Technology Development

associated with the

Idaho High Level Waste (HLW) Calcine Disposition Project (CDP)

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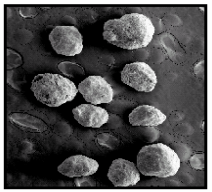
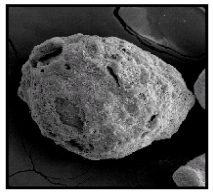
What Is Calcine?

- ***Calcine is high level waste (HLW) by source definition***
  - First cycle raffinate from reprocessing of spent nuclear fuel
- ***8-9M gallons liquid HLW converted to 4400 cubic meters of granular solid***
  - 7 to 1 volume reduction achieved
    - *Average particle size is 0.4 cm*
  - Contains roughly 44 metric tons heavy metal
    - *Acidic, abrasive, and hydroscopic*

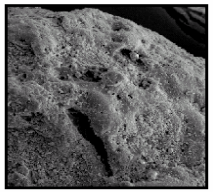
Calcine Bed Material 40x



Calcine Bed Material 150x



Calcine Bed Material 500x

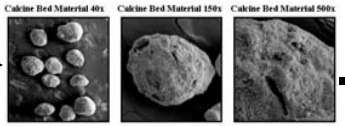


- ***Currently stored in 43 bins in 6 bin-sets***
  - Designed for safe storage for several hundred years
  - Stored under 10-year RCRA Part B Permit issued 11/06

- ***Calcine is also classified as hazardous waste as it:***
  - Exhibits hazardous waste characteristics for toxicity for metals
    - *Waste numbers D004 through D011*
  - Contains listed wastes
    - *Spent solvents (hazardous waste numbers F001, F002, and F005)*
    - *Discarded hydrogen fluoride (hazardous waste number U134)*
- ***Chemical analysis has been performed on samples from:***
  - New Waste Calcining Facility (NWCF) Campaign H-4 (1998)
  - *NWCF Campaign H-3 (1993)*
  - *Alumina and zirconia calcine from CSSF 2 (1978)*

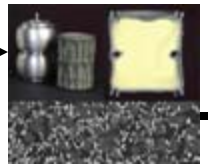
Potential Disposal Options for Calcine Remain as Follows:

- ***Package and dispose of as is (direct disposal option)***
  - Idaho baseline approach – highest regulatory risk, potential lowest cost
  - Requires conditional exemption from RCRA
  - Granular waste form



- ***Hot isostatic pressing***
  - Forms volume reduced glass ceramic
  - Being evaluated by BEA and ANSTO, Inc.
  - Monolithic waste form – requires delisting
  - Could compact (>50% volume reduction) steam reformed or untreated calcine

>30% volume reduction



>50% volume **reduction**

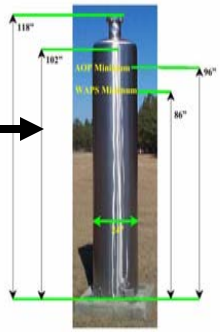
- ***Vitrification of high-activity fraction after separations***
  - Highest facility cost – lowest disposal volume
  - Requires re-dissolution of calcine
  - Produces 20,000 m^3 of grouted low activity fraction
  - Monolythic waste form – requires delisting

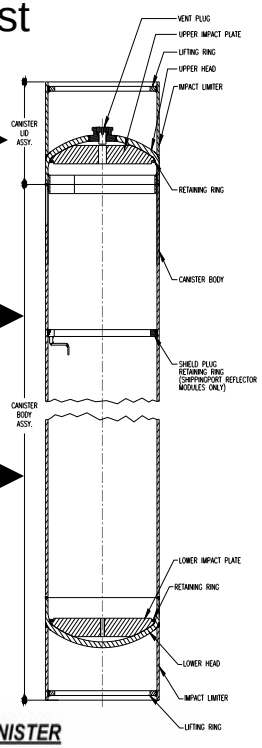
>50% volume reduction

Plus LLW Grout

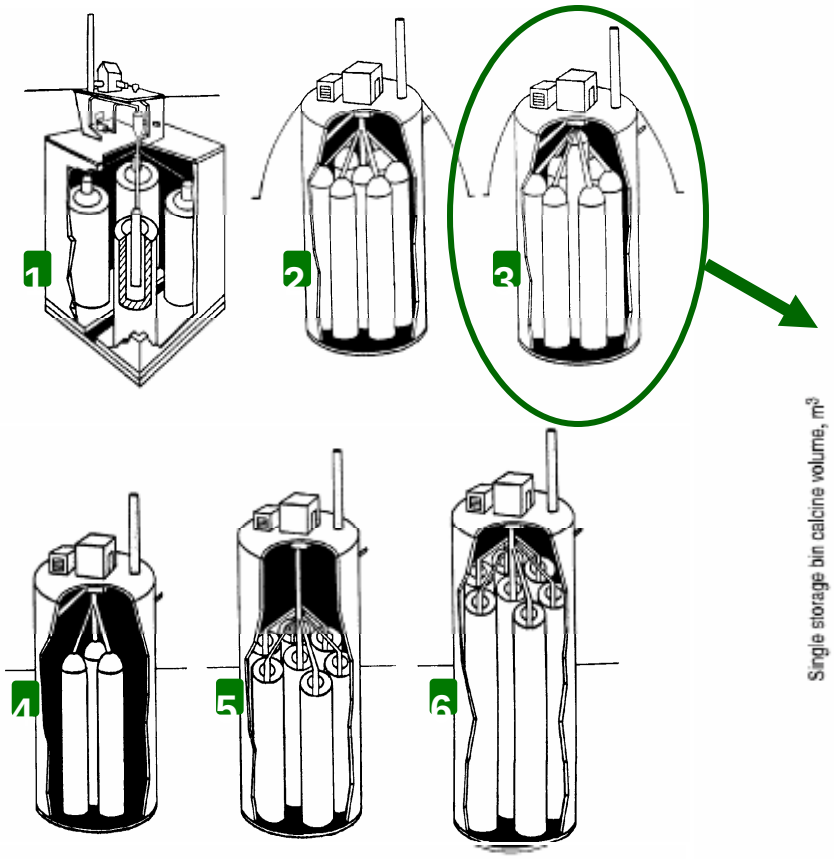
- ***Direct vitrification (State EIS PA)***
  - Monolythic waste form – requires delisting
  - Lowest regulatory risk – highest cost and disposal volume

