

Sludge Mass Reduction SR-07-19-01

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Project Description

- **DOE has a significant volume of HLW that must be vitrified in borosilicate glass for disposal.**
- **Technologies that reduce the mass of HLW or increase the rate of treatment via improved waste throughput or waste loading are beneficial to reducing storage, treatment, and/or disposal costs.**



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Project Description – Technical Strategy/Approach

- **Increased sludge mass estimates at SRS revived interest in an Al Dissolution process to reduce DWPF canisters.**
- **Develop a flowsheet for a low temperature process to dissolve the gibbsite form of Al.**
 - Al-dissolution, washing, and SRAT/SME processing
 - initial dissolution studies indicated primarily gibbsite in the demonstration tank waste
 - later XRD studies indicated the tank waste was composed of 90% boehmite
 - Glass formulation, melt rate, and waste throughput issues



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Project Description – Technical Strategy/Approach

- **SRNL tasked with demonstrating the proposed dissolution flowsheet on a sample from Tank 51H**
 - **Test Conditions**
 - **Conducted at 55 °C with agitation**
 - **Add 50 wt% NaOH to provide**
 - **An initial OH concentration of 4.3 M**
 - **5:1 molar ratio of OH to Al**
 - **Test duration of 21 days with periodic sampling**
 - **Settle sludge and decant (characterize both phases)**
 - **Gravity settling**
 - **Temperature maintained at 35 °C during settling**



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Project Description – Technical Strategy/Approach

- **Sludge washing and DWPF processing demonstration also conducted on the sample**
 - **Matched number of washes (3), Na concentration, and wt% insoluble solids**
 - **Not possible to fully match Tank Farm plan; SRNL washing does not include addition of Tank 7 PUREX sludge**
 - **Conducted simulated DWPF SRAT, SME, and vitrification activities**
- **Evaluated impacts of Al-dissolution on glass formulation and melter processing issues**
 - **Paper study assessments**
 - **Melt rate testing**

Composition of As-Rcvd Slurry & Supernate

Major Components of Tank 51H Sludge

Analyte	Average Wt% TS
Al	15.6
Na	14.5
Fe	7.4
Mn	1.7
Hg	1.7
U	1.5
Ni	0.6
Si	0.4
Mg	0.3
Cr	0.04

Tank 51H Supernate

Analyte	Average M
Na	1.05
Al	0.013
Cr	7E-04
OH⁻	0.032
NO₃⁻	0.29
NO₂⁻	0.49
SO₄²⁻	0.03
C₂O₄²⁻	0.003

