Idaho National Engineering and Environmental Laboratory

ACERC Influence on Radioactive Waste Calcination

Richard Boardman,
Ph.D. – 1990 (BYU)
Consulting Engineer, INEEL

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Idaho Operations Office

BYU Chemical Engineering Graduates who have worked at the "Chem Plant"

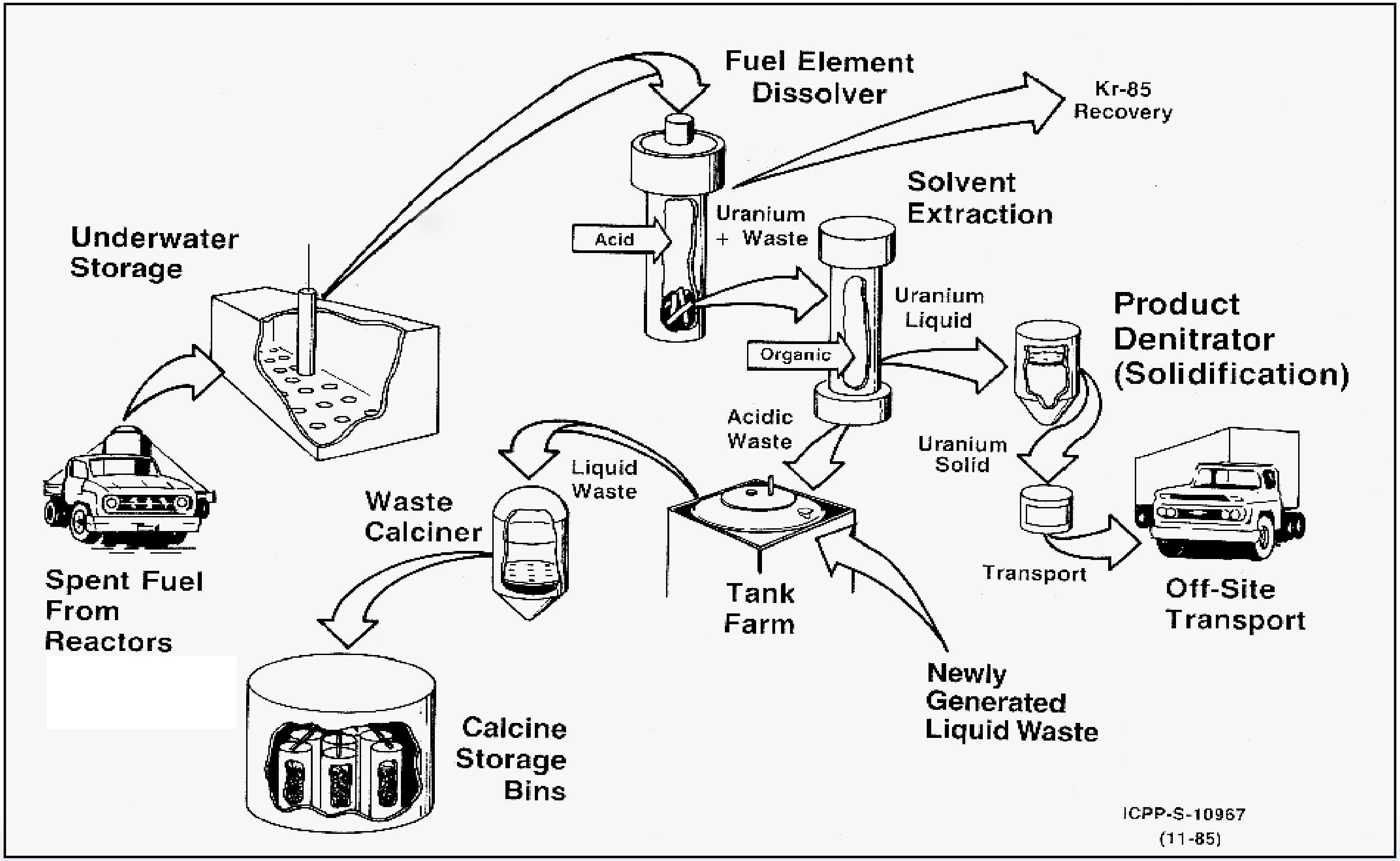
ANDERSON, MICHAEL
ARGYLE, MARK
BLACK, DOUGLAS
BOARDMAN, RICHARD
BROWN, BLAINE
CALDWELL, MICHAEL
ELDREDGE, BRAD
FITCH, CLAIR
HATFIELD, KENT
ILLUM, DOUGLAS
JACOBSON, VICTOR
KIRKHAM, ROBERT
LUKE, DALE
MARSHALL, DANIEL
MARSHALL, DOUGLAS
MIYASAKI, DEAN
NICHOLS, TODD
OWENS, PAUL
PALMER, BRENT
POCOCK, GARY
SIMPSON, GARY
SMITH, RON
SMOOT, DOUGLAS
SOELBERG, NICK
STAIGER, DANIEL
SWENSON, KIRK
SWENSON, MIKE
WILLIS, NORM
WOOD, RICHARD
WOODARD, JULIE

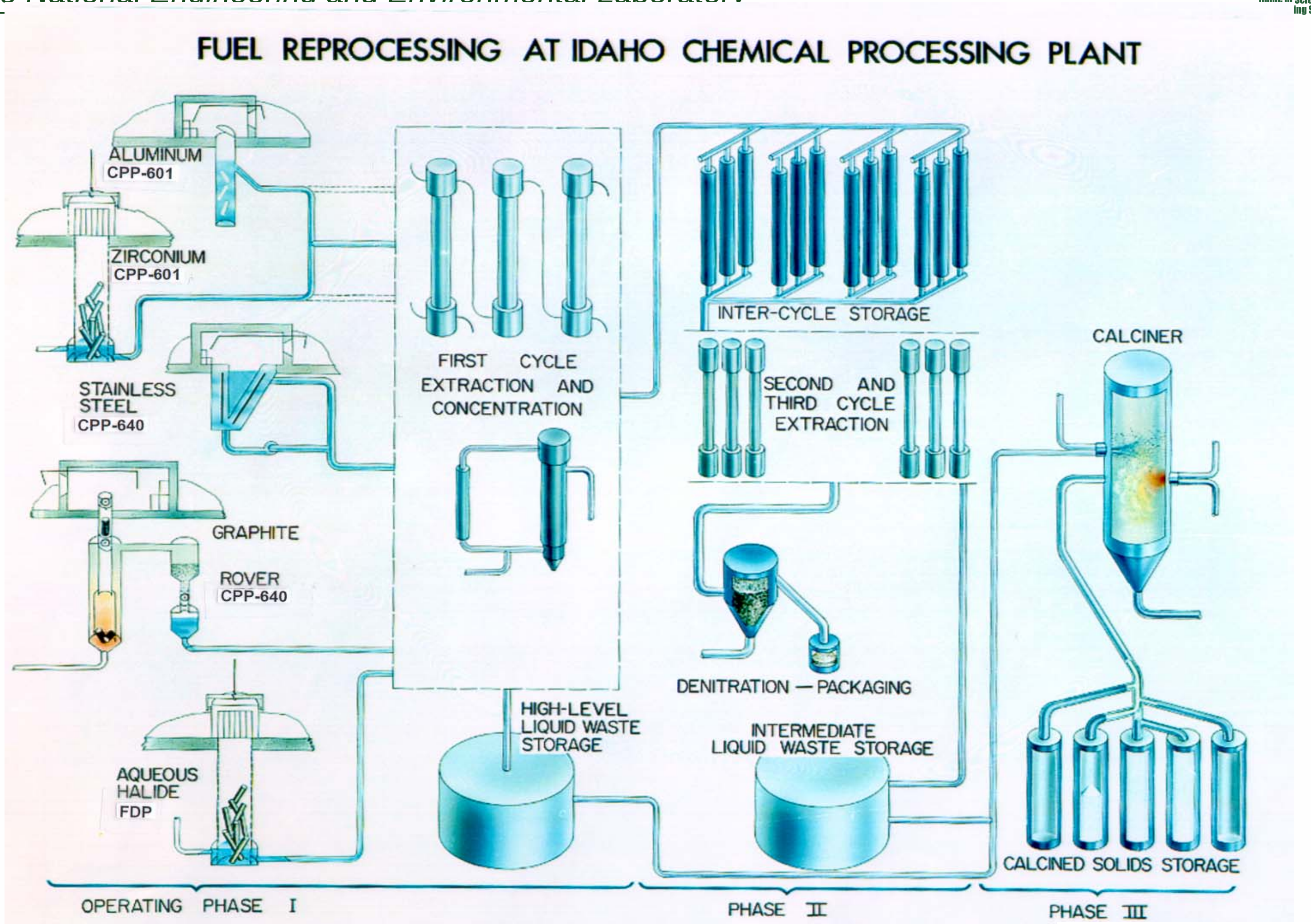
Calciner Applied Technology R&D

- 1990-1992: SCR NOx Abatement Pilot Plant Test Operations
- 1993 – 2004: NO_x/THC/CO Staged Offgas reburner
- 1994 – 2000: New Calcination Flowsheets
  - Sugar addition (redox reaction)
  - High Temperature
- 1998 – 2001: EPA Sampling Method Development
  - Revised collection and analytical methods
  - Emissions compliance tests


99-204-2-4

INTEC Spent Fuel Management Process Flow





FUEL DISSOLUTION | 1ST CYCLE EXTRACTION | 2ND & 3RD CYCLE EXTRACTION | CALCINATION

Fuel Reprocessing Activities

- *Designed for recovery of U-235*
- ***Aluminum fuels*** *– Dissolved in nitric acid with mercuric nitrate catalyst. Tributyl phosphate (TBP) used for first cycle extraction, hexone (methyl isobutyl ketone) used used for second/third cycle extractions*
- ***Zirconium fuels*** *– Dissolved in hydroflouric acid. TBP and hexone used for extraction.*
- ***Stainless steel fuels*** *– dissolved in sulphuric/nitric acid or with electric current.*
- ***Graphite fuels*** *– oxidized to reduce graphite. Uranium materials dissolved in hydroflouric acid*

Reprocessing Wastes Generated

- ***First-cycle raffinates** containing ~99% of the waste radionuclides, high in decay heat, stored in high-level waste storage tanks with cooling coils*
- ***Second/third-cycle raffinates**, containing the remaining ~1% of the waste radionuclides, stored in intermediate-level storage tanks without cooling coils*
- *Radioactive **liquid wastes from decontamination** activities in support of operations and maintenance, from calcination off-gas scrub systems, from filter leaching and debris treatment activities, and from contaminated facility sumps. (Evaporator systems used to concentrate dilute waste streams prior to storage in the tank farm)*


96-648-1-1

General Characteristics of Reprocessing Waste

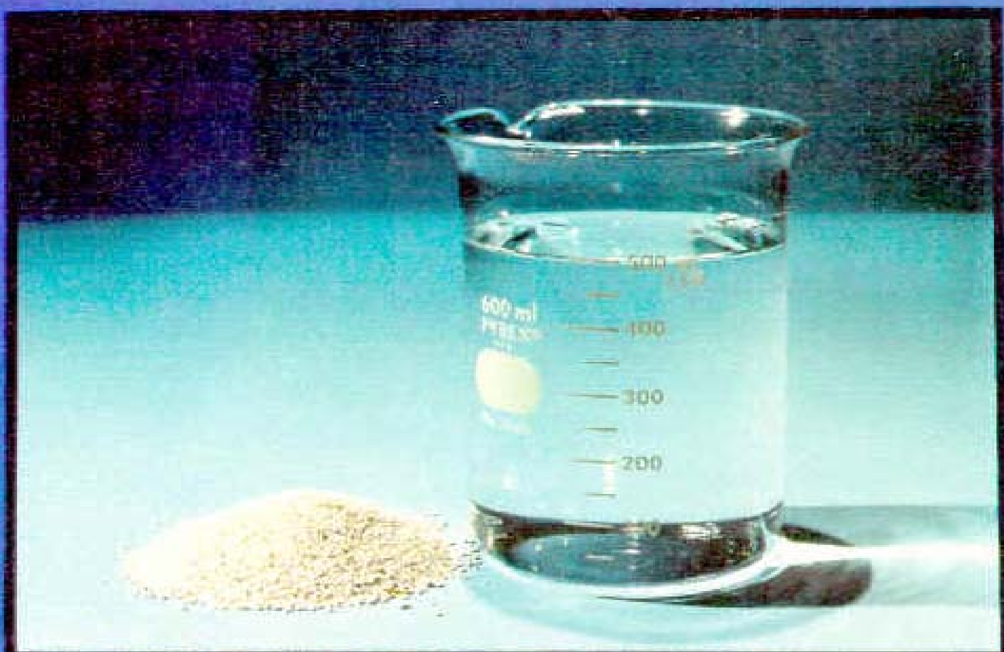
- *In all, ~ 9 million gallons of highly acidic liquid waste have been stored the tank farm as a result of fuel reprocessing activities – (**stainless steel storage tanks** allowed storage of acid waste without neutralization)*

- *Some small solid particles exist in the liquid waste – they form a thin (up to a few inches) layer on the tank bottoms – solids are typically light and relatively easy to move*

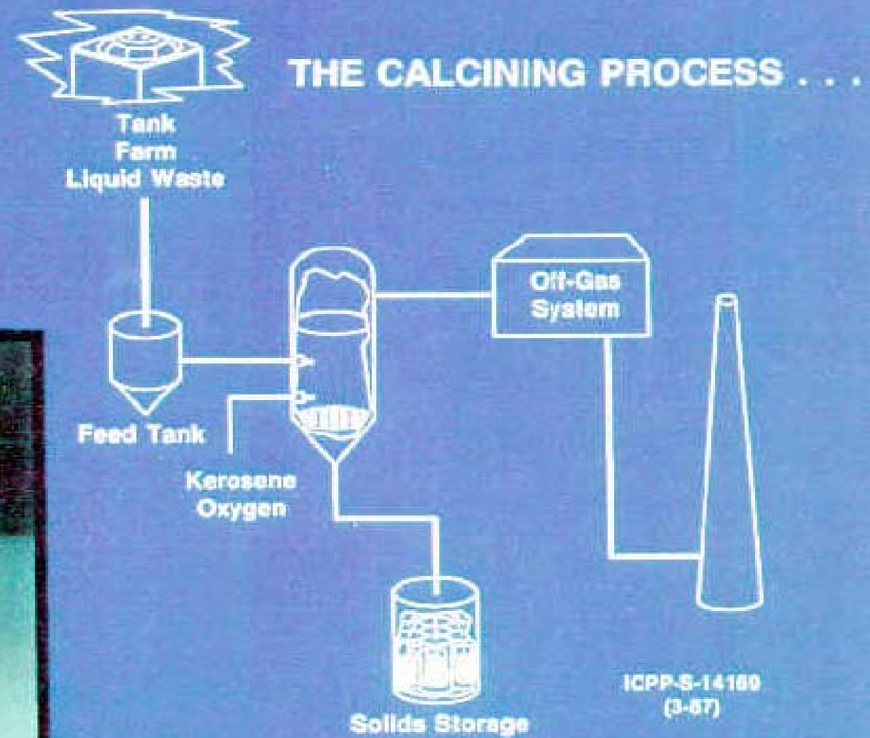
- *Waste contains constituents identified as "hazardous" under RCRA regulations*

