Technical Bases for DWPF Glass Product Control Program

M. J. Plodinec
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5, 6. Product Consistency

- Specification:
  - Control process so glass better than benchmark glass — "EA glass" — (lower release of Li, Na, B on Product Consistency Test)
  - Verify mean reported value 2 standard deviations below mean of benchmark glass

- Volume 5 describes strategy, technical bases, and qualification testing
  - Control of feed composition is key to compliance
  - Occasional glass sampling will confirm compliance
  - Reporting will be done on basis of macro-batch

- Volume 6 (Glass Product Control Program) details control actions and reporting during production
  - Implementation of strategy

Technical Bases for Product Consistency

- Key parameter to control is glass composition
- Best controlled through control of feed composition, in last feed preparation vessel
- Free energy of hydration a useful "metric" to evaluate feed composition
- Have developed software system to assure product quality, while satisfying process constraints

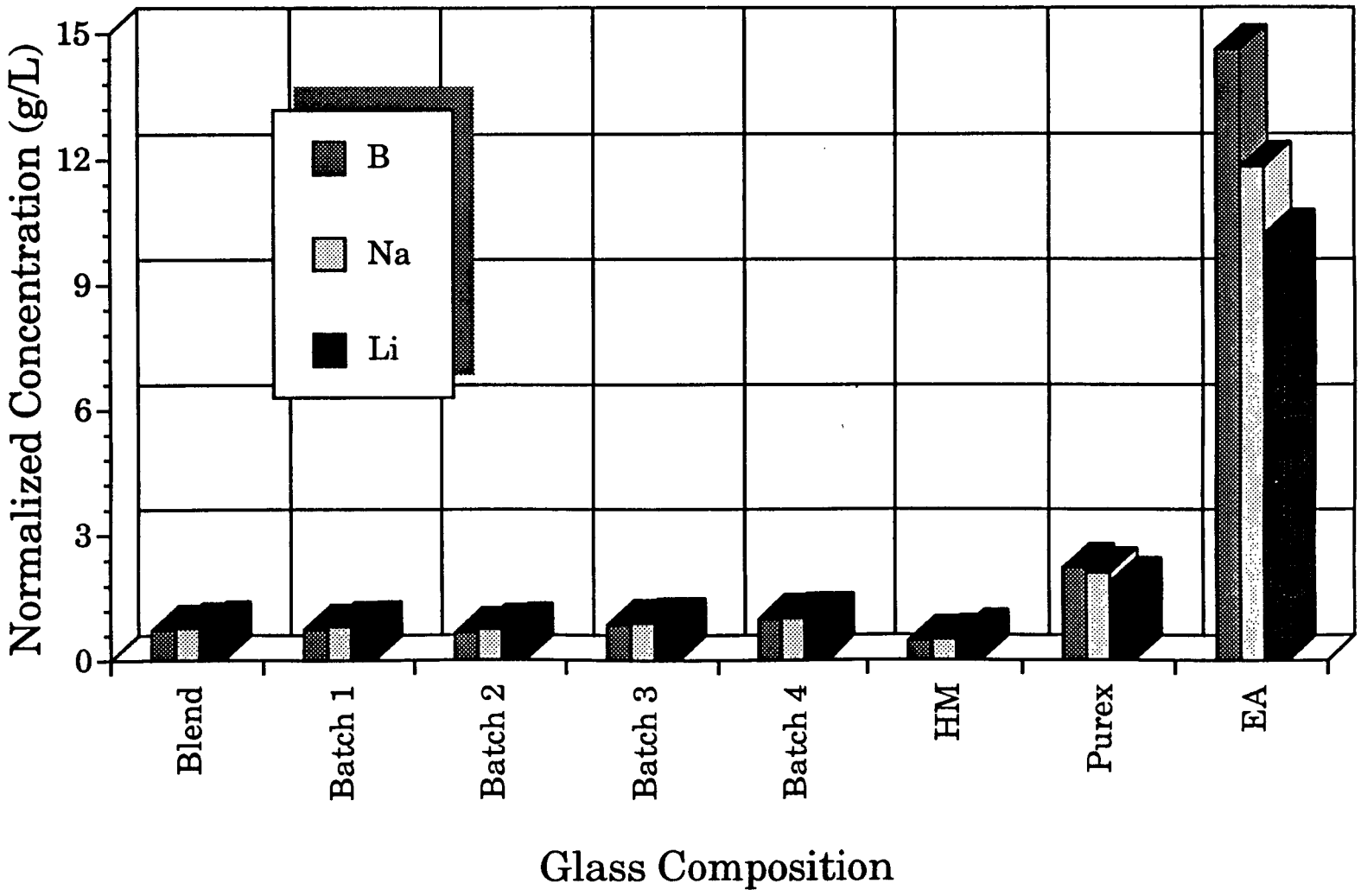
Importance of Glass Composition

- Performance of glass on PCT (or any leach test) depends on:
  - Glass composition
  - Water composition, Eh, pH
  - Temperature of interaction
  - Water flow rate
  - Ratio of glass surface area to solution volume
  - Time of contact between glass and water