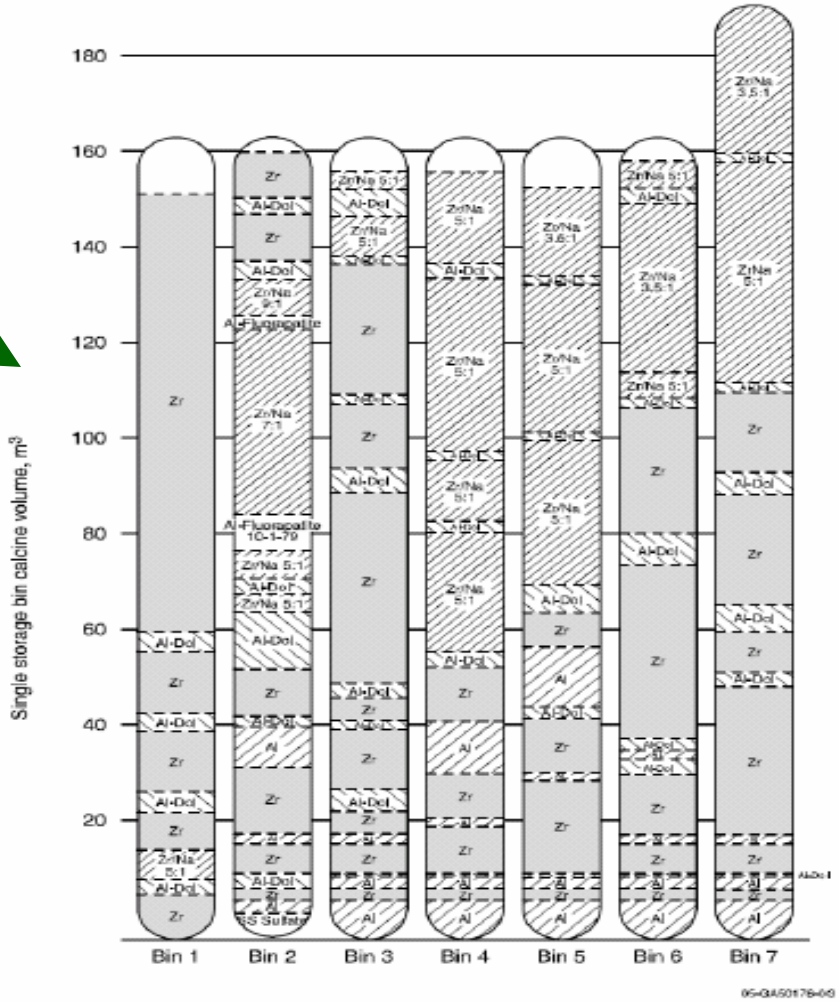
~100% volume increase





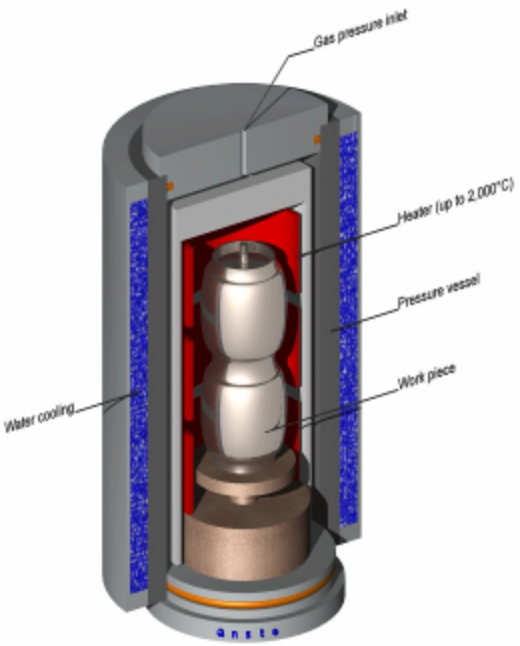
Technical Challenge: Layering of Calcine (Bin Set #3 shown)





Basic Hot Isostatic Pressing Process

- ***HIP patented in the US by Romp in 1941.***
  - Battelle patented HIP process to diffusion bond nuclear fuel in 1964.
- ***Technology consists of a pressure vessel containing an electrically heated furnace.***
- ***Components are placed in a sealed can inside the furnace and isostatically pressed with argon to maximum density***
  - Temperature to 2000 C (3600 F)
  - Pressure to 100 MP (15000 psi)
- ***Pressure vessels are built to stringent ASME codes, and include active and passive safety systems.***
  - Can isolates pressure vessel from contamination (less than .1% failure rate)