Calcining Process

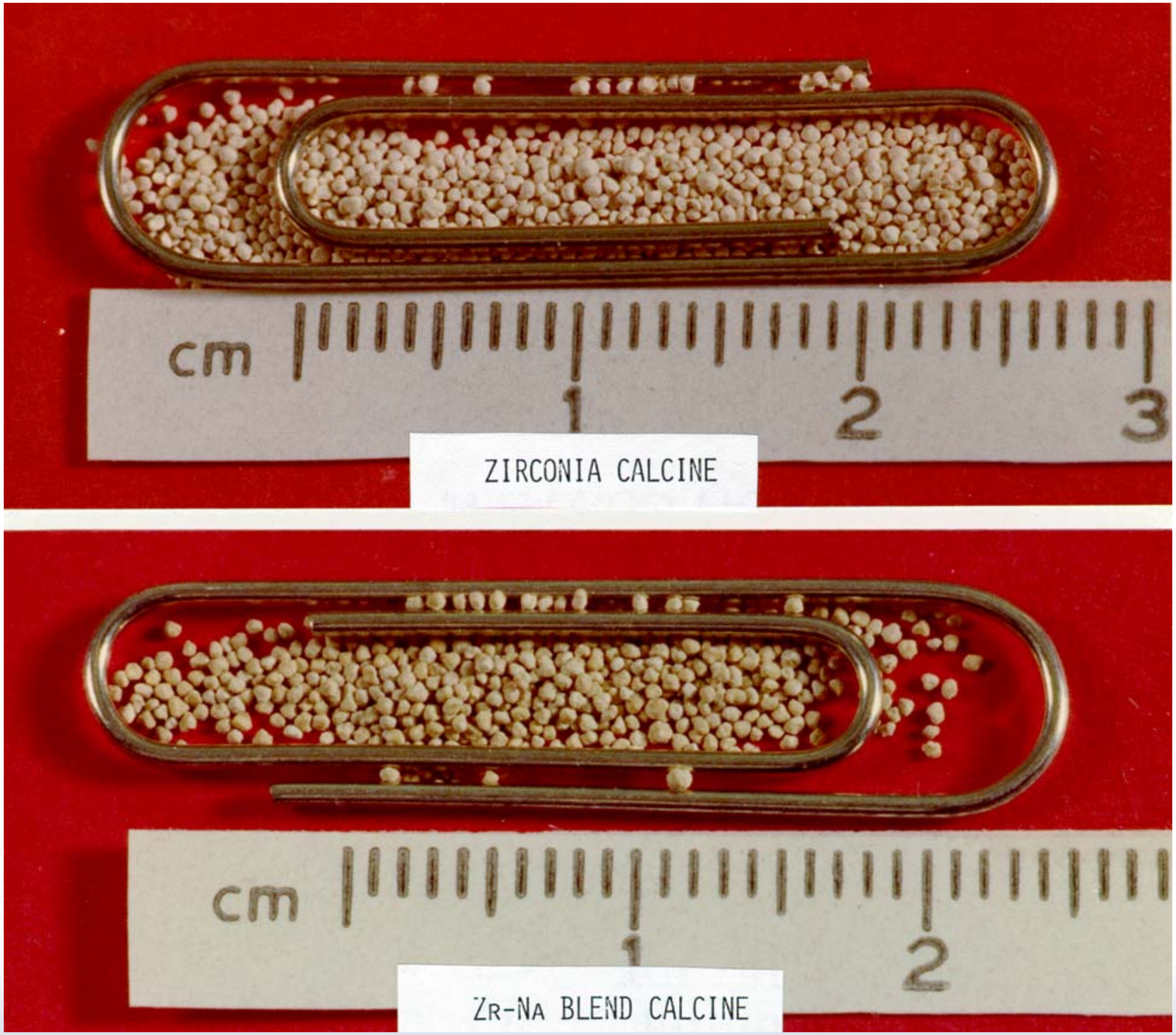
- Conversion of liquid, high-level radioactive waste to solid by calcination (high temperature drying) process.
- Fluidized bed produces solidified granular high-level radioactive waste.
- Pneumatic transfer of solid waste to bin set storage.
- Sophisticated effluent cleanup system.

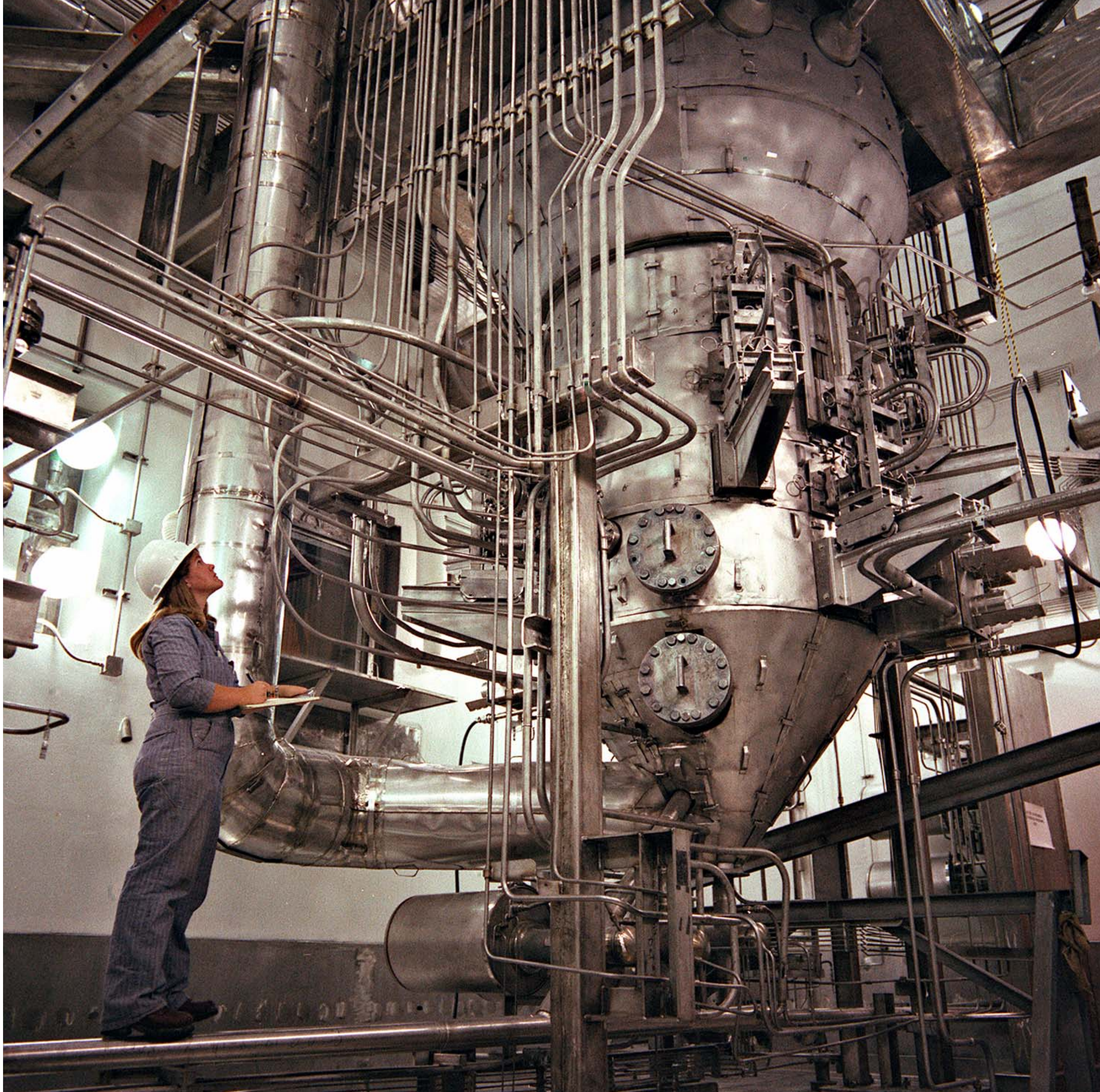


74-1171

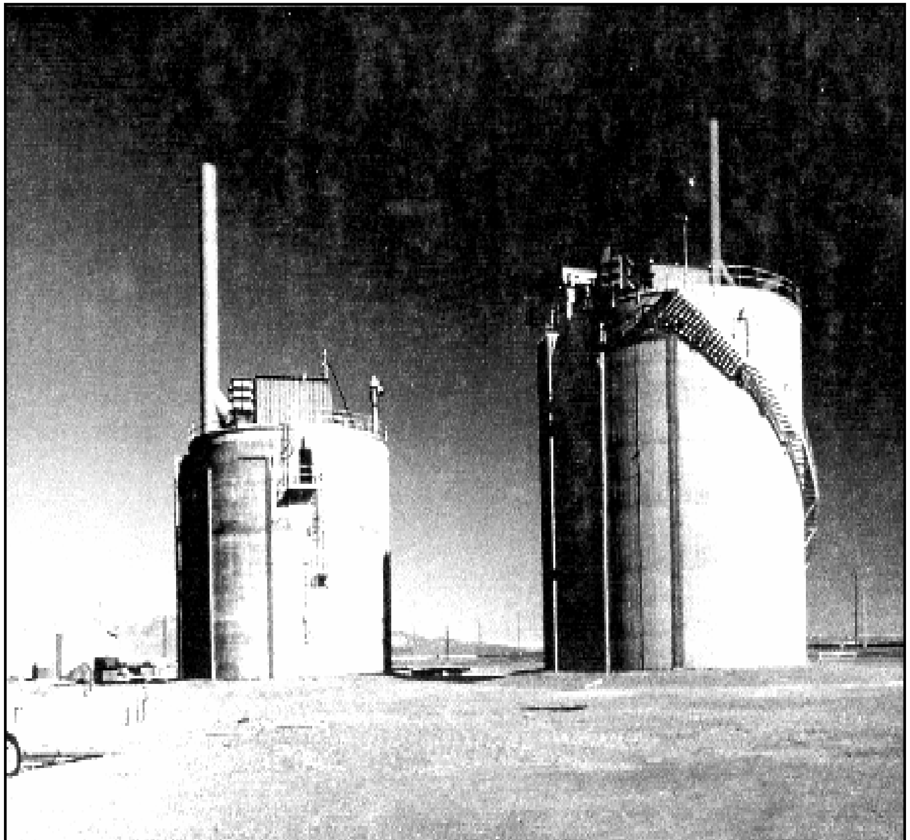


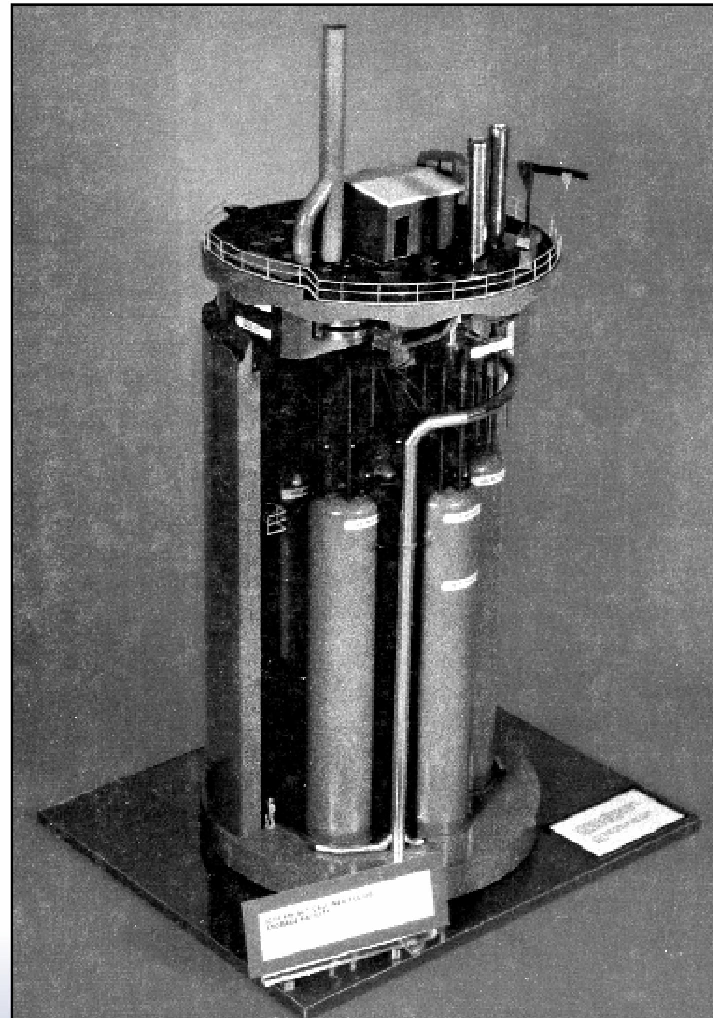
ICPP-S-14037
(6-87)

