Pb, Cd, Cr^{+6} and Ni Alternatives for Surface Finishing

Peter A. Gallerani, MSF, AESF Fellow

Integrated TECHNOLOGIES, INC.

My Journey to Toxics Use Reduction

- 1980s…Process Optimization, Waste Minimization, Pollution Prevention (P2) or Toxic Waste Reduction (TWR)
- 1990s…Focus shifts to TUR
  - TUR isn't synonymous with TWR
  - TUR can increase hazardous waste generation
  - TUR can be a distraction from working the low hanging fruit of TWR
  - TUR gets all the money
  - TUR can be a distraction from effective hazard management
- Present…TUR, Hazard Management (HM) and TWR …Lean and Six Sigma

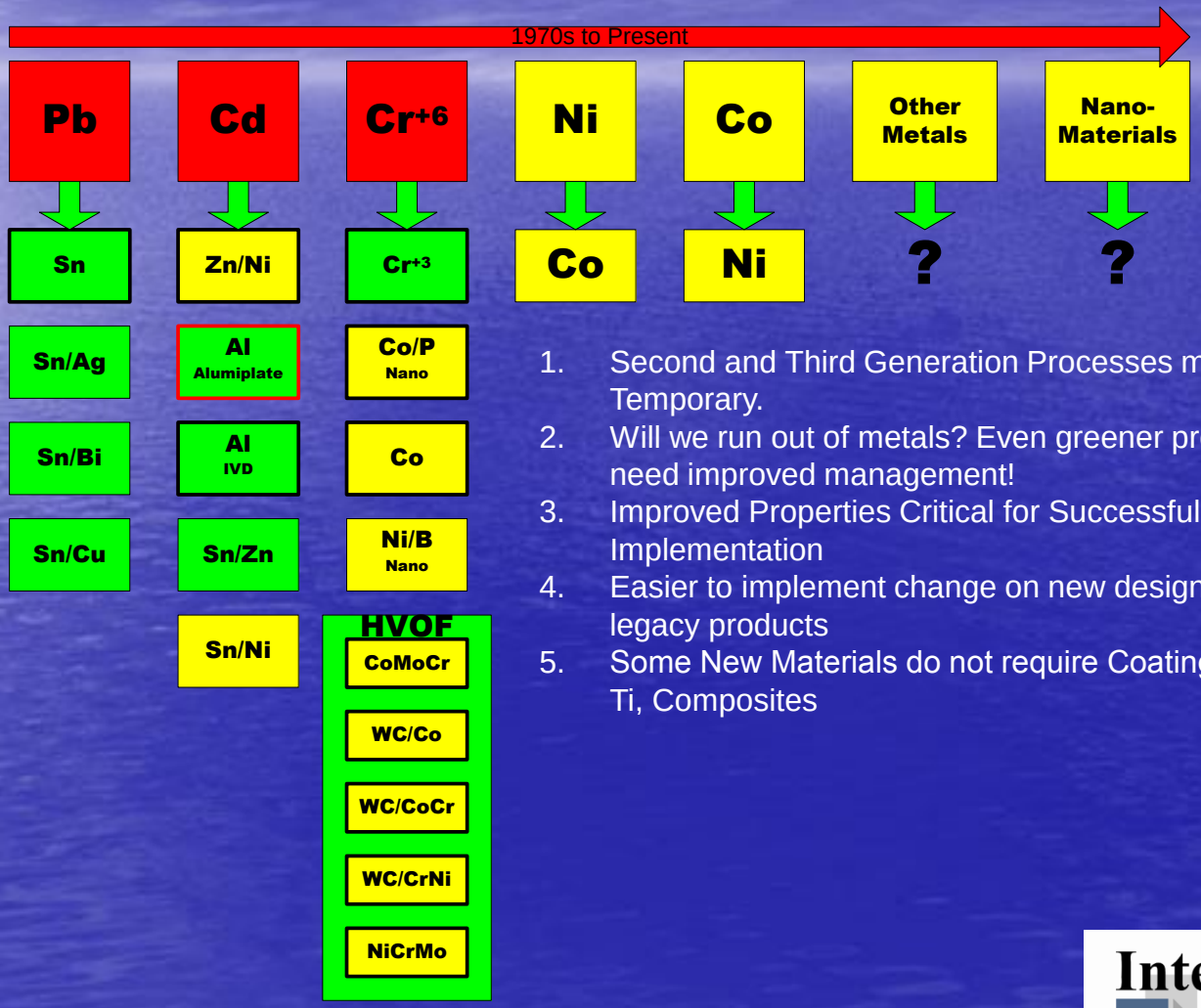
Integrated TECHNOLOGIES, INC.

Hazard Management…the Other Side of Green

Purely Green
Chemistries/Processes
are Currently Not Viable for
Most Surface Finishing Requirements
so
we Must Devote as
much Effort to Effectively
Manage Hazards
as we do to Seek New Alternatives!

Integrated
TECHNOLOGIES, INC.

Regulatory Trends and Green Alternatives

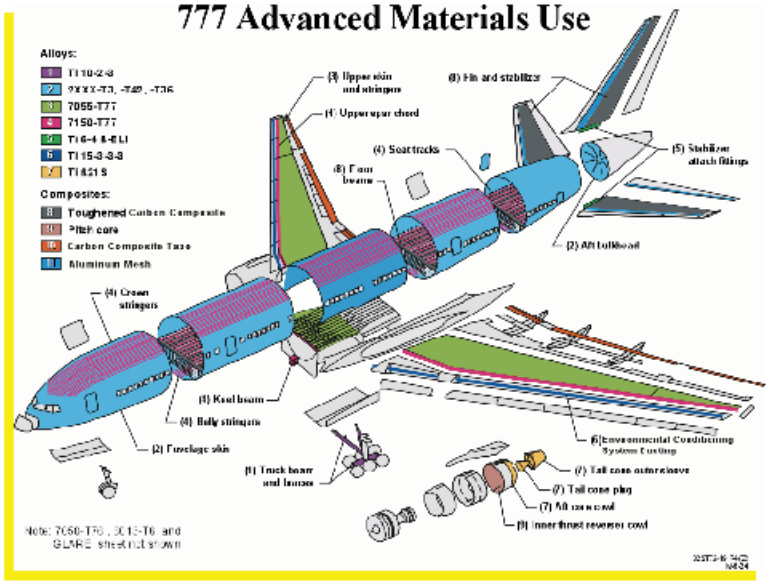


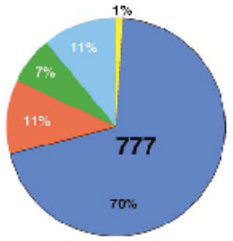
1. Second and Third Generation Processes may be Temporary.
2. Will we run out of metals? Even greener processes need improved management!
3. Improved Properties Critical for Successful Implementation
4. Easier to implement change on new designs than on legacy products
5. Some New Materials do not require Coatings…CRES, Ti, Composites

Integrated TECHNOLOGIES, INC.

777 Advanced Materials Use

Boeing Technology





- Steel
- Titanium
- Composite
- Misc.
- Aluminum

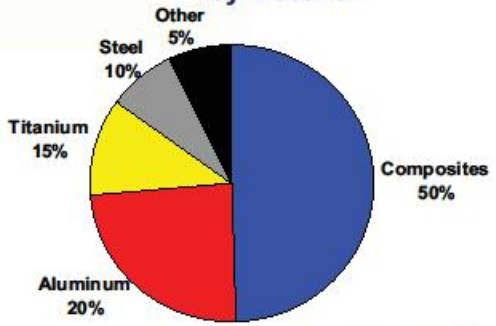
Integrated TECHNOLOGIES, INC.

787 Composites Use

Boeing Technology

- Carbon laminate
- Carbon sandwich
- Fiberglass
- Aluminum
- Aluminum/steel/titanium pylons

Primary Structure Weight by Material



Integrated TECHNOLOGIES, INC.

Cadmium Plating Alternatives - JSF

Table 7. Summary of recommendations by rough order of usefulness for the JSF.

Options	Critical issues for application	Comments
Components		
IVD Al (sputtered Al for IDs)	Needs alternative to chromate conversion Higher coating density (more ion bombardment)	Full production process, available in depots ID coating method now available
Sn-Zn	Hydrogen embrittlement Chemical uniformity	Concern over whisker growth and phase changes
Zn-Ni	Hydrogen embrittlement Chemical uniformity	More subject to galling than Sn-Zn
Al-Mn	Property and performance database OSH, removal of salt from interstices after plating	Under development at NAWC May be good option if performance is good and OSH tractable for depots.
High strength stainless steel	Property and performance database Qualification	Ideal for landing gear if can be qualified in time. O&R replacement possibility. Avoids stress corrosion cracking failures.
Aluminum-ceramic (SermeTel)	High curing temperature Embrittlement issues seen in some cases	Production use on landing gear, engines
Thermal spray Al	Roughness, line-of-sight	Limited production use on landing gear
Fasteners		
Sn-Zn	Hydrogen embrittlement	Under evaluation by Boeing
Zn-Ni	Hydrogen embrittlement	Not for high strength alloys
Electroplated Al	Availability OSH	Sole source proprietary coating
Al-Mn	Property and performance database OSH	Under development at NAWC May be best option if performance is good.
Metal-polymer	Thread-filling Aerospace performance Damage by lightning strikes?	Tests well for land vehicles
MOCVD Al	Deposition temperature	Sole source proprietary coating
Electrical connectors		
Sn-Zn	Whisker growth concerns	Under evaluation by Boeing
Electroplated Al	Availability OSH	Sole source proprietary coating
Zn-Ni	Hydrogen embrittlement, soldering	Especially for Al
Al-Mn	Property and performance database OSH	Under development at NAWC Too high coating temperature for Al alloys
MOCVD Al	Deposition temperature	Sole source proprietary coating. Too high deposition temperature for most Al alloys
Color code:	**Best options**	**Promising new technologies**

Integrated TECHNOLOGIES, INC.

Alumiplate

- Very Good Coating
- Limited Availability (one supplier)
- Expensive
- Hazardous
  - Toluene Based
  - Pyrophoric

Integrated TECHNOLOGIES, INC.

IVD Al and Sputtering

- Corrosion Resistance not equal to Alumiplate
  - Cleaners & Deicing Fluids
- Solderability
- Cost
- Line-of-Sight (limited ID plating with sputtering)

Integrated TECHNOLOGIES, INC.