Further Technical Evaluation of HIP Option Appears Warranted

Consolidation:	HIP	Direct Vitrification (JHM)
Matrix:	glass-ceramic	borosilicate glass
Waste loading:	**60-90%**	**20-35%**
Durability (PCT-B):	10-100 x EA glass	10 x EA glass
Final volume: (relative to untreated calcine)	**30-45% reduction**	**~100% increase**
Temp:	1200°C (2200°F)	1150°C (2100°F)
Pressure:	31 MPa (4500 psi)	atmospheric
Off-gas:	minimal	medium-high
Facility		
Future Mission Flexibility:	diverse/flexible	extremely limited/inflexible

Cold calcine in glass-ceramic matrix

Direct SBW compaction (no additives)

Metal encapsulation of uneconomic feeds (Swedish SNF in copper shown)

Technology Initiative: HIP Evaluation Funded by EM-20

- ***Contract between Battelle Energy Alliance and the Australian Nuclear Science and Technology Organization, Inc. was signed 2/28/2008***
  - **Funded at $3.5M** to date
  - Will provide data necessary to fairly **evaluate HIP treatment of calcine** with other options for proper down-selection among other calcine treatment alternatives
    - Also evaluate other HIP challenging material treatment/confinement applications
- ***Calcine surrogate produced at STAR Center and shipped to ANSTO for HIPing and testing of resultant waste form against repository criteria***
  - Three distinct alumina-calcine and zirconia calcine simulants containing low, medium, and high mercury and cadmium concentrations respectively
  - All other RCRA constituents held at maximum

Sample of simulated alumina calcine showing fines (bottom ~10% of total), product (vast majority) and agglomerates (~1%).

- ***HIP unit is installed in the HFEF hot-cell at the INL***
  - Using to evaluate conduct of necessary remote operations (filling/crimping/welding) and HIPing of surrogate calcine spiked with radionuclides, followed by HIPing of actual calcine
  - Planning to evaluate treatment of a wide range of challenging EM materials difficult to incorporate into glass such as:
    - *Cesium/Strontium, technicium,* ***radioactive sludges (e.g. Hanford K-basin),*** *alpha ashes, impure actinides,* ***corroded spent fuel pins****, et*

Technology Initiative: HIP Evaluation Funded by EM-20 (cont)

- ***Results to date indicate viability of HIP treatment of calcine***
  - Direct HIPing (no treatment additives) generates >50% volume reduction
    - *Direct HIPing of aluminum calcine actually exceeds the regulatory universal treatment standard (UTS via TCLP test) without treatment additives (direct HIPing)*
    - *Resultant monolythic waste form facilitates transport to a repository or MRS*
  - HIPing of treated calcine (80% loading) results in a glass-ceramic waste form
    - *Chemical durability of treated zirconium calcine handily exceeds UTS and environmental assessment (EA) requirements while achieving >35% volume reduction*
    - *Evaluation of treated aluminum calcine is currently underway*
  - Preparations are being made for HIPing actual calcine at MFC (HFEF hot cell) and HIPing a large (70 pound) Al surrogate can in Sydney, Australia
    - *All work is being performed under the NRC-approved QA program (RW-0333P)*

Direct HIPed alumina calcine showing a 69%+ volume reduction

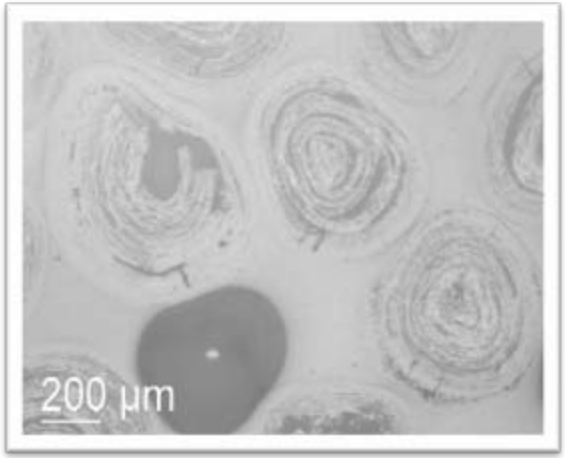
HIPed treated zirconia calcine inside the MFC HFEF hot cell

Evolution of HIP can design will further enhance volume reduction

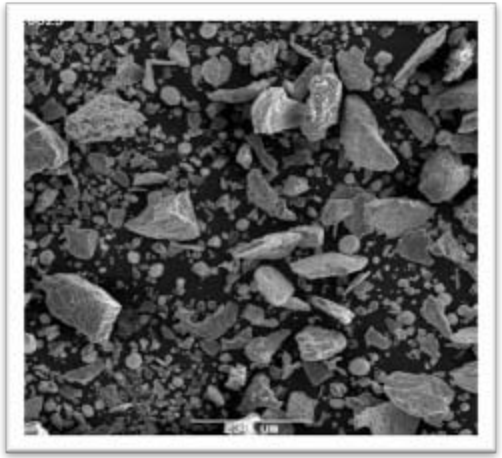
Calcine RCRA Surrogate Material Produced At STAR Center

