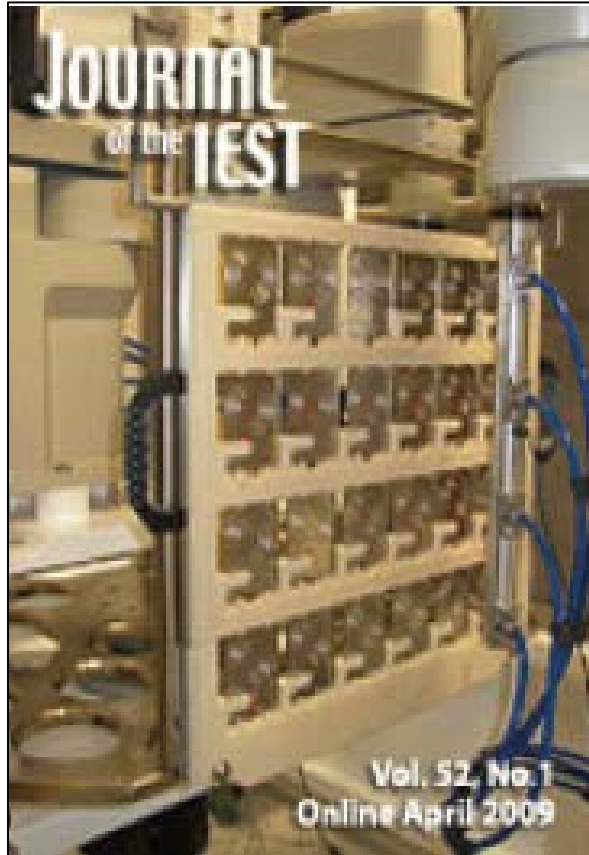


Dimension 3

Manufacturing Process and Equipment Compatibility



Cost-Benefits



Cleaning Cost Comparison Between DI/US Immersion and CO₂ Composite Spray™ Cleaning

Deionized Water
(Immersion/Drying)

\$0.12-\$0.13/part

CO₂
(Dry Spray)

\$0.015-\$0.06/part

**50% - 88% cost reduction -
fully burdened**

Economics

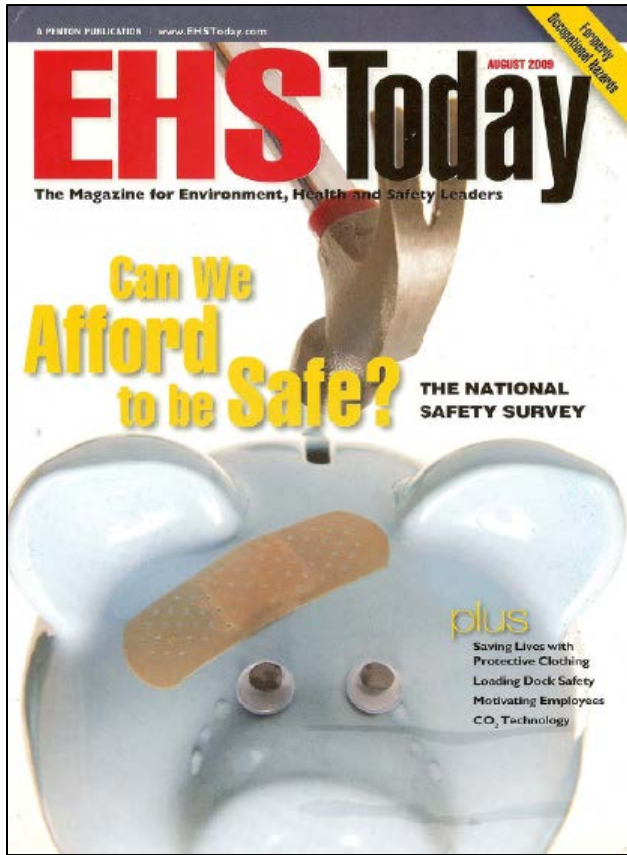
Low Cost of Operation
Less Space
Lower Energy
Lower Labor
No Waste Treatment
Faster Processing
Cash Flow Recovery

Reference:

1. "Automated CO₂ Composite Spray Cleaning System for HDD Rework Parts", G.W. Knoth et al., Journal of the IEST, Volume 52, Number 1, April 2009.



