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ANALYSIS OF TANK 241-AN-106 CHARACTERIZATION AND GROUT PERFORMANCE CRITERIA

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EXECUTIVE SUMMARY

This report provides an assessment of how well we can resolve the following issues, given the current state of information:

- how well we can characterize the contents of 241-AN-106
- whether the degree of characterization is sufficient to use 241-AN-106 wastes to develop tests of grout adequacy.

The wastes must be characterized not only to ensure grout adequacy but also to provide assurance that the wastes can be successfully and safely transferred. In this report, we evaluate the adequacy of characterization for transfer and tests of grout adequacy, and we evaluate the current status of acceptance criteria and grout formulation experiments.

CHARACTERIZATION

The adequacy of waste characterization is determined by the ability to make decisions in light of differences between acceptance limits and estimated concentrations when associated uncertainties are taken into account, as discussed in Section 2.0. As explained in Section 4.0, it is conservative to evaluate characterization adequacy solely in terms of 241-AN-106 wastes. For the 241-AN-106 constituents with sufficient data to analyze, we conclude that characterization is adequate, relative to the acceptance criteria in Hendrickson (1991), except for phosphate, carbonate, and nitrite. For the combined contents of 241-AN-106 and 241-AP-102, characterization is adequate except for carbonate and phosphate. It is not clear whether organics have been adequately characterized. Furthermore, it is not clear how important it is to characterize organics. It is important to note that the acceptance criteria have not yet been formally adopted by DOE. Until they are, characterization results must be considered preliminary and subject to change.

TRANSFER

The formation of solids and questions of grout adequacy both affect the decision to transfer.

Formation of Solids. The formation of crystalline gels, especially during initial stages of mixing in 241-AP-102, is a procedural concern. Formation of solids is not expected to be a major problem during transfer because the wastes in 241-AN-106 are quite dilute. Plans for transfer have been developed to minimize mixing during transfer, and there are procedures for mixing transferred wastes so that solids remain suspended until temperatures become high enough for them to redissolve. For the reasons cited, we believe that procedural issues are of secondary importance relative to formulation issues.

Grout Adequacy. It is highly undesirable to transfer 241-AN-106 wastes without reasonable assurance that an adequate grout can be formed. Based on comparisons of characterization results with current grout feed acceptance criteria, we believe that the risk is small that 241-AN-106 wastes will prove unacceptable for grout. We find no compelling reasons not to transfer them into 241-AP-102. Consequently, we recommend that the transfer of 241-AN-106 wastes proceed as planned so that the necessary grout acceptability tests can be conducted.

ACCEPTANCE CRITERIA

Acceptance criteria for 241-AN-106 wastes were developed after sampling in order to evaluate the adequacy of characterization results. In reality, quantitative acceptance criteria should have been established to guide development of a sampling plan. Moreover, the acceptance criteria developed by WHC and used in this report have not been formally adopted by DOE. Until all necessary formulation experiments have been completed and the criteria are formally adopted, any conclusions presented in this report must be considered preliminary and subject to change.

We have noted several other difficulties with the current acceptance criteria. These include the following: 1) Some acceptance criteria, especially those related to performance, have a weak or obscure technical basis; 2) there are discrepancies between the list of 241-AN-106 analytes and constituents for which acceptance criteria are given; 3) there is a need to separate regulatory and process requirements; 4) there are no models that relate criteria imposed at one point in the grout formulation process (e.g., to the grout) to those imposed at another point (e.g., waste feed concentrations); and 5) existing documents provide little insight as to which of the many regulated constituents are of greatest concern. Finally, the extent to which heat will be treated as a performance issue rather than an engineering issue should be resolved.

GROUT FORMULATION

The greatest source of uncertainty involves the composition of and properties that the final grout waste form must possess. A dry blend grout formulation has been adopted by WHC, but solid statistical evidence is required to demonstrate that an acceptable grout can be made with this composition. To date, only one experiment has been conducted in which both the dry blend composition and the waste feed were varied jointly, and results of that experiment are not yet available. Additional testing is required. The tests should use the target dry blend formulation and expected waste feed composition, and both should be varied jointly over the compositional ranges expected during processing. Moreover, the tests should be statistically designed, and insofar as possible, they should be conducted under operating conditions.

ACKNOWLEDGMENTS

The authors acknowledge the support of Wes Nicholson and Rich Hanlen. The many helpful discussions we had with Wes and Rich have resulted in significant improvements in the clarity and content of this report.

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1.0 INTRODUCTION

The purpose of this report is to present an assessment of the completeness and reliability of the characterization of waste in Tank 241-AN-106. This characterization will be used to determine 1) whether that waste can be safely and efficiently transferred to and mixed with the waste in Tank 241-AP-102 and 2) whether the resulting wastes can be used to form a grout (i.e., waste form) with suitable properties for long-term storage in a disposal facility (i.e., vault). The objective of long-term storage is to ensure health and safety.

The objective of this report will be achieved in part by answering the following general questions:

- How well do we know the contents of 241-AN-106? What confidence do we have in current characterization/composition estimates? Using existing information, can we adequately characterize 241-AN-106?

- Can we use existing data to determine grout adequacy? Specifically, can we use 241-AN-106 data to develop the composition of simulated waste for development and testing of potential grout formulations?