- ***Produced using a fluidized bed calciner***
  - 200-300 lbs produced (aluminum and zirconium calcine combined)
- ***All RCRA characteristics @ maximum except for cadmium and mercury that were produced at low, transition, and maximum concentrations for Zr and Al calcine surrogate respectively***

Sample of Al calcine surrogate showing fines (bottom ~10% of total), product (vast majority), and agglomerates (~1.5%)



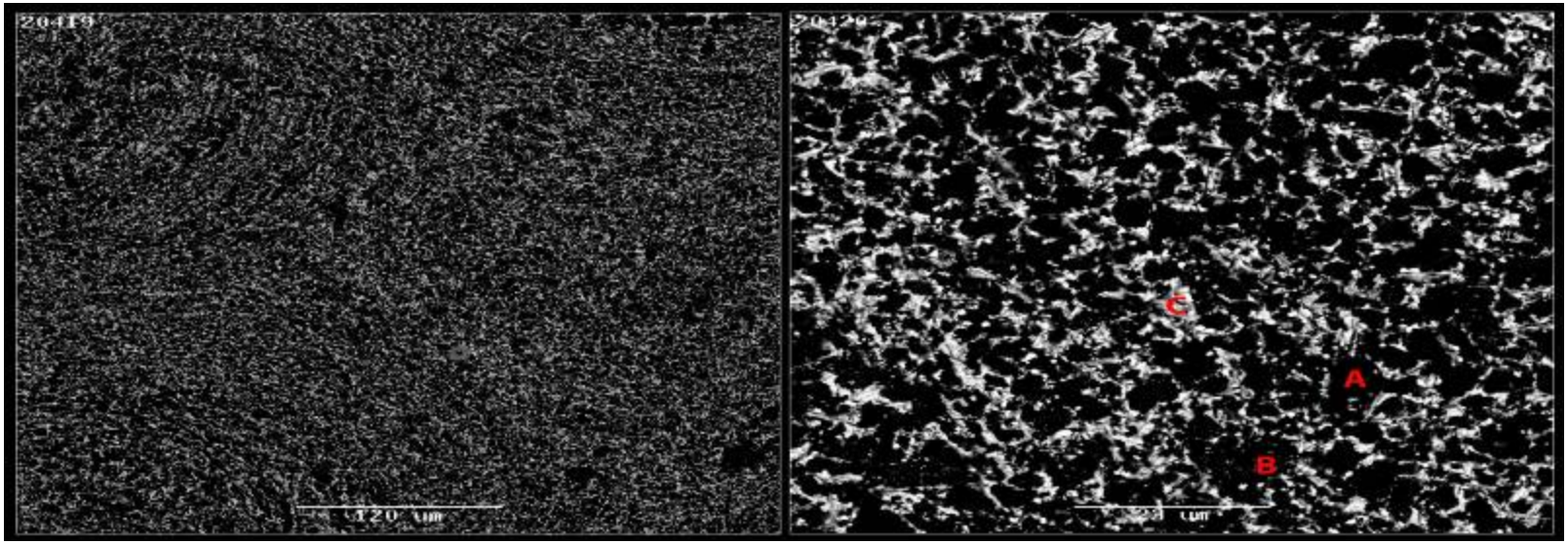
Optical micrograph 50X magnification of Zr maximum RCRA composition surrogate showing onion-ring type layering particle growth.



Scanning electron micrograph 100X magnification of Al maximum RCRA composition

Technology Initiative: HIP Evaluation Funded by EM-20 (cont)

- ***Scanning electron microscope (SEM) images of untreated Zr (direct disposal volume reduction) cross-section indicating predominant phases***
  - **A** – Calcium Fluoride
  - **B** – Alumina (predominantly Al, with minor Na element)
  - **C** - Zirconia (predominantly Zr, with minor Al, Ca, and Cd elements)



Backscattered electron images of Zr at magniifcations of 200X and 1000X respectively showing the phases formed in the bulk ceramic

TCLP Results: Max Cd Zr Calcine Before and After Direct HIP

TCLP Summary Table: ***Direct HIP of Zirconia Calcines Maximum RCRA (1124 DB2)***

Metals in TCLP	Type of Sample	TCLP/UTS Nonwastewater Standard	Blended Zr Maximum RCRA Starting Powder	Direct HIPed Zr Calcine Maximum RCRA
Extraction Fluid Used	-		1	1
pH of Final Leachate	pH units	_	6	4.97
Antimony in TCLP	mg/L	1.15	0.2	0.2
Arsenic in TCLP	mg/L	5.0	<0.05	<0.05
Barium in TCLP	mg/L	21	1.3	0.09
Beryllium in TCLP	mg/L	1.22	<0.01	<0.01
Cadmium in TCLP	mg/L	0.11	600	150
Chromium in TCLP	mg/L	0.6	15	9.3
Lead in TCLP	mg/L	0.75	0.09	<0.03
Mercury in TCLP	mg/L	0.025	0.27	<0.0005
Nickel in TCLP	mg/L	11	4.1	0.05
Selenium in TCLP	mg/L	5.7	<0.12	<0.12
Silver in TCLP	mg/L	0.14	<0.02	<0.02
Thallium in TCLP	mg/L	0.2	<0.05	<0.05
Vanadium in TCLP	mg/L	1.6	<0.02	<0.02
Zinc in TCLP	mg/L	4.3	<0.02	<0.02