New Metal Alloys

QuesTek® INNOVATIONS LLC

FERRIUM® S53

Corrosion Resistant Ultrahigh-Strength Steel for Aerospace Structural Applications

Ferrium® S53 Mechanical Properties (typical)

YS (ksi)	UTS (ksi)	El (%)	Ra (%)	Hardness (HRC)	CVN (ft-lb)	K_{Ic} $(ksi\sqrt{in})$	K_{Iscc} $(ksi\sqrt{in})$
225	288	16-18	60-70	54	20	70	44

Other Key Properties

- Corrosion resistance has been measured in accelerated sea water tests and is less than 0.4 mils per year, comparable to 15-5PH.
- Limited fatigue testing at a number of R values and stress levels has shown equivalent performance to typical 300M values.
- S53 yields a Class A Weld. Welding studies have shown minimal impact on mechanical properties.

Materials by Design® Objective

Steels currently used in numerous aerospace applications, specifically landing gear, are not corrosion resistant and therefore require a protective cyanide-based cadmium plating process. Cadmium, a known carcinogen, represents significant environmental risks in both primary aerospace manufacture and at overhaul and repair facilities. The design objective of *Ferrium*® S53 was to create an ultrahigh-strength stainless steel that would eliminate the need for toxic metal plating.

Description

Ferrium S53 is a corrosion resistant ultrahigh-strength steel for structural aerospace applications. *Ferrium* S53 was designed to provide mechanical properties equal to, or better than, conventional ultrahigh-strength steels such as 300M and SAE 4340 with the added benefit of general corrosion resistance similar to 15-5 PH. This eliminates the need for cadmium coating processes, which are environmentally unfriendly and require subsequent hydrogen bake-out operations in order to avoid hydrogen embrittlement. *Ferrium* S53 has a greatly improved resistance to stress-corrosion cracking (SCC) over 300M and SAE 4340.

Ferrium S53 utilizes an efficient M_7C strengthening dispersion precipitated through tempering while avoiding other carbides. This maximizes strength, wear resistance, and toughness; resulting in a unique combination of mechanical properties for a stainless steel.

Ferrium S53 uses a stable passive oxide film for optimum corrosion resistance. It also has high hardenability, permitting less severe quench conditions for a given section size and resulting in less distortion during heat treatment.

For additional information regarding QuesTek's Ferrium S53 contact **Charles J. Kuehmann** by e-mail or call 847.425.8222.

QuesTek® INNOVATIONS LLC

FERRIUM® S53
Corrosion Resistant Ultrahigh-Strength Steel for Aerospace Structural Applications

Processing

Processing of *Ferrium* S53 is similar to other quench and tempered martensitic secondary-hardening steels. Vacuum heat treatment and vacuum tempering is recommended to avoid surface decarburization. After quenching to room temperature *Ferrium* S53 is subjected to cryogenic treatment to assure a complete martensitic transformation. *Ferrium* S53 is typically double-step tempered around 900°F (482°C) and has excellent thermal resistance approaching this temperature. This allows for higher grinding speeds without risk for grinding burns and more reliability in service.

Corrosion Resistance

The general corrosion resistance of *Ferrium* S53 is similar to typical precipitation-hardened stainless steels such as 17-4 PH and 15-5 PH. Linear polarization testing of *Ferrium* S53 measured an average corrosion rate of 0.40 mils per year versus a saturated Ag/AgCl reference electrode in 3.5% sodium chloride (NaCl) solution at ambient temperature. *Ferrium* S53 is rust resistant in 3.5% NaCl solution.

Density

The density of *Ferrium* S53 is 7.98 g/cc.

Product Forms

Ferrium S53 may be manufactured in typical ingot, bar, and billet forms. Sheet and plate also available upon request.

Other

Patent pending.

For additional information regarding QuesTek's Ferrium S53 contact **Charles J. Kuehmann** by e-mail or call 847.425.8222.

November 2005.
Copyright © 2005 QuesTek Innovations LLC.
All rights reserved.

Integrated TECHNOLOGIES, INC.

Alkaline Zinc Nickel

Zinc-Nickel vs. Cadmium Score Sheet

Properties	LHE Cadmium	IZ-C17 LHE Zinc-Nickel
Corrosion - Salt Spray	1000 hours	+ 1000 hours
Hydrogen Embrittlement (1a.1)	Pass	Pass
Hydrogen Re-Embrittlement - Water	Marginal	Pass
Hydrogen Re-Embrittlement - Salt Water	Fail	Pass
Throwing Power	Poor	Good
Fatigue	Good	Good
Lubricity	Good	Needs Lubricant
Electrical Properties	Good	TBD
Fluid Immersion	Good	Good
Strippability	Good	Good*

* Dilute HCl Solution - Strips Zn-Ni in 10 seconds and is Non-Embrittling

Integrated TECHNOLOGIES, INC.

Chromate Conversion Coatings

- Trivalent "Passivates" or "Chromites" are available for zinc plating and cadmium plating alternatives
  - Results vary for clear, yellow and black processes and top coats may be required to duplicate corrosion resistance and torque values with fasteners
  - No self healing with some exceptions
- Trivalent Processes based on the Navy TCP processes are effective on aluminum
  - 2024 alloy has been a greater challenge
  - Chromate/Primer Synergy…you can eliminate the chromate in the primer or the "chromate" but not both
    - Chromate primers are 25% by weight strontium chromate and relatively thick…chromates are thin films

Integrated TECHNOLOGIES, INC.

Chromate Alternatives

SERDP

ESTCP
Environmental Security Technology Certification Program

Options – Chromate conversion of coatings and Al alloys

Substitution, control options					Best DoD options	Projects			Gaps	Implementation
Current tech Options	Commercial Status	DoD Status R&D	DoD Status Qual	DoD Status Prod		Unsuccessful	On-going	Successful		
Trivalent chrome conversion	All vehicles and electrical equipment (EU ELV and RoHS compliance). Incs Al alloys; Zn, ZnNi coatings.	NAVAIR qualified: TCP			✓	ESTCP Non-Chromate Al pretreatments			Better treatments for 2000 and 7000 series Al alloys. Electrical cabinets. Bonding primers. Fasteners	Helos, EFV, Army vehicle road wheels
		Electrical performance under test (DDG 1000)								
Non-Cr conversion		NASA, TACOM, USMC: Alodine 5200, 5700			✓					
Paint adhesion promoters (sol-gels, Prekote)	Boeing production	USAF flight testing: Prekote			✓					
Phosphate	Production (steel sheet)	Army vehicles			✓				Wash primers	
Polymer coatings	Production (steel sheet, Kobe Steel)					SERDP electroactive polymers				

TOC

Integrated TECHNOLOGIES, INC.

Tri-Chrome Treatments (ESTCP)

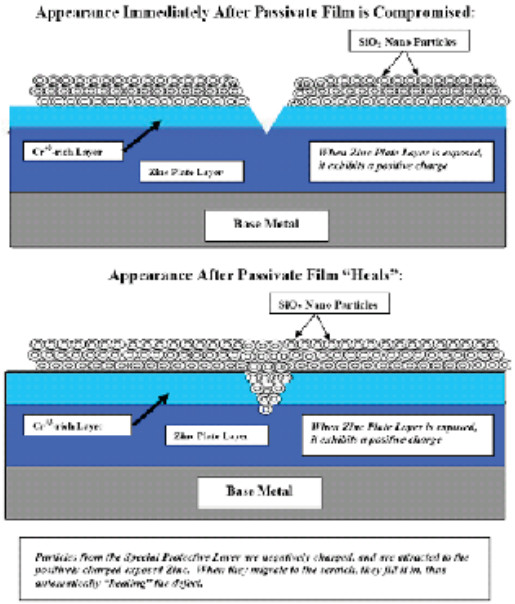
SERDP

ESTCP
Environmental Security Technology Certification Program

Description – Tri-chrome treatments

- Developed by NAVAIR and tested under ESTCP WP-0025
- Drop-in replacement for Cr^{6+} conversion coatings/sealers
- Cr^{3+} with Zr inhibitor
- Licensed and sold as
  - B-K Aklimate
  - Lusteron Aluminescent
  - Iridite TCP
  - Metalast TCP HF
  - Surtec ChromitAl TCP
- Other Cr^{3+}, such as Alodine 5900
- Commercial systems now often contain Co inhibitors and SiO_2 nanoparticles