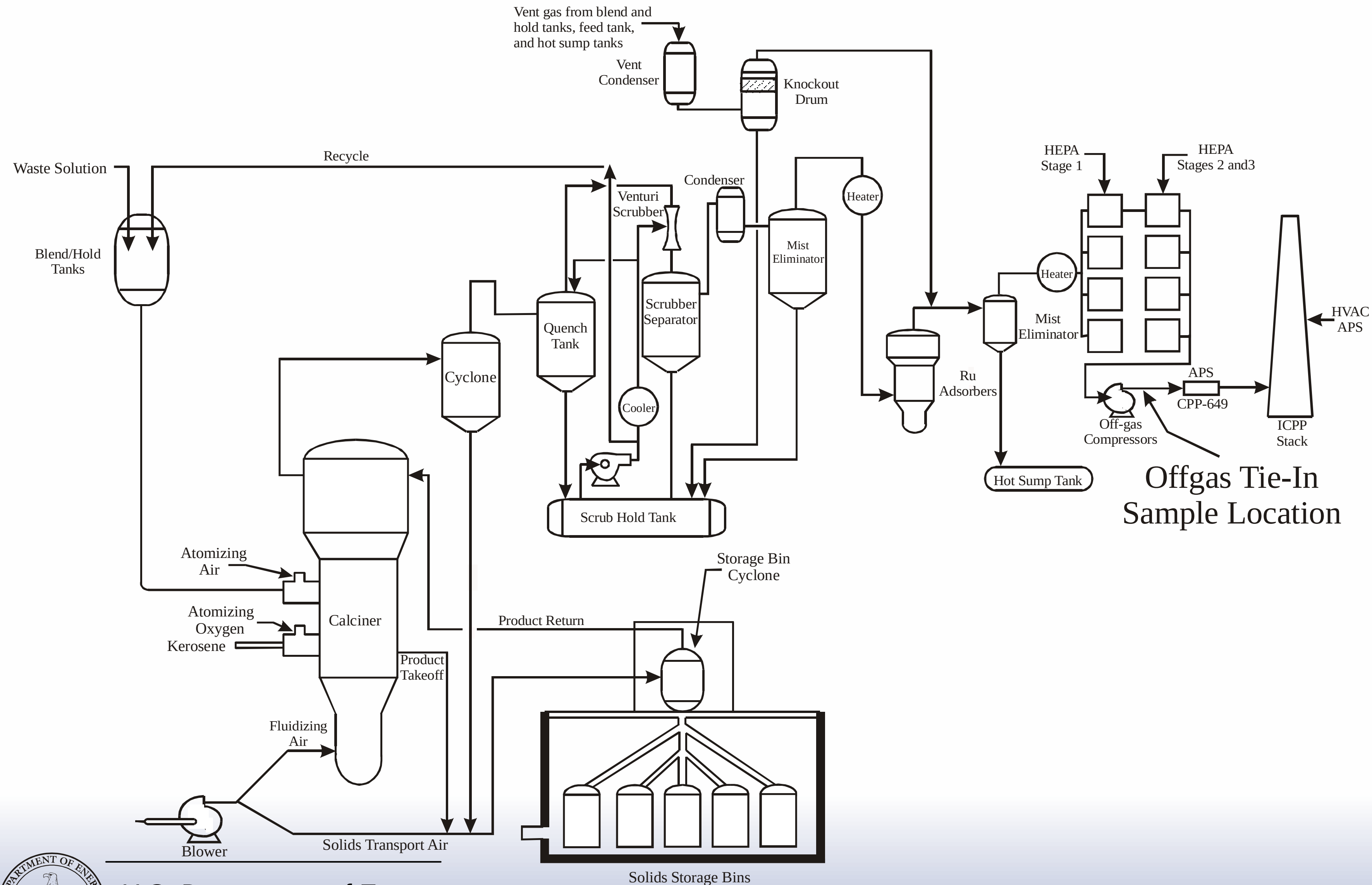

cm
1
2
3
ZIRCONIA CALCINE
cm
1
2
ZR-NA BLEND CALCINE



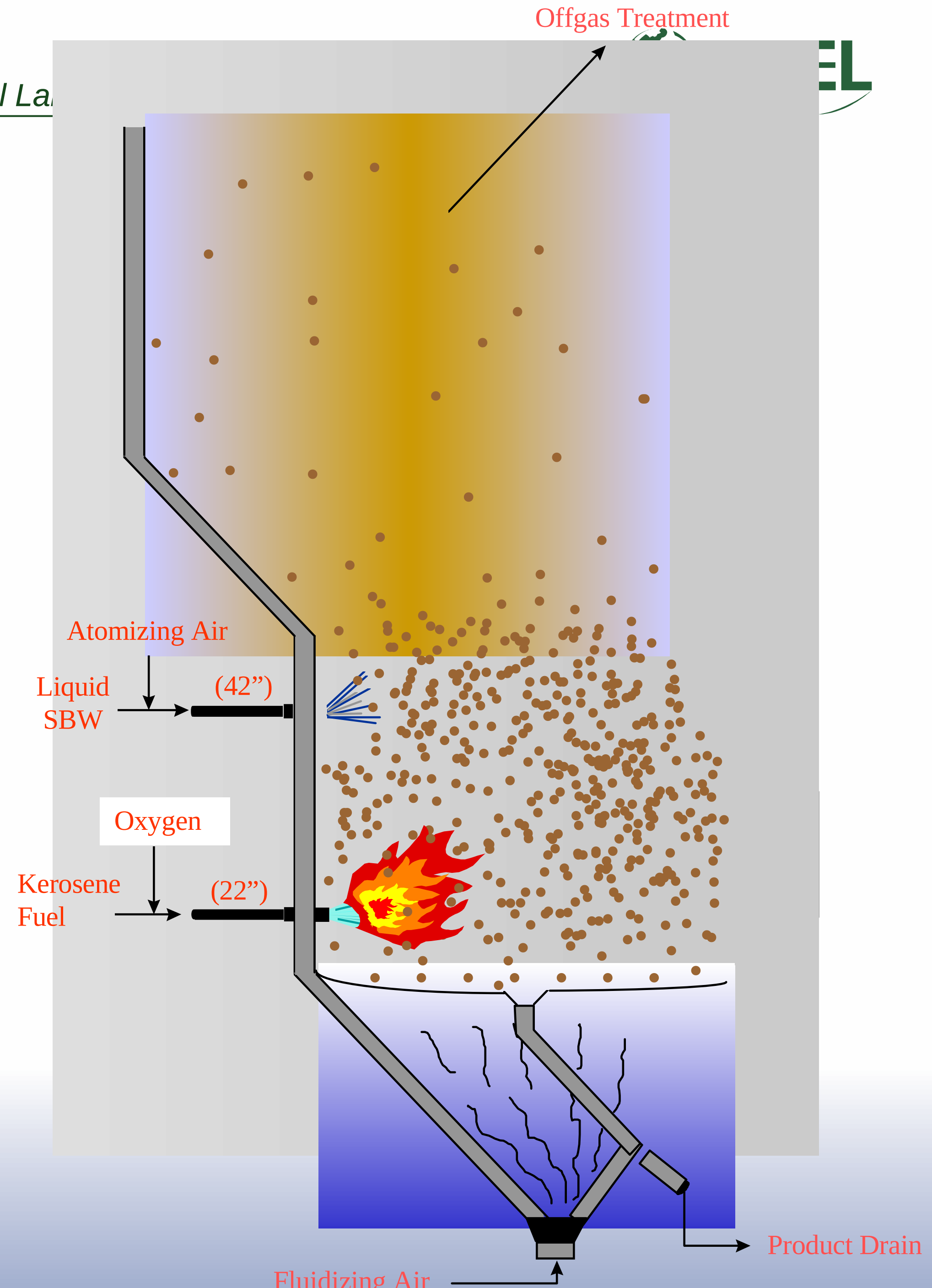
Calcine Bin Sets



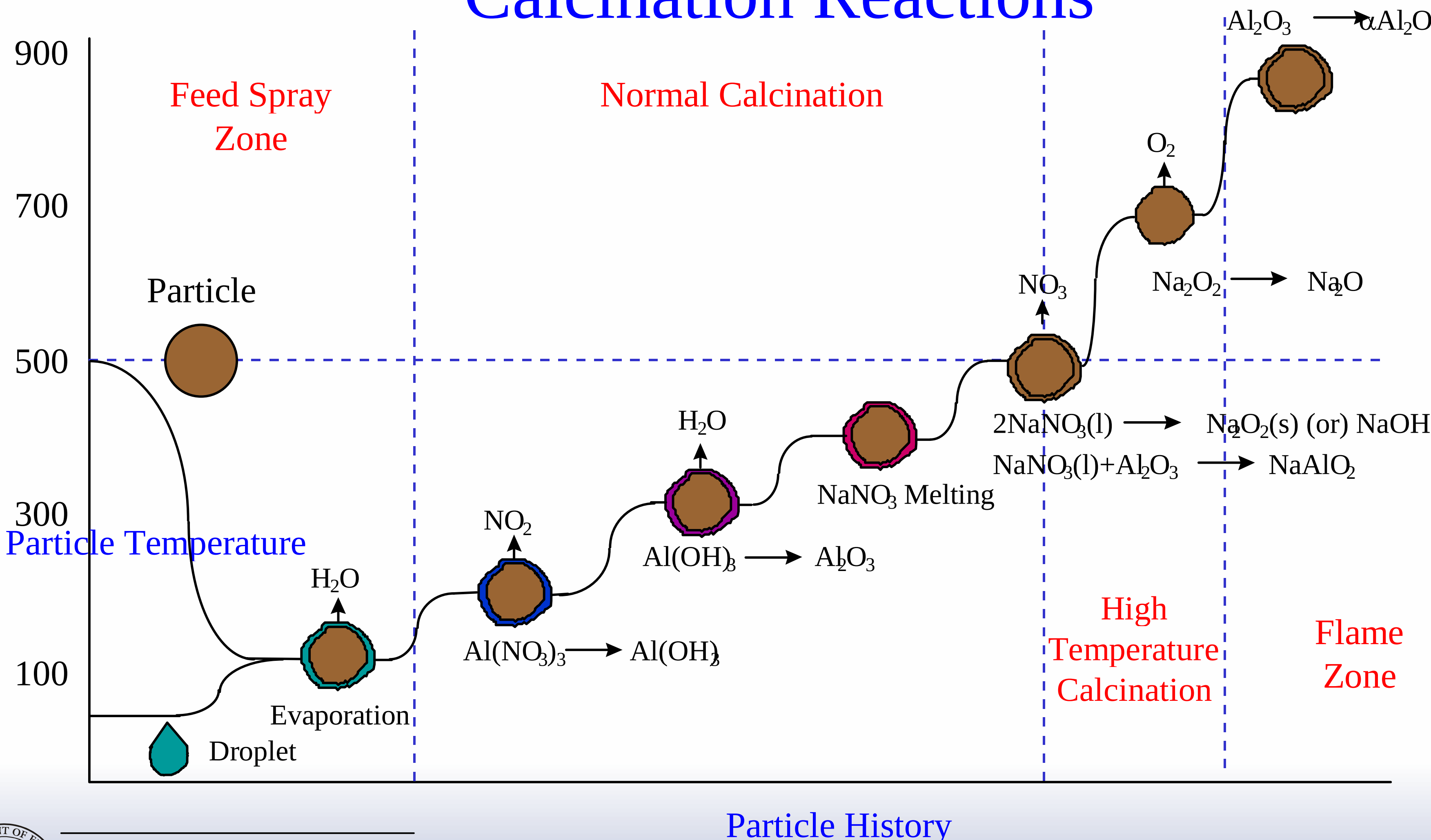



Vent gas from blend and hold tanks, feed tank, and hot sump tanks
Vent Condenser
Knockout Drum
Recycle
Waste Solution
Condenser
Heater
HEPA Stage 1
HEPA Stages 2 and3
Venturi Scrubber
Blend/Hold Tanks
Mist Eliminator
Heater
Scrubber Separator
Quench Tank
Mist Eliminator
HVAC APS
Cyclone
Ru Adsorbers
APS
CPP-649
Cooler
Off-gas Compressors
ICPP Stack
Hot Sump Tank
Offgas Tie-In Sample Location
Scrub Hold Tank
Atomizing Air
Storage Bin Cyclone
Atomizing Oxygen
Kerosene
Calciner
Product Return
Product Takeoff
Fluidizing Air
Blower
Solids Transport Air
Solids Storage Bins