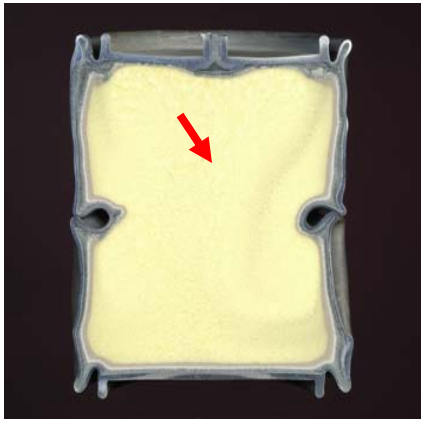
PCT Results: Max. Cd Zr Calcine After Direct HIP

PCT-B Summary of Elements in Excess 0.5 wt%: Direct HIP Zirconia Maximum RCRA Elements (1124 DB2)			
Element	**Weight %**	**EA Glass STD, g/L**	**Upper Limit on Normalized Conc.*, g/L**
Al	9.8		0.68
B	0.9	16.28	35.3
Ca	23.9		1.66
Cd	7.0		0.013
Fe	0.6		4
Na	0.8	12.92	57.7
Zr	16.3		0.000002

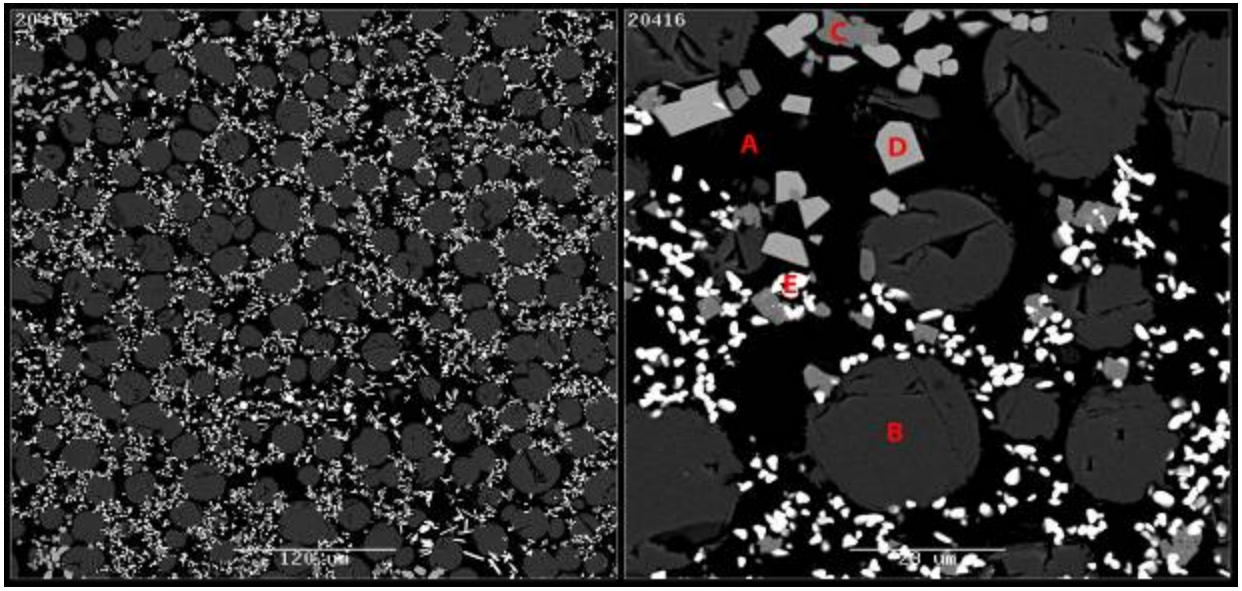
*95% confident that the true normalized concentration lies below this upper limit.

Microscopic Examination of Phases of Bulk Zr Glass Ceramic

- ***SEM investigation of the bulk of the treated Zr sample***
- ***Phase assemblage is consistent with the interfacial region:***
  - **A** – glass
  - **B** – calcium fluoride
  - **C** - $Fe(Cr,Al)_2O_4$ spinel
  - **D** – zircon
  - **E** - zirconia

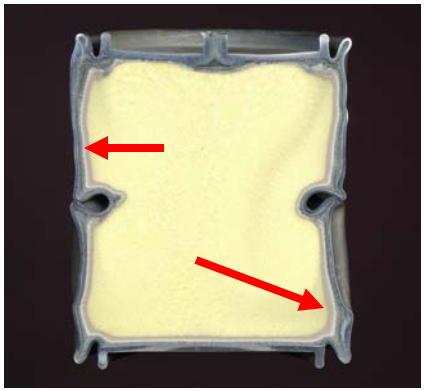


Backscattered electron images of transition treated zirconium calcine with 80% waste loading at magnifications of 200X and 1000X respectively showing the phases formed in the bulk ceramic

