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STATISTICAL ANALYSIS OF THE DWPF PROTOTYPIC SAMPLER (U)

by

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INTRODUCTION

The DWPF process will be controlled using assay measurements on samples of feed slurry. These slurries are radioactive, and thus will be sampled remotely. A Hydraguard™ pump-driven sampler system will be used as the remote sampling device.

A prototype Hydraguard™ sampler has been studied in a full-scale mock-up of a DWPF process vessel. Two issues were of dominant interest: (1) what *accuracy* and *precision* can be provided by such a pump-driven sampler in the face of the slurry rheology; and, if the Hydraguard™ sample accurately represents the slurry in its local area, (2) is the slurry *homogeneous* enough throughout for it to represent the entire vessel?

To determine Hydraguard™ Accuracy, a Grab Sampler of simpler mechanism was used as reference. This (Low) Grab Sampler was located as near to the intake port of the Hydraguard™ as could be arranged. To determine Homogeneity, a second (High) Grab Sampler was located above the first.

The data necessary to these determinations comes from the measurement system, so its important variables also affect the results. Thus, the design of the test involved not just Sampling variables, but also *some* of the Measurement variables as well. However, the main concern was the Sampler and not the Measurement System, so the test design included only such measurement variables as could not be circumvented (Vials, Dissolution Method, and Aliquoting). The test was executed by, or under the direct oversight of, expert technologists. It thus did not explore the many important particulars of "routine" plant operation (such as Remote Sample Preparation or Laboratory Shift Operation).

RESULTS & CONCLUSIONS

There was a *statistically discernible bias*¹ between the Hydraguard™ and the Reference Grab Sampler. Depending upon the element being assayed, this bias ranged from -2% to + 5% relative. The Hydraguard™ produced a Waste-rich and Frit-poor sample: as much as 2% low in Frit elements (Si, Li), up to 4% high in Sludge elements (Al, Fe), and up to 5% high in Precipitate Hydrolysis Aqueous (PHA) elements (K).

¹ A *statistically discernible bias* is not necessarily important operationally. It implies only that the average of the paired differences differs from zero by more than is explainable as noise. As the number of paired differences being averaged gets large, the standard error of this average gets small; and even inconsequentially small deviations from zero nonetheless become statistically discernible.

DISCUSSION: THE EXPERIMENTAL DESIGN

A *nested* experimental design was used to pattern the test, so that the sub-components of overall variance coming from the particular sub-sources of variation tested could be estimated.

These sources of variation were:

Sampler,
Vial-to-Vial within Sampler,
Type of Dissolution within Vial,
Dissolution Replicate within Type, and
Aliquot-to-Aliquot within a Replicate Dissolution.

The Samplers and Dissolution Type are regarded as *fixed effects* since those of them on test constitute all the candidates available. The Vials, Dissolution Replicates, and Aliquots are regarded as *random effects* since those of them on test are only random selections from a conceptually unlimited set of candidates.

The Samplers were:

Hydraguard™ (R)
 (Low) Grab Reference Sampler (G)
 (High) Grab Sampler (H)
 Tap Sampler (T).

Two kinds of Dissolutions were used:

Na₂O₂ Fusion & Acid Microwave,

thus forming the general hierarchy:

Sampler --> Vial --> Dissolution --> Aliquot.

The R-G contrasts determine Hydraguard™ Accuracy. They being the most consequential, the design *split-plot* them. That is: the R-vials and G-vials were collected in immediate sequence, paired together, and the resulting samples processed through Vitriification, Dissolution, and Measurement as closely together as procedures and laboratory equipment allowed. This insured that, as nearly as was possible, only the two Samplers differed between the pair. By cancelling out other extraneous variables which might have affected the pair in common, this split-plot arrangement makes the determination of Sampler Accuracy as precise as possible.

The *size* of the design was dictated by our interests. Since Sampler Accuracy was most important, the most degrees of freedom were devoted to the R-G contrasts. How many R-G pairs there should be depends on: (1) how large an effect must be relative to its imprecision before it is of practical consequence, and (2) what balance is struck between Type I and Type II error risks.² Using usual Gaussian theory, specifying the Type I risk to be 5% and the Type II risk to be 10% (both are arbitrary choices, but not unusual ones), assuming a basic error relative standard deviation of 5%, and requiring real effects of Δ% to be detected, gives the following numbers of paired differences needed:

Δ	5%	4%	3.3%	2%
n	21	32	48	128.