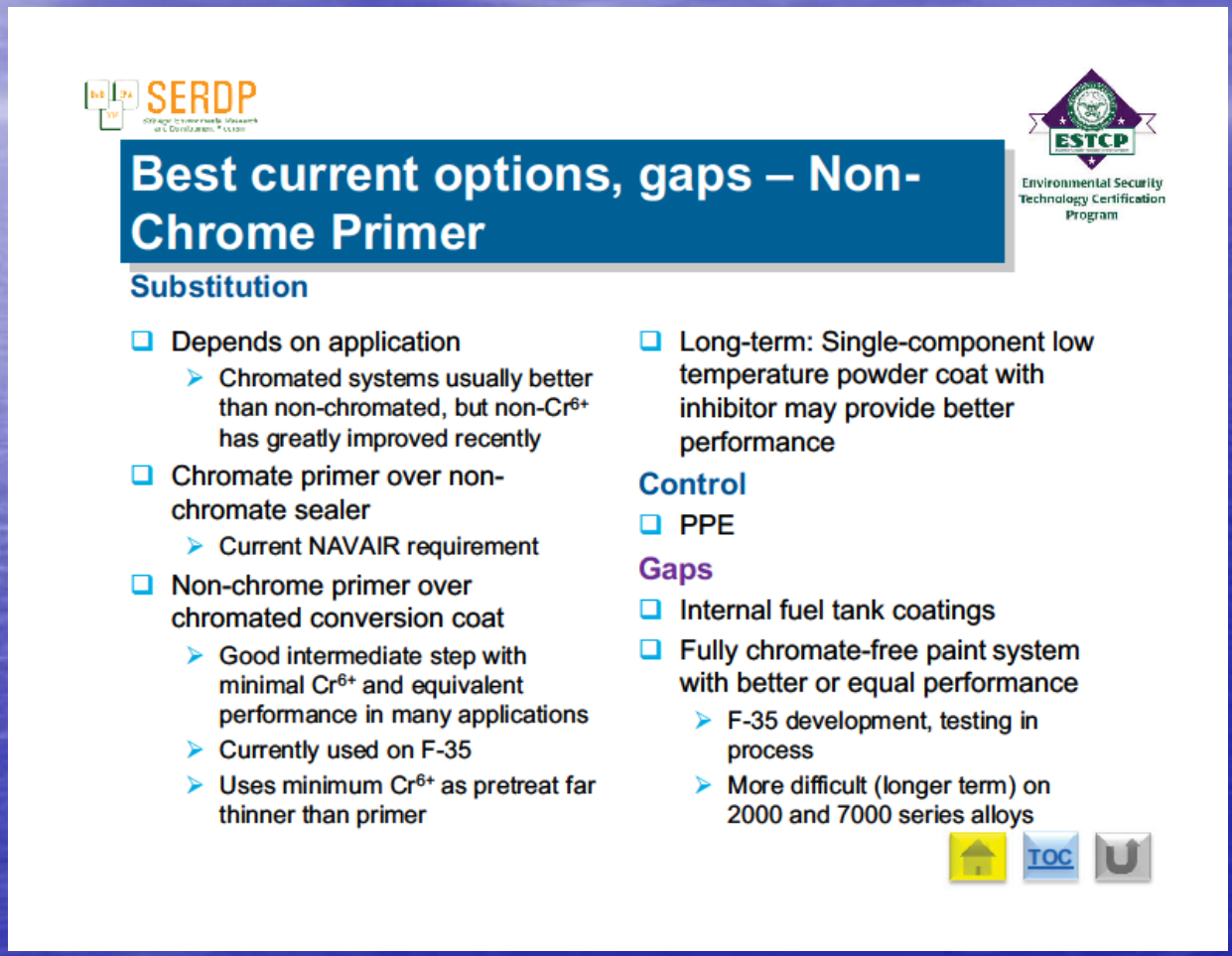
Click for additional Info



TOC

Integrated TECHNOLOGIES, INC.

Chromate/Primer Synergy



Integrated TECHNOLOGIES, INC.

Hard Chromium Plating Options

SERDP

ESTCP
Environmental Security Technology Certification Program

Options - Hard chrome plating

Substitution, control options					Best DoD options	Projects			Gaps	Implementation
Current tech Options	Commercial Status	DoD Status								
		R&D	Qual	Prod		Unsuccessful	On-going	Successful		
HVOF	All OEM mil and comm landing gear. some GTEs, acts	Being implemented at OO-ALC. Depot some GTE usage			✓	ESTCP HCAT HVOF: Completed			Spall-resistant coating for carrier a/c LG	A/c LG – new/MRO; hydraulics
Electroless Ni (internals)	Primary ID alt. Moderate and growing use, F-35	Some R&D, testing			✓	AFRL NLOS completed, Niplate 700. Not implemented			No qual ID chrome alt	Hydraulic IDs
Ni-based plate	Limited OEM use									
Other electroplates	Limited OEM use Co electroplates - GTEs	nCo-P electroplate dem/val, JAX			✓	SERDP nCo-P				
						ESTCP nCo-P D/V				
Gas/ion nitride	Some actuator rod				N/A					
Cr^{3+} electroplate	Decorative only				N/A					
Ta (gun barr, large)		Dem/val, firing test			TBD	"green gun barrel"			Qual alt for gun barrels	
Ta (gun barr, small)		R&D				SERDP CVD				
Ta (gun barr, small)		R&D				SERDP expl clad				
CONTROL OPTIONS										
Segregated line		In use (FRC-SE)			✓				Fit	FRC-SE
Enclosed line		In planning (WR ALC)			✓				Cost	
Surfactants		In use								

TOC

Integrated TECHNOLOGIES, INC.

Hard Chromium Plating Alternatives

- HVOF (Various)
- Nanocrystalline Co/P (Integran) looks promising but it has not scaled up well
- Issues
  - Cost
  - Line-of-Sight

Integrated TECHNOLOGIES, INC.

HVOF

SERDP

ESTCP
Environmental Security Technology Certification Program

Status – HVOF

Commercial/OEM

- Specified on all new landing gear programs
  - B787, B767-400, A380, A350
  - F-35 (all variants)
- Increasing use for hydraulics
  - Aircraft (OEM, MRO)
  - Caterpillar vehicle hydraulics (OEM, MRO)
- Specifications
  - AMS 2447, 2448, 2449
  - Boeing 5851

DoD

- Project to replace all EHC on LG at Ogden ALC
  - 38-128 qualified so far
- Advanced testing, Qualifications
  - Flight testing EA-6B (JAX), CH-53 (FRC-E)
  - C-2, P-2, P-3, C-130 propeller hubs WR-ALC, FRC-E
  - H-1 drive and rotor components, FRC-E
  - P-3 LG (FRC-SE) qual'd but not in production
  - TF33 GTE (OC-ALC)

TOC

Integrated TECHNOLOGIES, INC.

Decorative Chromium Plating

- Trivalent Chromium Plating and PVD are the best alternatives to Hexavalent Chromium Plating
- PVD "top coats" provide lifetime finish over nickel plating with excellent wear/abrasion resistance…decorative hardware and plumbing
  - Capital Costs
  - Process Flow
- Trivalent Chromium Plating provide a good alternative for automotive trim and other similar parts where corrosion resistance is primary non-decorative requirement
  - Hexavalent Chromium Plating can be Operated in a Closed Loop
  - Color is the only issue to complete conversion

Integrated TECHNOLOGIES, INC.

PVD Coatings

- Decorative Thin Films Only
  - Synergistic Coating over Electroplated Nickel

Integrated
TECHNOLOGIES, INC.

Nickel vs. Cobalt

- Continued debate regarding which element is more toxic
- Many alternatives to Cadmium Plating include Nickel Alloy Coatings or Substrates
- Most alternatives to Chromium Plating include Nickel and/or Cobalt Alloy Coatings
- Many alternatives to chromates include Cobalt in addition to trivalent chromium

Integrated TECHNOLOGIES, INC.

Hazardous Material vs. Hazardous Process Perspective

- Alumiplate…hazardous process produces nonhazardous material…pure aluminum
- Chromium Plating…hazardous process produces nonhazardous material…pure chromium
- Chromate…hazardous process produces hazardous material
- Cadmium….hazardous process produces hazardous material

Integrated TECHNOLOGIES, INC.

Hazard Management for Wet Processes

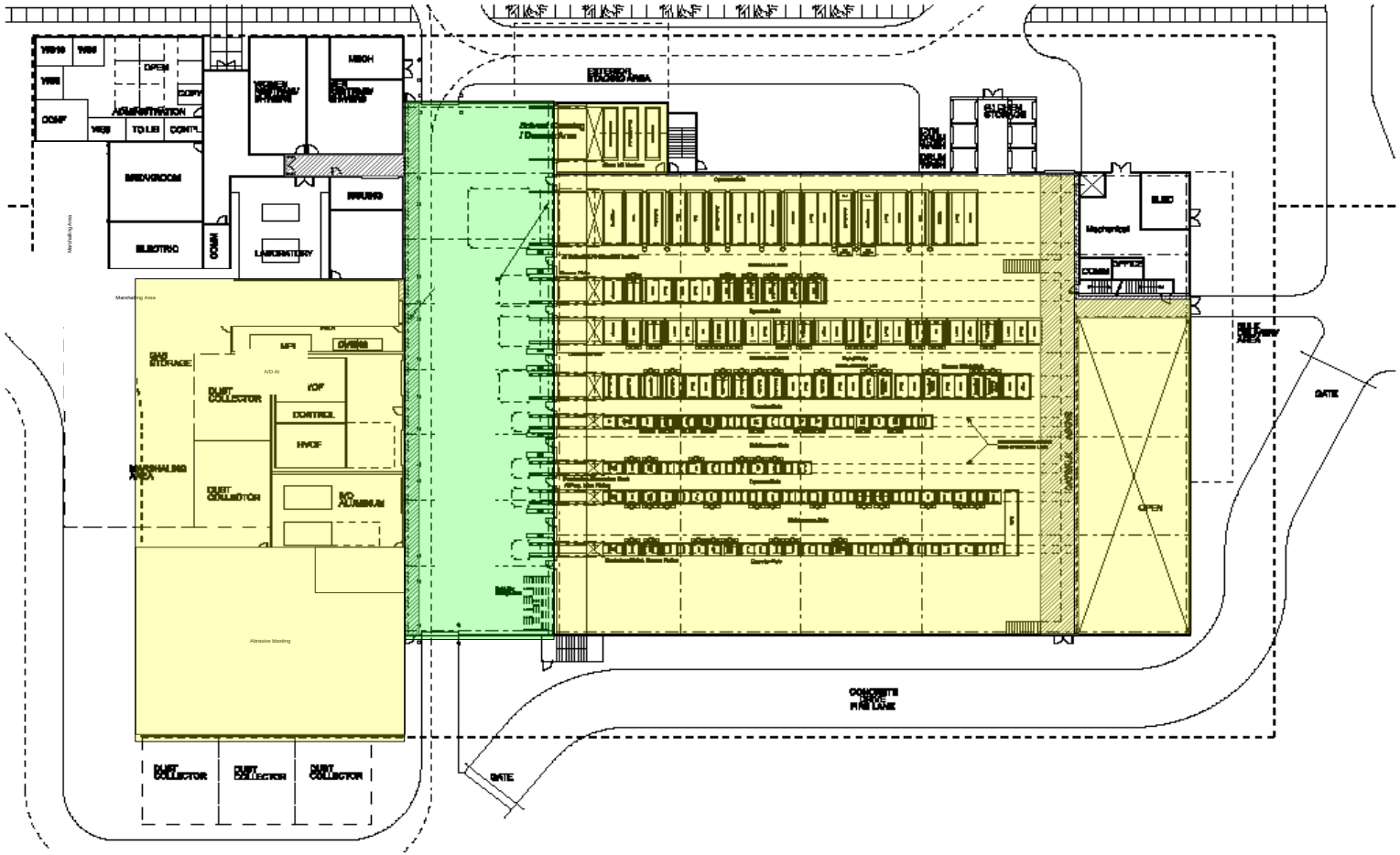
- Minimize Operator Exposure
  - Automation and Tooling
  - Enclosures
  - Automatic Covers
  - Ventilation System Design
  - Minimize Mist with Agitation Design
- Spill Prevention & Control – Asset Management & Preventative Maintenance
- PPE

Integrated TECHNOLOGIES, INC.