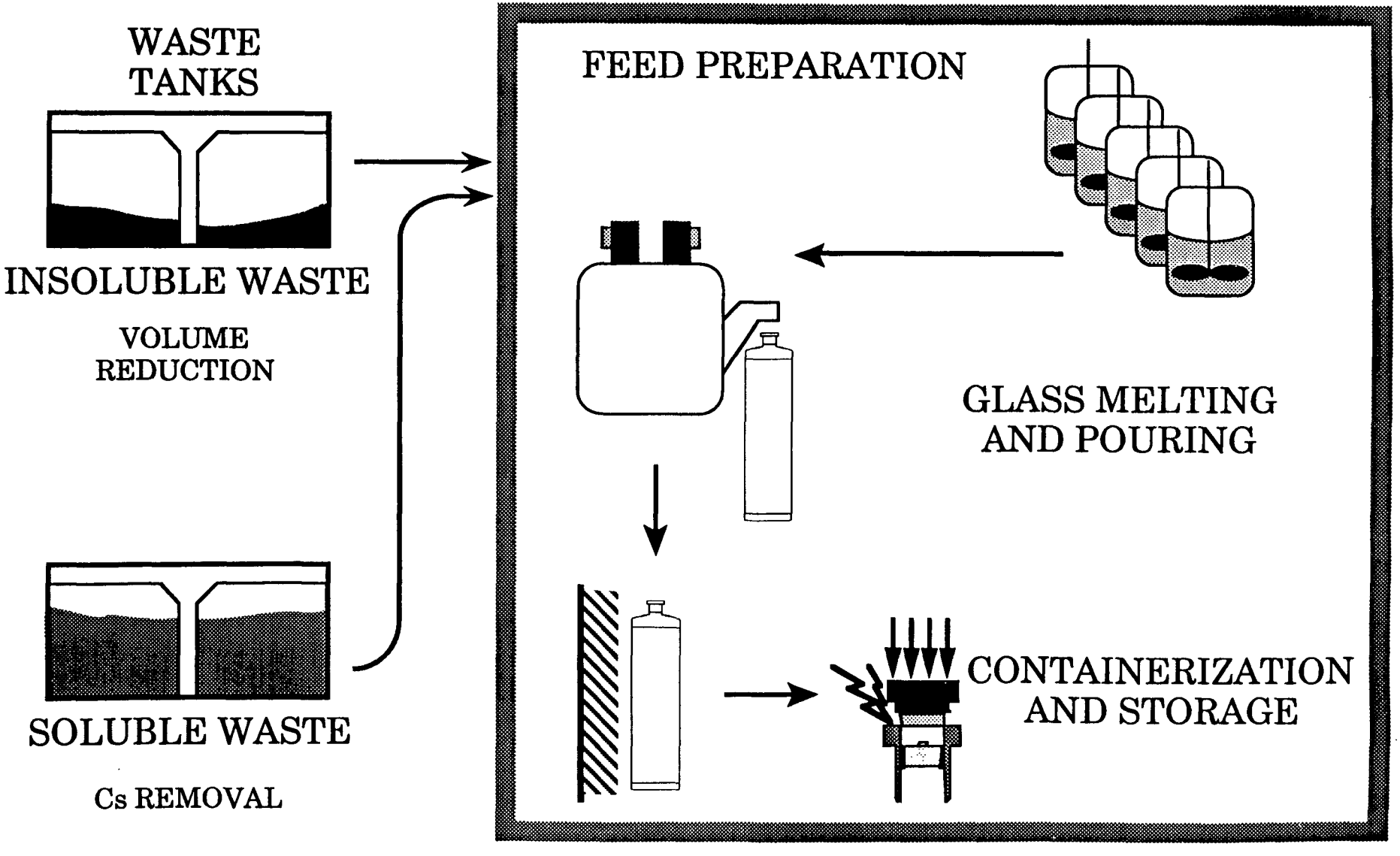
- The PCT fixes: water composition (DIW), temperature (90°C), flow rate (static), SA/V, time (7 days)

- Therefore, the DWPF must control the composition of the glass to meet the specification

PCT Results for Projected DWPF Glasses



DWPF Process



Control of Glass Composition

Objective: Make only glass which meets specification

Cause	Effect
• Cannot recycle bad glass	⇒ glass sampling of little value for control ⇒ must control feed composition
• Maximize effectiveness of control	⇒ control each process batch
• Minimize risk of undoing control	⇒ apply control after last routine addition, at last feed preparation vessel

Constraints on Composition Control

- SRS waste variable in composition; future waste compositions may differ from current waste

- Want to minimize needless shutdowns of process, while maintaining tight control over product

- Thus, need a tool to evaluate compositions which is
  - — Easy to use, and reliable, in production
  - — Able to take into account waste variability and effects of trace components consistently
  - — Wide range of applicability (both compositions and test conditions)

Hydration Thermodynamics Approach

- Assumes glass a mechanical mixture of components (SiO_2, B_2O_3, etc.)
- Each component has well-defined free energy of reaction with water
- Free energy of hydration of glass = sum of the free energies of hydration of individual components weighted by concentration of component in glass

$$\Delta G^{\circ}_{hydration} = \sum_{i} \Delta G^{\circ}_{i,hydration} \cdot m_i$$