Environmental, Health, and Safety



Environmental

- Renewable Resource
- No Water/Wastewater
- No Air Pollution
- No Environmental Permits
- No VOCs
- GWG Reporting Exempt

Facilities and Workers

- Non-Corrosive
- Non-Toxic
- Non-Flammable
- Non-Contaminating

Reference:

1. "Setting the Record Straight: CO₂ Technology is Part of the Solution", D. Jackson, EHS Today, August 2009.



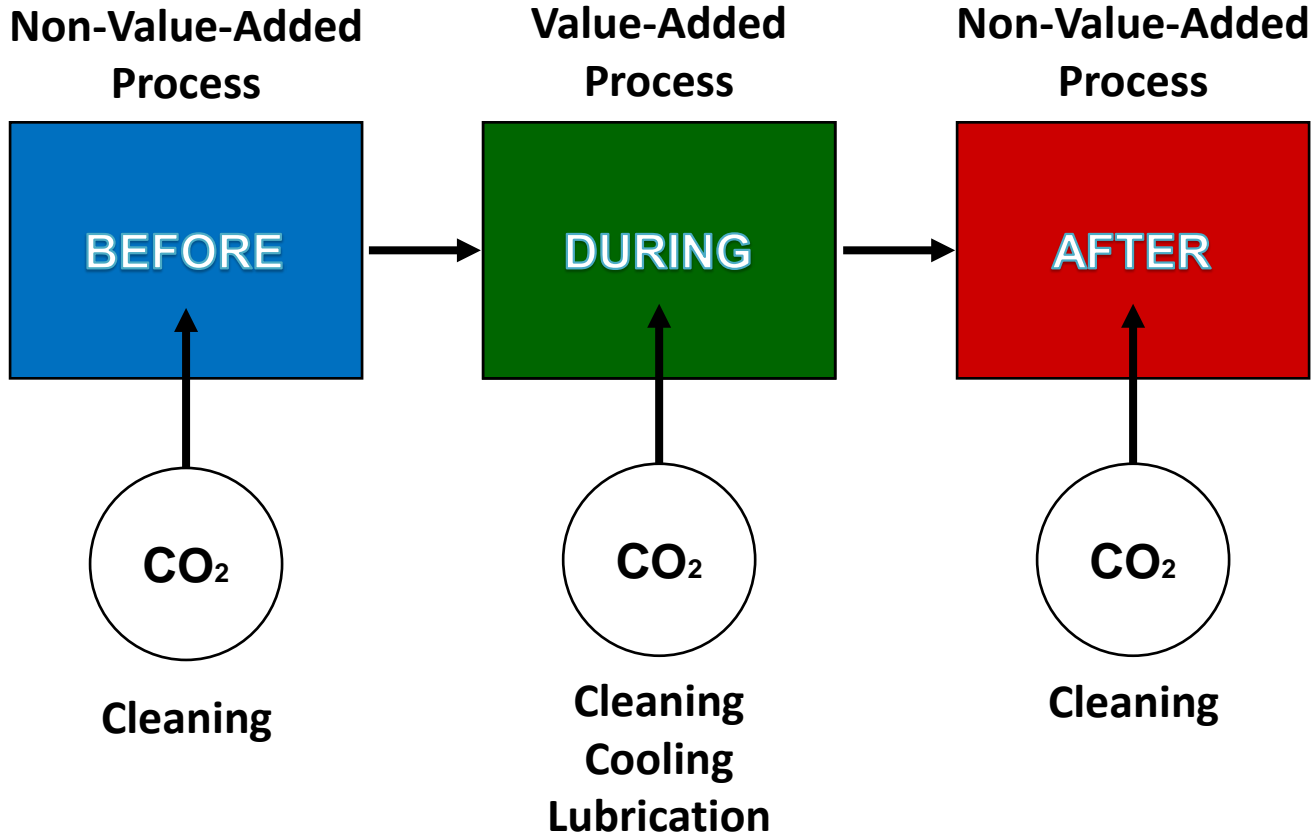
Transformative Implementations

Aspect	Examples
Processes	Plant Extraction, Fastening, Welding, Machining, Stamping, Thermal Spray, Coating, Molding, Testing, Inspection, Wire Bonding, and Adhesive Bonding...
Wastes	Motion, Space, Energy, Inventory, Transport, Tool Life/Changes, Safety, Scrap, Environmental Permitting, Pollution, Water, Labor, Capital, and Rework...
Functions	Value Extraction, Degreasing, Thermal Control, Disinfection, Defluxing, Bioburden Reduction, Outgas Removal, Surface Modification, and Dry/Near-Dry Cooling-Lubrication, Precision Drying, and Pressure Impregnation...
Implementations	Integrated with a Pressure Vessel, Process Tool, Conveyor, Stand-alone Tool, Cluster Tool, Mobile Tool, and Robotic Tool...
Quality	Higher Yields, Cleaner Environment, Safer Environment, Better Surface Finish, Higher CpK, Improved Product Performance, and Improved Dimensional Control...