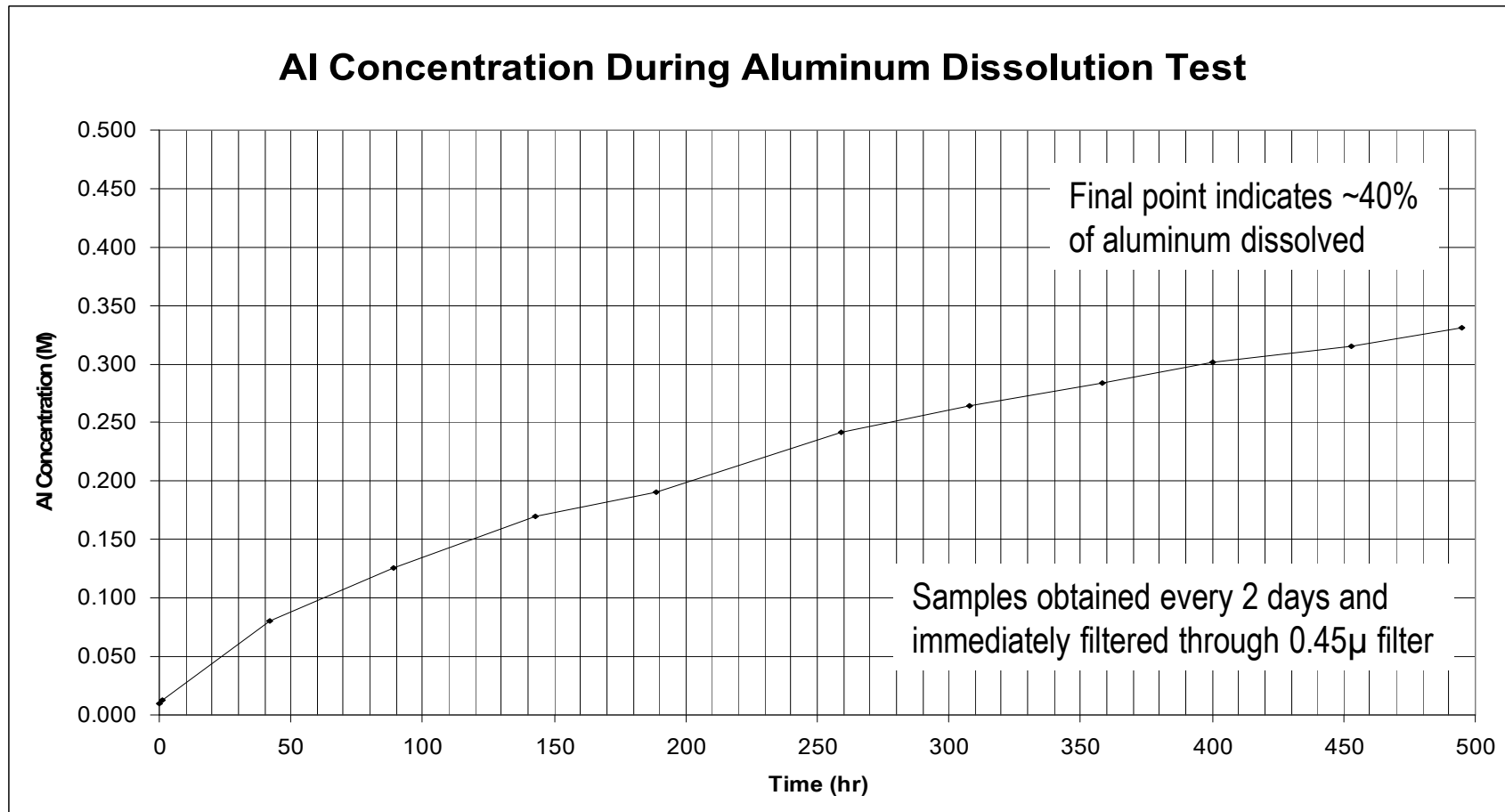


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Al Dissolution Process



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Al Dissolution Process

- **Conclusions from Al Dissolution Phase**
 - Approximately 40% of the Al in the sludge dissolved
 - Process appears to be **selective for Al** - no other major components of sludge dissolved to any appreciable extent
 - Dissolution of Al was **not complete** at the conclusion of the testing
 - Process had **minimal impact on sludge settling**
 - The Al rich **supernate** decanted from the process **was stable** with respect to precipitation over the course of several months
 - The slow Al dissolution rate in the test supports the fact that **Boehmite**, rather than Gibbsite, was the **predominate** form of Al

Sludge Washing

- **Observations During Sludge Washing**
 - **Wash 1:** settling slowed after 7 days; unable to decant enough supernate using a pump to reach plant target wt% insoluble solids (12.0 wt%)
 - **Wash 2:** sludge settled slowly over 7 days; unable to reach plant target wt% insoluble solids (12.4 wt%) after 7 days (8.9 wt%), after 14 additional days of settling achieved 12.0 wt%; Na concentration (1.42 M) near plant target (1.36 M)
 - **Wash 3:** not performed because measured Na was within 5% of the target, however wt% insoluble solids were below 13.6 wt% plant target

Sludge Washing

- **Conclusions from Sludge Washing Phase**
 - **35% of the Al** from the As-Received Tank 51 sample was **removed**
 - **Using the ratio of insoluble Fe to Al**
 - 21% removed in dissolution process
 - 14% removed during washing
 - **Based on soluble Na and insoluble solids balances, there may be some precipitation during washing**
 - **Washed sludge was very “sticky”**

Composition of As-Rcvd vs. Final Slurries

	As-Received Tk51	Post Al Diss/Washed
Al, wt% calcined solids	22.6	16.2
Fe, wt% calcined solids	10.5	11.6
Na, wt% calcined solids	21.0	26.3
NO ₂ ⁻ , M	0.49	0.11
NO ₃ ⁻ , M	0.29	0.051
OH ⁻ , M *	0.032	1.5
Calcine Factor (wt% calcined solids/ wt% total solids)	0.69	0.86

* As-Received supernate from titration of a supernate sample. OH on post-Al dissolution sample is from a titration of diluted slurry to a pH of 7



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Rheology Results

	Yield Stress (Pa)	Plastic Viscosity (cP)	Wt% IS
As Received Tank 51	5.8	4.6	9.39
Post Al Dissolution	9.3	19.4	6.44
Wash 1	4.7	9.0	6.52
Wash 2 First Decant	7.2	9.8	8.87
Wash 2 Second Decant = SRAT Receipt	19.9	18.2	12.0

Note: Tank Farm and DWPF yield stress limit: 10 Pa



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DWPF SRAT/SME Processing

- **Purpose: Make direct comparison of Tank 51 DWPF processing with and without Al dissolution**
- **Processing terminology:**
 - **SC-3 ≡ processing conducted with a October '06 Tank 51 sample taken prior to Al dissolution process**
 - **SC-4 ≡ processing conducted with a May '07 Tank 51 sample following Al dissolution and washing at SRNL**
- **Process parameters were chosen to make the two processing studies comparable**
 - **Due to the major difference in anion content between the two sludges, use of the same acid amounts in DWPF processing was not possible**



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DWPF SRAT/SME Processing

- **Observations and Issues:**
 - No mixing problems with SC-3 or SC-4
 - SC-4 sludge was prone to foaming
 - Due to a discrepancy between total base measurements, too little acid was added (select process criteria were not meet)
 - Difficult to measure total base in SRAT receipt slurry, hence a better understanding of how soluble Al affects total base measurements is needed
 - Al removed SRAT and SME products were more viscous
 - SRAT processing did improve rheological properties, so if acid was under added, additional improvement may be possible