- Kerosene-O_2 nozzles
- Air-atomized waste spray nozzles
- Nominally 500°C bed

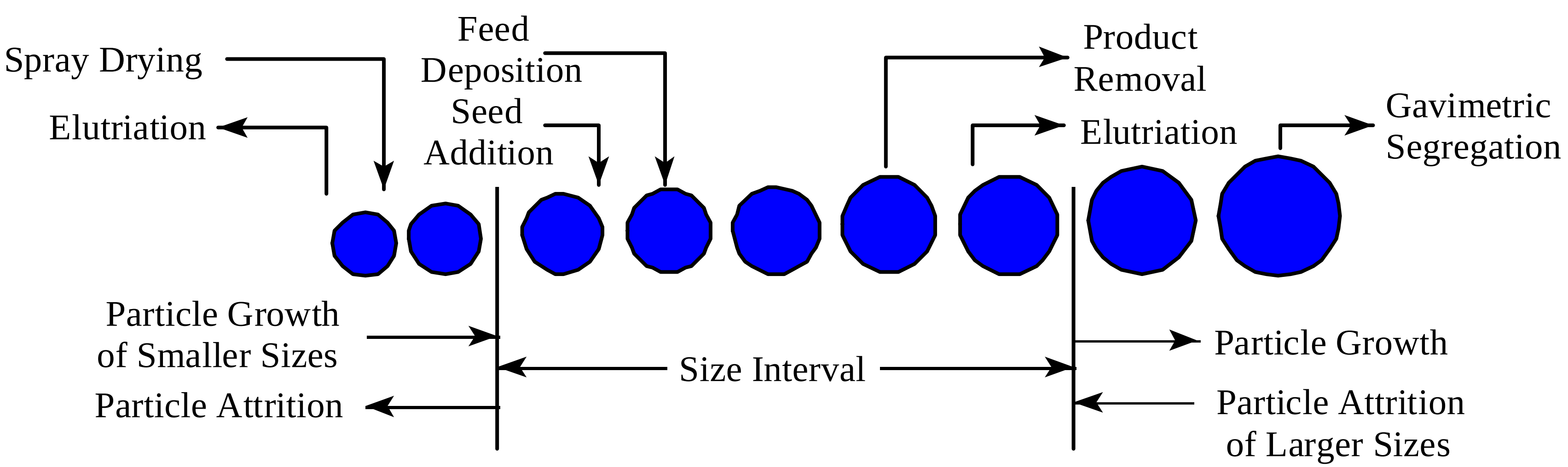


Calcination Reactions

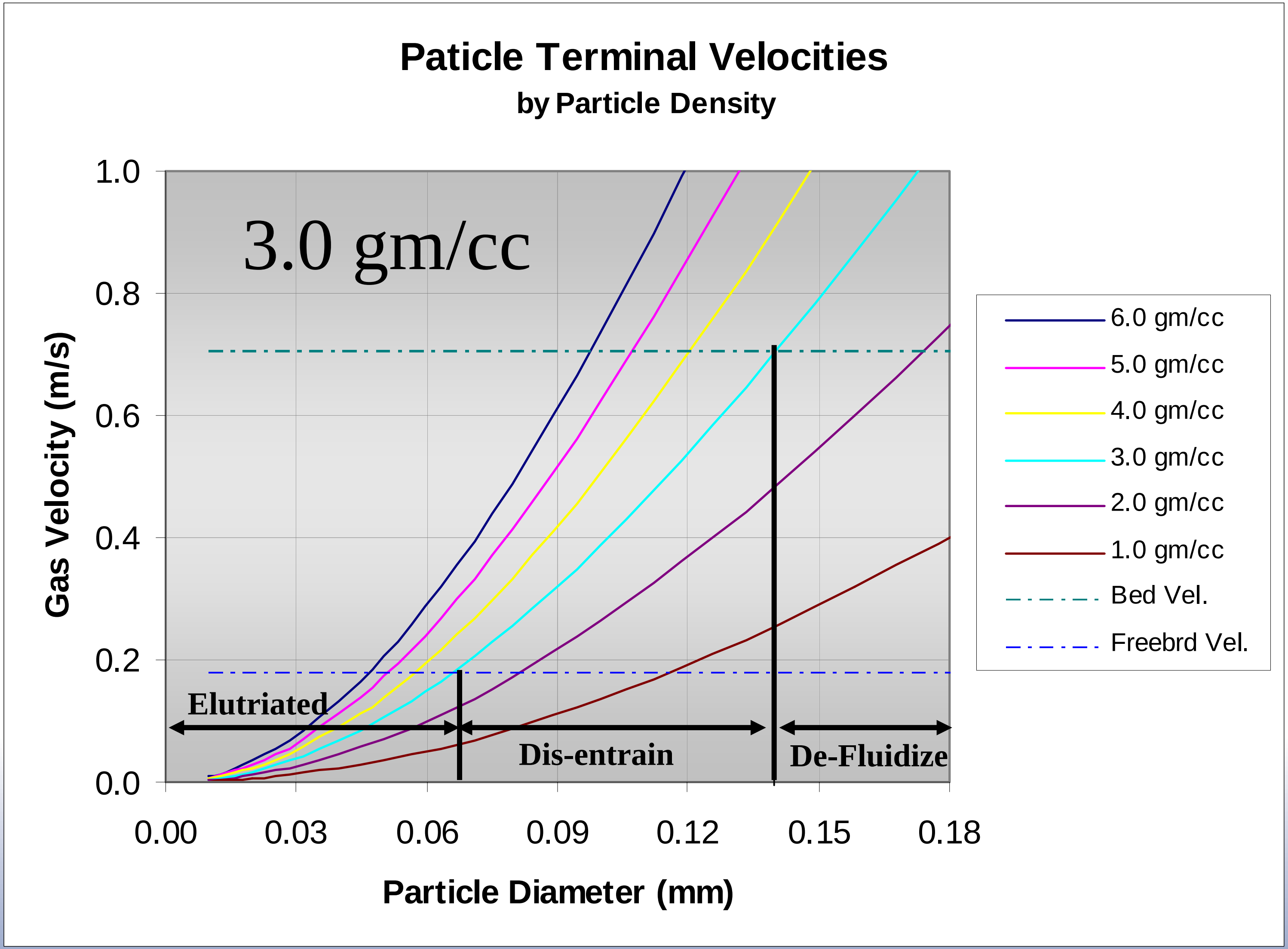


Component	Assumed Oxidation State in Production	Assumed Compounds Formed
Al	+3	Al_2O_3, $Al_2O_3 \cdot B_2O_3$, $CaO \cdot Al_2O_3$, $KAlO_2$, $NaAlO_2$
B	+3	$Al_2O_3 \cdot B_2O_3$, $CaO \cdot B_2O_3$, KBO_2, $NaBO_2$
Cd	+2	CdO, $CdO \cdot Al_2O_3$
Ca	+2	CaO, $CaO \cdot Al_2O_3$, $CaO \cdot B_2O_3$, CaF_2 $Ca_3(PO_4)_2$, CaSO
Cl	-1	KCl, NaCl, volatile
Cr	+6	K_2CrO_4, Na_2CrO_4
F	-1	CaF_2, KF, NaF
Fe	+3	$KFeO_2$, $NaFeO_2$
Pb	+2	PbO, $PbO \cdot Al_2O_3$
Mn	+4	MnO_2
Hg	--	volatile
Mo	+6	K_2MoO_4, Na_2MoO_4
Ni	+2	NiO, $NiO \cdot Al_2O_3$
NO_3	-1	NO, NO_3, $NO_2\uparrow$
PO_4	-3	$Ca_3(PO_4)_2$, K_3PO_4, Na_3PO_4
K	+1	$KaAlO_2$, KBO_2, KCl, K_2CrO_4, KF, $KFeO_2$, $NaNO_3$, Na_3PO_4, Na_2SO_4
Na	+1	$NaAlO_2$, $NaBO_2$, NaCl, Na_2CrO_4, NaF, $NaFeO_2$, $NaNO_3$, Na_3PO_4, Na_2SO_4
SO_4	-2	$CaSO_4$, K_2SO_4, Na_2SO_4
U	+6	K_2UO_4, Na_2UO_4
Zr	+4	ZrO_2, $CaZrO_3$

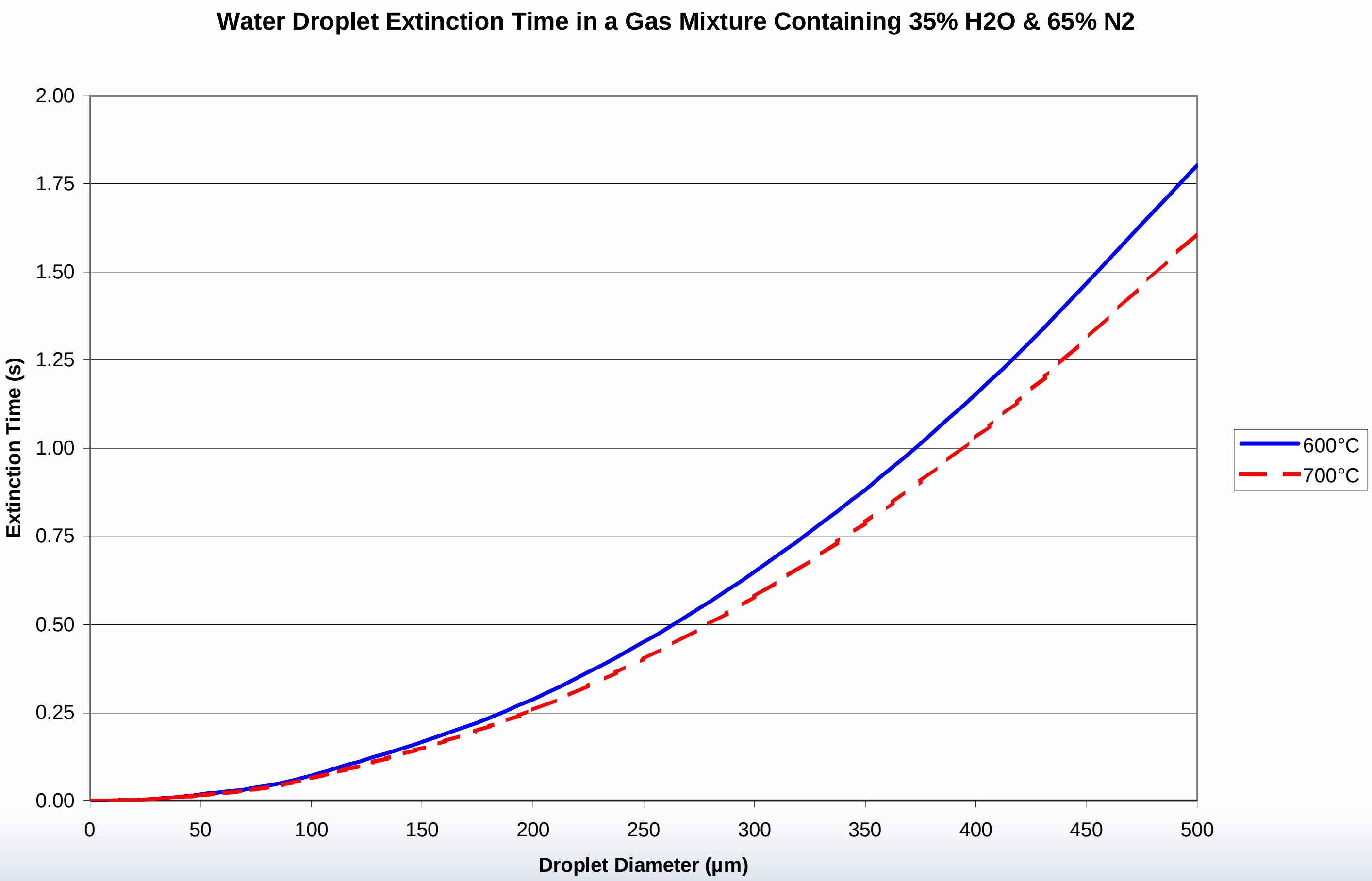
Particle Mechanics



Bed Fluidization Velocities



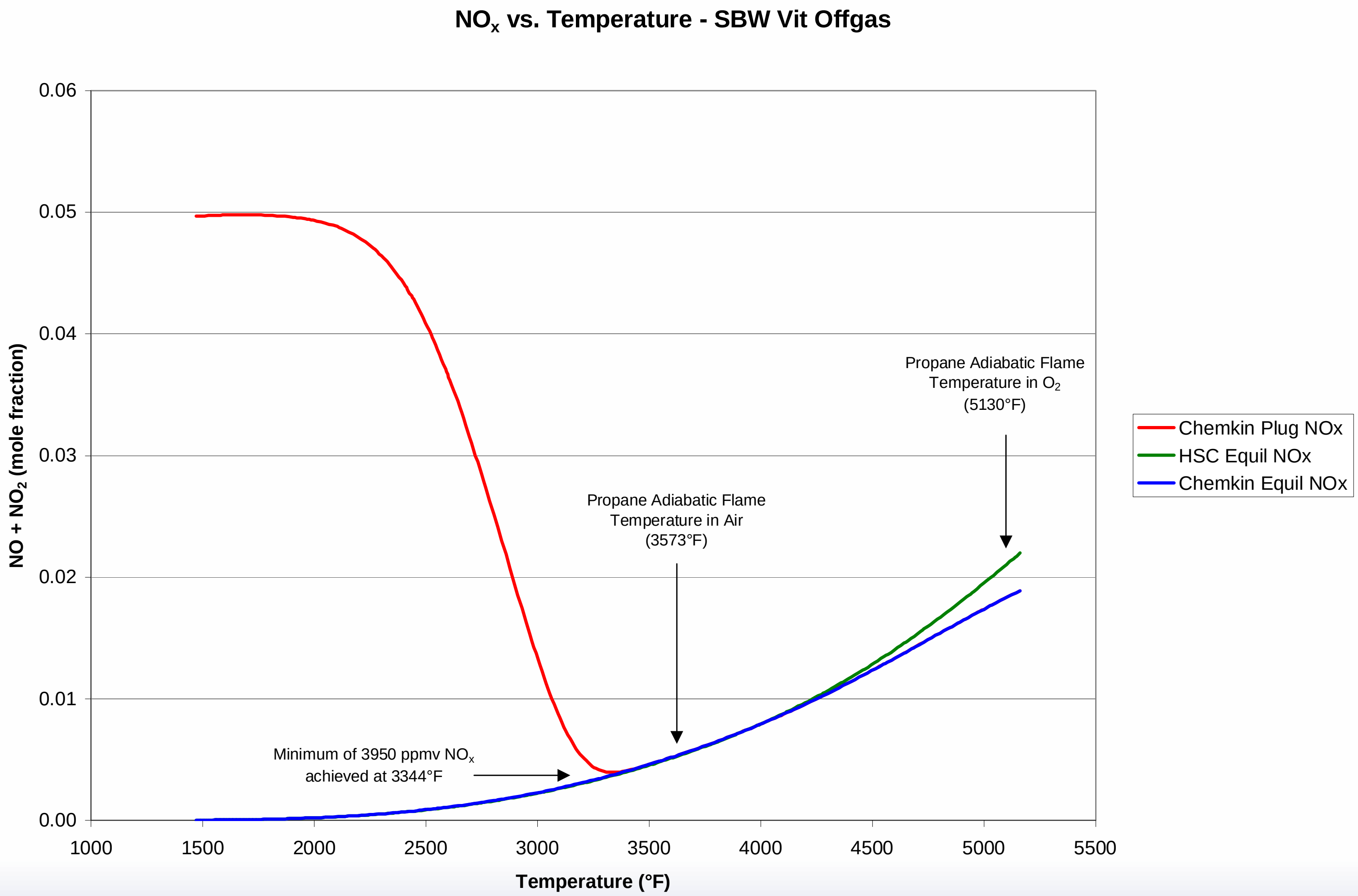
Droplet Evaporation Rate



- 20,000 – 35,000 ppm NO_X
- 0.25 – 0.5 vol.% CO/THC
- 5,000 – 40,000 µg/m^3

Offgas Cleanup Technology Developments

- **SCR- NOx Abatement Process**
  - *Mordenite/Zeolite Catalysts*
  - *High NOx concentrations*
- **Staged offgas reburner**
  - *NO_x reduction*
  - *CO/THC destruction*
- **Carbon Adsorption Beds**


NOx vs. Temperature - SBW Vit Offgas
0.06
0.05
0.04
0.03
0.02
0.01
0.00
NO + NO2 (mole fraction)
1000
1500
2000
2500
3000
3500
4000
4500
5000
5500
Temperature (°F)
Propane Adiabatic Flame Temperature in O2 (5130°F)
Propane Adiabatic Flame Temperature in Air (3573°F)
Minimum of 3950 ppmv NOx achieved at 3344°F
Chemkin Plug NOx
HSC Equil NOx
Chemkin Equil NOx

Technical Issues

- *Bed chemistry*
  - *Agglomeration of bed (alkali eutectic phases)*
  - *Bed attrition (alpha alumina formation)*
  - *Spray drying and film boiling (fines generation)*
- *Feed process rate*
  - *Cold chemical addition*
  - *Copious amounts of $Al_2(NO_3)_3$, $Ca(NO_3)_2$, and boric acid*
- *Offgas cleaning*
  - *Radionuclides*
  - *CAA regulated*
  - *RCRA toxic compounds*

Technical Issues

Radiological emissions

- Volatiles: I-129, Cs-137/Cs-134, Ru-109
- Particulate

- NO_x emissions and opacity Air Permit
- Visibility of plume (Impact on Regional Class I Air Sheds)
- Potential PAH, SVOC, VOC, D/F emissions
- Mercury emissions
- 1998 MACT Rule for HWC
- EPA Sampling and Analysis Methods (high acids)

INEEL SCR NOx Process Development

- 1978 – 1988: Developed & Patented SCR Process
  - High NO_x Levels (4 vol.%)
  - Mordenite/Zeolite catalysts
  - Three stage reactor with interstage cooling
- 1988 – 1992: SCR Pilot Plant Construction and Operation
  - Three Stage, variable bed diameter design
  - 50 scfm
  - Actual NWCF slip stream
  - Dupont/INEEL UV Spectrophotometer developed
    - Online, CEM for NH_3, NO_2, NO
- 1992: Determined N_2O generation rates