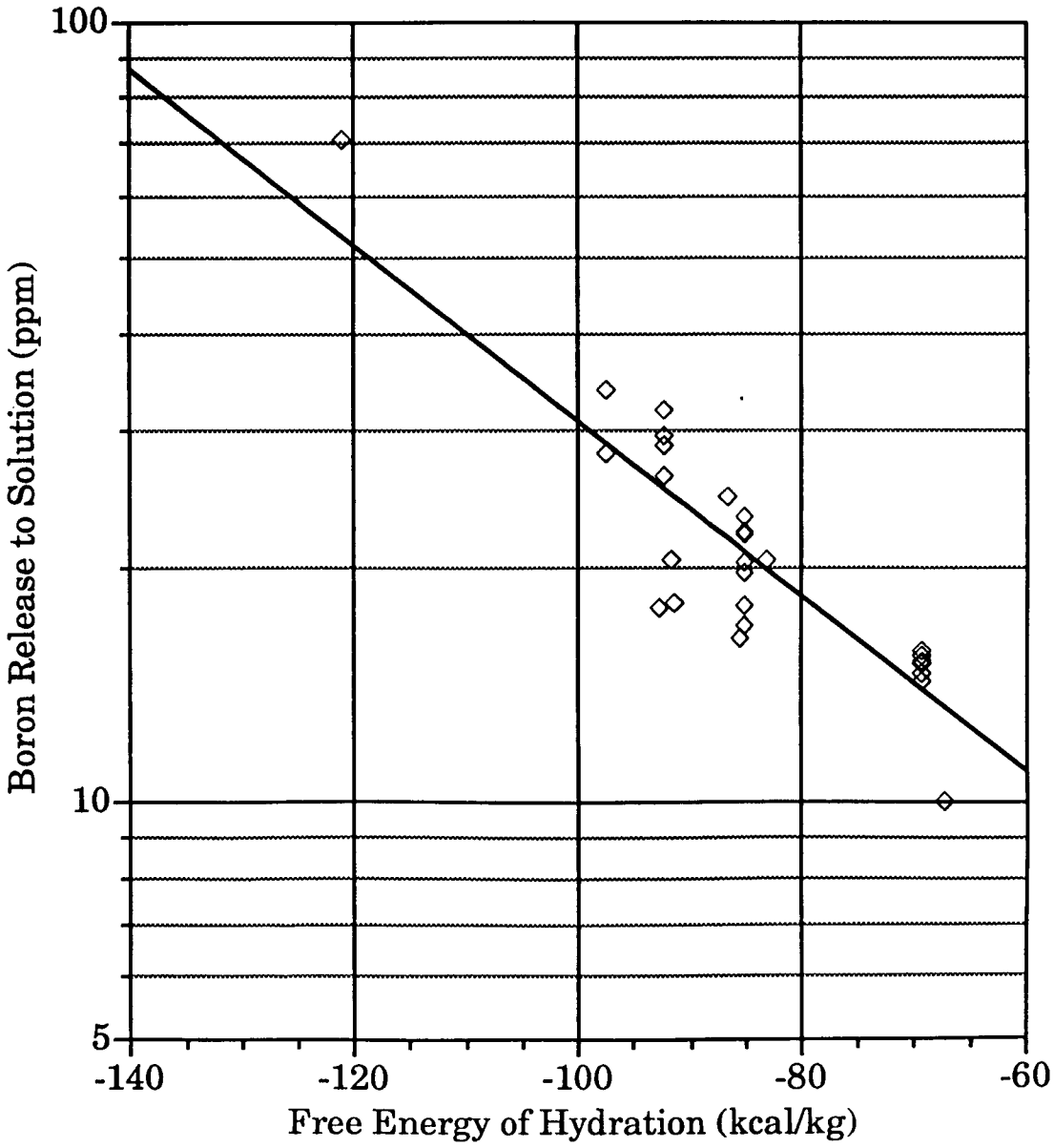
Glass Components for Hydration Approach

Glass Component	Hydrated Species	$\Delta G°$ (kcal/mol)
Li_2SiO_3	Li^+, H_2SiO_3	-22.740
Na_2SiO_3	Na^+, H_2SiO_3	-28.815
K_2SiO_3	K^+, H_2SiO_3	-41.735
Rb_2SiO_3	Rb^+, H_2SiO_3	-46.500
Cs_2SiO_3	Cs^+, H_2SiO_3	-46.820
$MgSiO_3$	Mg^{++}, H_2SiO_3	-13.888
$CaSiO_3$	Ca^{++}, H_2SiO_3	-16.116
$SrSiO_3$	Sr^{++}, H_2SiO_3	-24.400
$BaSiO_3$	Ba^{++}, H_2SiO_3	-30.570
$PbSiO_3$	Pb^{++}, H_2SiO_3	-8.810
$NiSiO_3$	Ni^{++}, H_2SiO_3	-14.347
$FeSiO_3$	Fe^{++}, H_2SiO_3	-14.609
$MnSiO_3$	Mn^{++}, H_2SiO_3	-14.871
Co_2SiO_4	$2Co^{++}$, H_2SiO_3	-46.820
$ZnSiO_3$	Zn^{++}, H_2SiO_3	-2.400
$USiO_4$	UO_2, H_2SiO_3	27.700
$ZrSiO_4$	$ZrO(OH)_2$, H_2SiO_3	45.100