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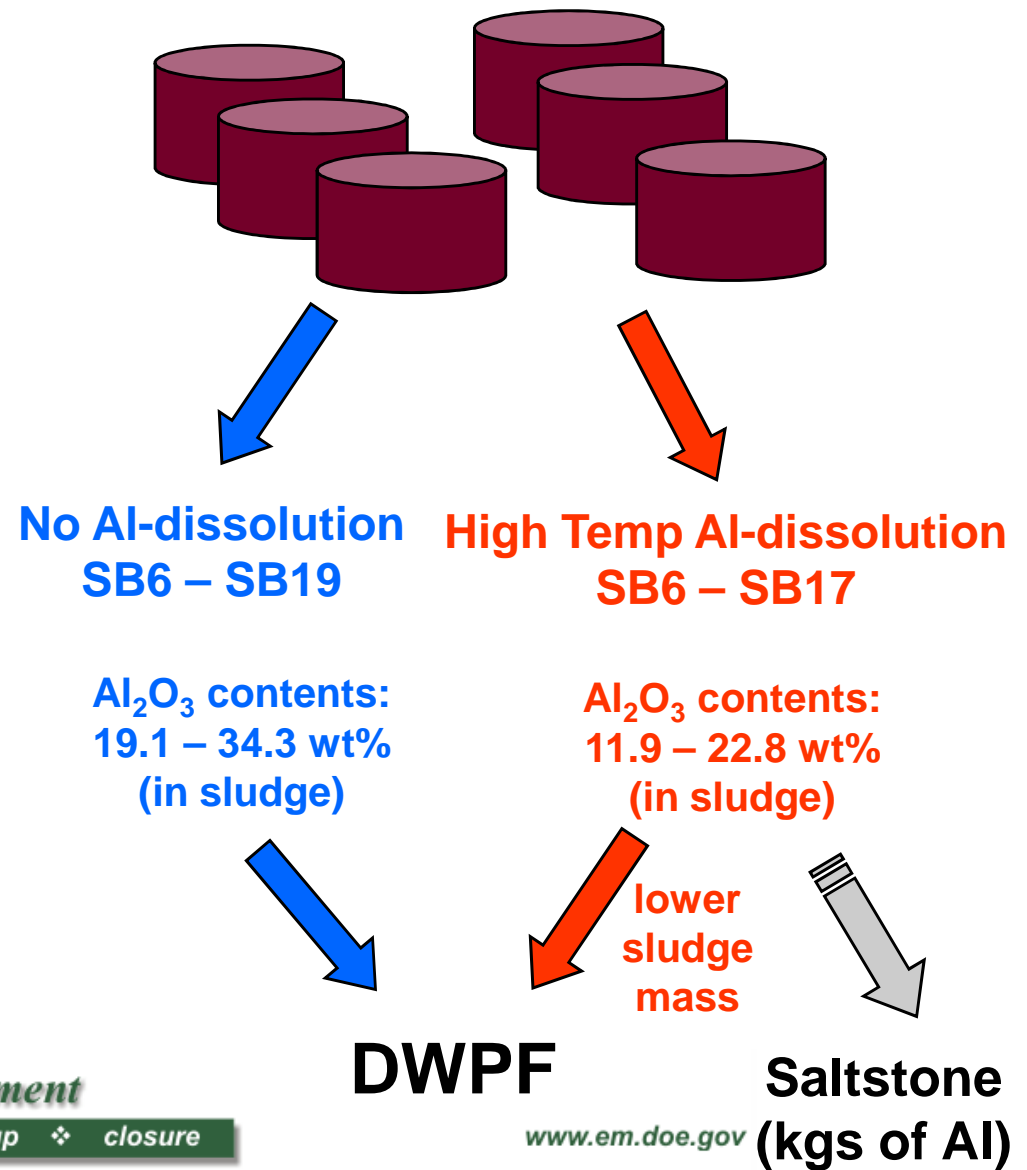
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Glass Formulation: Objectives

- Al-dissolution process was successful in removing sludge mass → translate in fewer canisters assuming same targeted WL can be achieved
- Questions regarding the impacts of Al-dissolution on glass formulation, melt rate, and/or waste throughput
 - Can frits be developed for higher/lower Al-based sludges?
 - Does the implementation of Al-dissolution have an impact on the ability to target higher waste loadings?
 - Melt rate (rheology impacts)?
 - Does sludge mass reduction result in the optimum flowsheet?
 - Number of cans minimized or waste throughput maximized

Overview: Paper Study Assessment

- Compositions from LWO representing with and without Al-dissolution
 - High temperature dissolution baseline
- 14 SBs without
 - SB6 – SB19
- 12 SBs with
 - SB6 – SB17
- Paper study results documented in WSRC-STI-2007-00688



Assessments: Impacts to DWPF

- Paper Study Assessments
 - Based on PCCS model predictions and current constraints
 - Frit “grid or array” approach (1755 frits)
 - Projected operating windows (in terms of an acceptable WL interval) defined using DWPF process control algorithms
- Possible results could indicate or identify (“*what if’s*”):
 - Show-stoppers for Al-dissolution decision
 - Example: One flowsheet (with or without Al-dissolution) does not provide adequate operating windows for any or most sludge batches
 - Problematic sludge batches
 - Example: Specific sludge batches which have no or limited operating windows; insufficient Al_2O_3 remaining (Al_2O_3 in frit?)
 - Ability of frit development efforts to compensate for pretreatment strategies
 - Example: Projected operating windows essentially identical for both with and without Al-dissolution



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Projected Operating Windows

Sludge Type	Projected Operating Window Width (in points of WL) in the WL Interval from 25% to 50%																						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23
WALD - SB6	64	101	107	82	103	102	90	65	44	14	1												
WALD - SB7	24	33	42	50	46	52	53	66	54	80	81	65	92	73	47	55	34	19	9				
WALD - SB8	47	40	51	50	56	66	76	76	82	63	93	61	41	45	24	13	1						
WALD - SB9	35	37	43	42	49	55	47	41	48	49	77	57	60	77	57	58	49	32	28	8	3		
WALD - SB10	46	43	46	50	42	48	48	67	56	164	50	80	43	61	46	20	21	7					
WALD - SB11	44	46	47	48	42	47	48	53	49	75	66	80	73	69	78	67	22	35	12	3	1		
WALD - SB12	24	42	39	49	43	33	40	39	50	48	51	60	64	75	85	65	72	73	44	44	16	10	
WALD - SB13	31	47	46	39	33	36	50	44	60	56	63	83	61	95	90	43	59	50	24	8	4		
WALD - SB14	28	38	44	51	48	59	67	61	92	69	77	99	67	45	47	31	11	2					
WALD - SB15	48	59	59	57	86	75	105	65	58	78	38	19	17	7									
WALD - SB16	46	38	50	46	50	54	55	53	82	70	94	55	76	60	35	21	19	4					
WALD - SB17	42	43	42	44	47	56	42	80	68	75	59	76	87	34	66	31	16	13	3				
WOALD - SB6	27	35	64	51	85	96	133	130	103	81	61	27	4										
WOALD - SB7	20	37	22	30	38	20	43	26	35	53	49	55	97	109	92	94	95	64	30	7			
WOALD - SB8	41	13	40	19	40	39	18	47	36	26	56	49	65	74	87	116	98	63	71	41	11		
WOALD - SB9	35	27	30	43	14	43	36	23	48	47	29	48	75	75	96	103	84	82	66	35	16	3	
WOALD - SB10	35	33	23	43	17	41	43	19	44	43	40	42	77	68	104	99	89	85	67	27	17	3	
WOALD - SB11	22	36	19	43	12	45	27	32	47	24	43	61	58	80	95	109	112	72	55	34	17	1	
WOALD - SB12	42	13	41	29	29	45	23	36	49	41	29	53	59	79	93	89	101	84	54	49	24	2	
WOALD - SB13	38	19	46	42	35	33	53	69	73	89	96	105	94	90	56	32	9						
WOALD - SB14	48	58	69	75	89	86	101	98	95	75	54	24	4										
WOALD - SB15	42	41	17	44	40	21	42	52	50	39	72	81	91	111	106	71	56	43	11				
WOALD - SB16	22	44	15	39	39	22	49	34	25	51	50	49	60	86	90	96	106	78	57	40	19	1	
WOALD - SB17	14	44	15	39	21	30	28	40	36	52	48	76	65	77	78	68	84	77	67	65	29	14	1
WOALD - SB18	22	40	36	50	54	68	80	83	84	86	80	76	74	72	64	43	25	6	1				
WOALD - SB19	28	48	53	65	94	75	92	85	89	81	77	76	59	46	14	1							