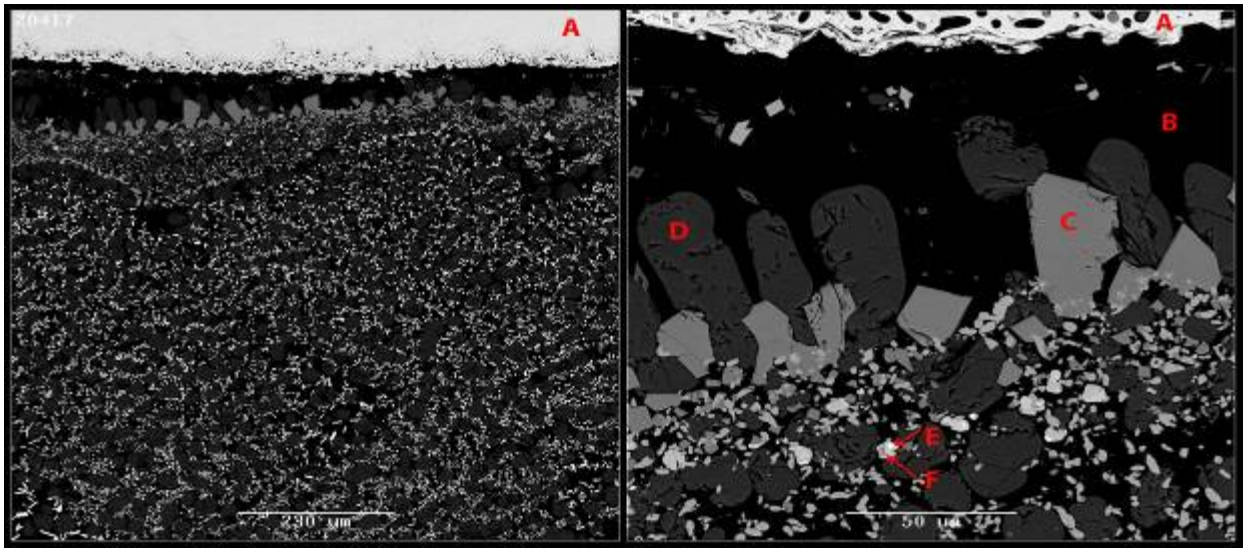


Microscopic Examination of Phases at Zr Can Interface

- ***SEM investigation of discoloration at the treated Zr HIP can interface***
- ***Phase assemblage at the interface consists of:***
  - **A** - can
  - **B** – glass
  - **C** – $Fe(Cr,Al)_2O_4$ spinel
  - **D** – calcium fluoride
  - **E** – cadmium metal or sulphide
  - **F** – iron nickel sulphide



Backscattered electron images of transition treated Zr calcine with 80% waste loading at magnifications of 100X and 500X respectively showing the phases formed at the HIP can interaction zone



TCLP Results: Treated Zr Calcine with Baseline RCRA

TCLP Summary Table: ***Treated HIP of baseline RCRA calcine (1136 DB2)***

Metals in TCLP	Type of Sample	TCLP/UTS Nonwastewater Standard	Zr Baseline RCRA Starting Powder	Solid HIPed Zr Baseline RCRA
Extraction Fluid Used	-		1	1
pH of Final Leachate	pH units	_	5.5	4.88
Antimony in TCLP	mg/L	1.15	<0.15	<0.15
Arsenic in TCLP	mg/L	5.0	<0.05	<0.05
Barium in TCLP	mg/L	21	0.87	<0.01
Beryllium in TCLP	mg/L	1.22	<0.01	<0.01
Cadmium in TCLP	mg/L	0.11	4.4	0.01
Chromium in TCLP	mg/L	0.6	20	0.01
Lead in TCLP	mg/L	0.75	<0.03	<0.03
Mercury in TCLP	mg/L	0.025	0.18	<0.0005
Nickel in TCLP	mg/L	11	2.6	<0.02
Selenium in TCLP	mg/L	5.7	<0.12	<0.12
Silver* in TCLP	mg/L	0.14	0.04	<0.02
Thallium in TCLP	mg/L	0.2	<0.05	<0.05
Vanadium in TCLP	mg/L	1.6	<0.02	<0.02
Zinc in TCLP	mg/L	4.3	<0.02	<0.02

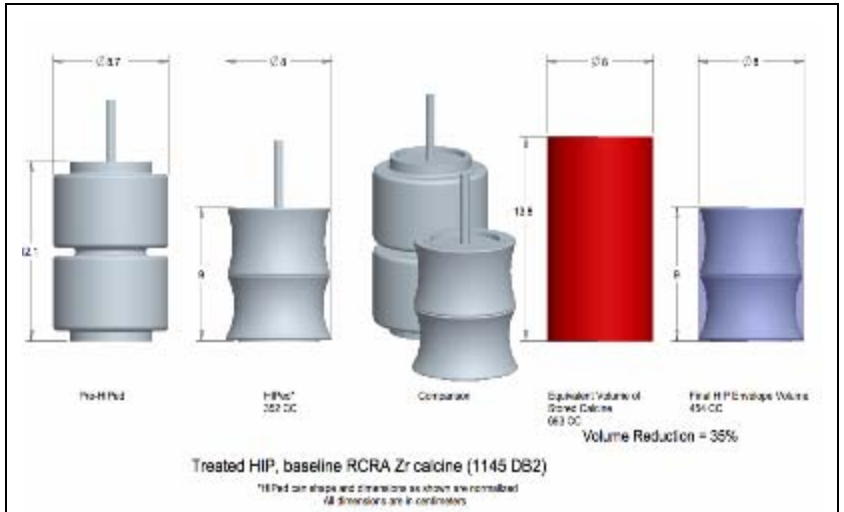
PCT Results: Treated Zr Calcine with Baseline RCRA