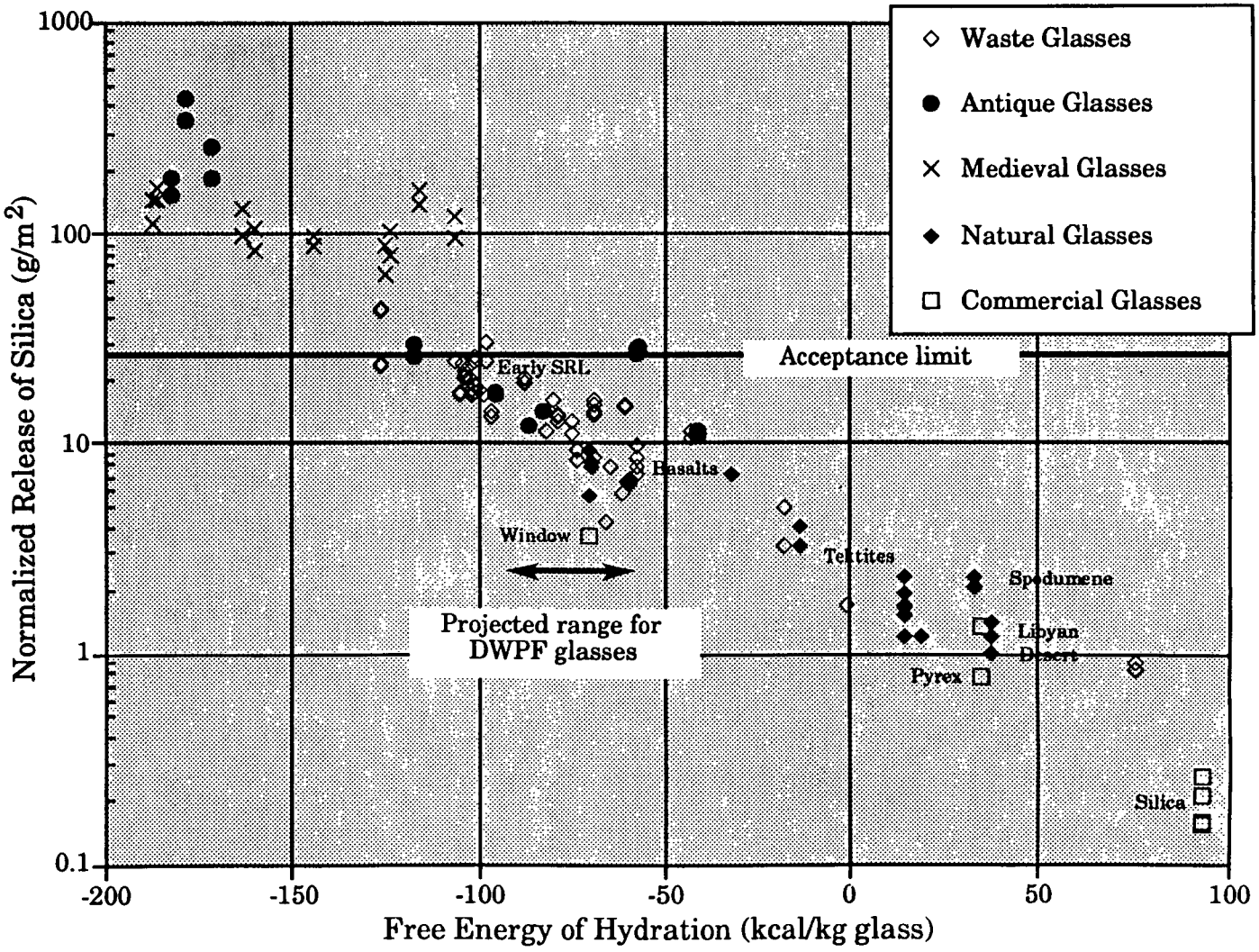
Glass Components (continued)

B_2O_3	$2H_3BO_3$	-9.930
Al_2O_3	$AlO(OH)$	3.040
SiO_2	H_2SiO_3	5.590
Fe_2O_3	$Fe(OH)_3$	15.500
TiO_2	$TiO(OH)_2$	15.990
TeO_2	H_2TeO_3	19.980
UO_3	$UO_2(OH)_2$	-6.800
CuO	Cu^{++}	-10.024
$CdSiO_3$	Cd^{++}, H_2SiO_3	-12.345
$MoO_3 + OH^-$	MoO_4^{--}	-21.750
P_4O_{10}	$4H_3PO_4$	-107.241
ThO_2	Th^{++++}	-2.533
Y_2O_3	$2Y(OH)_3$	-12.954
Ce_2O_3	$2Ce(OH)_3$	-26.390
Nd_2O_3	$2Nd(OH)_3$	-28.320
La_2O_3	$2La(OH)_3$	-31.140
Cr_2O_3	$2Cr(OH)_3$	37.360
CeO_2	Ce^{++++}	11.345
SnO	$Sn(OH)_2$	0.570