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Paper Study: General Observations

- For most sludge options, there are multiple frits that could be used that provide relatively large operating windows (mid 20 – low 40s)
 - Exceptions:
 - SB6 with and without Al-dissolution – very restrictive windows
 - SB8 with Al-dissolution
 - SB15 with Al-dissolution
 - SB14 without Al-dissolution
 - SB19 without Al-dissolution
- In general, more compositional flexibility in frit selection for the without Al-dissolution cases
 - Higher potential to maximize melt rate?

MAR Results: General Observations

- No clear distinction based on projected operating windows to drive Al-dissolution decision (i.e., comparable operating windows can be achieved)
 - If frit development efforts can compensate for pretreatment strategies (with respect to providing the same or equivalent operating windows or maximum WL targets), the lower sludge mass from Al-dissolution would result in minimizing the number of cans.
 - Does targeting same WL yield same waste throughput?
- Is a reduction in the mass going to DWPF the only parameter of interest?
 - What about facility (Tank Farm and DWPF) operating time? Life cycle costs?
 - Dependent (in part) upon melt rate and waste throughput issues
 - MAR assessment provides no insight into melt rate issues

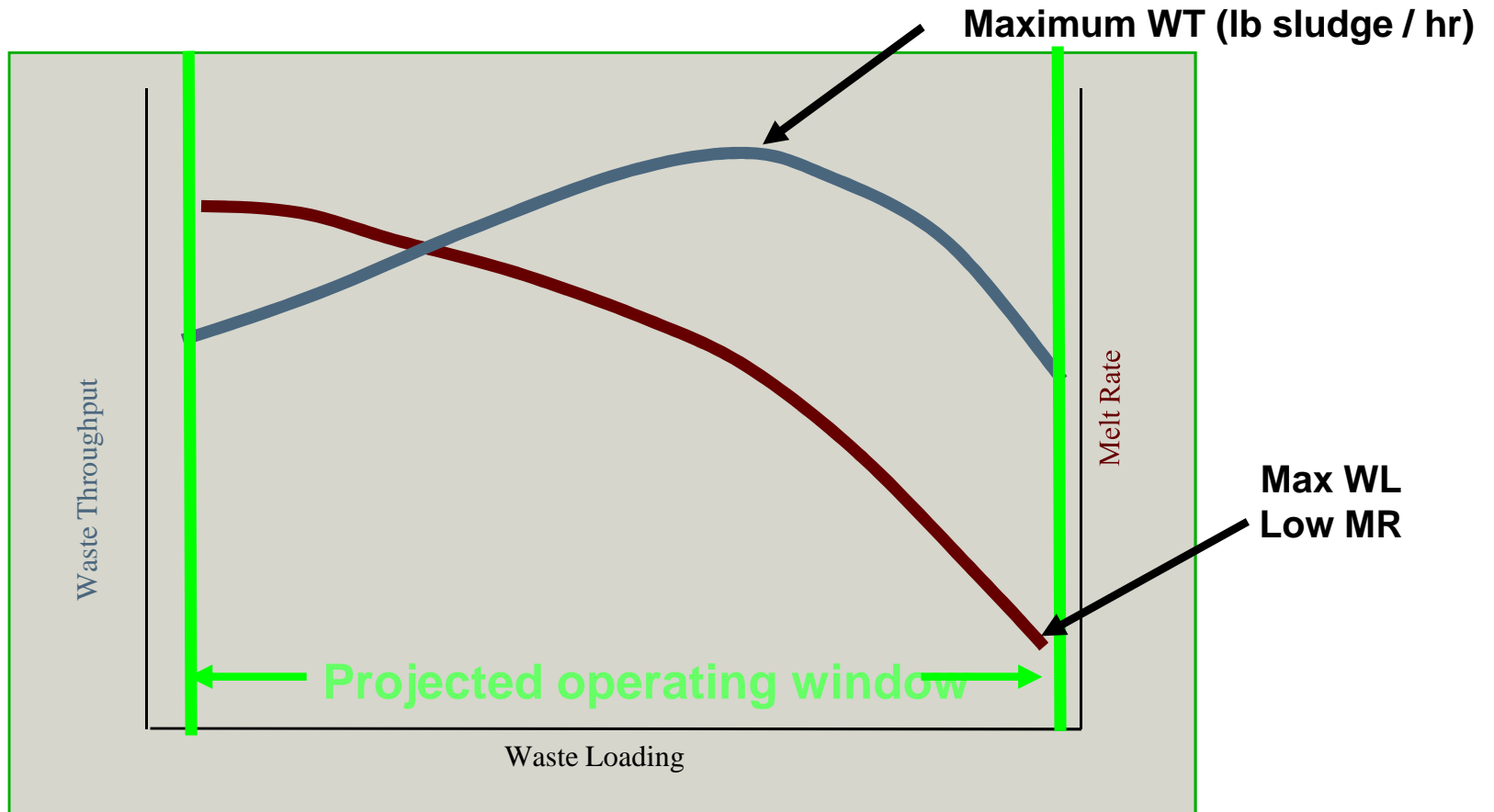


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Melt Rate and Waste Throughput as a f(WL)