PCT-B Summary of Elements in Excess 0.5 wt%: Zirconia Treated Baseline 80-20 (1136 DB2)					
Element	Weight %	EA Glass STD, g/L	Upper Limit on Normalized Conc.*, g/L		
Al	9.3			0.01	
B	1.1	16.28		0.6	
Ca	20.4			0.4	
Cu	2.2			0.0006	
F	16.3			0.03	
Fe	3.0			0.007	
Na	0.7	12.92		0.5	
Si	3.5			0.3	

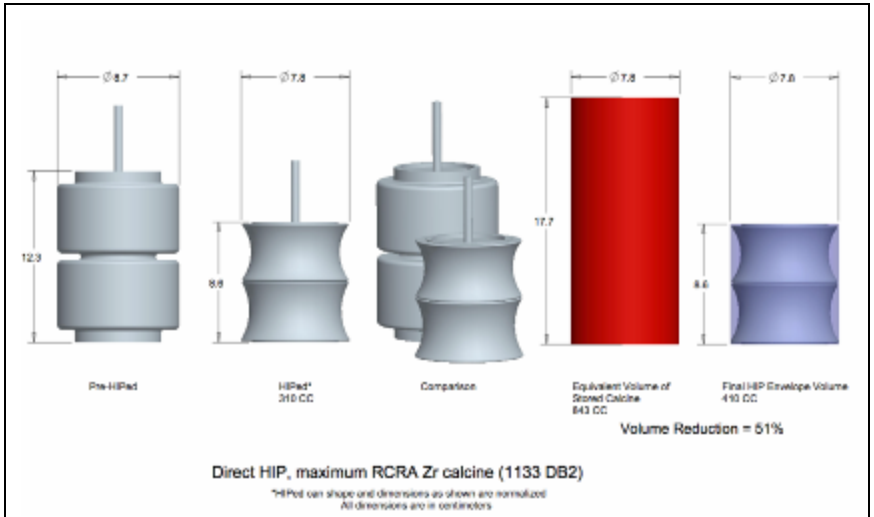
*95% confident that the true normalized concentration lies below this upper limit.

Volume Reduction Ranges from 70% (Direct Al) to 35% (Treated Zr)

- ***Treated and direct Zr HIPed volume reduction (35% and 51% respectively)***
  - ***Untreated Al volume reduction approaches 70%***