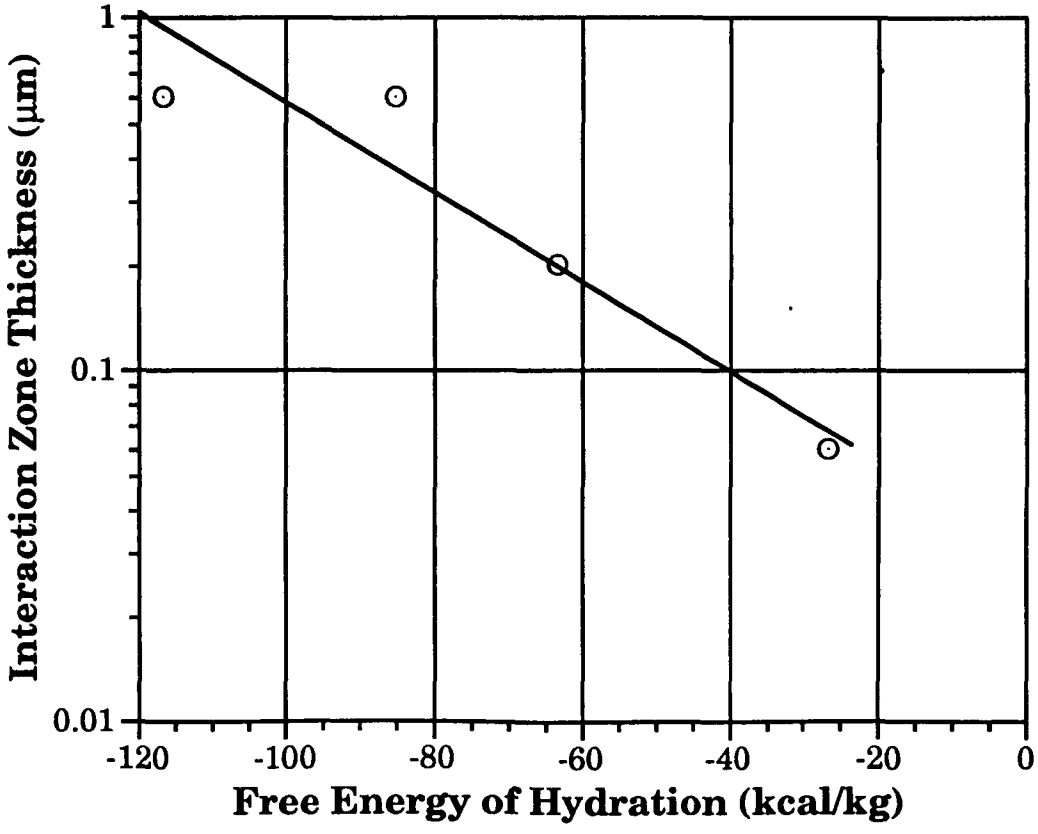
DWPF Product Consistency Test (7 d, 90°C)



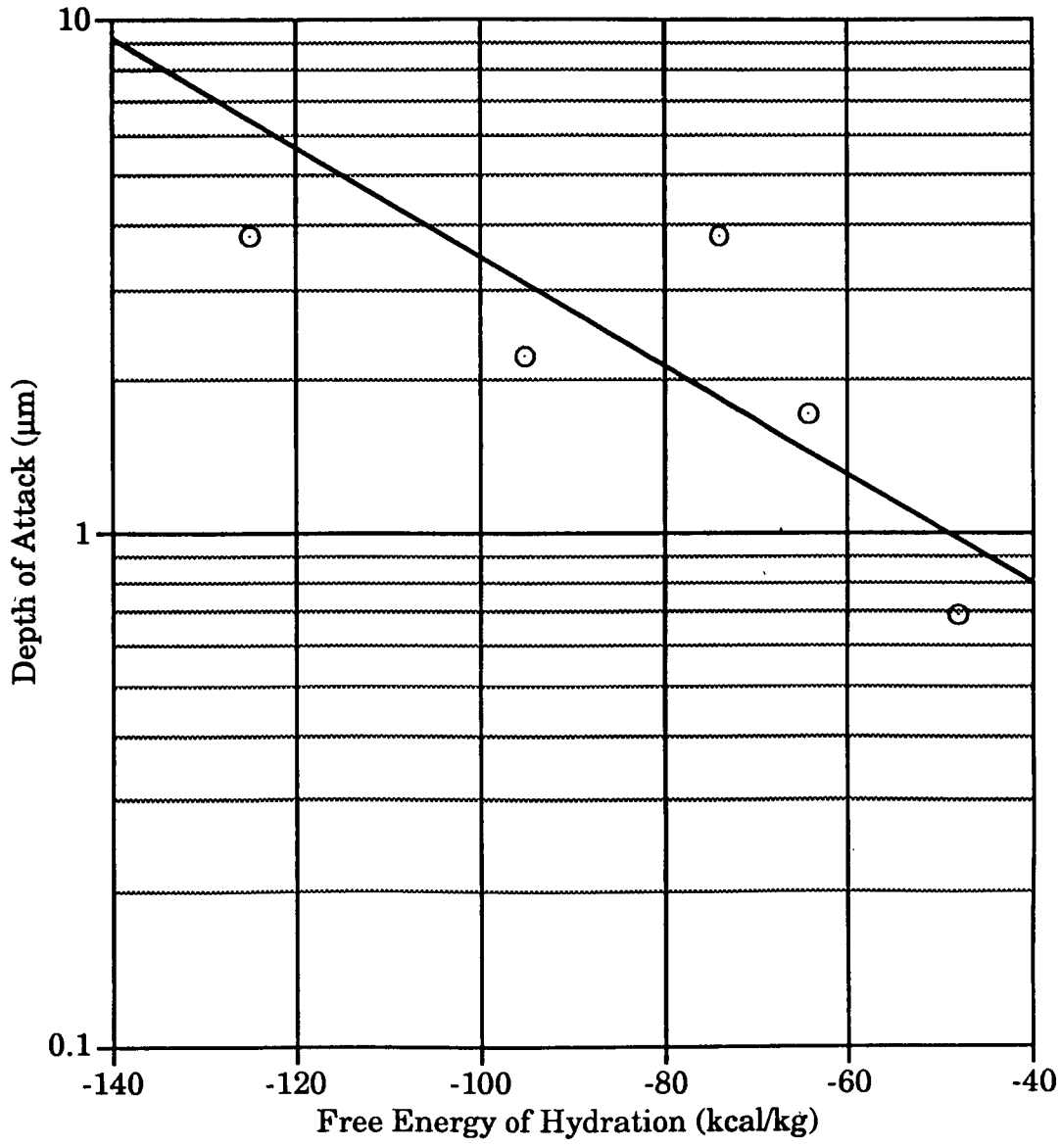
MCC-1 Tests (28 d, 90°C)