General trend



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Other Possible Impacts

- Examples:
 - If there are more frit options for the without Al-dissolution flowsheet, does that provide a higher probability of optimizing melt rate and waste throughput (WT) relative to the Al-dissolution flowsheet?
 - If so, does the higher WT off-set the lower mass with the Al-dissolution flowsheet?
 - What are the implementation costs / risks for Al-dissolution and the possible impacts of higher Al going to Salt Stone (gel time, PA, etc.)?
 - What are the trade-offs to consider and account for in a cost – benefit analysis decision for Al-dissolution?
 - High temp, low temp, or no-Al-dissolution?
 - What will meet contractual and/or processing expectations?
 - Possible impacts of melter feed rheology on melt rate?

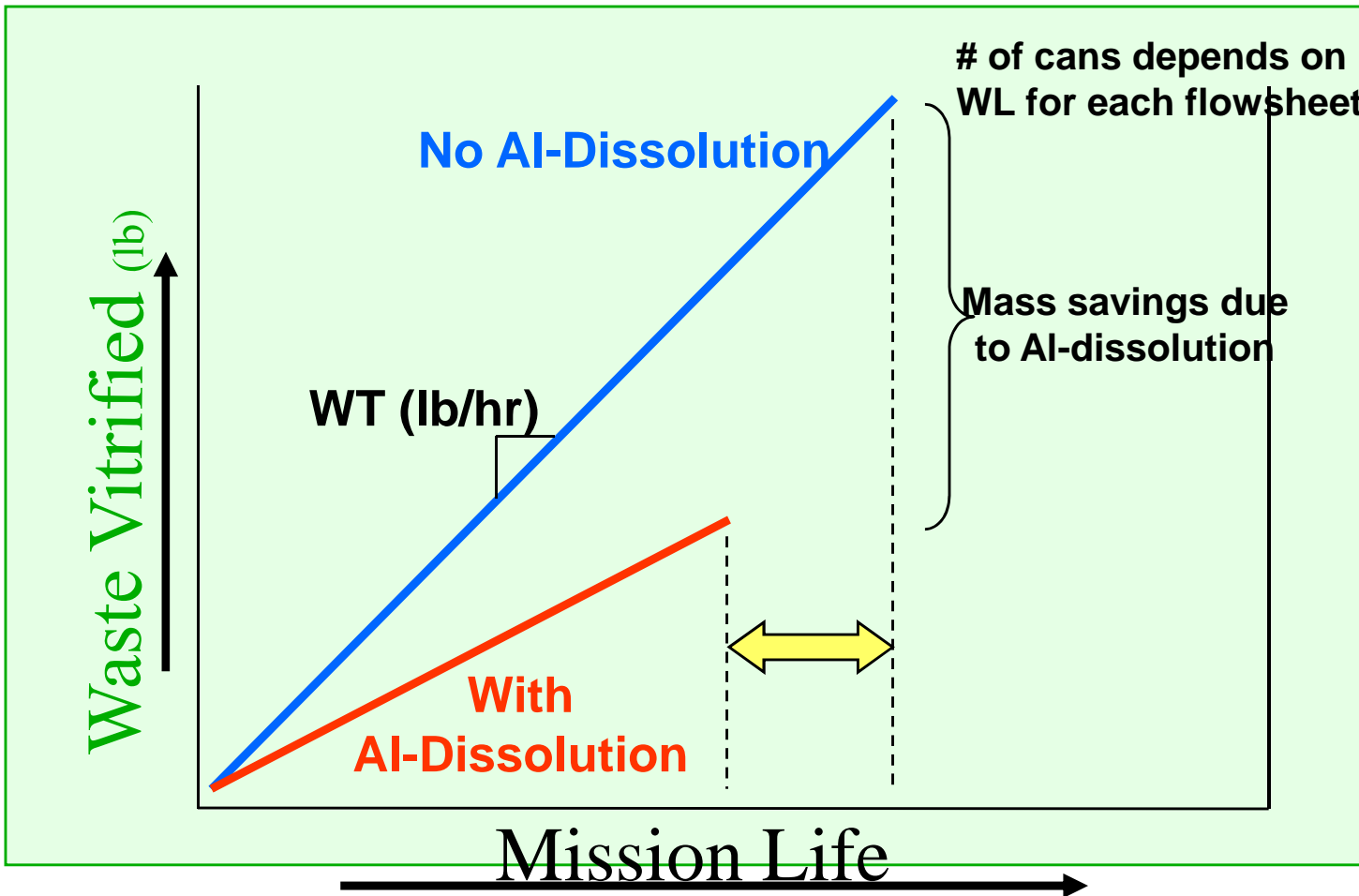


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Mission Life as a Function of Waste Throughput and Sludge Mass