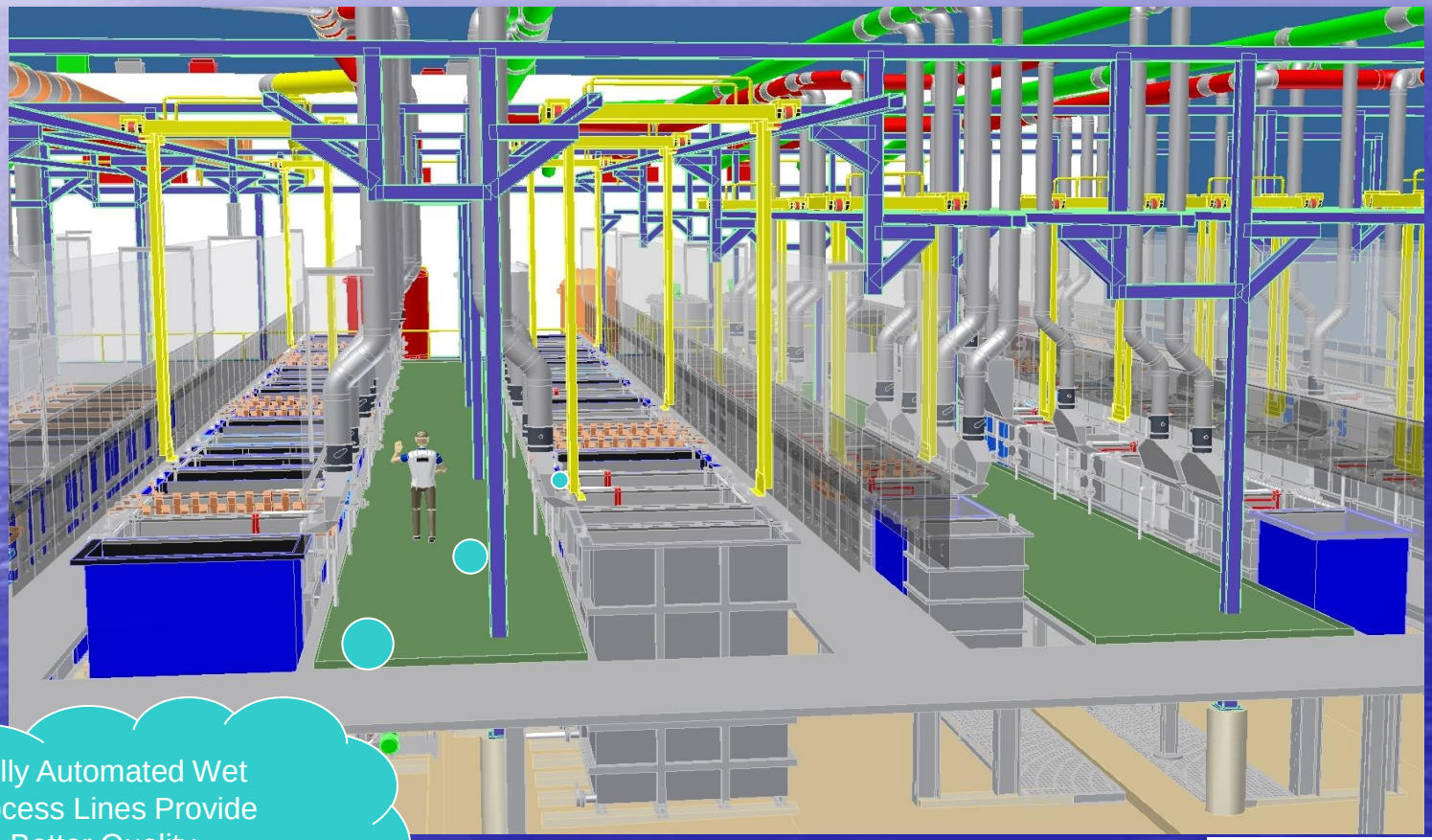
RAFB AMFF

Designing for LEED

Leadership in Energy and Environmental Design



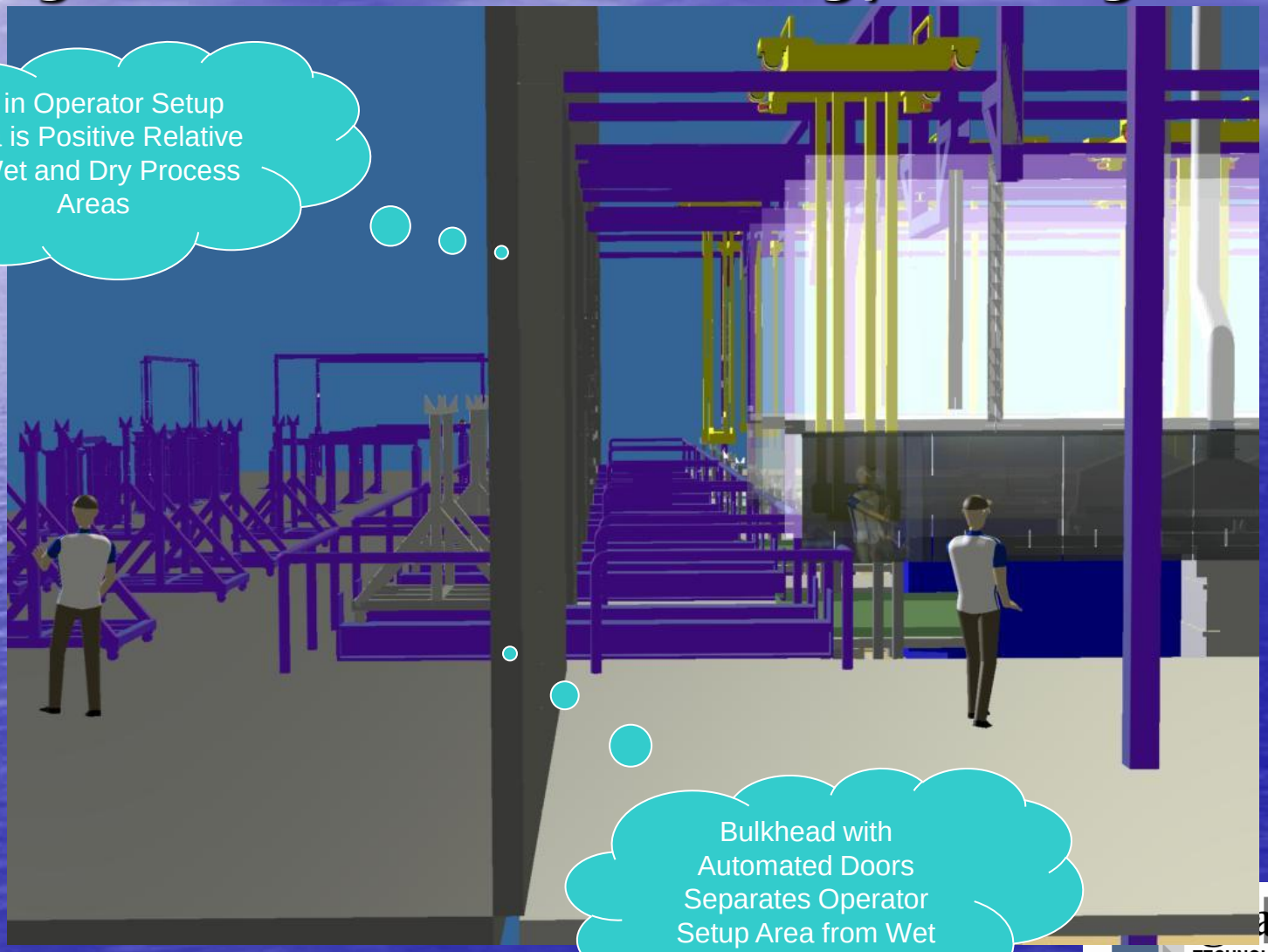
Robins AFB Process Automation



Fully Automated Wet Process Lines Provide Better Quality, Productivity and Safety

Integrated TECHNOLOGIES, INC.

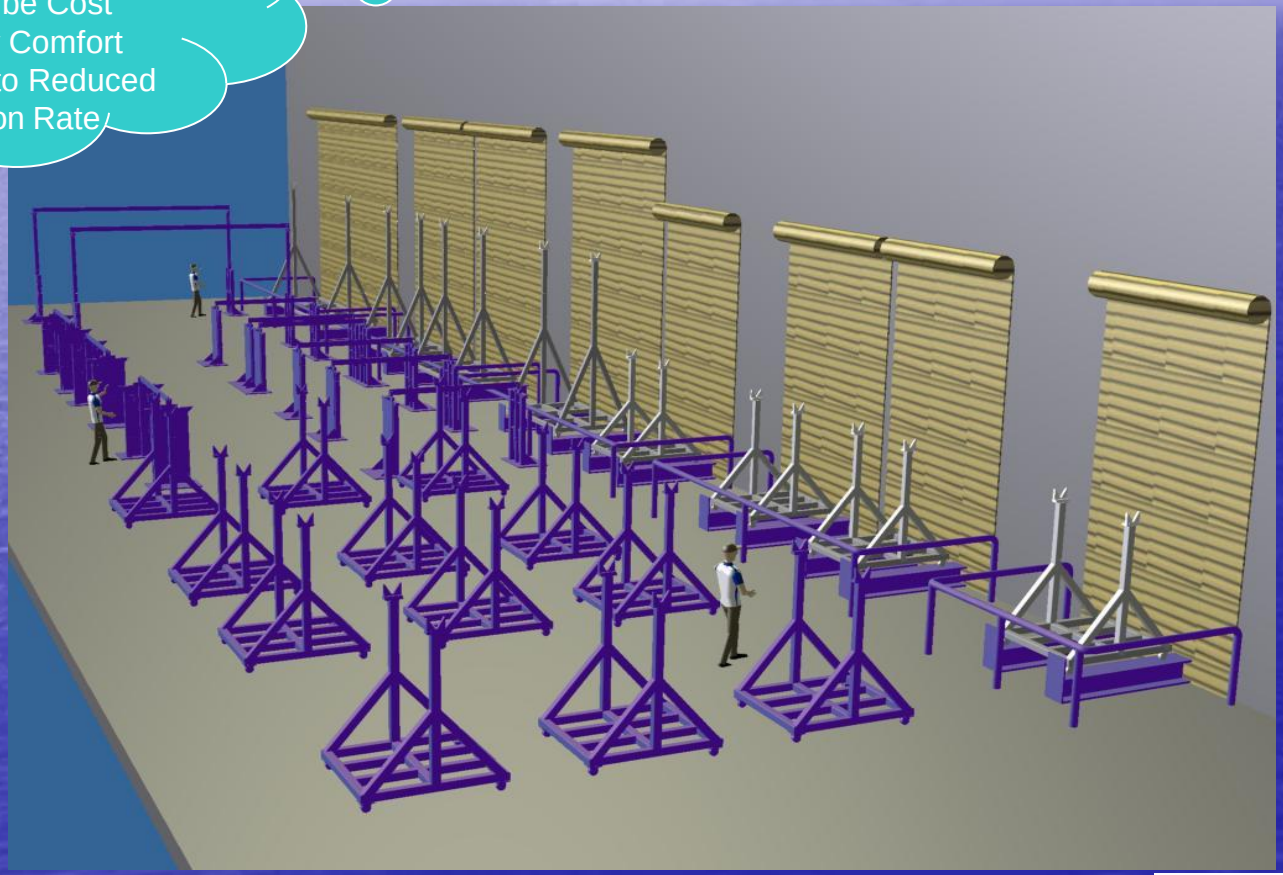
Integrated Hazard and Energy Management



ated
TECHNOLOGIES, INC.