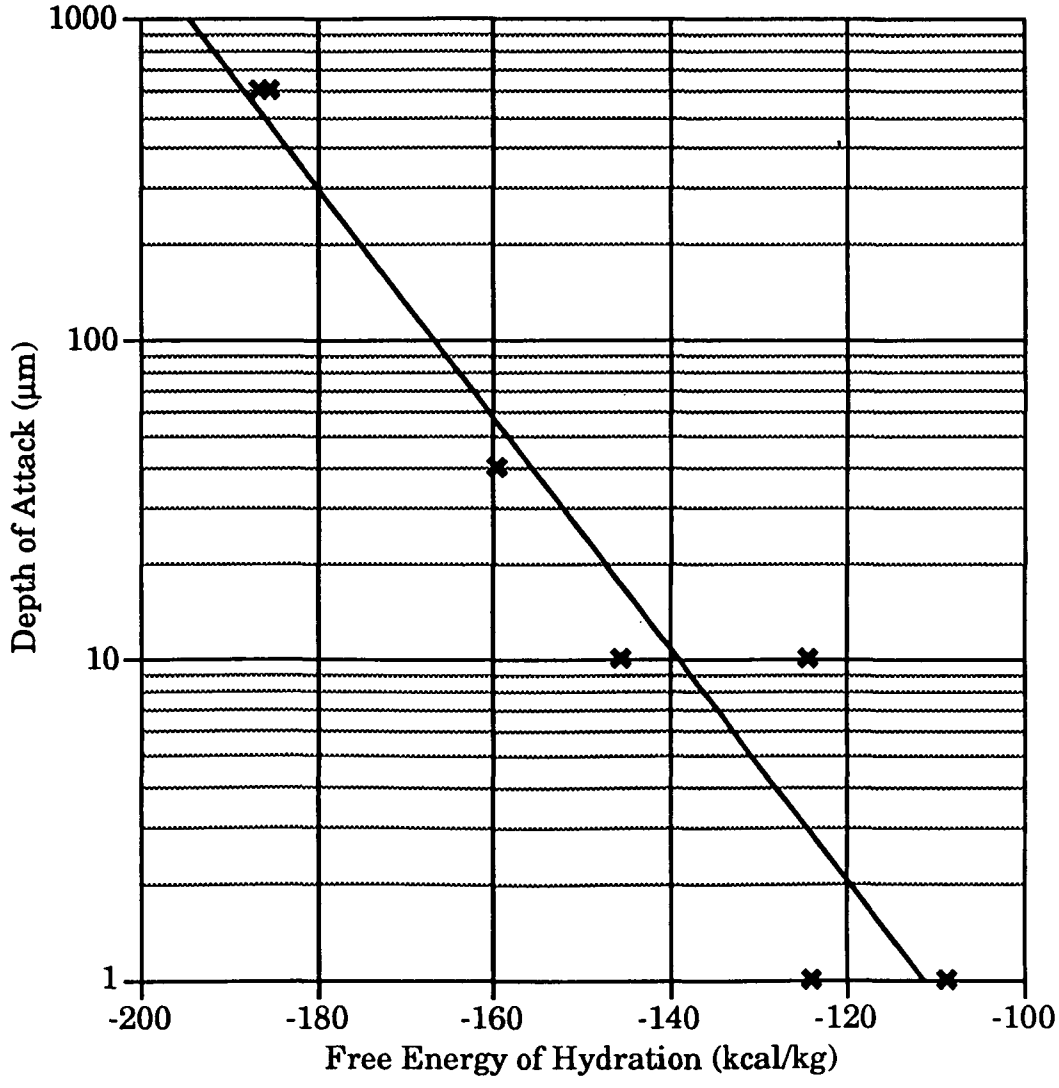
Glasses Buried One Year in Ballidon



Glasses Buried Two Years in Stripa (90°C)



Glasses Buried Five Years in Ballidon (UK)