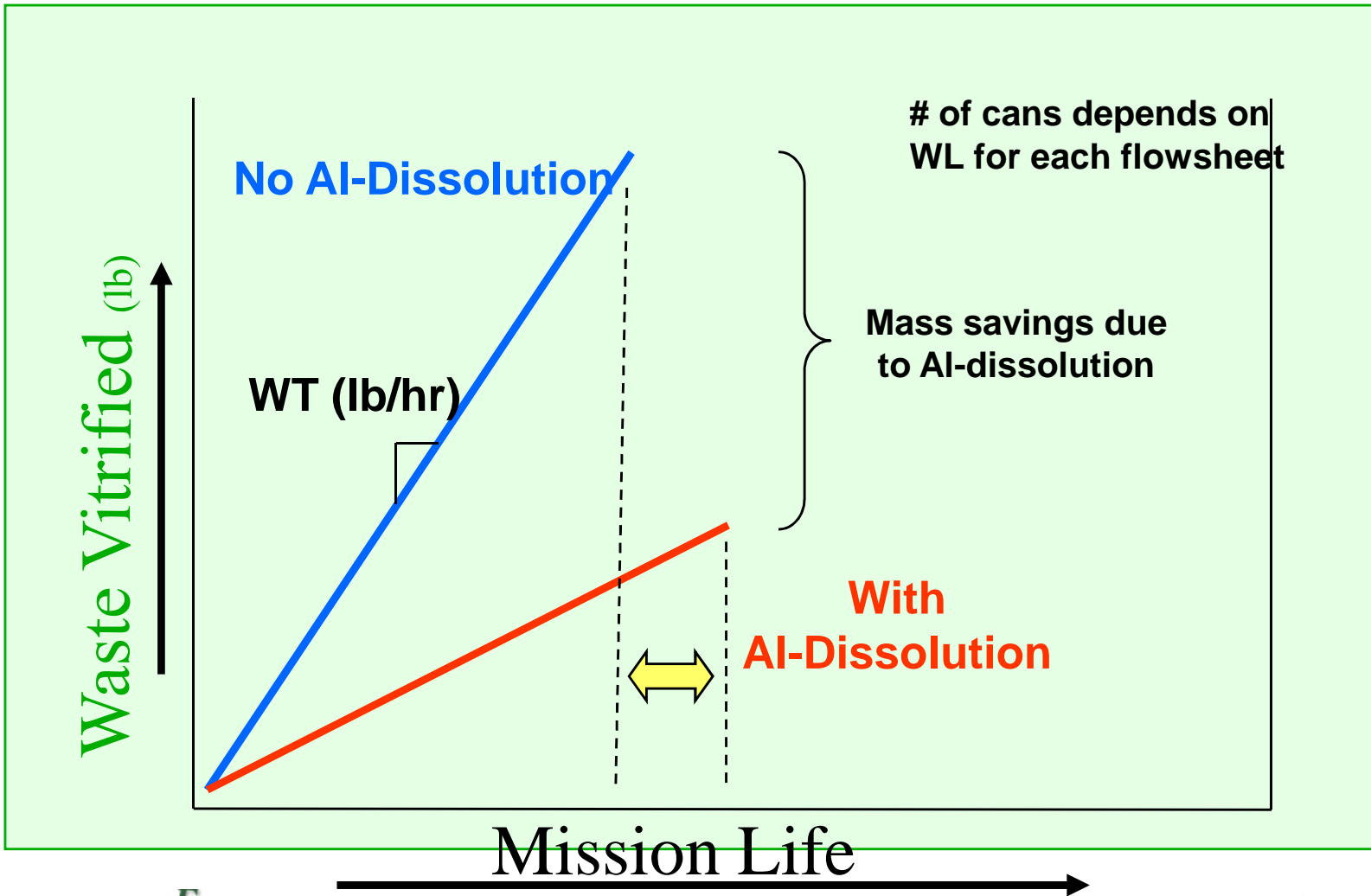
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POSSIBLE EXAMPLE

Mission Life as a Function of Waste Throughput and Sludge Mass



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POSSIBLE EXAMPLE

Programmatic Challenge

- How to select frits for each flowsheet option that provide the best opportunity for maximum MR or WT?
 - Given 14 sludges with no Al-dissolution and 12 sludges with Al-dissolution, melt rate testing can not be performed on all individual sludges
 - Potential for different optimal frits with each sludge batch
 - observed with SB3 (low Al) and SB4 (high Al)
 - Can generic sludge be identified and studied to make “global” statements about the melt rate, waste throughput, and waste loading interactions?
 - “Cluster” approach based on similarities among sludge compositions (Al_2O_3 , CaO , Fe_2O_3 , MnO , Na_2O , NiO , and TiO_2)