Treated Zr



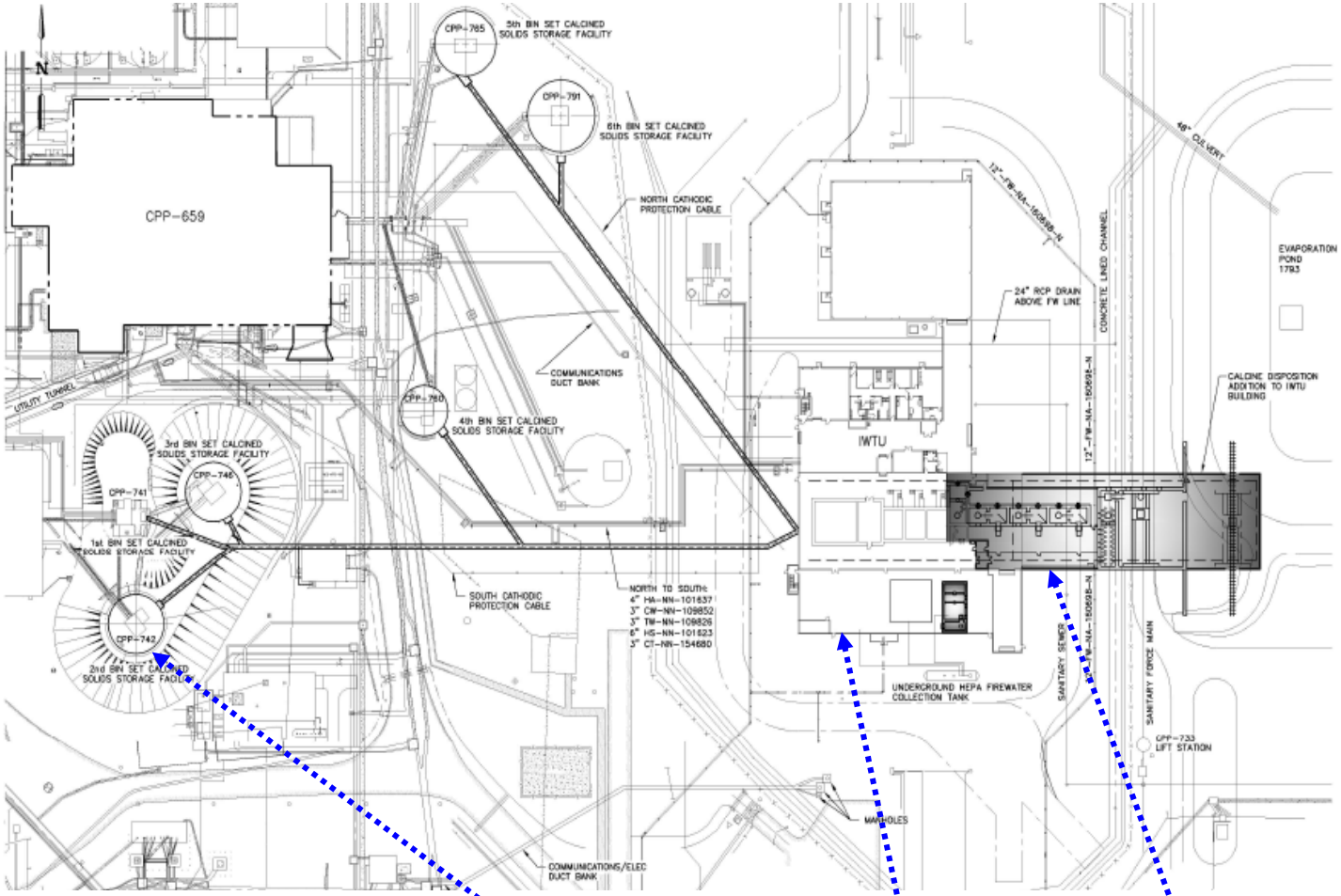
Untreated Zr

- ***Future can optimization will further reduce volume as packaged***

HIP Technology is Safe and Industrially Mature

- ***BEA/ANSTO have reviewed performance/safety record of US HIP industry***
  - HIPs of up to 64-inch diameter operate above calcine pressure and temperature requirements
  - Operated in 24/7production environment over 30 years
    - *Work pieces up to 10,000 pounds are routinely HIPed*
  - Main safety issue raised was asphyxiation (argon gas)
    - *Not a significant concern in a restricted hot-cell environment*

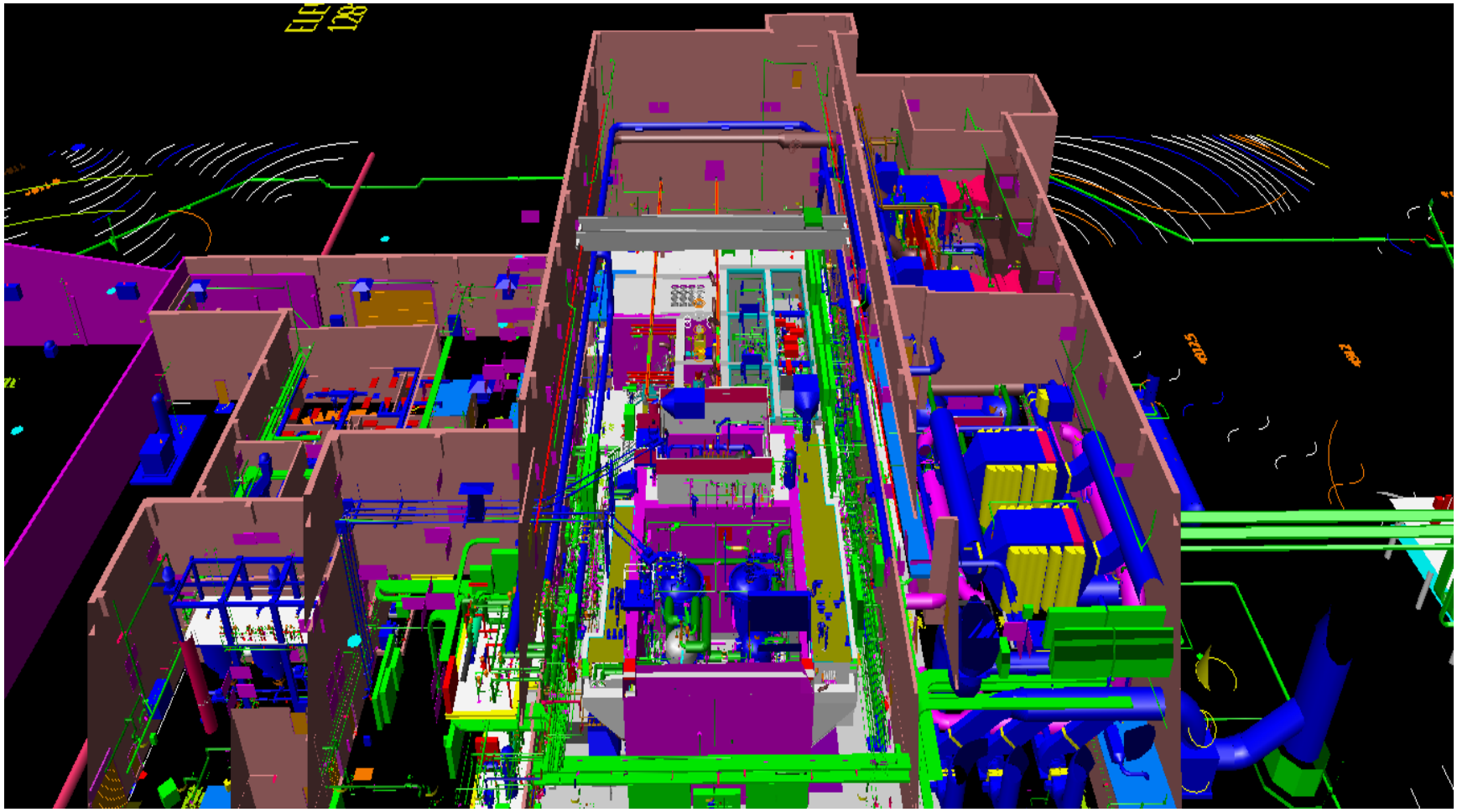
Calcine Retrieval and Delivery (Development EM-20 Funded) to IWTU



Prototype retrieval arm

Bin sets (typical)

IWTU

Potential packaging annex

IWTU Internal View