The focus of this assessment is on existing sampling data, primarily that obtained from samples taken from Tank 241-AN-106 (Welsh 1991) by Westinghouse Hanford Company (WHC) in 1989.

The two questions are closely related. The first question, which pertains to the characterization of 241-AN-106 wastes, is driven by the second. The second question, which concerns grout adequacy, is the key question from a programmatic perspective. The waste in 241-AN-106 must be adequately characterized to determine whether it can be used to formulate a grout with acceptable waste form properties. A secondary concern is whether the wastes in 241-AN-106 can be safely and successfully transferred to the grout feed tank (241-AP-102). In other words, information about waste processability is also a desired result of characterization. Because the basic concerns during the assessment were waste transfer and grout formulation, the following overview of each is presented below. Detailed descriptions and analyses are to follow.

1.1 WASTE TRANSFER

The main concern about pumping 241-AN-106 wastes to the feed tank for the grout treatment facility (241-AP-102) is the possibility of crystallization. In laboratory samples of 241-AN-106 wastes, solids formed when the sulfate and phosphate wastes were mixed at low relative temperatures; i.e., at temperatures less than 30°-35°C. Thus the mixing induced by transfer operations could result in plugged or blocked transfer lines. Also after 241-AN-106 wastes are transferred into 241-AP-102 and thoroughly mixed with existing waste, crystallization could occur in 241-AP-102 if temperatures fall below approximately 35°C. The combined contents of both tanks in 241-AP-102 will be referred to as the "waste feed."

1.2 GROUT FORMULATION

To be an acceptable waste form, a grout must meet both regulatory and performance criteria. Regulatory criteria are imposed by various agencies to ensure that certain safety standards and release limits are met. Land disposal restrictions are the primary determinant of regulatory criteria: In particular, regulations require that the waste feed meet the definition of low-level waste. Performance criteria are set to ensure that the grout will have certain physical properties, such as sufficiently high leach resistance and compressive strength.

The wastes in 241-AN-106 are to be mixed with the existing heel in 241-AP-102. The resulting mixture must either be adequate for making an acceptable grout or it must be amenable to treatment to make it adequate. After transfer a final determination of adequacy will be made by characterizing the final contents of the feed tank (241-AP-102) before the waste it contains is grouted. It is highly desirable, however, to determine the adequacy of the waste before the contents of 241-AN-106 are transferred to 241-AP-102, in order to avoid contaminating the existing heel in 241-AP-102 and incurring the cost of retransfer.

The contents of 241-AN-106 and the heel of 241-AP-102 must both be characterized in order to estimate the composition of the final grout feed, if the final feed characterization is to be estimated before the waste in 241-AN-106 is transferred. In other words, the acceptability of grout cannot be determined solely from the contents of 241-AN-106, even though the majority of the waste may come from that tank. The composition of waste in both tanks must be known to evaluate grout performance before transfer.

2.0 MEASURES OF CHARACTERIZATION AND PERFORMANCE

Measures of characterization and performance of tank waste are defined in this section. These measures provide a quantitative basis for answering the two questions posed in the previous section. Statistical confidence intervals are used to describe the adequacy of characterization. Significance levels determined for confidence intervals that are created so their limits match performance limits are used to quantify the likelihood of acceptable performance. Obviously, the more precisely we have characterized the wastes in question, the more confident we can be of our performance evaluation.

2.1 CHARACTERIZATION

The first question posed in Section 1.0 has to do with characterization: How well do we know the concentrations of constituents of 241-AN-106 waste? To address this question, we will present confidence limits for sampled constituents of 241-AN-106 waste. For each constituent, these confidence limits take the form

$$(\bar{x} - t_\alpha S, \ \bar{x} + t_\alpha S) \qquad (1)$$

where $\bar{x}$ is a suitable estimate of the sample average, s is the estimated standard deviation of $\bar{x}$, and t_α is a selected percentage point from the t distribution. The value t_α is chosen so the intervals in (1) have a specified probability of covering the true underlying constituent concentration. For example, if α is chosen to be 0.975, then t_α is the 97.5th percentile of the t-distribution, and (1) yields a 95% (two-sided) confidence interval for the constituent.

The width of the interval in (1), which is determined by the product of t_α and s, can be regarded as a measure of characterization. The smaller interval, the more precise is our estimate of concentration. Confidence intervals for sampled constituents of 241-AN-106 wastes are presented in Section 4.0.

2.2 PERFORMANCE

The second question posed in Section 1.0 has to do with performance: How confident are we that constituent concentrations satisfy certain regulatory or performance limits? As noted in Section 1.0, performance limits may be imposed to meet either regulatory or process requirements. Performance has to do with our confidence that constituent concentrations fall within certain specified acceptance limits. If intervals with high confidence coefficients fall within the stated acceptance intervals, then the risk is small that the acceptance criteria will not be met. Conversely, if the only confidence intervals that fall within the acceptance intervals have low confidence coefficients, then the risk is high that the acceptance criteria will be violated. In this case, we want to determine a value of t_α, and the corresponding significance level α, so that $\bar{x} + t_\alpha s$ or $\bar{x} - t_\alpha s$ (whichever is closer to a limit) equals the stated acceptance limit. For a significance level α determined in this way, the quantity $(1 - \alpha)$ is a measure of the risk that the acceptance criteria is violated. For constituents of waste from 241-AN-106 that have been sampled, risk coefficients (significance levels) are presented in Section 4.0.