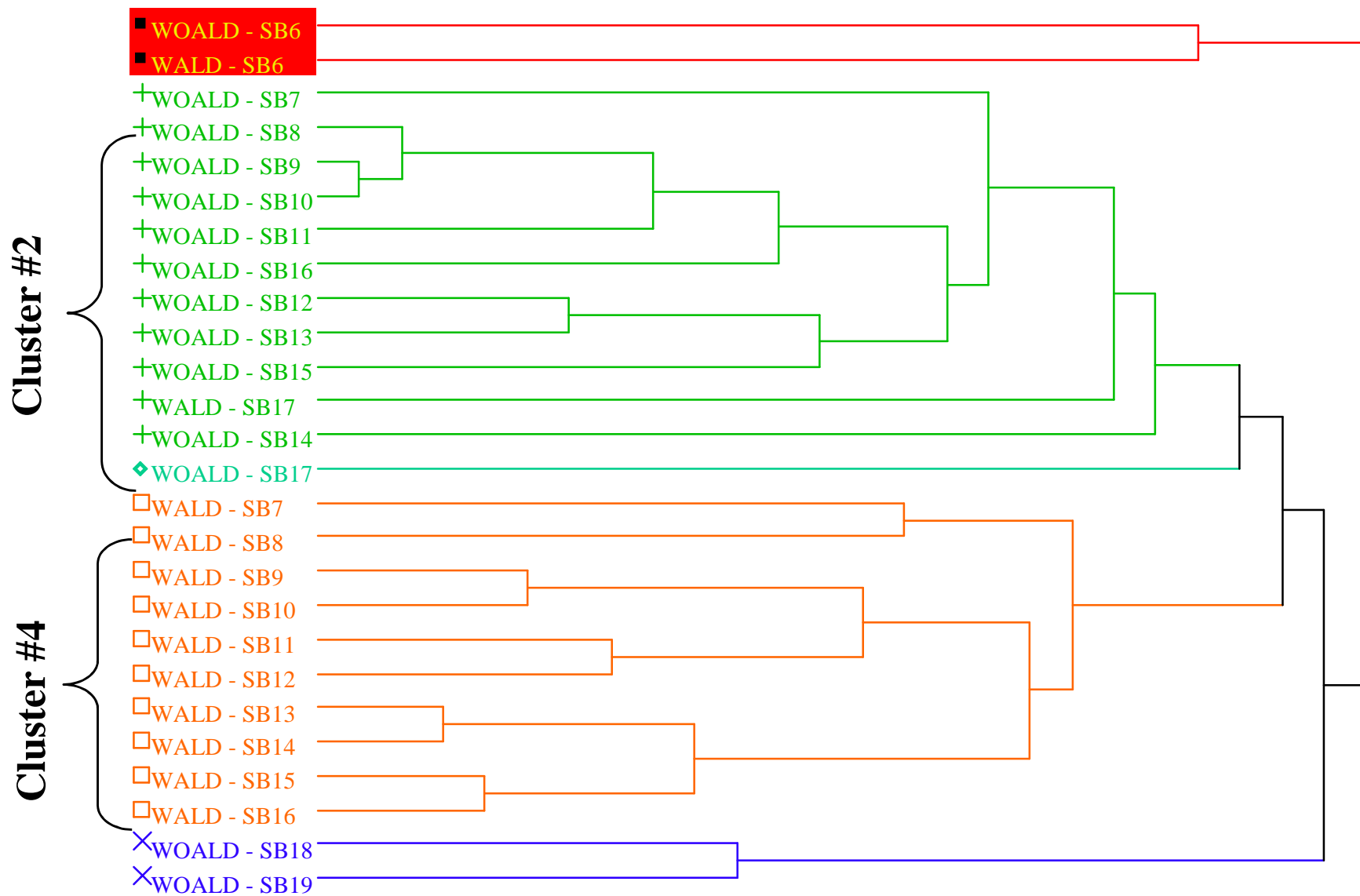


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Clusters



Clusters: Average Compositions

- Cluster #2: without Al-dissolution
 - 23.1 wt% Al₂O₃
- Cluster #4: with Al-dissolution
 - 14.6 wt% Al₂O₃
- Utilize clusters to assess “global” impacts of Al-dissolution (high temp) on melt rate and/or waste throughput
 - Identified candidate frits for each cluster
 - Based selection on historical trends observed in SRNL testing and DWPF processing

Oxide	Cluster 2 avg	Cluster 4 avg
Al ₂ O ₃	23.10	14.62
BaO	0.21	0.25
CaO	2.63	3.26
Ce ₂ O ₃	0.55	0.58
Cr ₂ O ₃	0.27	0.34
CuO	0.08	0.11
Fe ₂ O ₃	30.81	35.17
K ₂ O	0.18	0.23
La ₂ O ₃	0.20	0.22
MgO	0.41	0.47
MnO	4.00	5.17
Na ₂ O	20.25	21.21
NiO	1.16	1.28
PbO	0.24	0.25
SO ₄	0.20	0.25
SiO ₂	3.35	5.09
ThO ₂	1.00	1.20
TiO ₂	3.29	2.77
U ₃ O ₈	7.44	6.76
ZnO	0.13	0.16
ZrO ₂	0.50	0.61



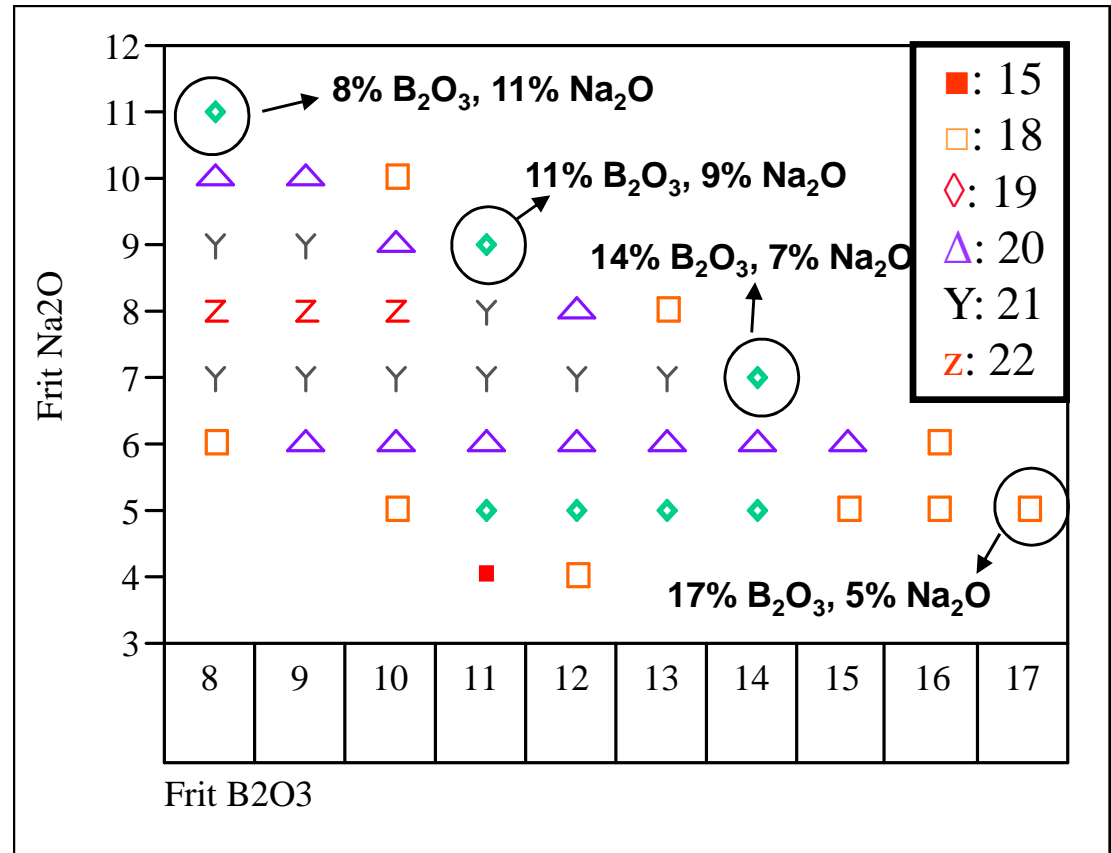
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Candidate frits for Cluster #2 (high Al_2O_3)