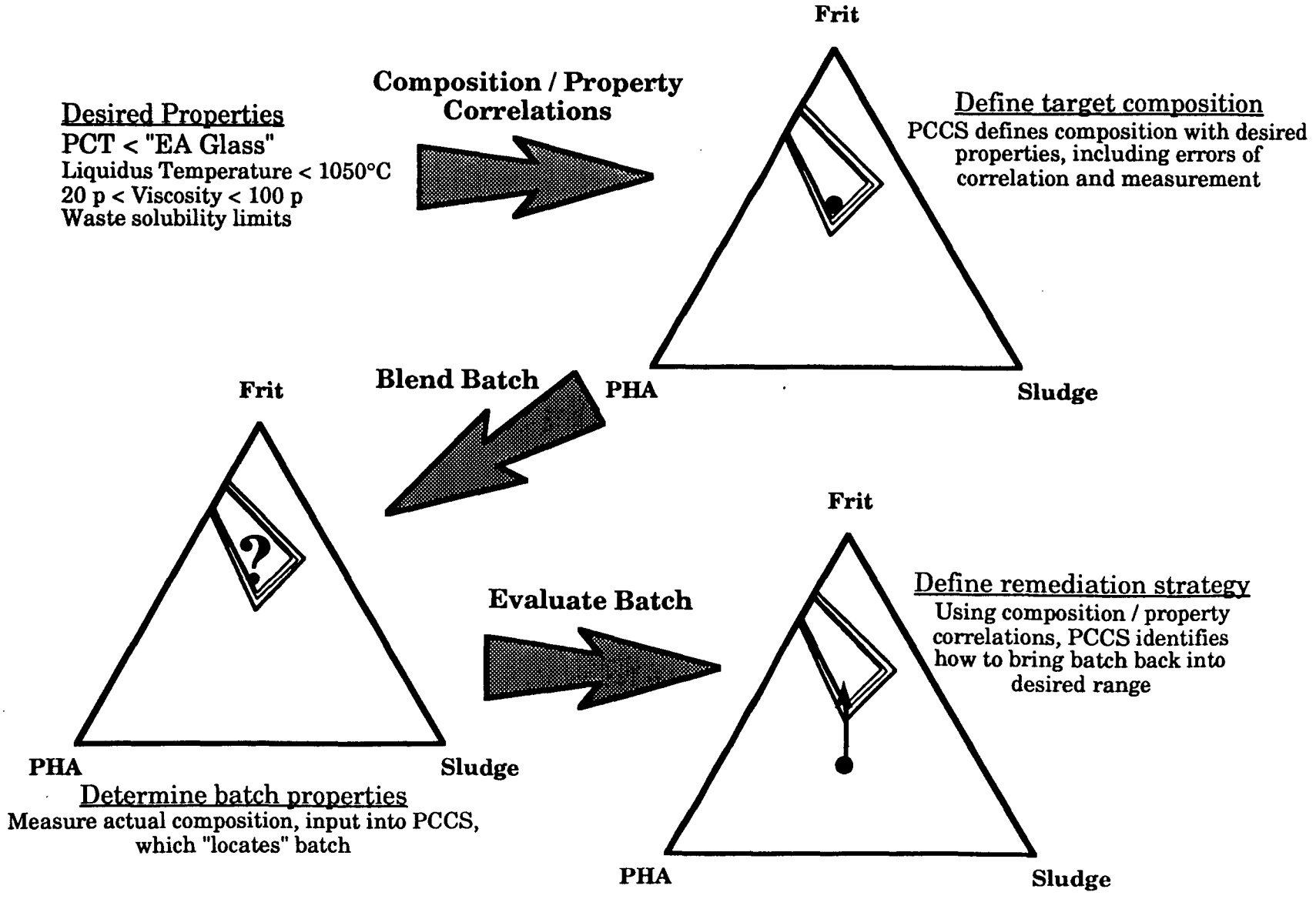
Product Composition Control System — Need

- Equipment sets limits on process safety and reliability which may compete with product needs
  - Durability
  - Corrosion
  - Volatility
  - Waste solubility

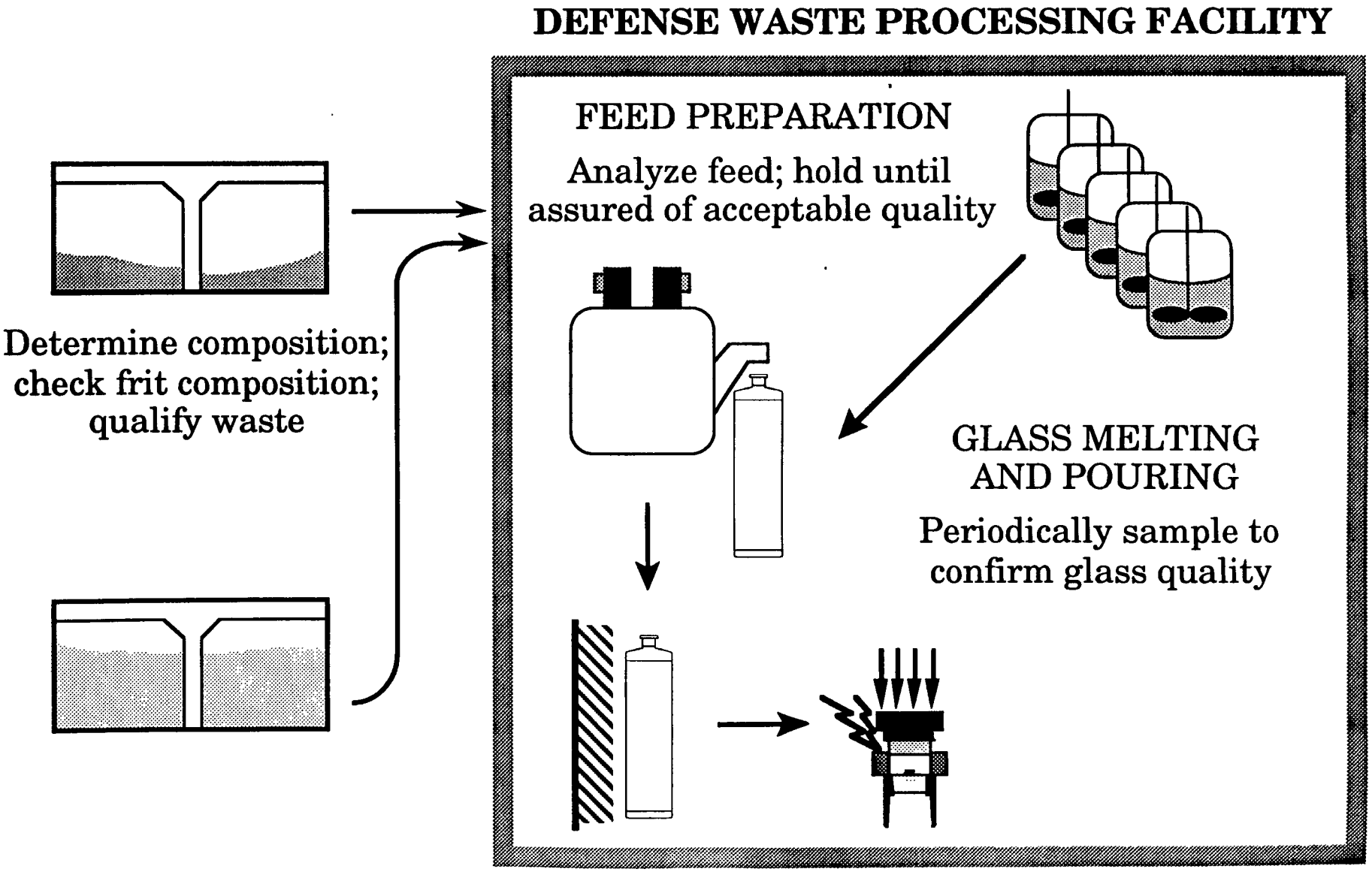
- Specification requires use of multi-variate statistical process control algorithms for process control