Unlimited Utilization

Production Line



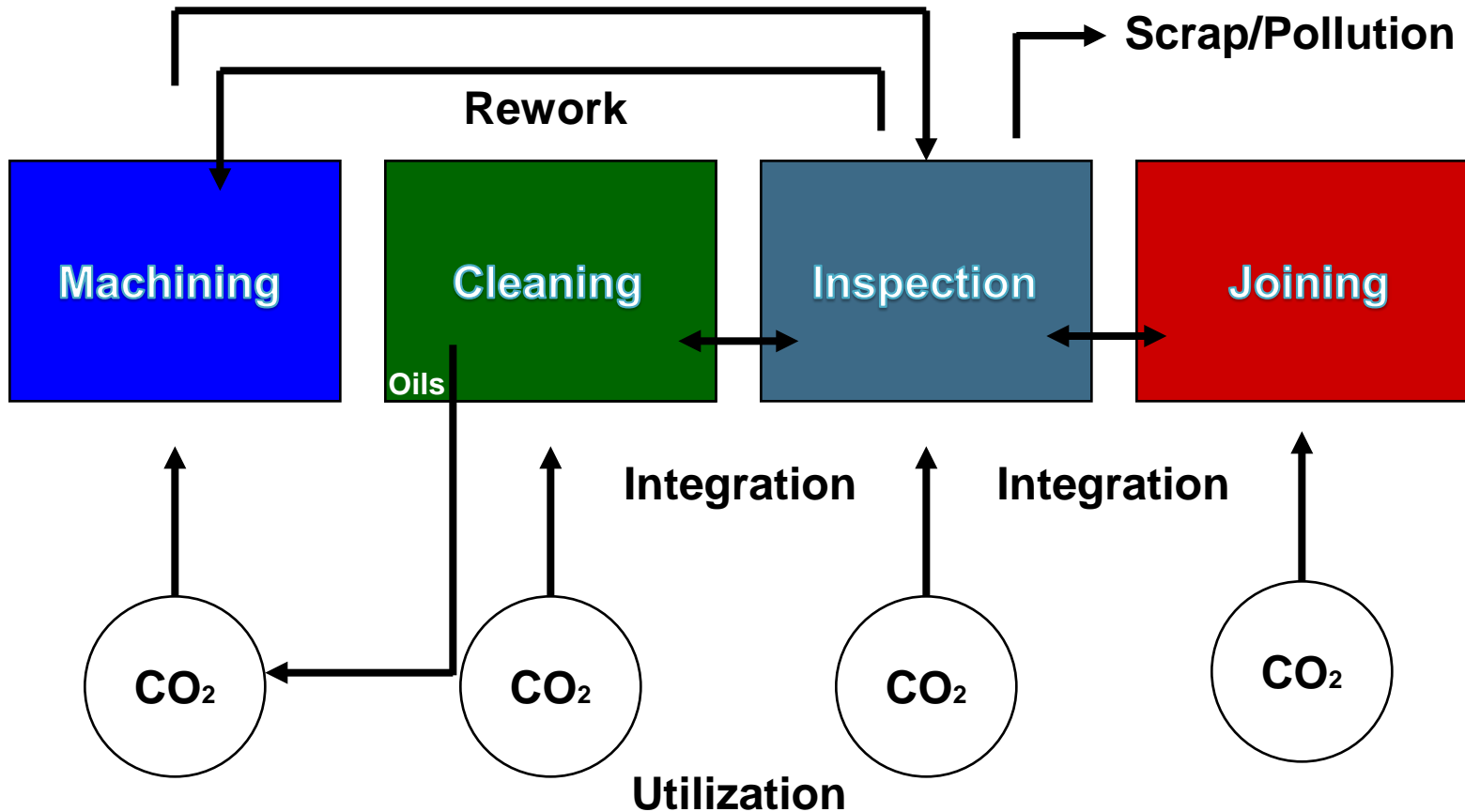
Optimized Production Lines

Time/Space/Energy/Labor



Skip Step

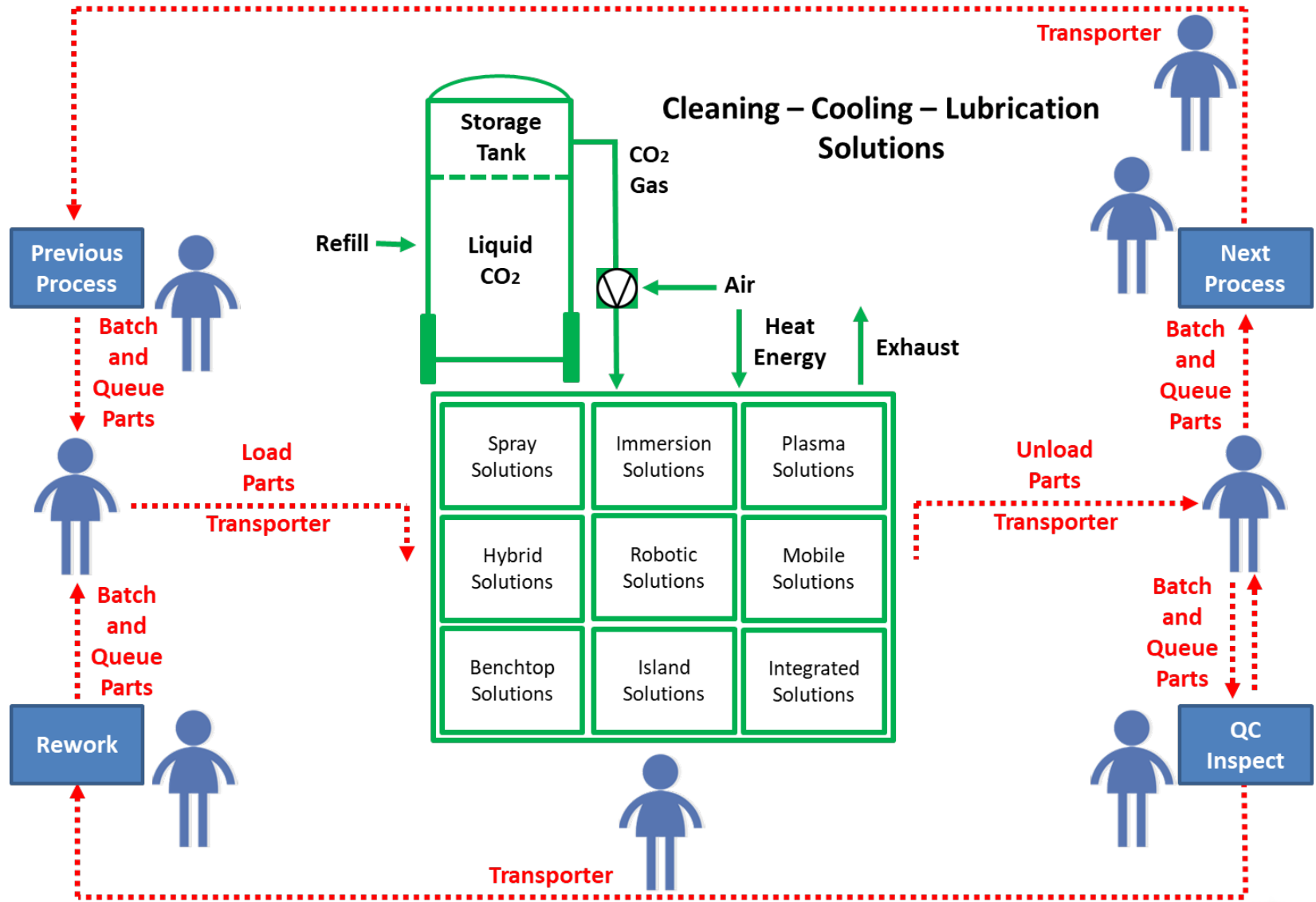
Scrap/Pollution



In-the-Tool, On-the-Line, In-the-Cell

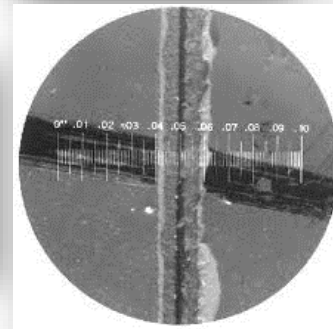
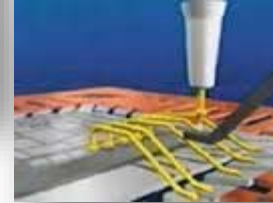