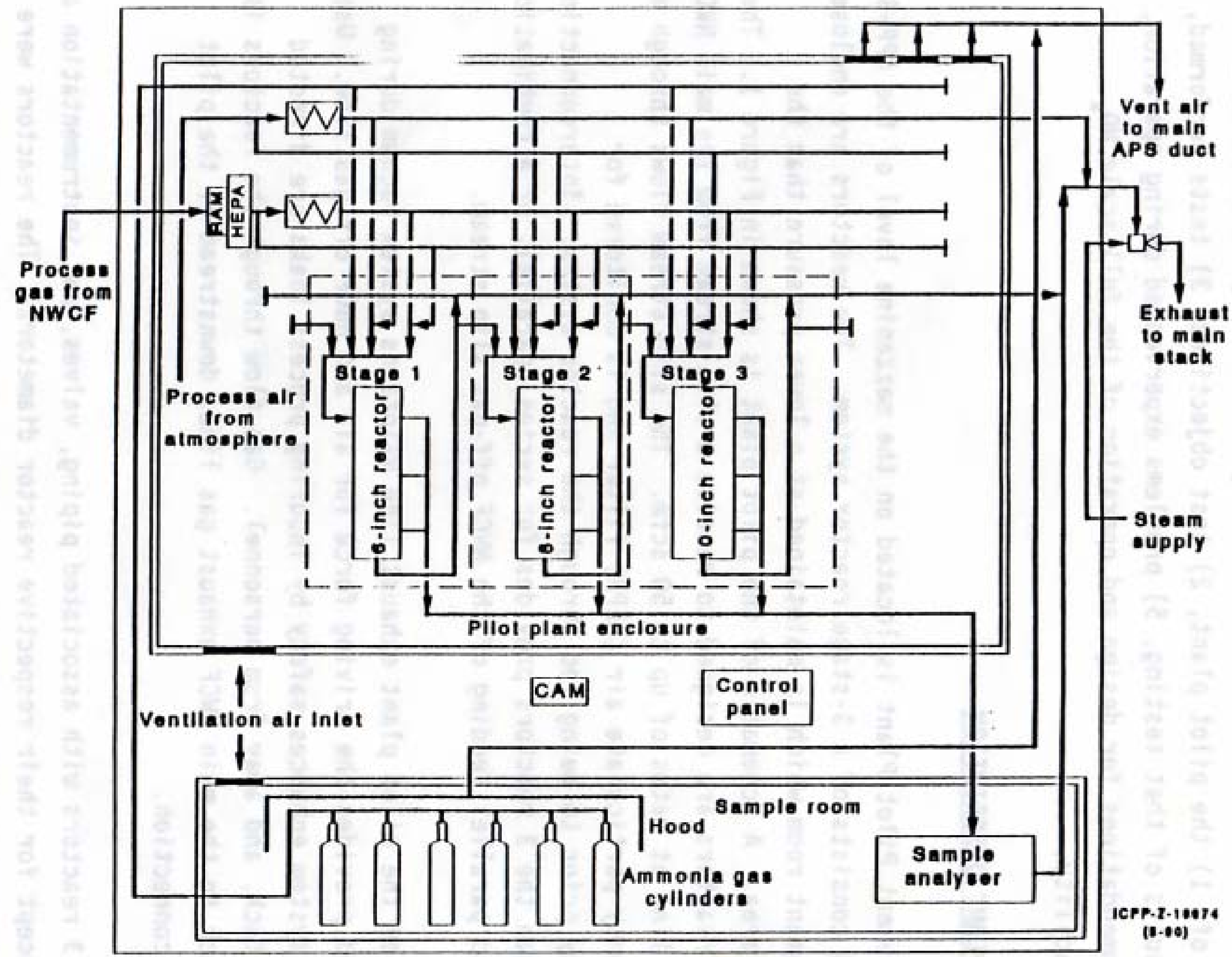


Figure 1. NOx Abatement Pilot Plant

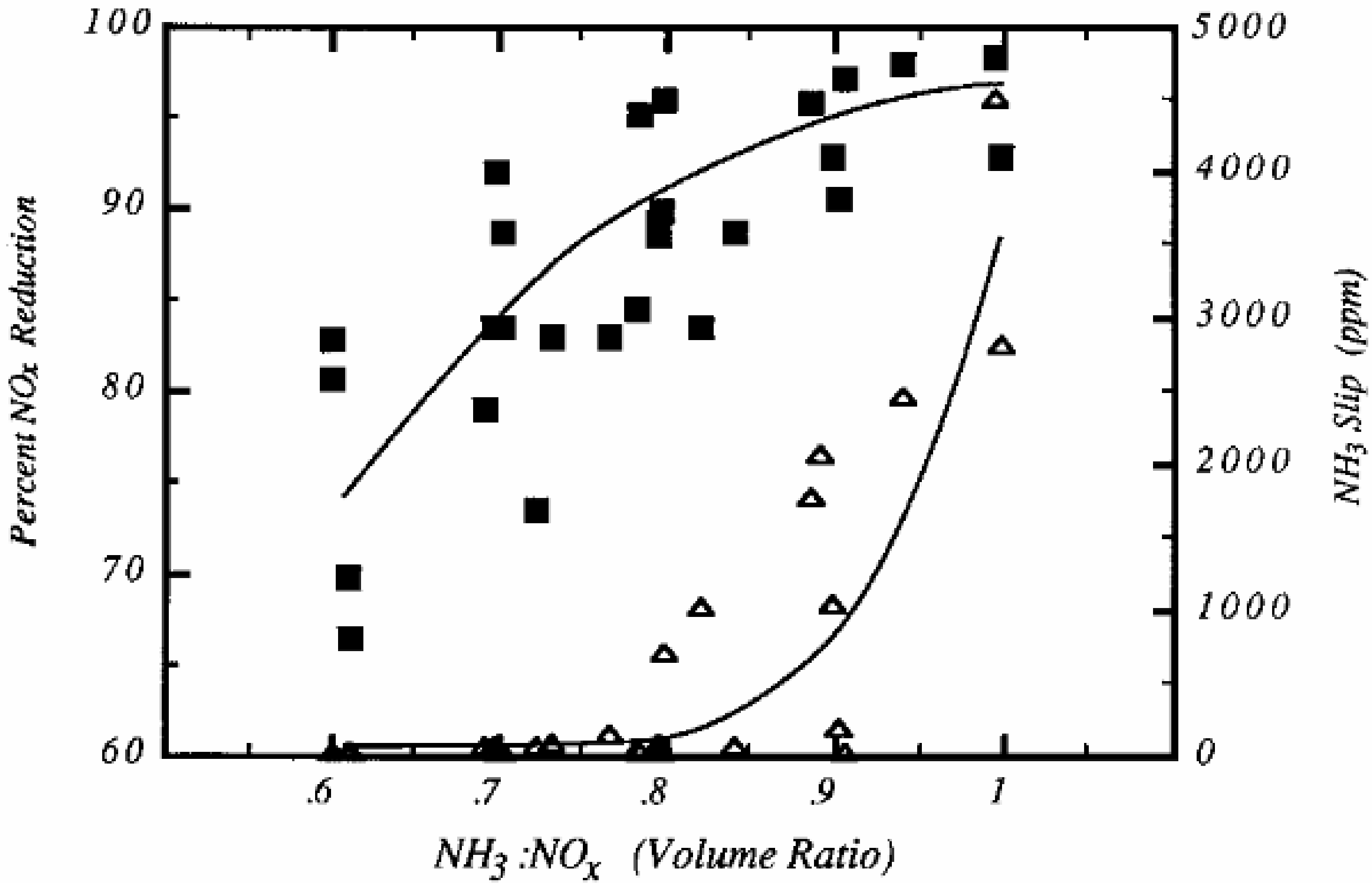
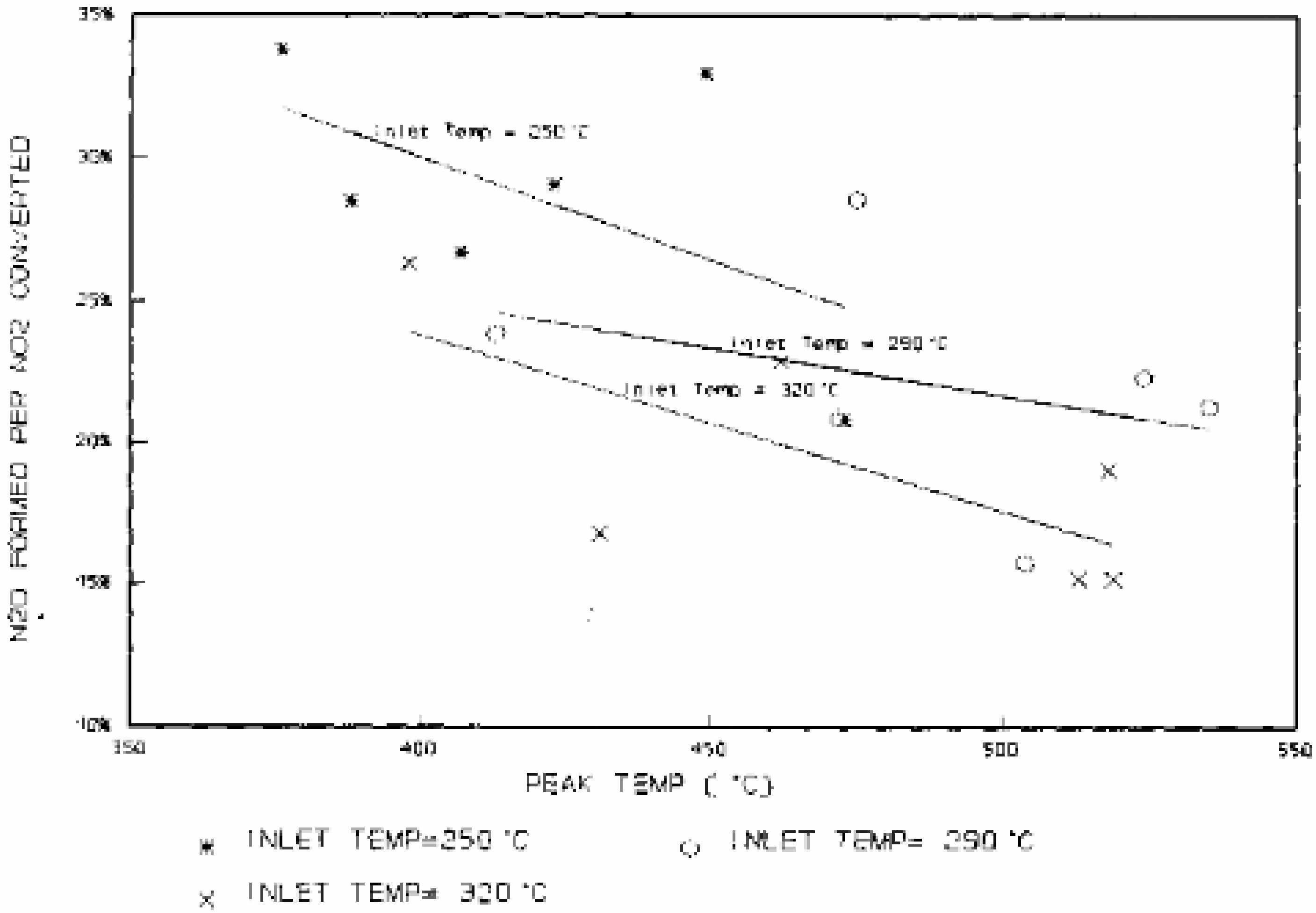


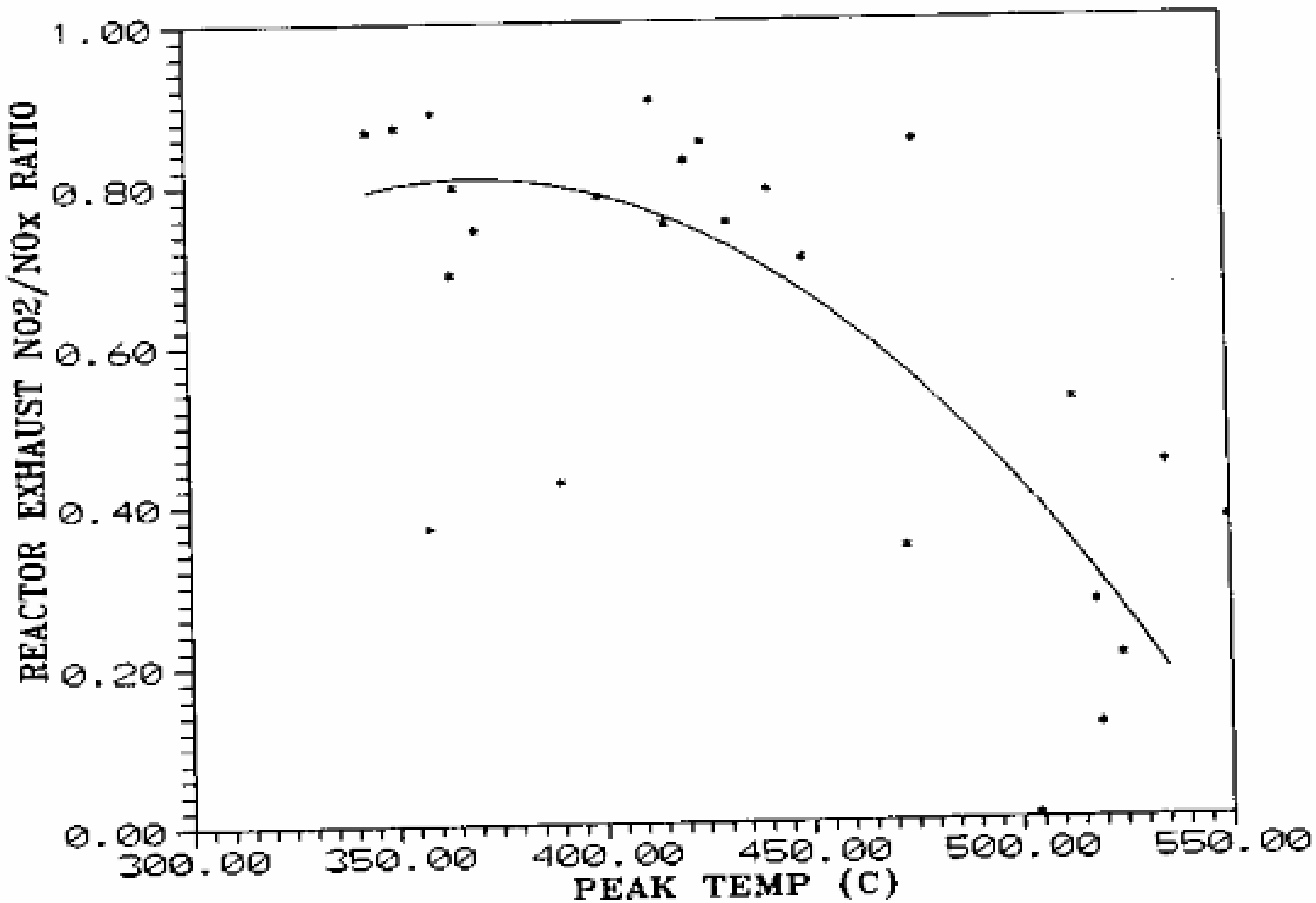
Figure 7. NOx reduction (left) and NH_3 slip (right) trends at a space velocity of **25,000** (1/hr).