We chose n = 48 to be the number of R-G pairs so that real Sampler biases of about 3% or so could be detected. (Since the basic error standard deviation turned out to be substantially less than 5%, we were actually able to detect differences of 1% or less). For those elements which could be dissolved both by Fusion and by Microwave, these n = 48 pairs resulted from:

² A Type I error is: wrongly declaring random noise to indicate a significant effect. A Type II error is: wrongly declaring a significant effect to be random noise.

$n = (6 \text{ Vials per Sampler}) * (2 \text{ Types of Dissolution per Vial}) * (2 \text{ Replicate Dissolutions per Type of Dissolution}) * (2 \text{ Aliquots per Replicate Dissolution}) * (1 \text{ measurement per Aliquot}) = 48$

The design was built up from small Blocks which defined the split-plot contrasts. The Vials were all filled in design order from the various Samplers during one 24-hour day. The samples from these vials were vitrified, but over a longer time. The Dissolutions and Measurements required a considerably longer elapsed time, but the design order was preserved to the extent that the equipment allowed. As a further precaution, various Standards and Blanks were inserted into the measurement sequence to monitor drift and flag inconsistencies, and preserve the design's built-in precision for estimating this essential contrast.

For illustration, the first design Block using Fusion Dissolution was (the numbers indicate the time order of measurement):

Block 1: (St1)[(R₁₁₁-G₁₁₁) T](St2)[H (R₁₁₂-G₁₁₂)](St3)[(R₁₂₁-G₁₂₁) T](St4)[H (R₁₂₂-G₁₂₂)](St5)
 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17

(St1)...(St5) represent 5 replicate standard glass samples inserted to check for instrument drift. The R_{1jk} denote the 4 measurements made on the Fusions from the first Hydraguard™-Vial. The G_{1jk} denote the 4 measurements made on the fusions from the first Low Grab-Vial. The j=1 denotes the first of 2 Fusion Dissolutions and j=2 denotes the second. The k=1 denotes the first Aliquot from the dissolution, and k=2 denotes the second. Thus, (R_{1jk}- G_{1jk}) is the split-plot nested within the kth Aliquot from the jth Fusion Dissolution on the first sample Vial from each of the Hydraguard™ and Low Grab Samplers. See Figure 1 for further explication.

There was a corresponding Block 1 for Microwave Dissolution, so that there were 8 R-G paired contrasts per Block. There were 5 additional Blocks, for the total of (6)(8) = 48 R-G paired contrasts.

G-H contrasts determine In-Tank Homogeneity. Although not as consequential as the Sampler contrasts, these too were of essential interest and were similarly split-plotted in the design.

DISCUSSION: THE ANALYSIS

Initial exploratory histograms showed many of the sample distributions to be too diffuse, tail heavy, and/or irregular to support Gaussian formalism. Thus, to analyze the results we mostly used *nonparametric* methods based on orderings, since they are greatly less sensitive to distributional assumptions than are *parametric* methods based on magnitudes.

To assess the R-G split-plot pairs: The relative medians of the paired differences (taken as $\Delta = R - G$) and 95% confidence intervals³ around them for the various elements at the 2 solids levels were:

Source	Element	Solids Level	Relative Δ	95% CI	CI Include 0?
Sludge	Al	Hi (49%)	+3.0%	(+2.4, +3.7%)	No
	Fe	"	+3.1%	(+2.6, +3.7%)	"
	Mn	Hi (49%)	+3.0%	(+2.4, +3.6%)	No
	Ni	"	+3.3%	(+2.7, +3.9%)	"

³ using the sign method of Thompson & Savur cited in Hollander & Wolfe, *Nonparametric Statistics*, Wiley (1973), p48