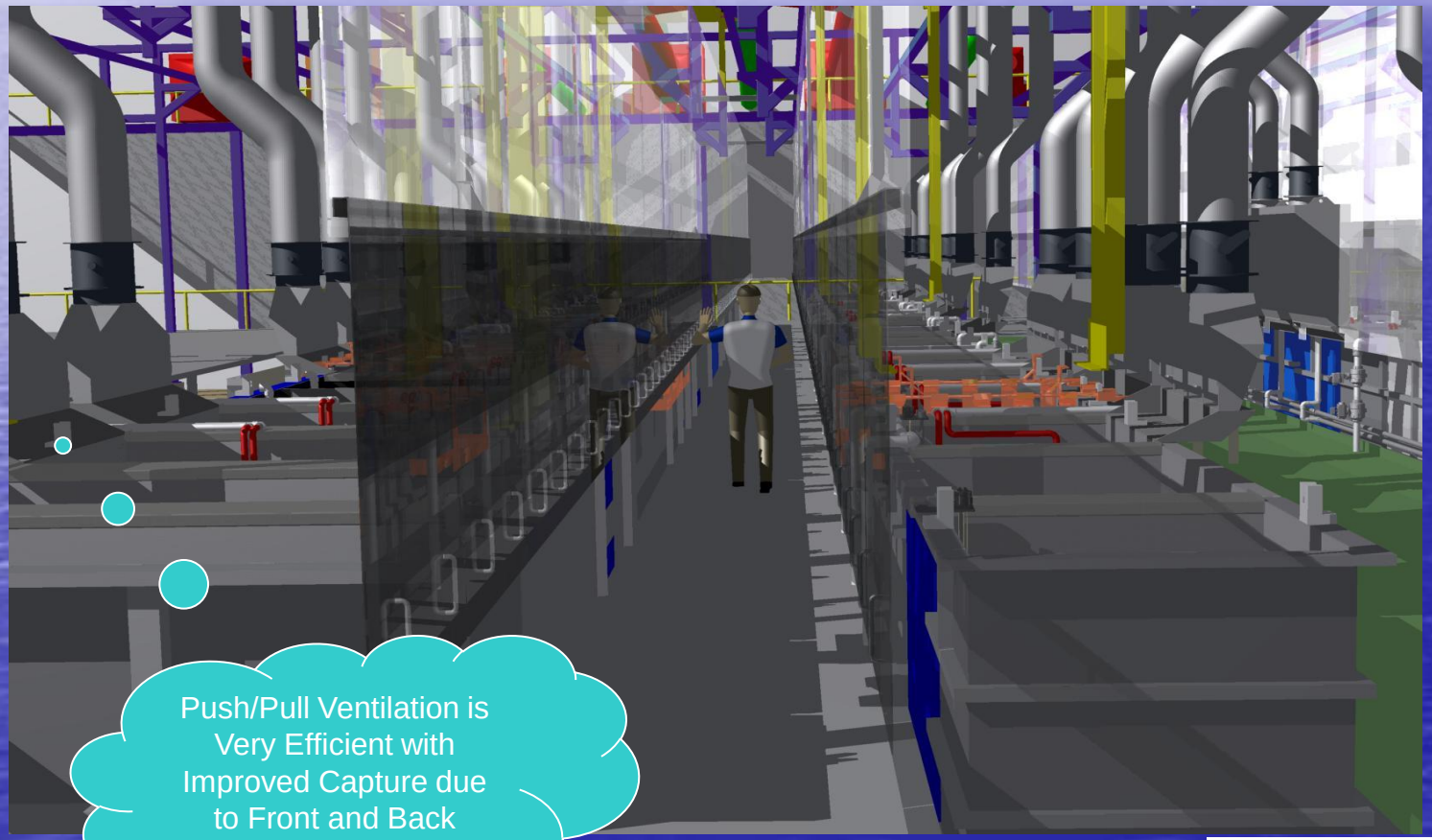
Integrated Hazard and Energy Management

Air in Operator Setup Area can be Cost Effectively Comfort Cooled due to Reduced Ventilation Rate



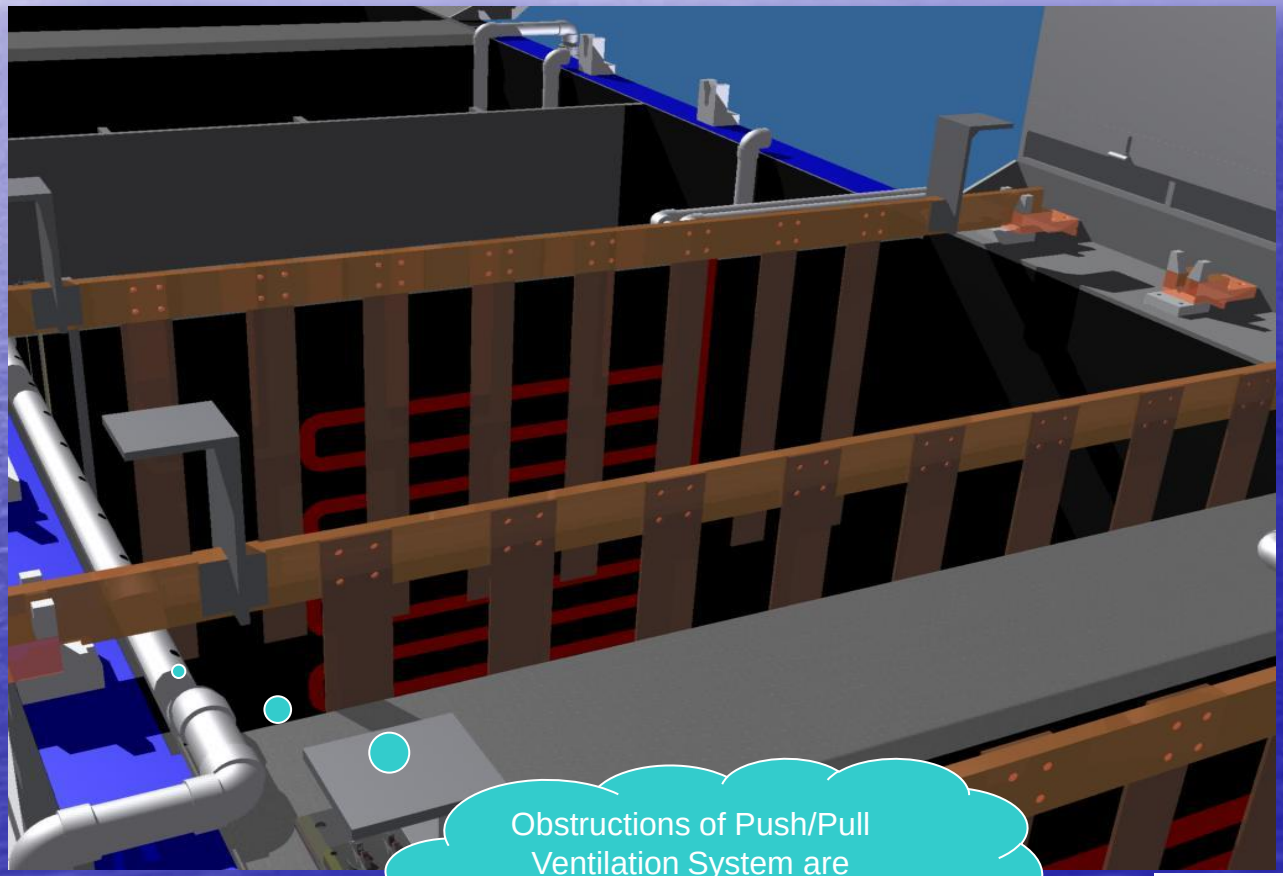
Integrated TECHNOLOGIES, INC.

Integrated Hazard and Energy Management



Integrated TECHNOLOGIES, INC.