- Need a means to define blending target, evaluate process batch, and recommend remediation strategy (if necessary)

Product Composition Control System

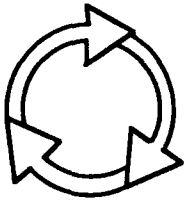


Glass Product Control Program



Startup Test Program

Facility



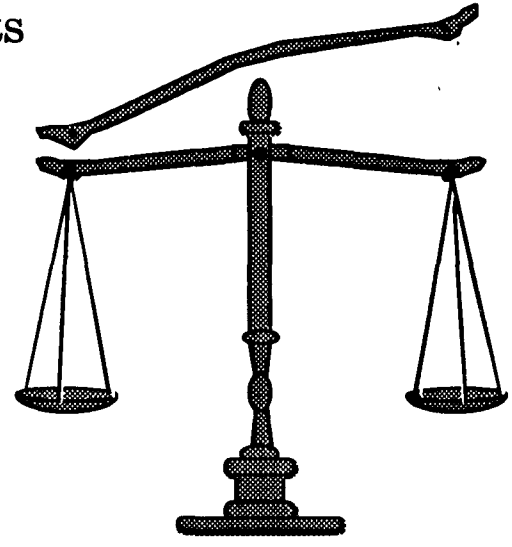
Shielding
Emergency Power
Crane Operations
HVAC

10 tests

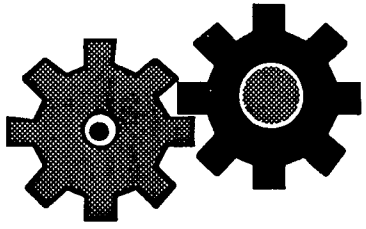
Product

Product Control Demonstrations
Glass Sampling
Welding
Foreign Materials
Temperature Profiles
Reporting

18 tests



Process



Integrated Operation with Water
Vessel Materials
Startup of each Vessel
Continuing Operation of each Vessel
Feed, OG, Waste Handling Systems

18 tests

Bases for Qualification Runs

- Objective: Demonstrate effectiveness of product control strategy under most adverse credible conditions

- Bases for program:
  - Glass durability controlled by composition
  - Composition will vary (because waste does)
  - Feed composition will be controlled by the Glass Product Control Program
  - Want to maximize value of runs

Qualification Runs

- Objective: Demonstrate effectiveness of product control strategy under most adverse credible conditions

- Will vary feed composition over widest credible range for facility
  - Small changes
  - Drastic decrease in viscosity, increase in density
  - Drastic increase in viscosity, decrease in density
  - Back to moderate conditions for first batch of radioactive feed

- Compare glass samples to canister contents, and both to PCCS predictions

Characterization of Qualification Run Canisters

- Each of 124 canisters will be sampled during pouring

- Most canisters will be destructively examined as well
  - Canisters filled during greatest changes in composition will be sectioned
  - Canisters filled when near steady-state will be sectioned
  - Most other canisters will have wall removed from side of canister

- Glass characterization
  - Product Consistency Test
  - Chemical composition (including glass redox)
  - Non-vitreous phase identification

Conclusions

- Controlling the composition of the glass is the key to compliance with the Product Consistency Specification
- Although variable in composition, DWPF glasses will meet the specification
- A detailed program is being implemented to ensure that the DWPF will make a glass which meets the specification
- Qualification Runs designed to provide crucial evidence that the DWPF will be able to control the product during production