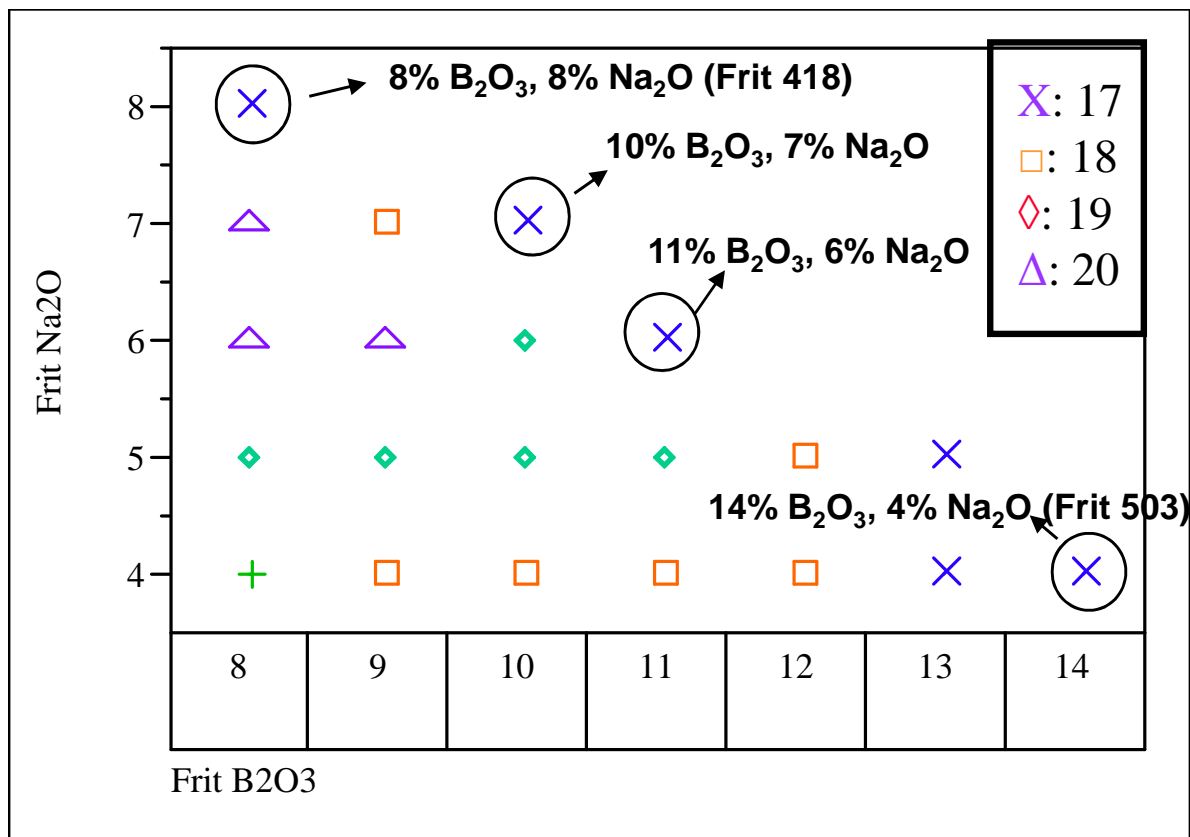
- Cluster #2: high $\text{Al}_2\text{O}_3 \rightarrow \text{SB4}$
 - Historically, high B_2O_3 and Na_2O frits melt faster
- Frit Na_2O ranges from 5% to 11%
- Frit B_2O_3 ranges from 8% to 17%



○ Candidate frits for Cluster #2

Candidate frits for Cluster #4 (low Al_2O_3)

- Cluster #4: low $\text{Al}_2\text{O}_3 \rightarrow \text{SB3}$
 - Historically, high Na_2O frits melt faster
- Frit Na_2O ranges from 4% to 8%
- Frit B_2O_3 ranges from 8% to 14%



○ Candidate frits for Cluster #4

Melt Rate Program

- Initial assessments for each “cluster” with specific frits as a function of WL
 - Initial MRF testing → SRAT redox questions?
 - Fully oxidizing which could have masked compositional impacts
 - Formic acid added to SRAT products
- Phase 2 MRF testing in progress
- Report to be issued

Note: Al_2O_3 solubility for no-Al dissolution flowsheet should not be an issue for DWPF (SB19 – 35% Al_2O_3 in sludge)
(SRNL/PNNL/VSL → mid-to-high 20's Al_2O_3 glasses produced which were acceptable)



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Summary

- AI-Dissolution Demonstration
 - Approximately 40% of the AI in the sludge dissolved
 - Dissolution of AI was not complete at the conclusion of the testing
- Washing Impacts
 - Additional AI removed
 - Identified potential risks in the areas of sludge settling and rheology behavior
 - After decanting the supernate, yield stress and consistency were high and sludge settling rates were slow
 - “Sticky” sludge
- SRAT/SME Demonstration
 - AI-dissolution feed prone to foaming
 - SRAT reactions were not complete → acid addition / OH issue
 - SRAT and SME products were more viscous after AI-dissolution

Summary

- **Glass Formulation** (based on future comp projections)
 - No clear distinction based on projected operating windows to drive AI-dissolution decision (i.e., comparable operating windows can be achieved)
 - More compositional flexibility for “without” AI-dissolution flowsheets → potential to optimize melt rate or increase waste throughput?
 - Melt rate program in progress
 - Concept of reduction in canister counts versus mission life