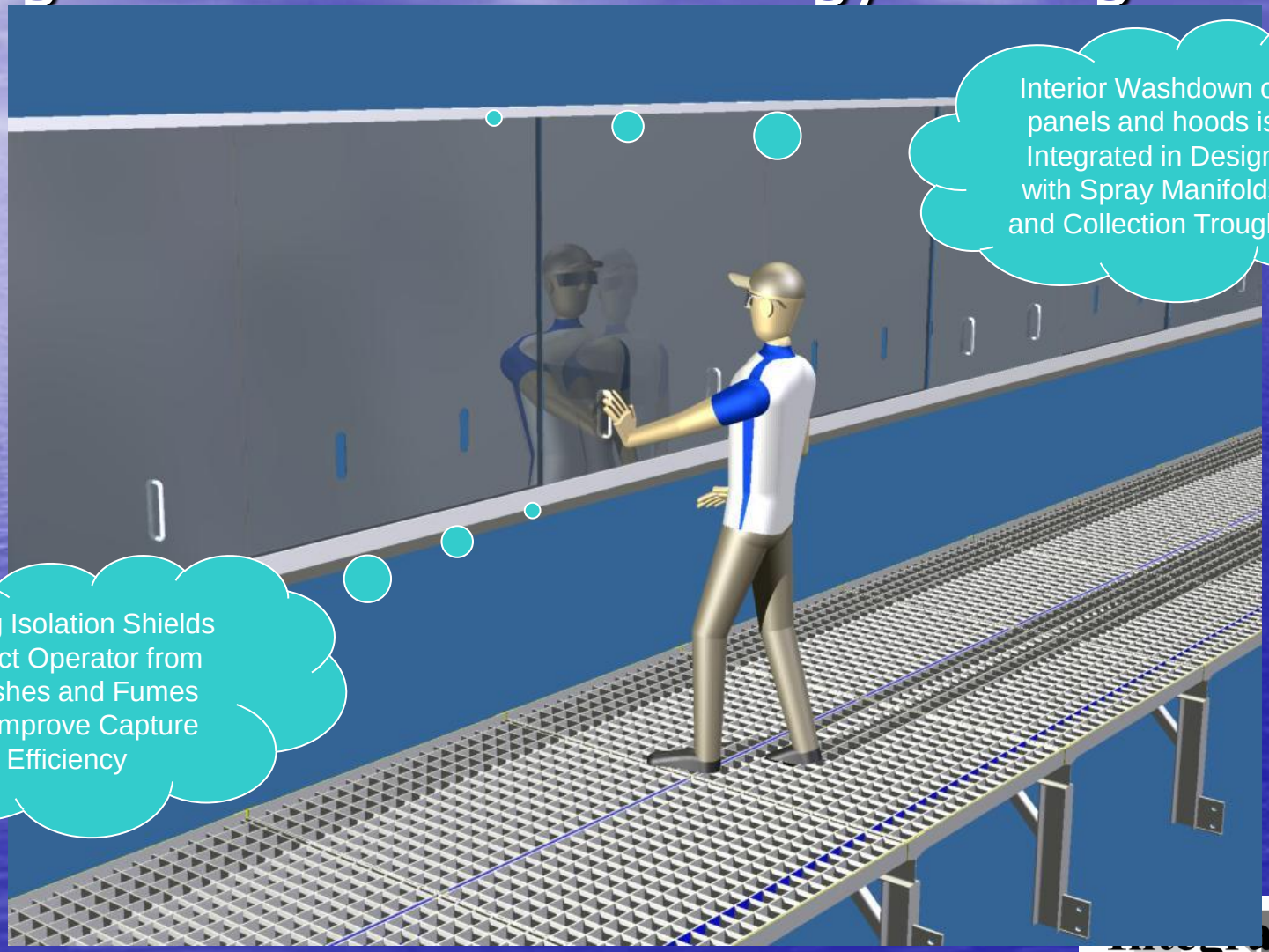
Integrated Hazard and Energy Management



Obstructions of Push/Pull Ventilation System are Minimized

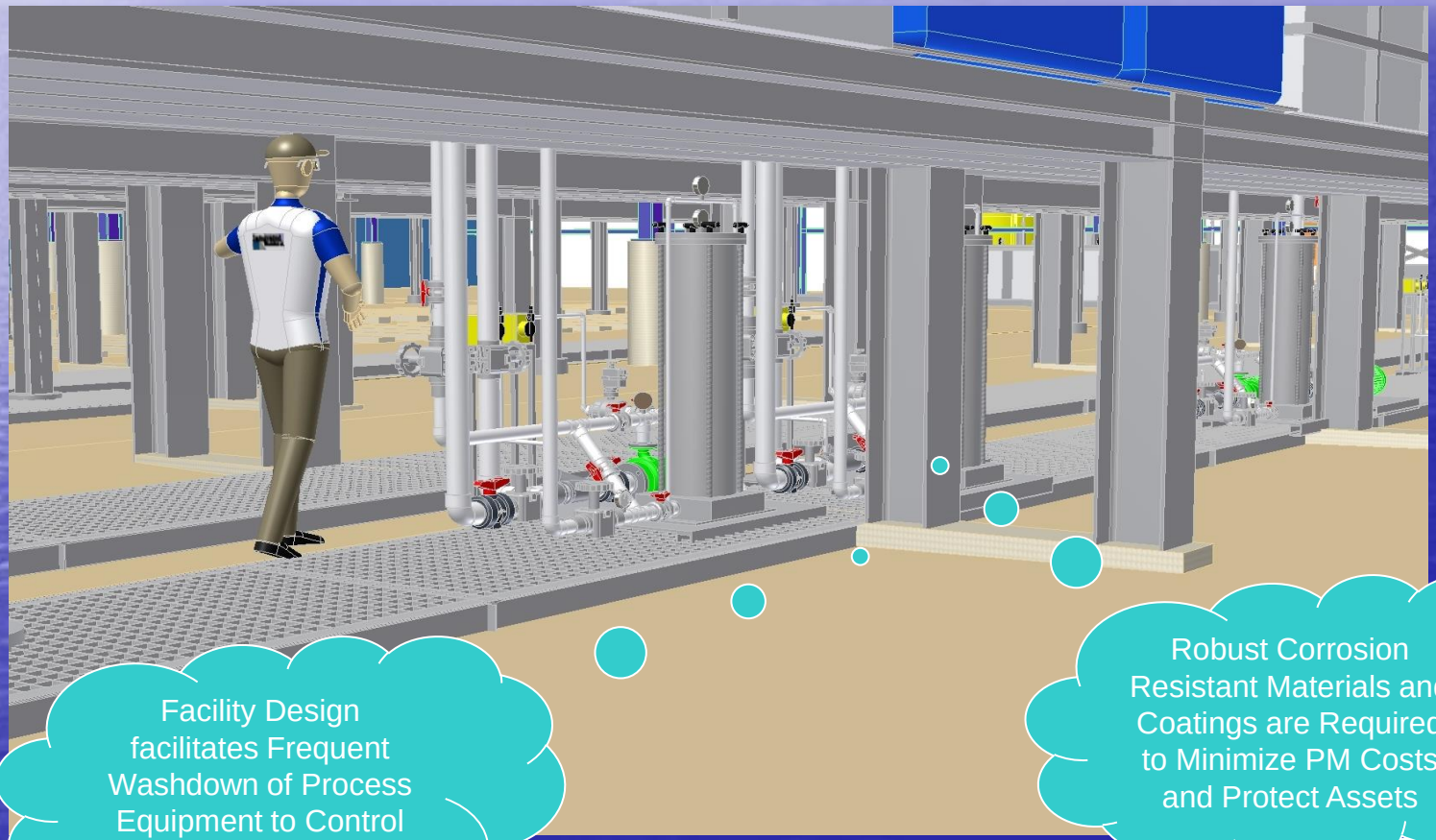
Integrated TECHNOLOGIES, INC.

Integrated Hazard and Energy Management



TECHNOLOGIES, INC.

Preventative Maintenance and Asset Management



Facility Design facilitates Frequent Washdown of Process Equipment to Control Corrosion

Robust Corrosion Resistant Materials and Coatings are Required to Minimize PM Costs and Protect Assets

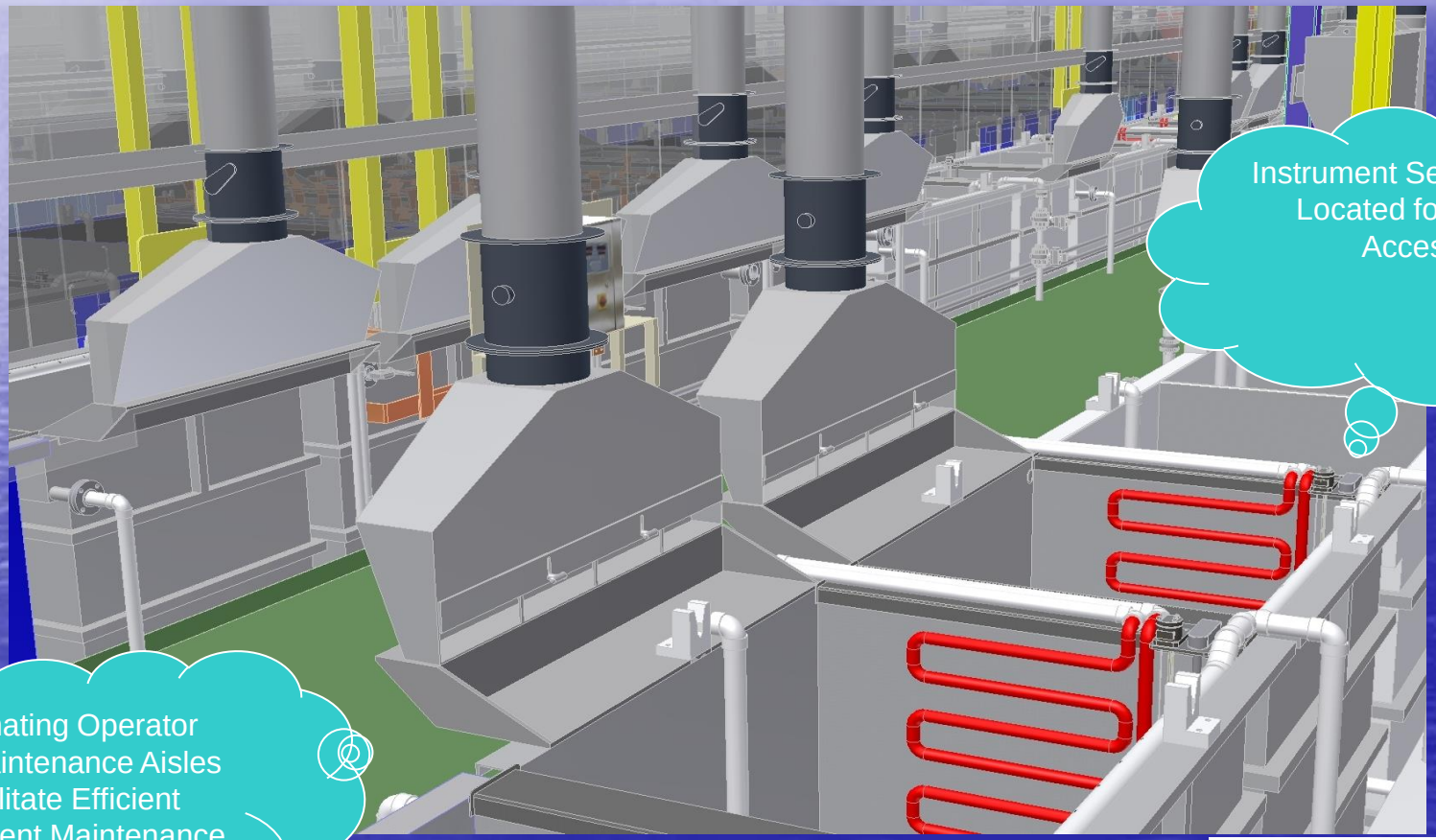
Integrated TECHNOLOGIES, INC.