Note that in the latter case, the confidence coefficient α is determined (via t_α) from the distance between $\bar{x}$ and its acceptance limit, i.e., the significance coefficient is determined from interval width. By contrast, for characterization, the interval width is determined from the confidence coefficient. For example, the 95% confidence limits for cesium-137 were calculated using $\bar{x}$ = 211000 and $s(\bar{x})$ = 4177[a] with effective degrees of freedom equal to 1. In this case,

$$t_{0.975,1} = 11.2$$

so the width of the confidence interval is

$$t_{0.975,1} * s(\bar{x}) = 46782$$

Thus 46782 (or 22%) is the measure of characterization for cesium-137. The measure of performance for cesium-137 is obtained by first taking the difference between the acceptance limit (L = 371800) and $\bar{x}$ to determine the interval width:

$$L - \bar{x} = 371800 - 211000 = 160800$$

The interval width, when divided by $s(\bar{x})$, gives t_α:

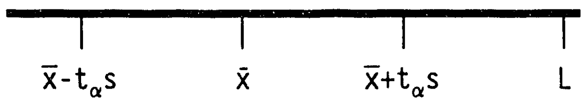
$$t_\alpha = w/s(\bar{x}) = 160800/4177 = 38.5$$

The one-sided significance level that corresponds to a t-value of 38.5 with one degree of freedom is α = 0.989. The corresponding risk that the acceptance criteria will not be met is $(1 - \alpha)$ = 0.011. Figure 1 may be helpful in understanding the distinction between characterization (intervals determined for a specified confidence level) and performance (confidence level determined for a specified interval width).

(a) All measurements are in μCi/L.

a) Characterization

- Confidence coefficient (α) is selected
- Standard deviation (s) is computed
- Interval width ($t_\alpha s$) is computed



b) Confidence/Risk

- Acceptance limit (L) is given
- Standard deviation (s) is computed
- Width (w) is computed:

$$w = | L - \bar{x} |$$

- t-value is computed:

$$t = w / s$$

- Significance level (α) is determined from t-distribution
- Risk ($1 - \alpha$) is computed

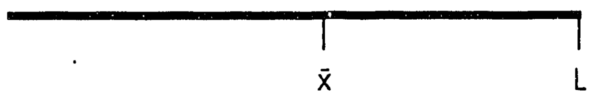


Figure 1. Steps in Determining Characterization and Acceptance Risk

3.0 THE COMPOSITION OF TANK WASTES

Some general information about the sources and composition of wastes in Tanks 241-AN-106 and 241-AP-102 is summarized in this section.

3.1 TANK 241-AN-106 WASTE

The waste in 241-AN-106 is primarily concentrated phosphate waste from the 100-N Area. Other waste in the tank consists of salt well liquid and minor amounts of dilute waste. The 241-AN-106 waste is separated from other wastes because of the deleterious effects that phosphate crystals have on evaporator operations (Hendrickson 1991). The actual amount of evaporation relative to potential evaporation was limited because of crystallization in the evaporation process, and a correspondingly large volume of waste was retained. Consequently, concentrations in 241-AN-106 are less than 40% of those in tanks containing wastes from slurry feeds, such as 241-AW-101. For example, the concentrations of Cs-137 in 241-AN-106 and 241-AW-101 are 0.185 and 0.483 Ci/L, respectively.

Liquid waste in 241-AN-106 is believed to be layered, with, from top to bottom, 1) a high phosphate layer, 2) a mixed phosphate-sulfate layer, and 3) a high salt layer. The salt layer has not only a higher density than the phosphate layer, but also higher concentrations of Na and SO_4. There may also be a layer of sludge/solids at the bottom of the tank. In 1989, the solids layer may have had a depth of approximately 7 inches (Hendrickson 1991). There is no further measurement history on the solids layer in 241-AN-106. These solids represent less than 2% of the total contents of Tank 241-AN-106, and there are no plans to transfer them during the current campaign. Therefore, solids are not considered in subsequent discussions of characterization adequacy.

Because evaporation was limited, the liquid wastes layers in 241-AN-106 are dilute (relative to other waste sources) and have extremely low viscosities. No solids were observed floating in samples taken from this tank, so there is no reason to suspect that the tank contains significant quantities of floating solids.

There is a natural tendency for the liquid wastes in 241-AN-106 to remain layered because of differences in their densities. However, large concentration gradients are not expected within layers, particularly at a given height within a layer. There is a tendency for the mixed sulfate-phosphate layer to form solids, so concentration gradients in this layer should be fairly constant. It is possible that thermal effects on solubilities could result in greater concentrations of dissolved sodium phosphate near the center of the tank where it is warmer. However, this effect is not expected to be significant because 241-AN-106 has a comparatively low temperature.

Physical theory suggests that concentrations in the layers of liquid in 241-AN-106 will, through diffusion, tend toward equilibrium with time. On the other hand, there could be mechanisms in operation in 241-AN-106 that mitigate the effects of pure diffusion. These include the existence of nucleating sites where crystals form at lower temperatures in the mixing layer. If such mechanisms are operative, it is possible that the tank now contains a greater accumulation of solids than that reported in 1989 (Hendrickson 1991). It is not known whether nucleating sites do exist within the tank nor is there any physical or field information to confirm the continued accumulation of solids.