Source	Element	Solids Level	Relative Δ	95% CI	CI Include 0?
Sludge	Al	Lo (41%)	+4.3%	(+3.7, +4.9%)	No
	Fe	"	+4.6%	(+3.9, +5.3%)	"
	Mn	"	+4.2%	(+3.4, +5.0%)	"
	Ni	"	+4.1%	(+3.2, +4.8%)	"
PHA	K	Hi	+2.0%	(+1.0, +3.0%)	No
	K	Lo	+5.5%	(+4.1, +6.9%)	"
Frit	Si	Hi	-0.9%	(-1.6, -0.2%)	No
	Mg	"	-1.3%	(-1.7, -0.9%)	"
	Li	"	-1.5%	(-1.8, -1.2%)	"
	Si	Lo	-2.0%	(-2.9, -1.2%)	No
	Mg	"	-2.3%	(-2.6, -2.0%)	"
	Li	"	-2.4%	(-2.7, -2.1%)	"

Thus, the conclusion: *The Hydraguard™ produced a Waste-rich and Frit-poor sample; as much as 2% low in Frit elements, up to 4% high in Sludge elements, and up to 5% high in PHA elements.*

To assess the G-H split-plot pairs: Using the same non-parametric methods and expressing the paired differences as $\Delta = G - H$, we see that:

Source	Element	Solids Level	Relative Δ	95% CI	CI Include 0?	
Sludge	Al	Hi (49%)	0.0%	(-0.7, +0.7%)	Yes	
	Fe	"	-0.5%	(-1.2, +0.0%)	" (but barely)	
	Mn	"	+0.4%	(-0.3, +1.3%)	Yes	
	Ni	"	+0.2%	(-0.7, +1.0%)	"	
	Al	Lo (41%)	-1.9%	(-3.1, -0.6%)	No	
	Fe	"	-1.9%	(-3.3, +0.1%)	Yes (but barely)	
	Mn	"	-1.7%	(-3.2, -0.1%)	No	
	Ni	"	-1.5%	(-3.3, +0.5%)	Yes	
	PHA	K	Hi	-0.4%	(-1.3, +0.9%)	Yes
		K	Lo	-1.7%	(-3.5, +0.0%)	No
Frit	Si	Hi	+0.5%	(-1.0, +1.1%)	Yes	
	Mg	"	+0.4%	(+0.0, +0.9%)	" (but barely)	
	Li	"	+0.5%	(+0.2, +0.8%)	No	
	Si	Lo	+0.9%	(-0.9, +2.5%)	Yes	
	Mg	"	+1.4%	(+0.4, +2.3%)	No	
	Li	"	+1.4%	(+0.6, +2.5%)	"	

These data are more diffuse and thus not as conclusive as those for Sampler Accuracy, but indications are: *There is a detectible inhomogeneity at the Lo Solids content. There is about 2% more PHA and Sludge, and 1-2% less Frit from the High Grab Sampler than from the Low.*

There is no strong evidence of inhomogeneity at the Hi Solids content although Fe is an anomaly for the Sludge elements, and Li is an anomaly for the Frit elements. Both behave at Hi Solids as they do at Lo Solids.

To assess the precision of the Hydraguard™ and Grab Samplers: The (im)precision of each Sampler is taken to be the relative standard deviation Vial-to-Vial within that Sampler. The nested arrangement of the design allowed this variance component to be estimated separately from others, like that due to differences between 2 separate Fusion Dissolutions on the same sample, and that between 2 Aliquots taken from a single sample prep. The Vial-to-Vial standard deviations reflect variation attributable to the Sampler System, divorced from Dissolution and Aliquot effects more fairly attributed to the Preparation and Measurement Systems. The Vial-to-Vial relative standard deviations for the Samplers R, G, & H⁴ were:

Source	Element	Solids Level	Vial SD for R	Vial SD for G	Vial SD for H	Pooled SD
Sludge	Al	Hi (49%)	0.2%	1.8%	Negative Est. ⁵	1.1%
	Fe	"	1.9%	0.8%	0.3%	1.3%
	Mn	"	1.3%	2.1%	1.4%	1.7%
	Ni	"	Negative Est.	1.6%	Negative Est.	0.5%
	Al	Lo (41%)	Negative Est.	Negative Est.	2.7%	0.6%
	Fe	"	1.4%	1.7%	4.5%	2.4%
	Mn	"	2.5%	2.2%	4.4%	2.9%
	Ni	"	0.6%	1.6%	4.4%	2.3%
PHA	K	Hi	4.2%	2.9%	3.2%	3.5%
	K	Lo	3.7%	2.3%	4.7%	3.5%
Frit	Si	Hi	0.9%	1.3%	0.8%	1.0%
	Mg	"	0.5%	0.4%	Negative Est.	0.3%
	Li	"	0.5%	Negative Est.	Negative Est.	0.2%
	Si	Lo	1.3%	1.4%	1.8%	1.5%
	Mg	"	1.7%	1.7%	2.0%	1.7%
	Li	"	0.9%	0.8%	2.1%	1.2%