Design for Maintenance

Efficient Mechanical Design and Layout Reduces Maintenance Time and Cost

Integrated TECHNOLOGIES, INC.

Main Level Maintenance Aisles

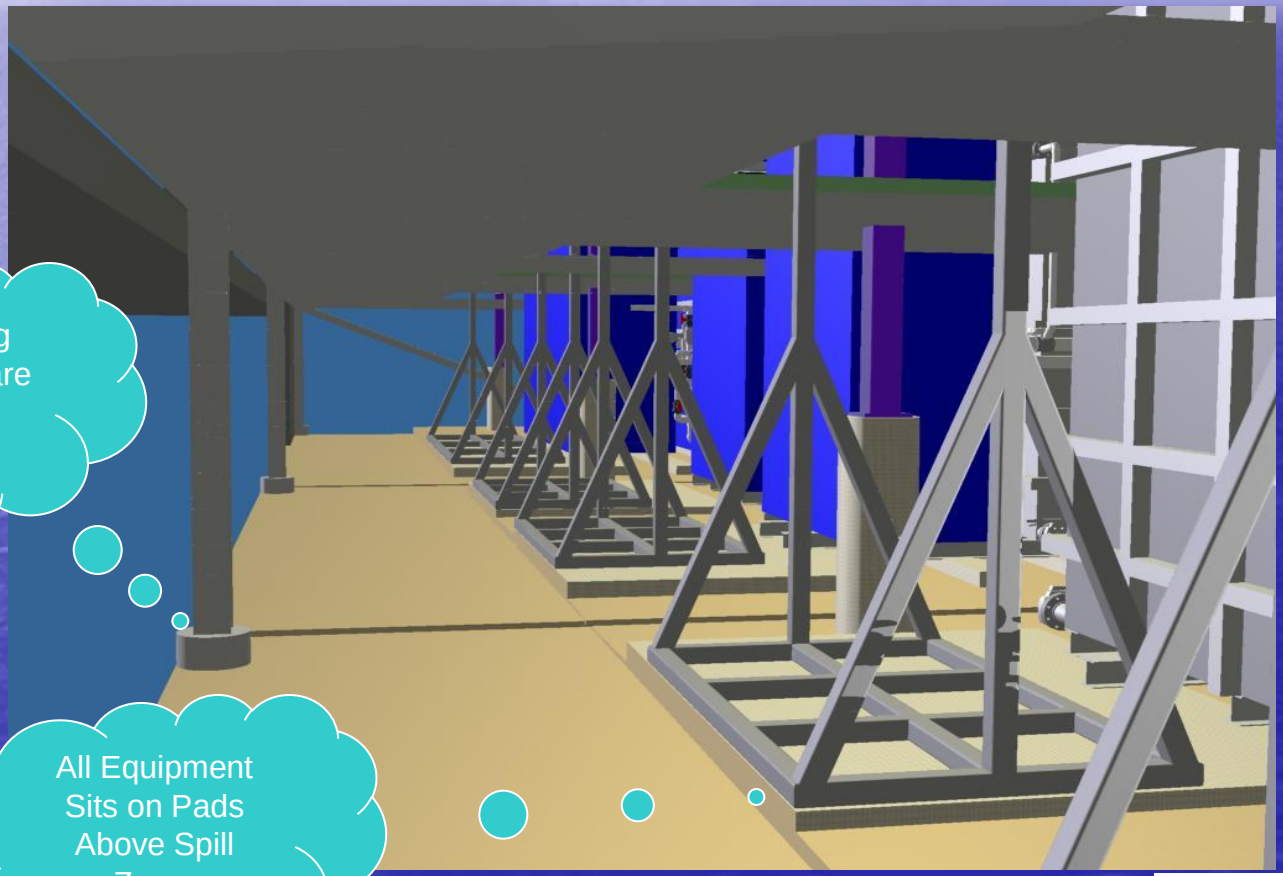


Instrument Sensors are Located for Easy Access

Alternating Operator and Maintenance Aisles Facilitate Efficient Equipment Maintenance

Integrated TECHNOLOGIES, INC.

Integrated Spill Prevention/Control and Corrosion Management

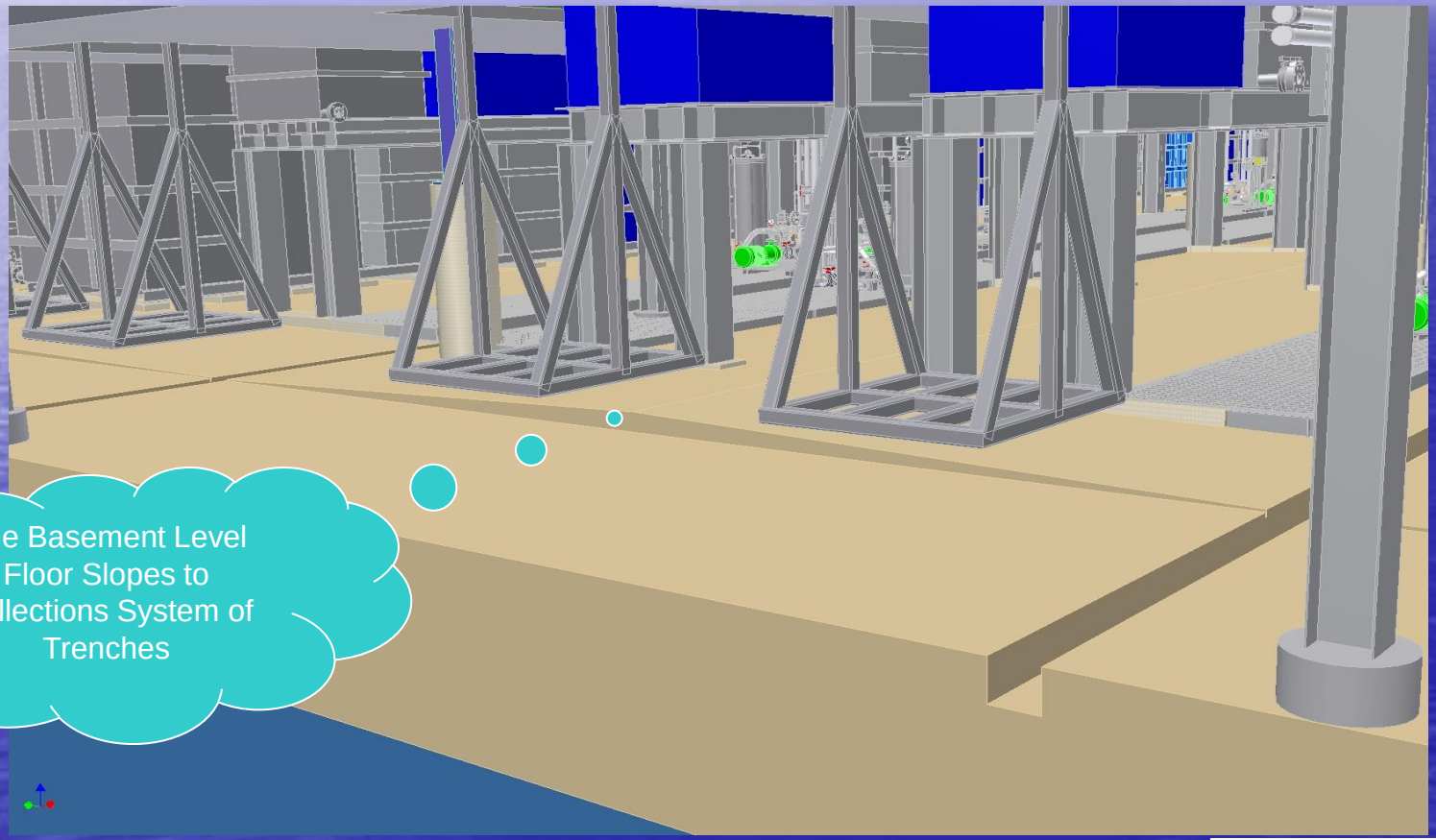


Floor Coating Penetrations are Above Spill Zone.

All Equipment Sits on Pads Above Spill Zone.

Integrated TECHNOLOGIES, INC.