3.2 TANK 241-AP-102 WASTE

The waste heel present in 241-AP-102 is composed of residual phosphate-sulfate waste, leachate returns from Vault 101 (218-E-16-101), and chemical additions from the PUREX Plant. Sodium nitrite and sodium hydroxide were transferred into 241-AP-102 from the PUREX Plant to increase the pH of liquid in 241-AP-102. The tank contains approximately 71,775 gallons of phosphate-sulfate waste, three additions of grout leachate totaling approximately 56,725 gallons, and two PUREX Plant additions totaling approximately 7,150 gallons. The total volume of waste in 241-AP-102 is approximately 135,650 gallons. Volumes and calculated (not measured) concentration estimates are given in Appendix A of WHC-SD-WM-TP-136.[a] The waste transfer history for 241-AP-102 is presented in Appendix B of that report.

(a) This report is a draft document: Hendrickson, D. W., and T. L. Welsh. *Hanford Grout Disposal Program Campaign 102 Sampling and Characterization Plan*. Rev. A. WHC-SD-WM-TP-136. Westinghouse Hanford Company, Richland, Washington.

4.0 REVIEW AND ANALYSIS OF CURRENT SAMPLING DATA

This section presents the results of a statistical analysis of the waste in 241-AN-106 and 241-AP-106 using the existing sampling data. The analysis was performed to answer the questions regarding characterization and performance for both tanks.

4.1 ANALYSIS OF TANK 241-AN-106 SAMPLES

A statistical sampling plan was designed to ensure spatial coverage of the tank, given that its contents were believed to be layered (see Hammitt and Claghorn 1989). Twelve samples were recovered from 241-AN-106 in 1989 according to the specified sampling plan. Details of the sampling plan, including the specification of the locations for the twelve samples, are given in Hammitt and Claghorn (1989). Sampling locations are shown in Figure 2. Each sample was split into two subsamples (denoted as a and b) and submitted "blind" to the analytical laboratory where analyses were performed on both. Each subsample was analyzed for 33 inorganic constituents. Of these 33 constituents, 14 were observed at concentrations greater than detection levels. In addition, the density of each sample was measured. The constituents observed at concentrations greater than detection limits are identified in Welsh (1991) and also in Figure 3 of this report. Differences between a- and b-subsamples are used to estimate analytical (replicate) variability.

A composite sample was also analyzed. The composite sample was obtained by combining equal amounts of the individual samples. The composite sample was analyzed for the 33 constituents of the individual samples and some additional constituents, including organics. Results of the analysis are presented in Welsh (1991). A check on the internal consistency of the data can be made by comparing the volume-weighted average of constituent concentrations from individual samples with the concentration measurement obtained from the composite sample. The reliability of the data (our confidence in them) and their "representativeness" are discussed further in Section 5.0.

Results of our exploratory statistical analysis of the 241-AN-106 sampling data are presented in this section. These results serve to expose the internal structure of the wastes and relationships among the waste constituents. The results presented here supplement those presented in Welsh (1991). The main difference is that the results in Welsh (1991) are given for individual constituents whereas the results presented here are based on a simultaneous analysis of all sampled constituents.

Figure 3a shows a profile of results for the "a" subsamples. For each constituent, Figure 3a shows the measured value for each of the 12 samples. Constituent values for each subsample are connected by a line to produce the sample profile. All concentration measurements have been converted to comparable units (mg/L). Cs-137 is expressed in (μCi/L). To facilitate presentation of all data on a single plot, all measurements have been scaled by an by an arbitrary volume unit as indicated on the plot. Thus, aluminum