Numerous Manufacturing Solutions

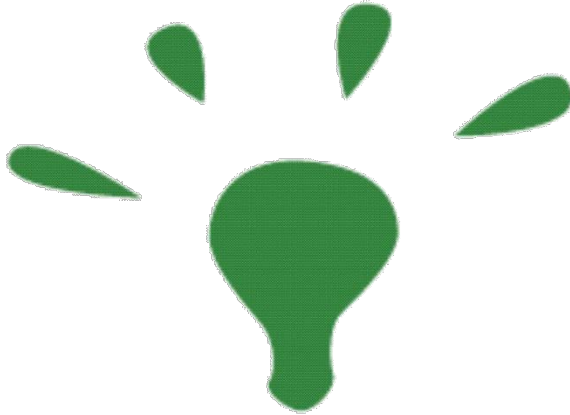


Unlimited Process Integration Schemes

- Clean-Dispense-Join-Cure
- Clean-Placement-Solder-Inspect
- Polish-Clean-Inspect
- Clean-Modify-Inspect-Coat
- Drill-Cool-Lubricate-Clean
- Milling-Cool-Clean
- Clean-Thermal Spray Coat-Cool
- Injection Mold-Clean
- Clean-Assemble-Test-Clean
- Clean-Weld
- Clean-Rework-Clean
- Clean-Wire Bond
- Clean-Treat-Adhesive Bond
- Clean-Test-Clean
- Machining-Clean
- Clean Machining
- Clean Grinding
- Clean Dicing
- Clean Lasing...



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