Integrated Spill Prevention/Control and Corrosion Management

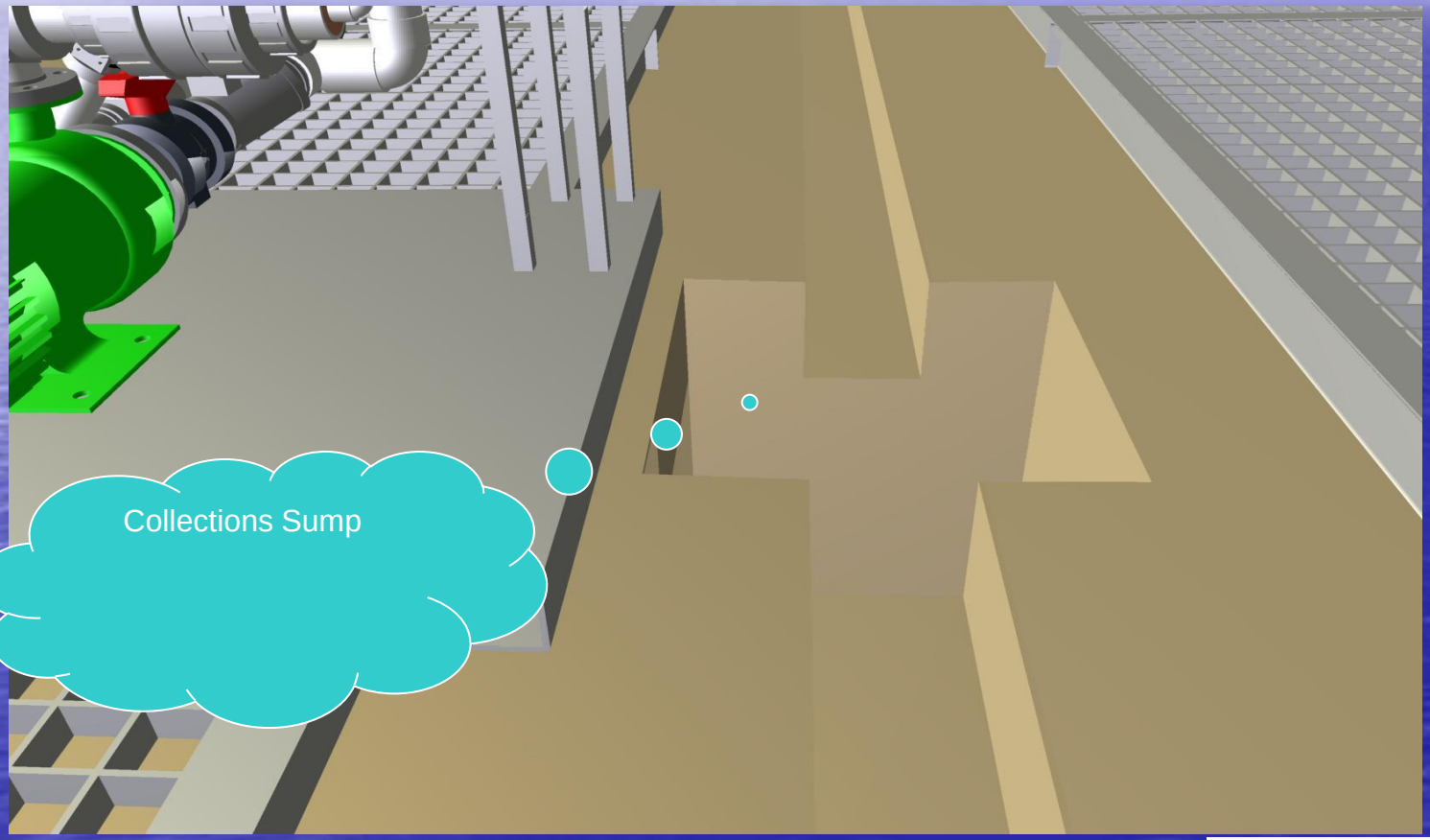


Integrated TECHNOLOGIES, INC.

Integrated Spill Prevention/Control and Corrosion Management

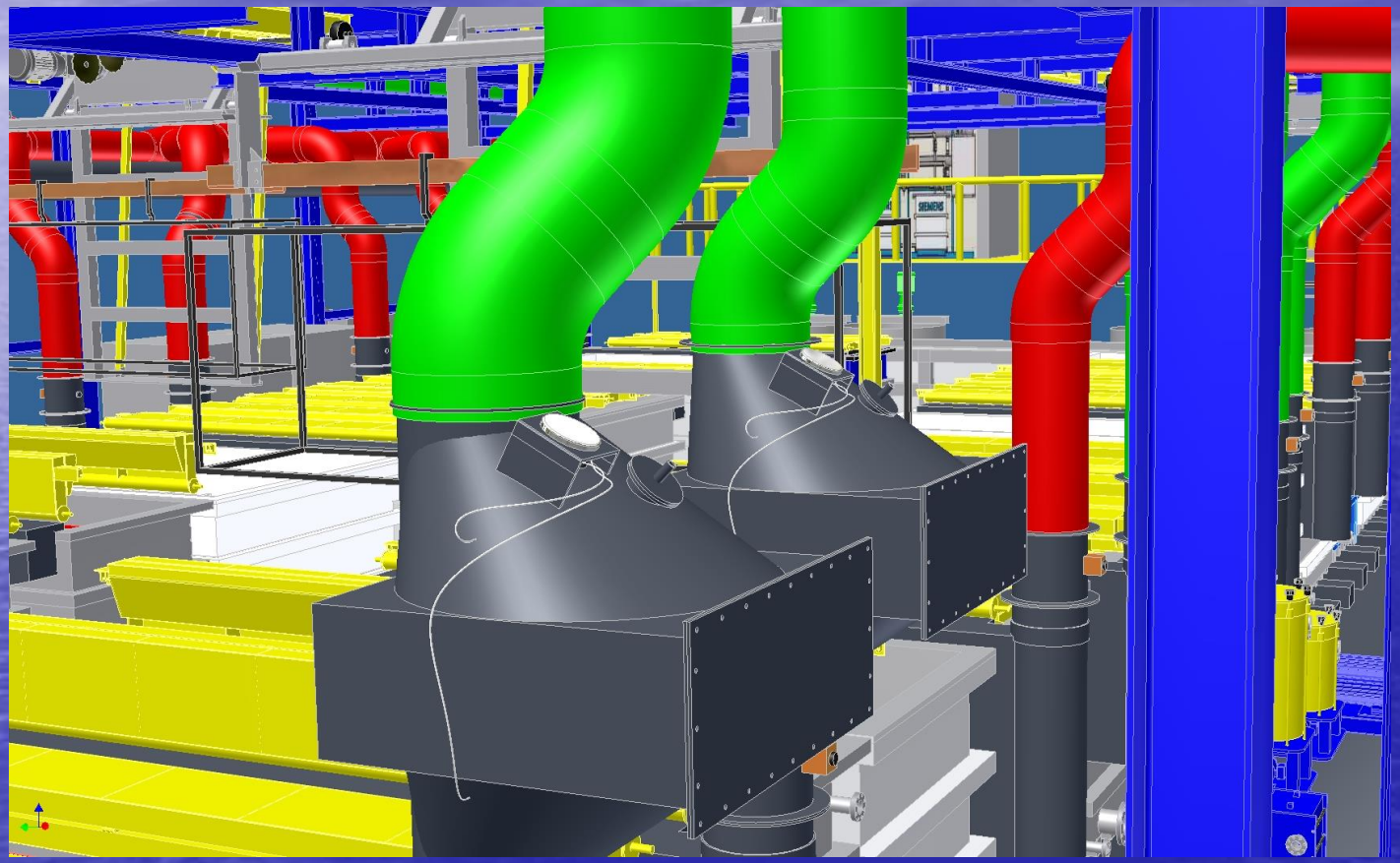
Integrated
TECHNOLOGIES, INC.

Integrated Spill Prevention/Control and Corrosion Management



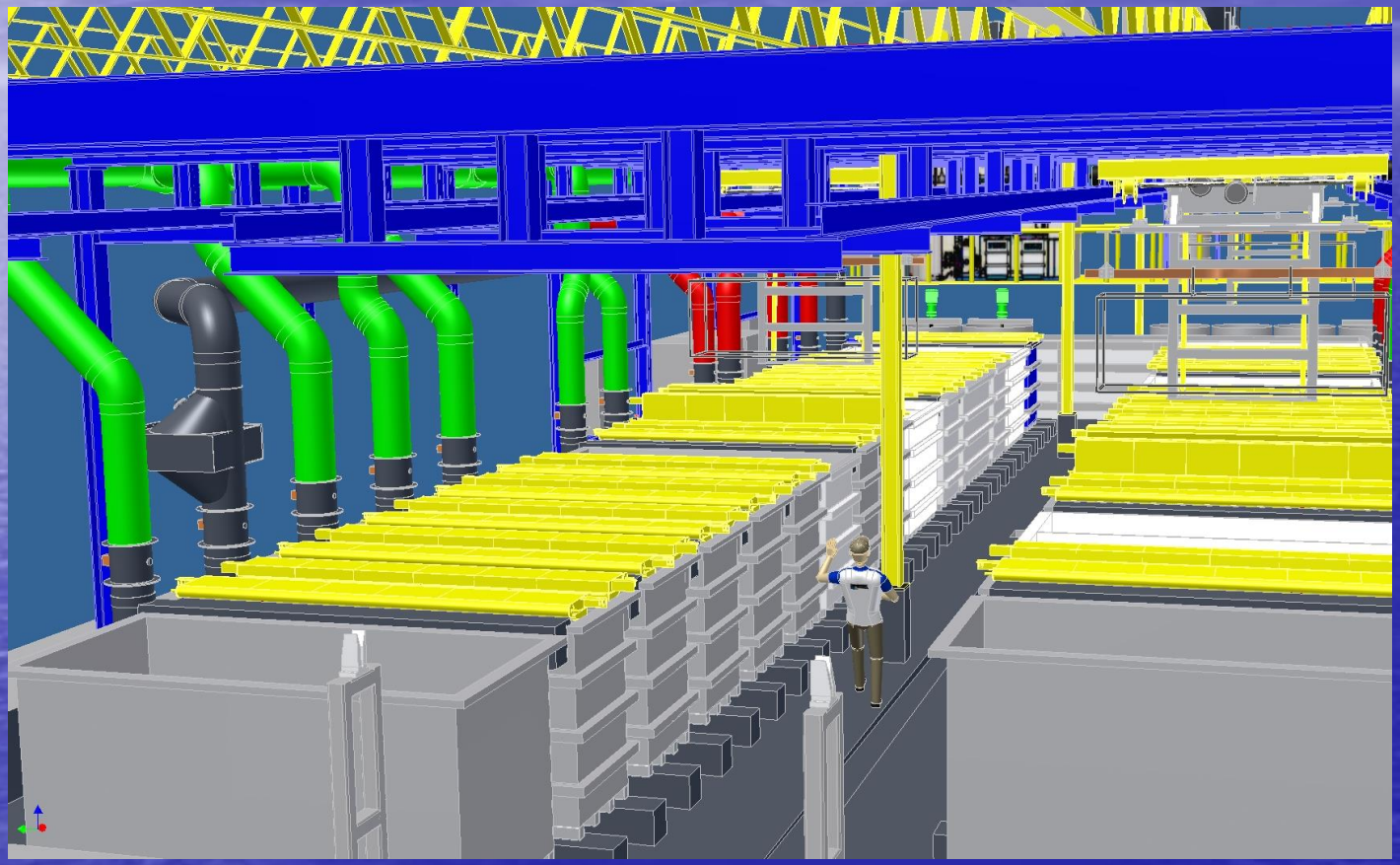
Integrated
TECHNOLOGIES, INC.

Automatic Covers



Integrated TECHNOLOGIES, INC.

Automatic Covers



Integrated
TECHNOLOGIES, INC.

Resources

- NASF Online Data Library
  - www.nasf.org
- ASETSDefense (HCAT/JCAT)
  - www.hcat.org
  - www.materialoptions.com
  - www.asetsdefense.org
  - www.hazmat-alternatives.com

Integrated TECHNOLOGIES, INC.