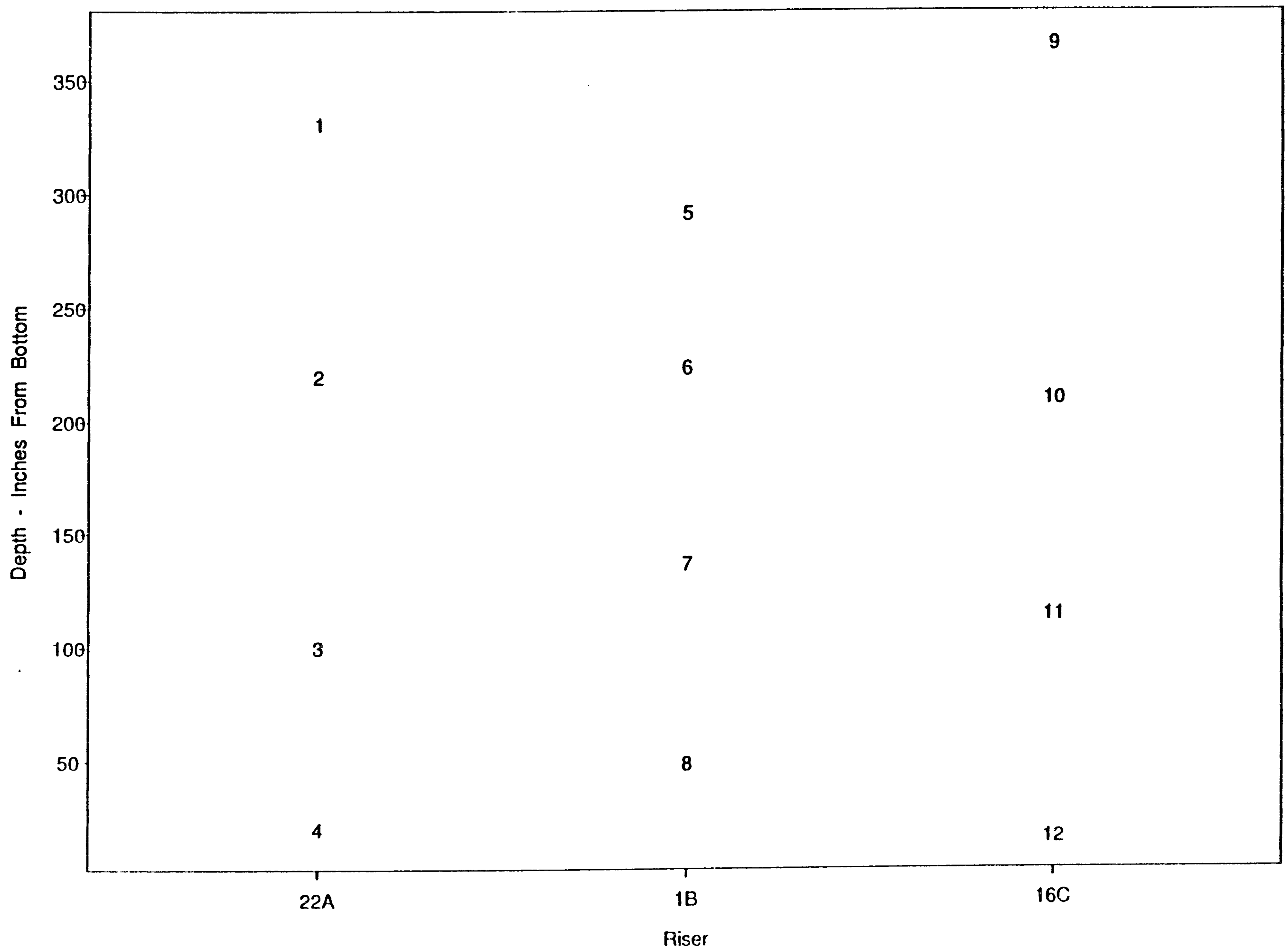


Figure 2. Tank 241-AN-106 Sample Locations

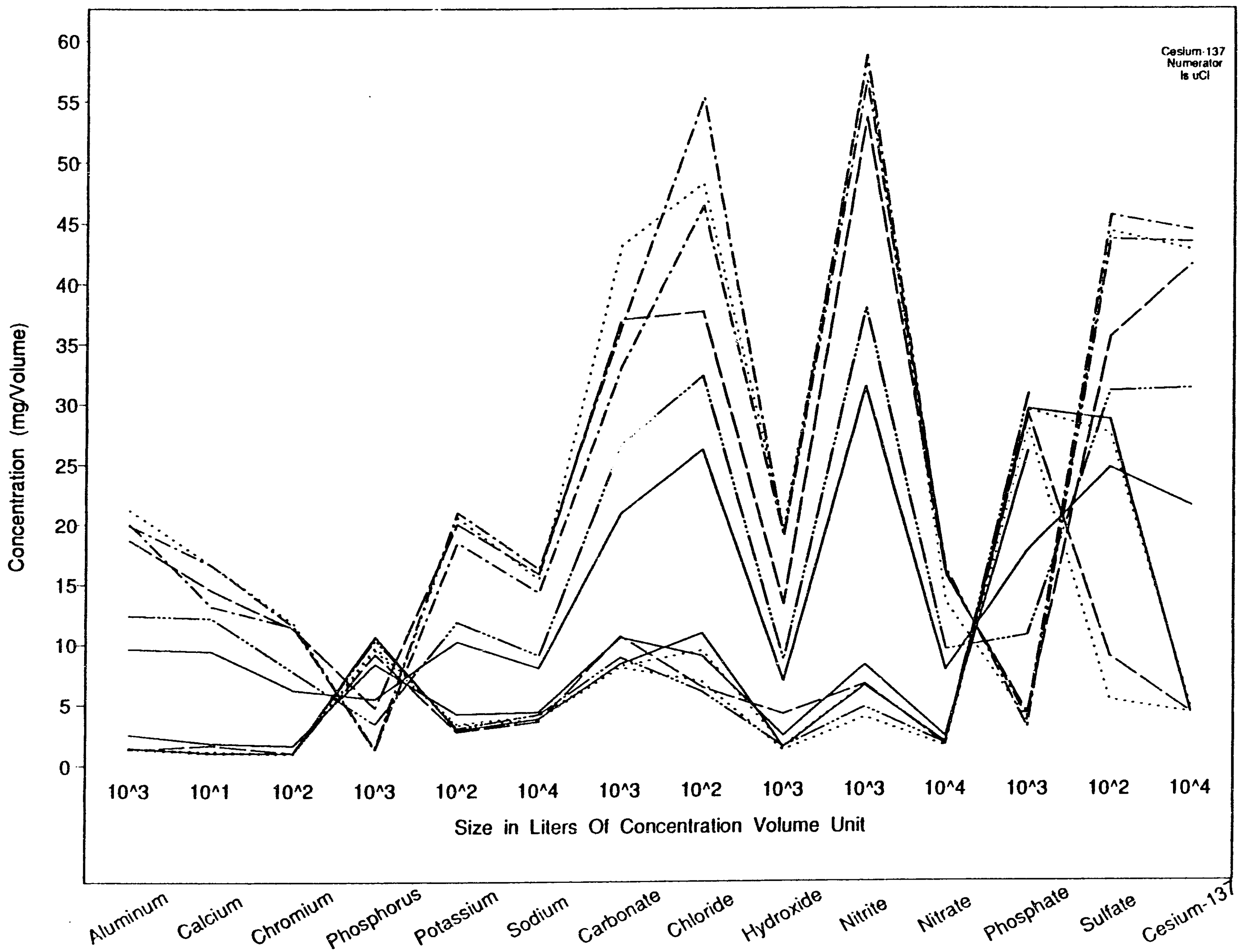


Figure 3a. a - Sample Constituents - Variable Volume Units

concentrations are expressed in mg per 1,000 L; calcium is expressed in mg per 10 L; etc. Below threshold observations (less-than values) are not shown in Figure 3a, nor in subsequent figures.

Figure 3b is similar to Figure 3a except that it shows the profile of results for "b" subsamples. Figure 3c shows the profile of results obtained by averaging corresponding "a"and "b" subsamples. Figures 3a to 3c all show similar very similar patterns.

Figure 4 shows the features of Figure 3c in greater detail. This figure was obtained as follows: The average value of each constituent is computed, and the deviation of each observation from its average is then plotted as in Figure 3. The most salient feature of these plots is that the 12 samples appear to fall into two groups.

- a lower group (LG), consisting of samples 3, 4, 8, 10, 11, 12
- an upper group (UG), consisting of samples 1, 2, 5, 6, 7, 9.

In addition, the lower group appears to cluster into two subgroups:

- LG1, consisting of samples 3, 4, 8, 12
- LG2, consisting of samples 10, 11

The solid dots in Figure 4 show the acceptance limits (converted to suitable units) given in Table 8-3 of Hendrickson (1991). The dots with arrows indicate that the acceptance limit is beyond the scale of the graph. The vertical line segments at the top of the plot show three standard deviations of the average, based on analytical variability in differences between "a" and "b" samples. For each constituent, the length of this segment is the approximate threshold above which observational differences are statistically significant. It is clear from the lengths of these segments that analytical variability (variability due to replicate chemical analyses) is quite small relative to other sources of sample-to-sample variability.

The above group definitions can be used as an outside check on the density measurements. Figure 5 shows density plotted by group. These measurements are expected to be more similar within groups than between groups. The most obvious feature is that in group LG1, the density of sample 4, is recorded at 1.6 g/cm^3, which is approximately 0.25 g/cm^3 higher than the other measurements in the group. This plot indicates a possible error in the density measurements. However, as mentioned earlier, this suspicion is unsubstantiated by any traceable records.

A cluster analysis across constituents was performed to test the significance of the clusters identified from Figure 4. The analysis was done after taking the log of the sampled data so that the scale differences could be de-emphasized while preserving the natural correlations. In general, these clusters are formed by assessing a measure of distance between samples among constituents and grouping those samples together that are closest. The