Thus, the conclusion: *The imprecision of the Hydraguard™ and Reference Grab Samplers was comparable.* Depending upon the element, there was 1% to 4% relative standard deviation between sample vials within each Sampler.

To assess measurement repeatability: The fundamental repeatability of a measurement is taken to be the standard deviation of the source lowest in the design hierarchy; that is, Aliquoting. Since repeat measurements were not made on an aliquot, the variance due to aliquoting confounds the effect of both aliquoting and the measurement process itself. We take the relative standard deviation of the Aliquot-to-Aliquot component to represent the basic repeatability of the measurement. Those values were:

⁴ Sampler T produced samples which were greatly more variable than the other 3. Accordingly, it was omitted from this summary analysis.

⁵ Due to the differencing of random estimators each of which holds only on the average, variance component estimates based on particular realizations of data can be negative. Since the variance itself cannot be negative, the proper way to treat this problem has been long debated in the statistical literature. No consensus has been reached. We indicate such cases here as "Negative Est." and interpret that crudely to mean the underlying true variance is "small".

Source	Element	Aliquot SD (Hi Solids)	Aliquot SD (Lo Solids)
Sludge	Al	1.4%	1.3%
	Fe	0.7%	0.6%
	Mn	0.7%	0.6%
	Ni	1.3%	1.6%
PHA	K	2.4%	1.9%
Frit	Si	0.4%	0.9%
	Mg	0.7%	0.6%
	Li	0.7%	0.5%

These assume that the Aliquot was taken from a *single replicate Dissolution* and the measurement made *within a single calibration* of the ICP measuring instrument. The way the design was blocked enabled the variation of the instrument between calibrations to be assessed as well. Adding in these additional sources to give a more realistic relative standard deviation gives the following:

Source	Element	Solids Level	Instr. Cal. SD	Rep. Diss. SD	Instr. + Rep. Diss. + Aliquot SD
Sludge	Al	Hi (49%)	3.5%	1.1%	<u>3.9%</u>
	Fe	"	0.8%	1.2%	<u>1.6%</u>
	Mn	"	0.8%	0.9%	<u>1.4%</u>
	Ni	"	2.7%	1.0%	<u>3.2%</u>
	Al	Lo (41%)	2.8%	1.1%	<u>3.3%</u>
	Fe	"	0.8%	0.8%	<u>1.3%</u>
	Mn	"	1.0%	1.4%	<u>1.8%</u>
	Ni	"	2.1%	0.7%	<u>2.7%</u>
PHA	K	Hi	2.0%	Negative Est.	<u>2.8%</u>
	K	Lo	2.1%	1.5%	<u>3.2%</u>
Frit	Si	Hi	0.0%	1.2%	<u>1.3%</u>
	Mg	"	0.8%	1.0%	<u>1.5%</u>
	Li	"	1.0%	0.5%	<u>1.3%</u>
	Si	Lo	0.0%	0.7%	<u>1.1%</u>
	Mg	"	0.8%	2.2%	<u>2.4%</u>
	Li	"	0.4%	0.8%	<u>1.0%</u>

Thus, the conclusion: *The fundamental repeatability of the measurements ranges between 1% and 4% relative standard deviation.*

To assess the effect of bias-correction : The RMSE of the 3 feedstream assays at the *Hi Solids* level contains a Bias term due to the Hydraguard™ Sampler. Thus, the $(\bar{x} - \mu)$ term is: $(\bar{x} - \mu) = (R - G)$ where the $(R - G)$ term is the previously detected real mean difference between the R-G pairs. Previous results and dividing the confidence interval widths by 4 to get the standard error σ of this bias gives:

<u>Source</u>	<u>Sampler Bias</u>	<u>SE of Sampler Bias</u>	<u>Vial SD</u>	<u>Instr. + Rep. Diss. + Aliquot SD</u>
Sludge	+4%	0.4%	2%	3%
PHA	+5%	0.8%	4%	3%
Frit	-2%	0.4%	2%	1.5%

The resulting RMSE's are:

$$\begin{aligned} \text{Sludge RMSE} &= \sqrt{[(+4)^2 + (0.4)^2 + (2)^2 + (3)^2]} = 5.4\% \\ \text{PHA RMSE} &= \sqrt{[(+5)^2 + (0.8)^2 + (4)^2 + (3)^2]} = 7.1\% \\ \text{Frit RMSE} &= \sqrt{[(-2)^2 + (0.4)^2 + (2)^2 + (1.5)^2]} = 3.2\% \end{aligned}$$

If these biases are corrected out, the RMSE's become:

$$\begin{aligned} \text{Sludge RMSE}_{BC} &= \sqrt{[(+0)^2 + (0.4)^2 + (2)^2 + (3)^2]} = 3.6\% \\ \text{PHA RMSE}_{BC} &= \sqrt{[(+0)^2 + (0.8)^2 + (4)^2 + (3)^2]} = 5.1\% \\ \text{Frit RMSE}_{BC} &= \sqrt{[(-0)^2 + (0.4)^2 + (2)^2 + (1.5)^2]} = 2.5\% \end{aligned}$$

The ratios of the $\text{RMSE}_{BC} / \text{RMSE}$ are ~ 0.7 , so that bias-correction at Hi Solids reduces total uncertainty to $\sim 3/4$'s of what it would otherwise be. Thus, the conclusion: *Removing these nuisance sources of error by bias-correction appreciably reduces the overall uncertainty of a given measurement.*

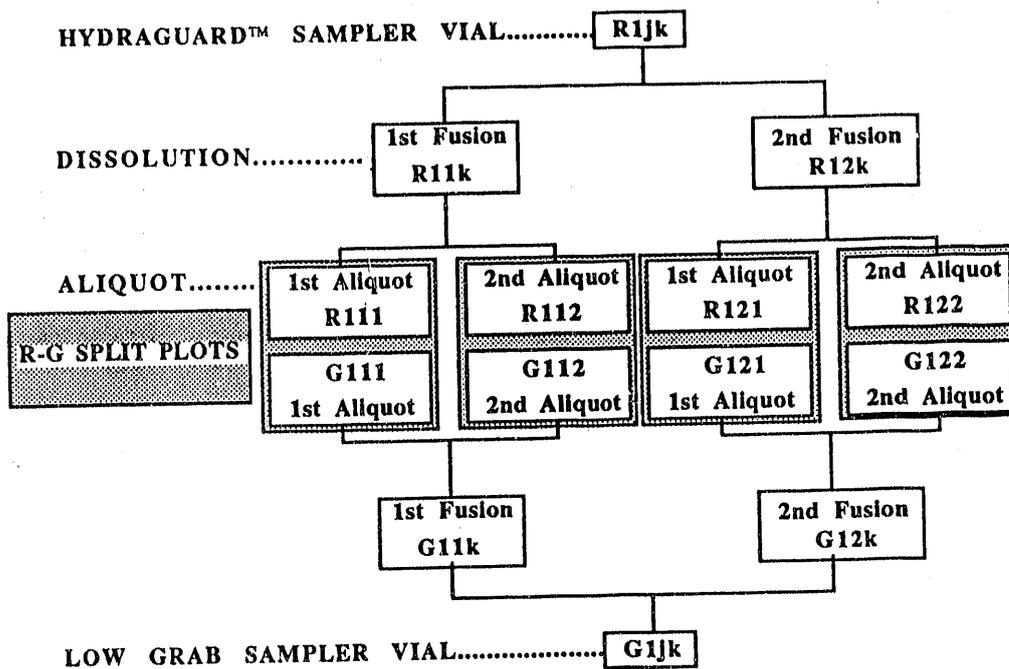
The Sampler and Inhomogeneity biases at Lo Solids partially cancel, so that this effect is not as noticeable. Presumably, however, the Hi Solids levels will be used in the interests of attainment.

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FIGURE 1

R-G SPLIT PLOTS FOR BLOCK #1 FUSION DISSOLUTIONS



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