Figure I. N_2O Formed Per NO_2 Converted Versus Reactor Peak Temperature



Data points are from tests resulting in greater than 85% NOx conversion

Figure 3. Reactor Exhaust NO_2/NO_x Volume Ratio Versus Peak Bed Temperature



SCR Applications

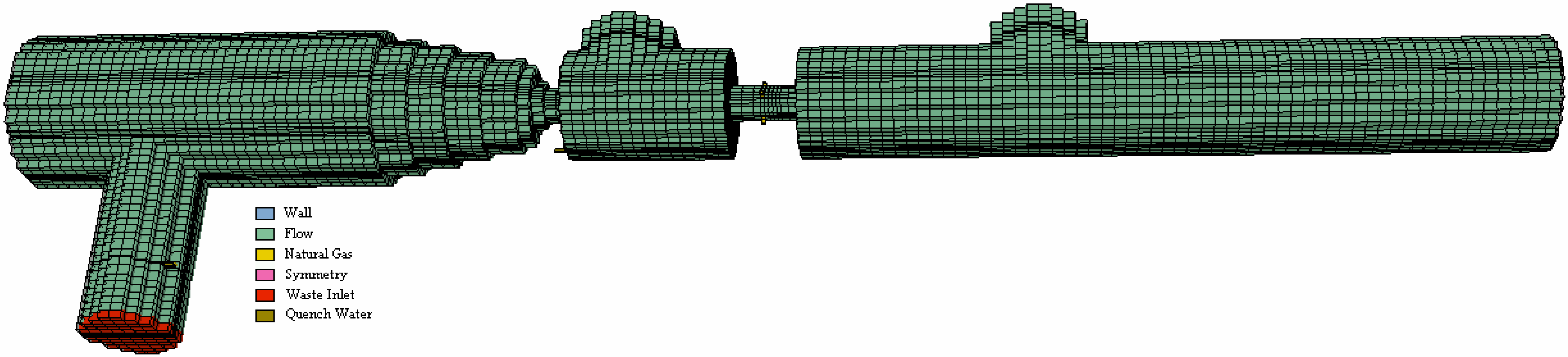
- West Valley melter
- Hanford Waste Treatment Plant melters

SCR Melter Test Skid

NO_x/THC/CO Staged Offgas Reburner Development

- 1993: ChemKin calculations
- 1995: CFD calculations (PCGC-3)
- 1996-1999: Test verification (John Zinc burner)
- 2000 – 2001: INEEL design
- 2003-2004: Pilot scale calciner construction and testing

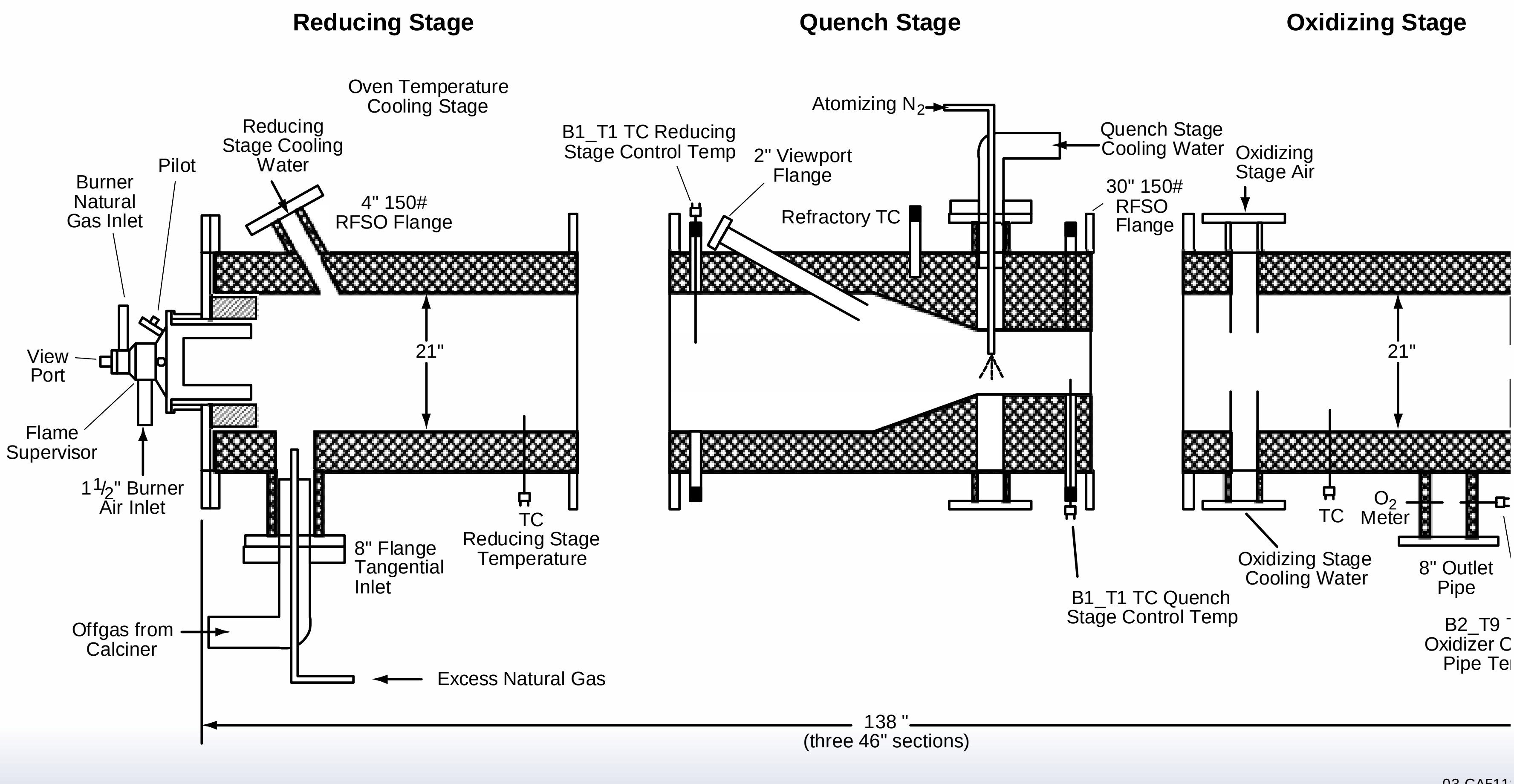
INEEL Offgas Reburner Development

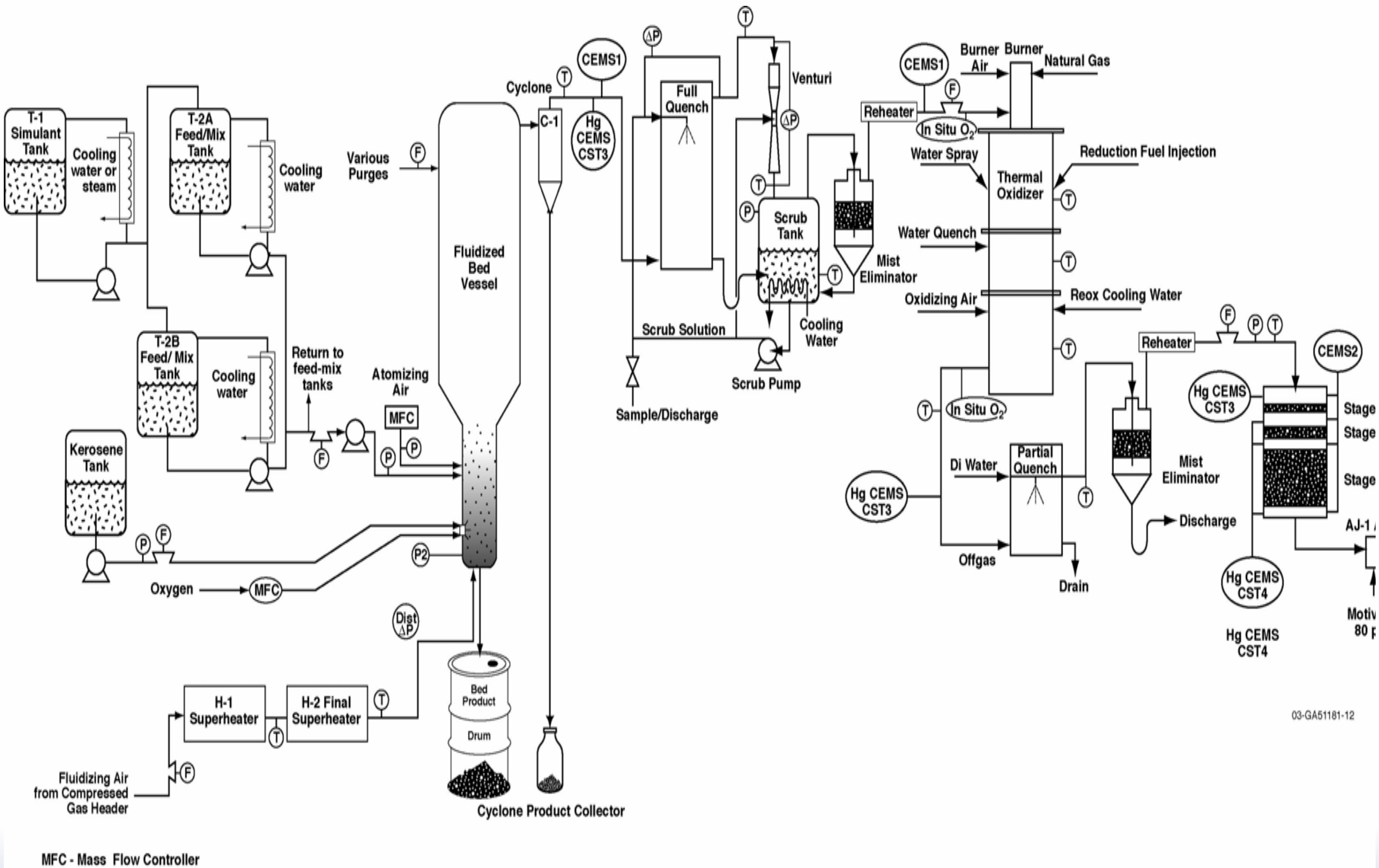


John Zinc Staged Burner Test Reactor

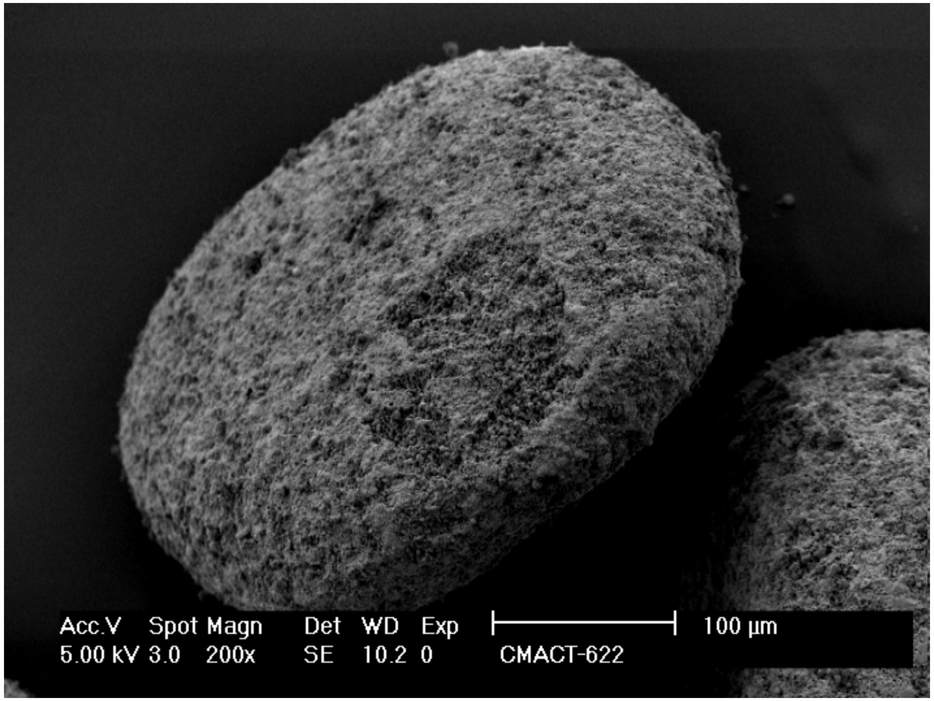
MSE Facility
Butte, Montana

Staged Offgas NOx/CO/HC Reburner

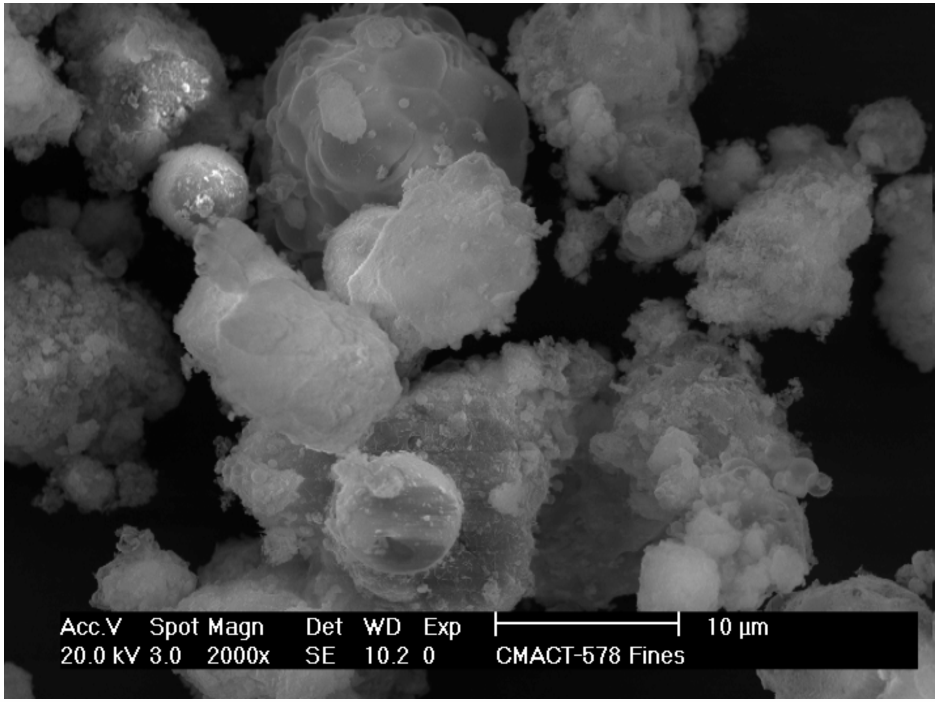



T-1 Simulant Tank
Cooling water or steam
T-2A Feed/Mix Tank
Cooling water
T-2B Feed/ Mix Tank
Cooling water
Kerosene Tank
Return to feed-mix tanks
Various Purges
Atomizing Air
MFC
Oxygen
MFC
Dist ΔP
P2
Fluidized Bed Vessel
Cyclone
C-1
CEMS1
Hg CEMS CST3
ΔP
Full Quench
Venturi
Scrub Tank
Mist Eliminator
Cooling Water
Scrub Solution
Scrub Pump
Sample/Discharge
H-1 Superheater
H-2 Final Superheater
Fluidizing Air from Compressed Gas Header
Bed Product Drum
Cyclone Product Collector
CEMS1
Burner Air
Burner
Natural Gas
Reheater
In Situ O_2
Water Spray
Thermal Oxidizer
Reduction Fuel Injection
Water Quench
Oxidizing Air
Reox Cooling Water
In Situ O_2
Hg CEMS CST3
Di Water
Partial Quench
Offgas
Drain
Mist Eliminator
Discharge
Reheater
CEMS2
Hg CEMS CST3
Stage
Stage
Stage
AJ-1
Hg CEMS CST4
Hg CEMS CST4
03-GA51181-12
MFC - Mass Flow Controller

Pilot Plant Test Calcine AAR = 1.75

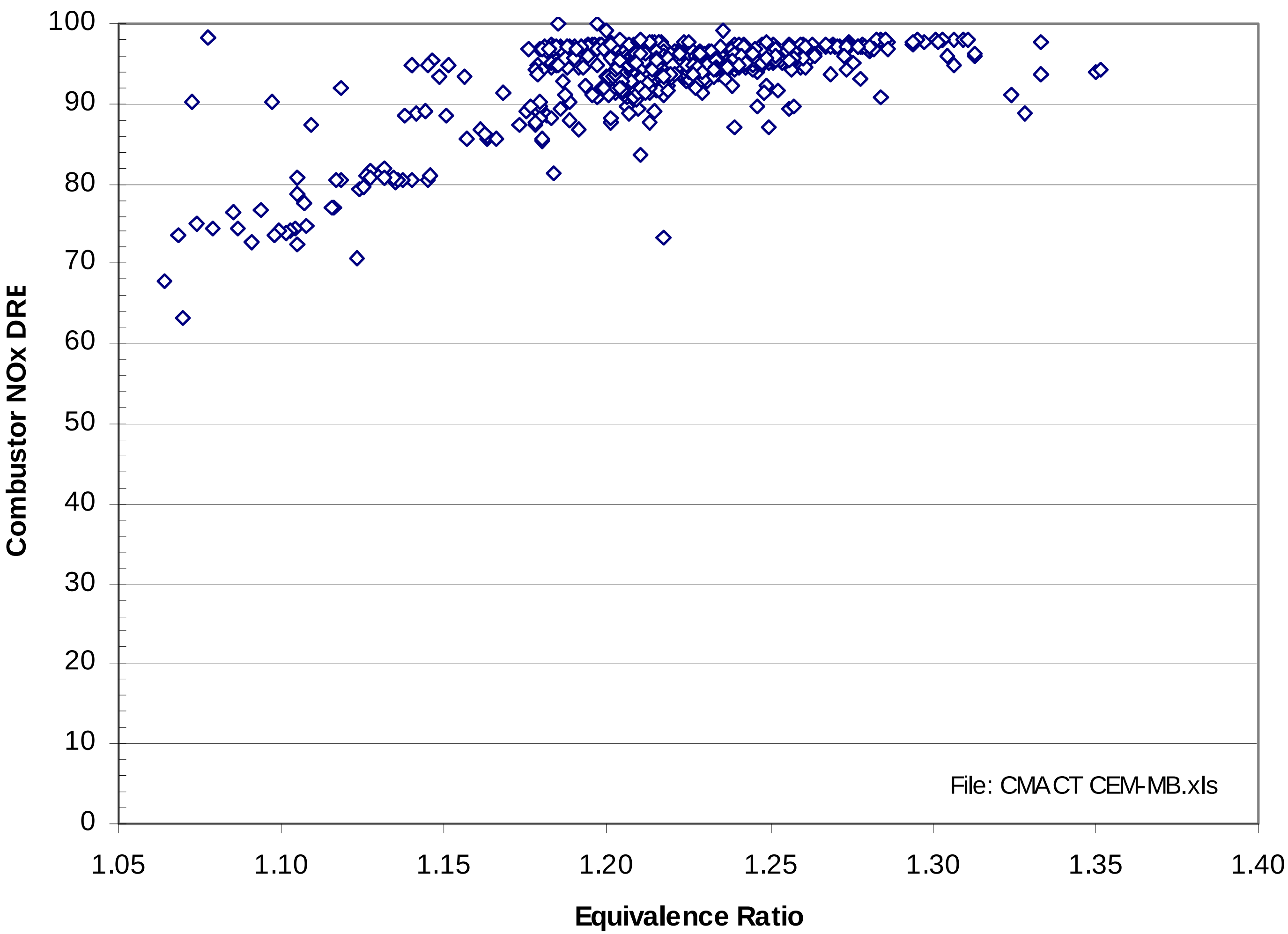


Bed Particles

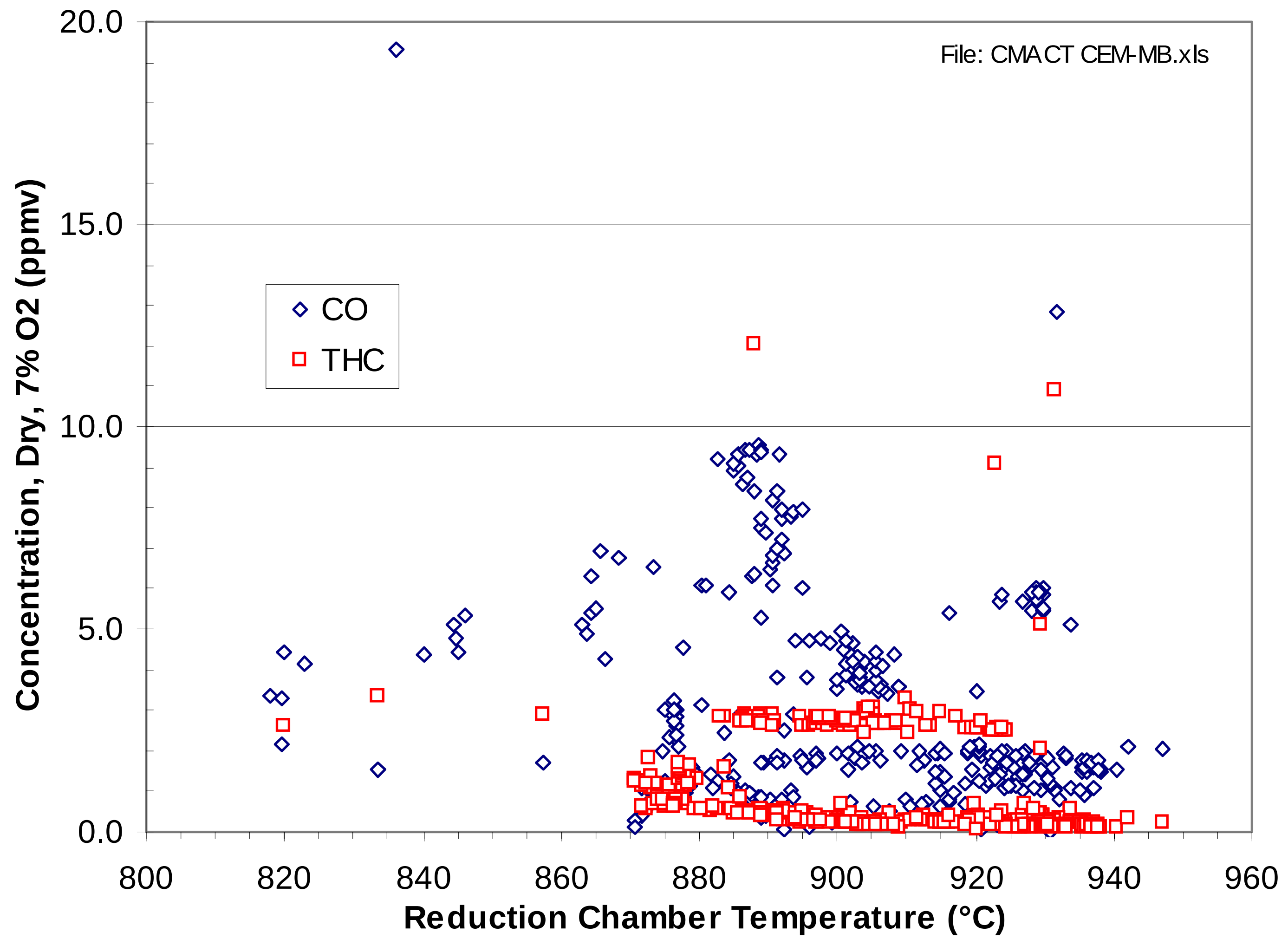


Cyclone Files

NOx Destruction Efficiency



CO/THC Emissions



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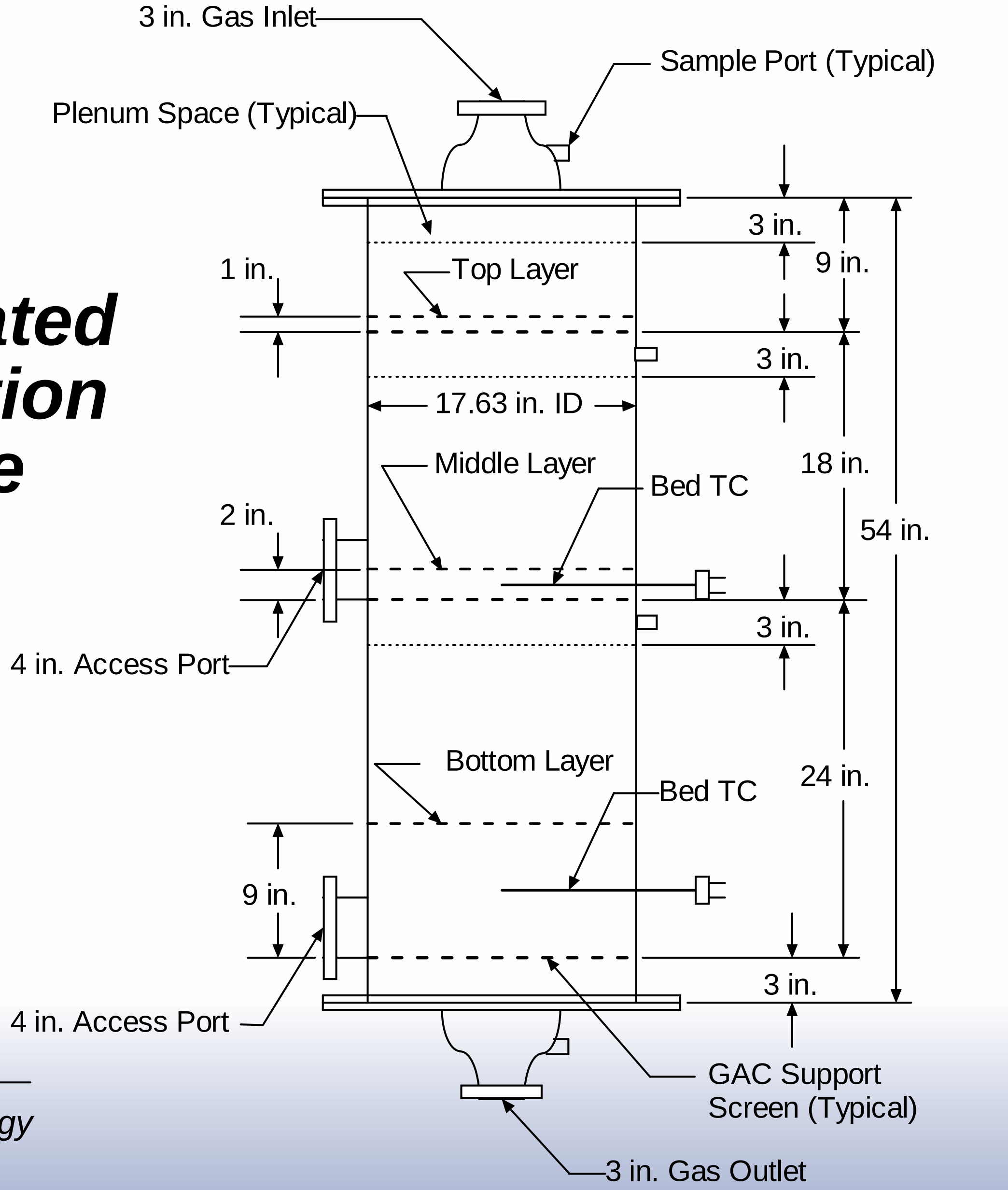
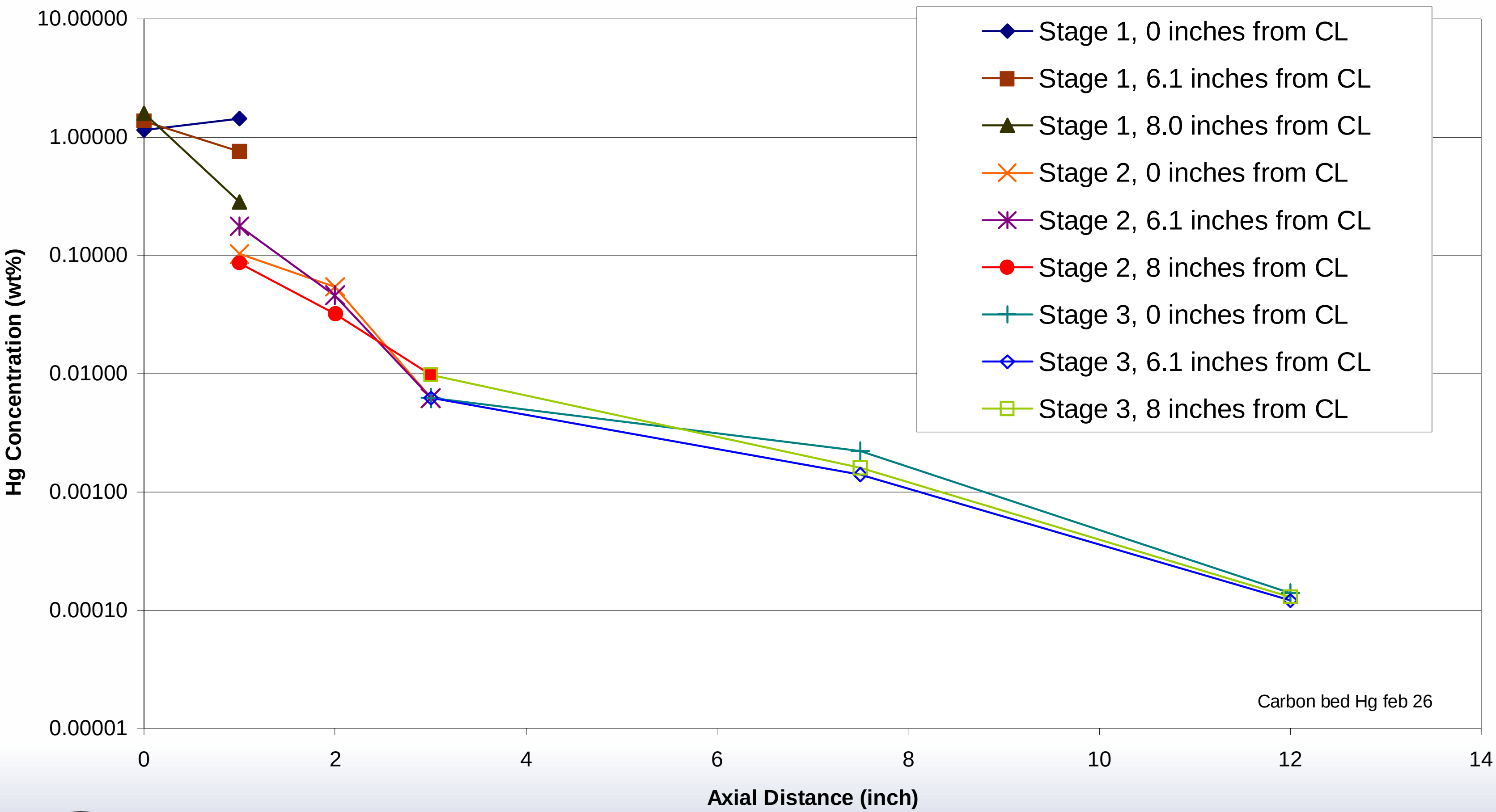
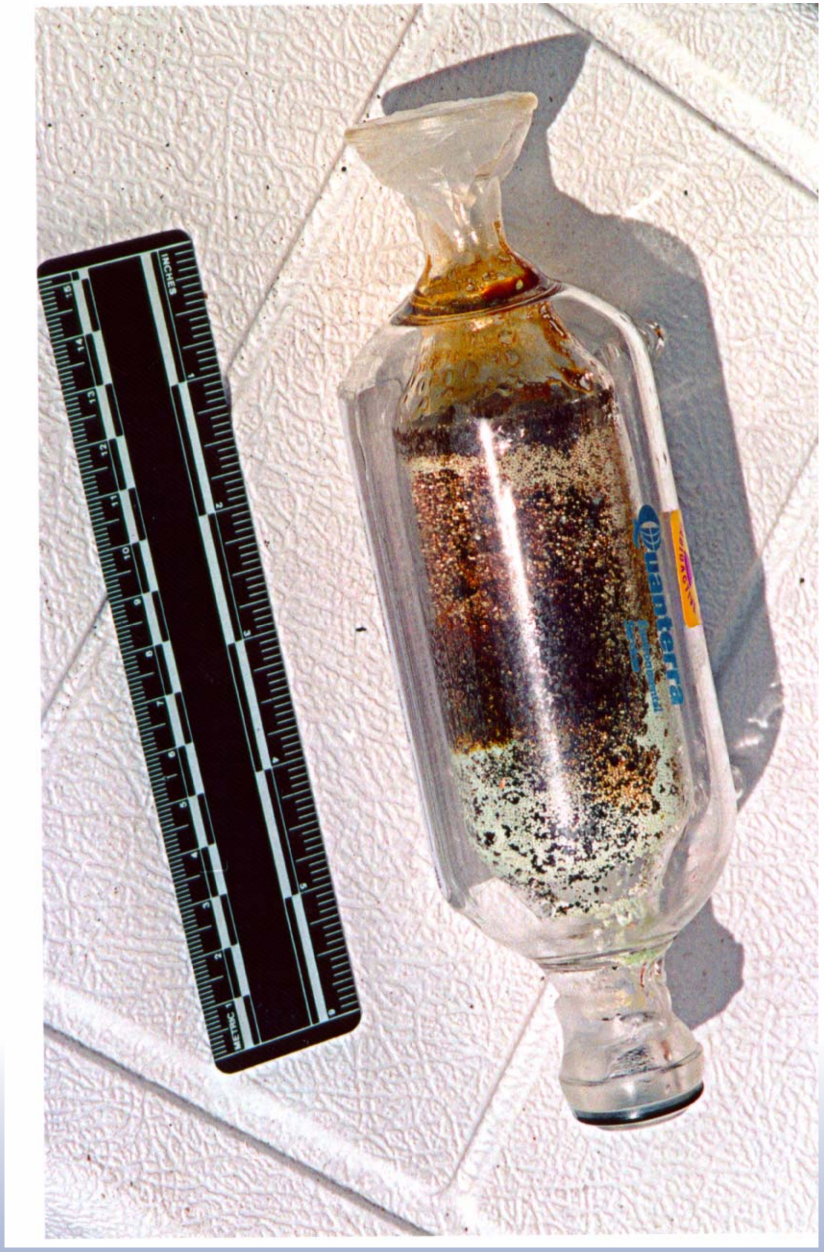
Sulfur-Impregnated Carbon Adsorption Mercury Capture Bed

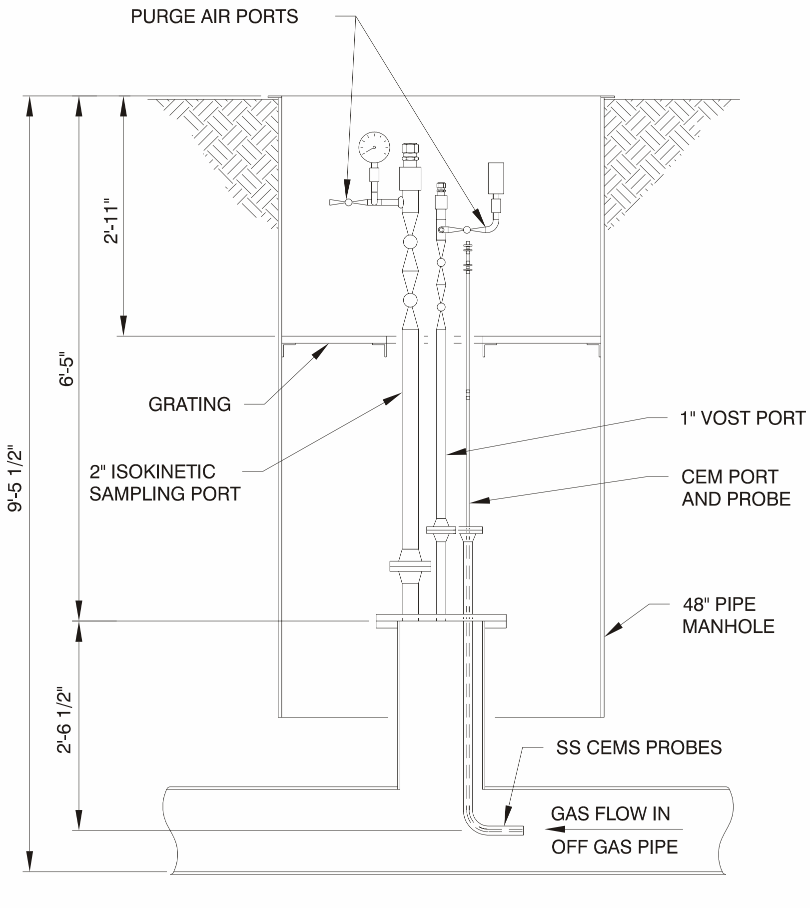


Mercury Adsorption Efficiency



XAD Resin Degradation





ELEVATION VIEW LOOKING NORTH

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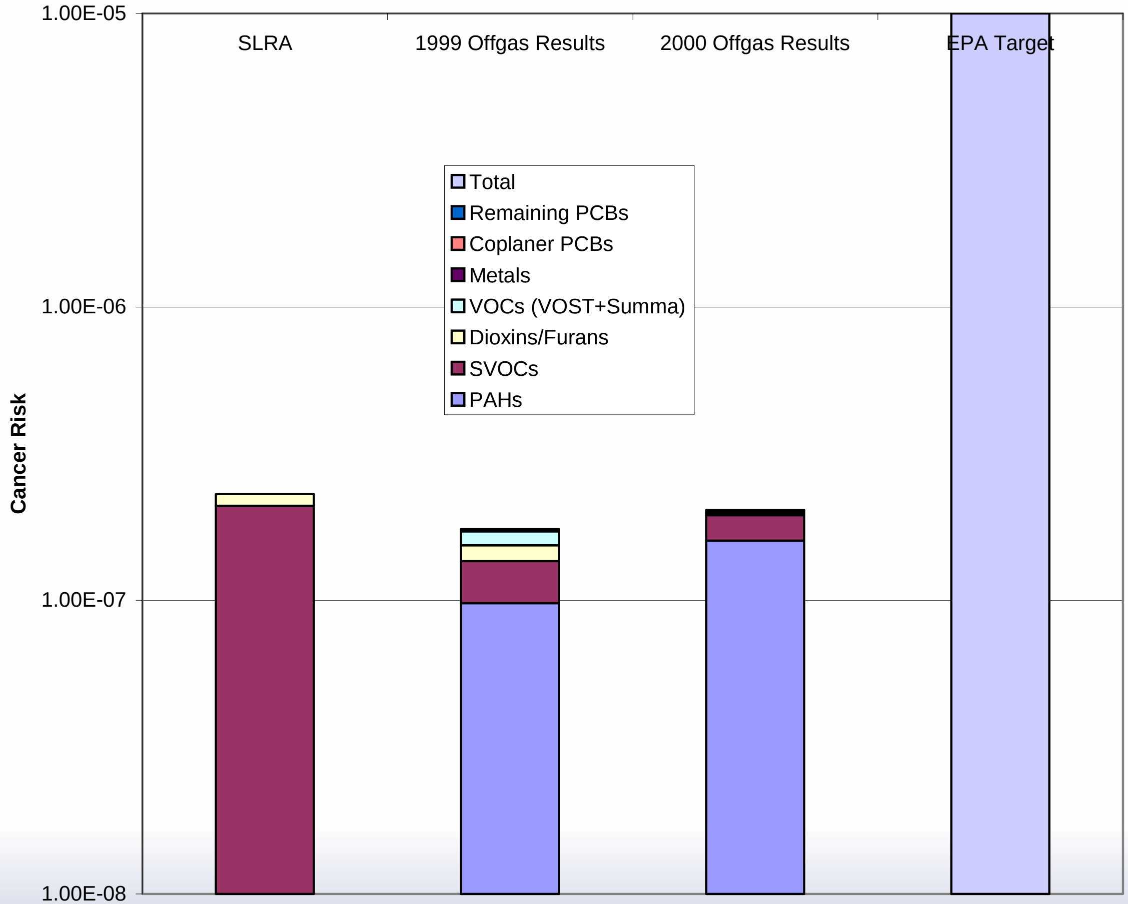
Date: 01/07/99 09:27 A.M.

NWCF Emissions Measurements

Comparison of SLRA and Measured Cancer Risk with EPA Criterion



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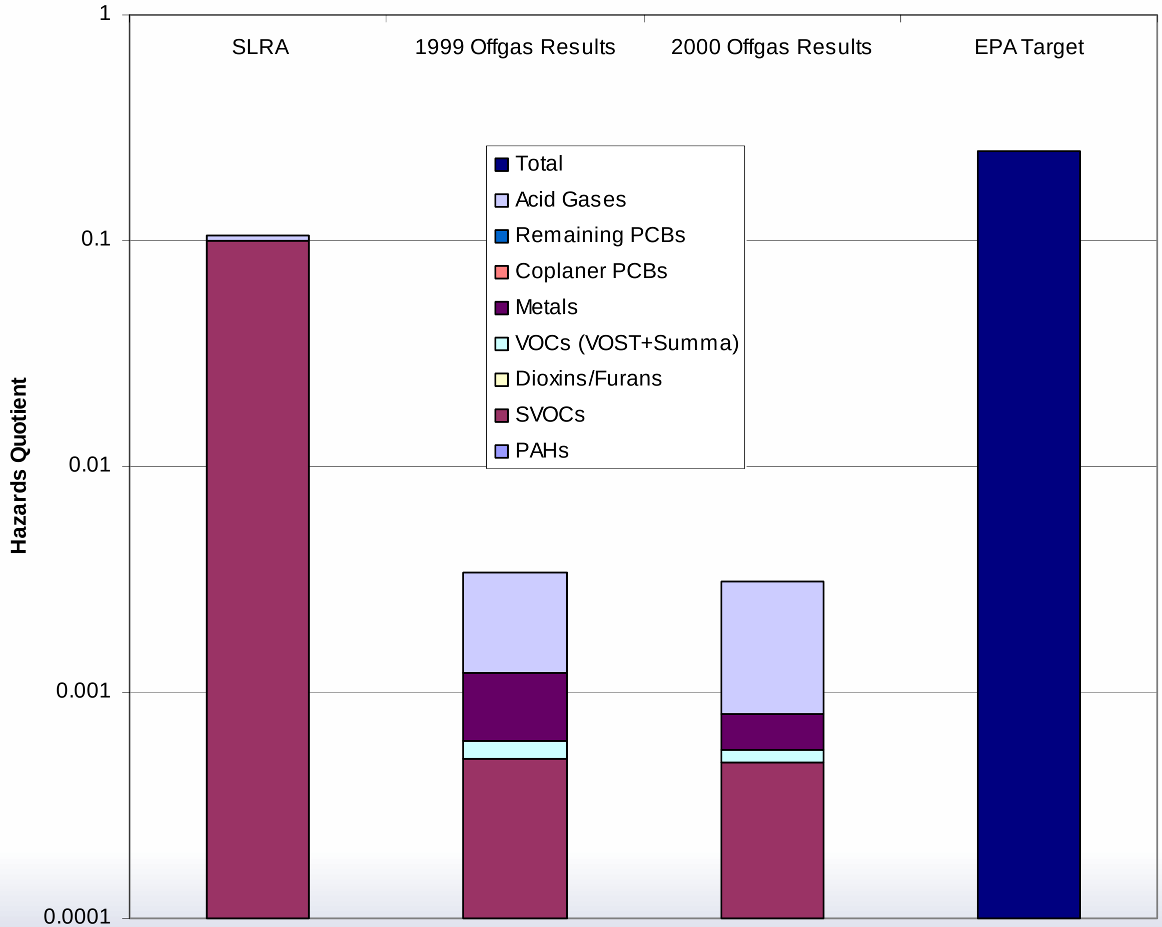
Comparison of SLRA and Measured Hazards Quotient with EPA Criterion



The INL

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