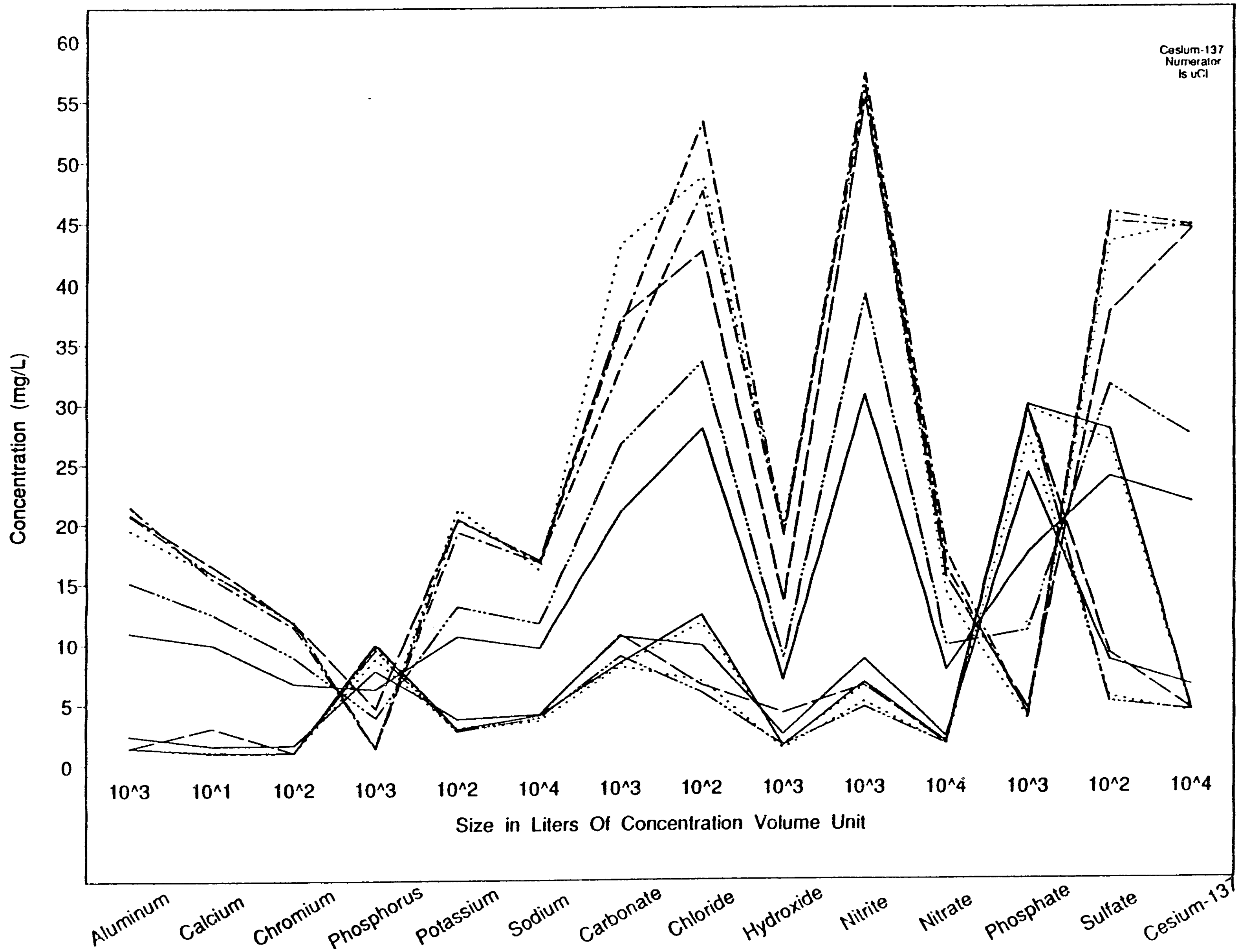


Figure 3b. b - Sample Constituents - Variable Volume Units

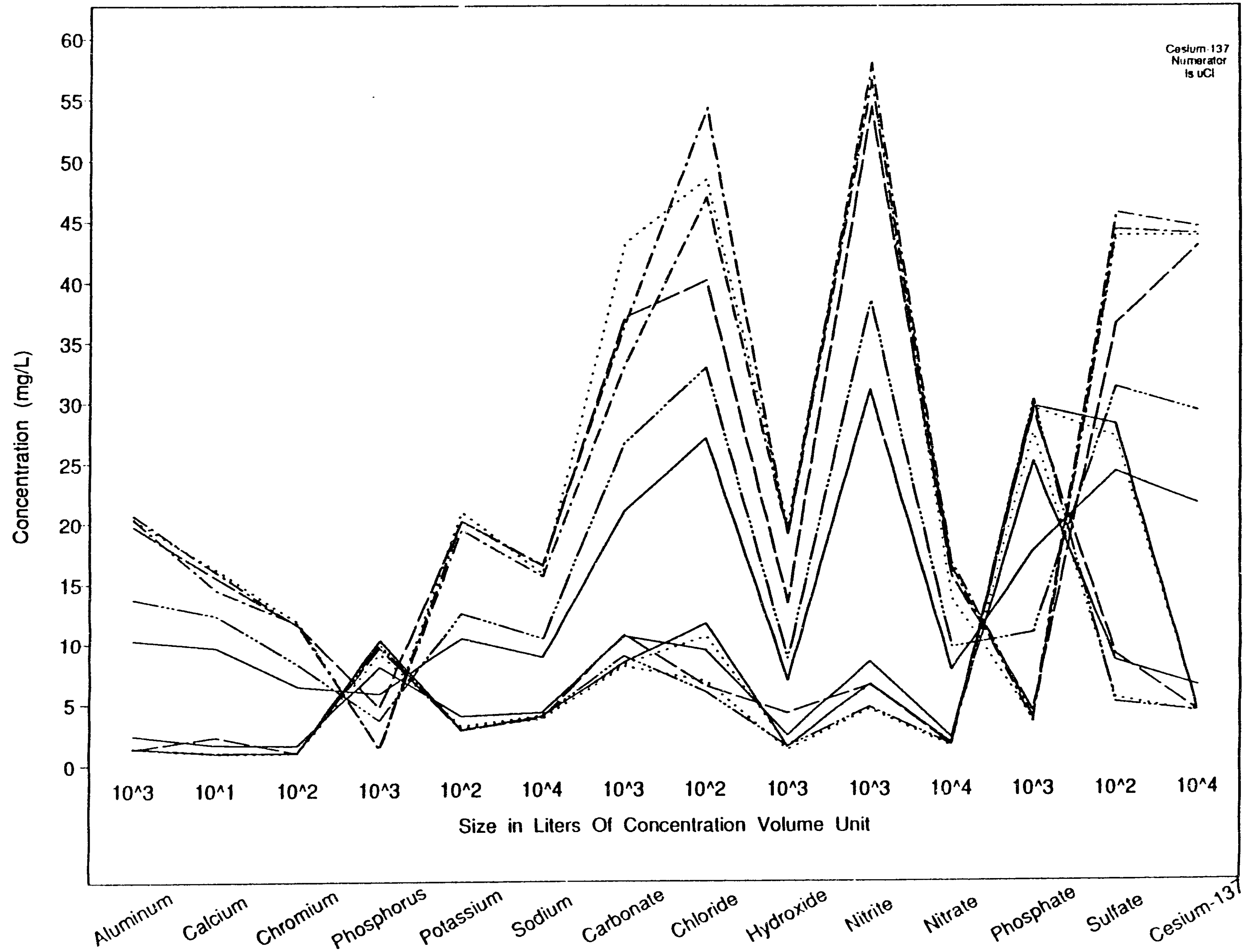


Figure 3c. Averaged a/b Sample Constituents - Variable Volume Units

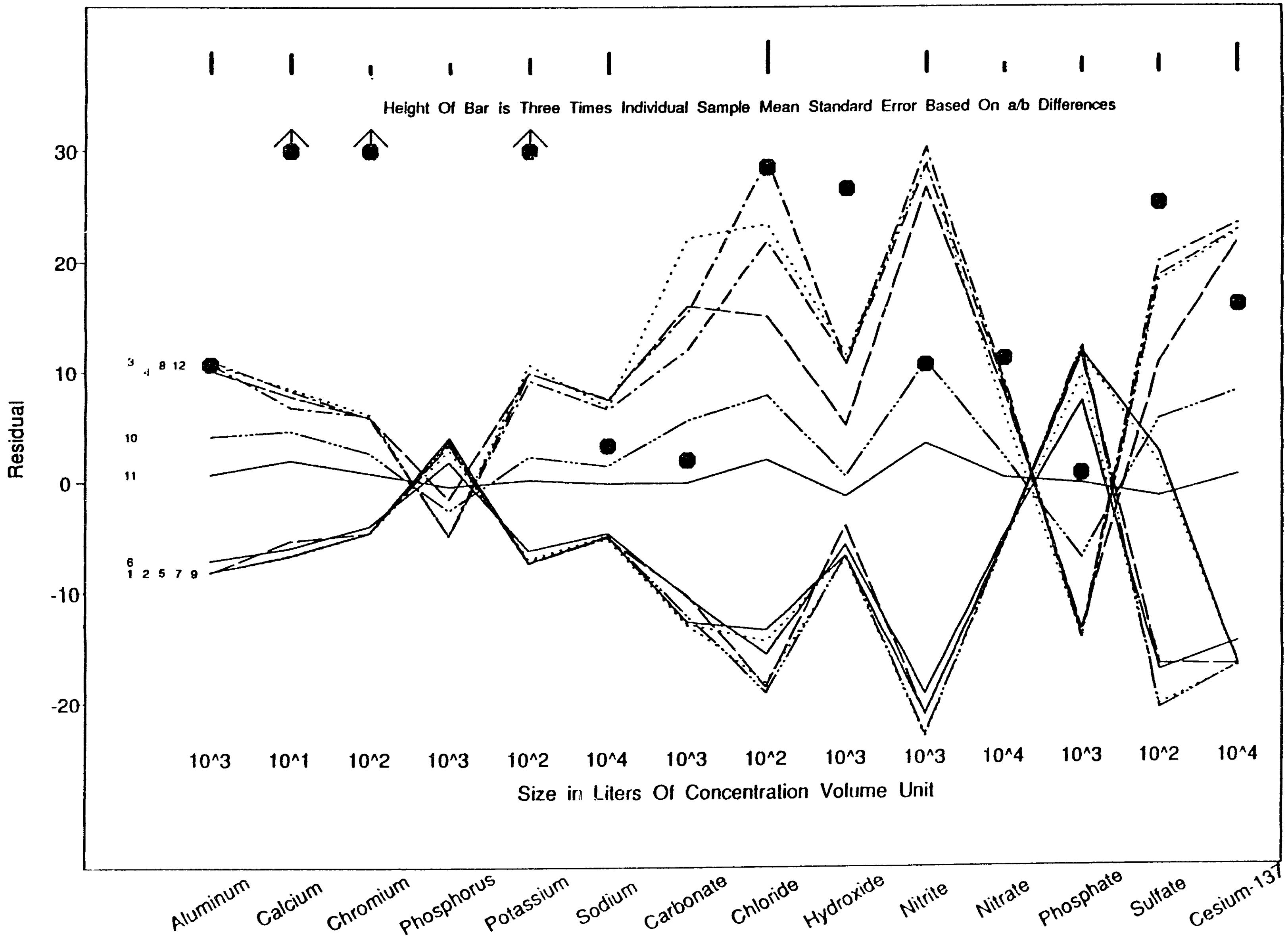


Figure 4. Averaged a/b Sample Constituent Residuals

results, which are shown in Figure 6, reveal that groups LG and UG have the greatest separation and that, within LG, LG1 and LG2 are the greatest distance apart. All other differences are negligible. For this analysis, the distance between two profiles was taken to be (1 - R) where R is a measure of pairwise correlation.

The interpretation of the analysis presented in Figure 6 is that the waste in 241-AN-106 form three distinct compositional regions. There is no plausible explanation for the fact that these regions are not (horizontal) layers as one might expect from what is known about the material in 241-AN-106 (see Section 5.0). If Samples No. 7 and No. 10 were interchanged, then the observed data would not contradict the layering hypothesis.

A second cluster analysis was performed, this time across samples. The results, shown in Figure 7, reveal the following three clusters:

- C1: phosphorus, phosphate
- C2: sulphate
- C3: aluminum, calcium, carbonate, cesium-137, chloride, chromium, hydroxide, nitrate, nitrite, potassium, sodium.

Differences among constituents in C3 are negligible. This means that, with respect to this class of constituents, the wastes in different compositional regions of 241-AN-106 differ only in the amount of dilution. Sulphate concentrations are not as highly correlated across samples with C3 constituents as are constituents within these clusters, but the significance of differences is questionable. Finally, the constituents in C1 (phosphorus, phosphate) behave

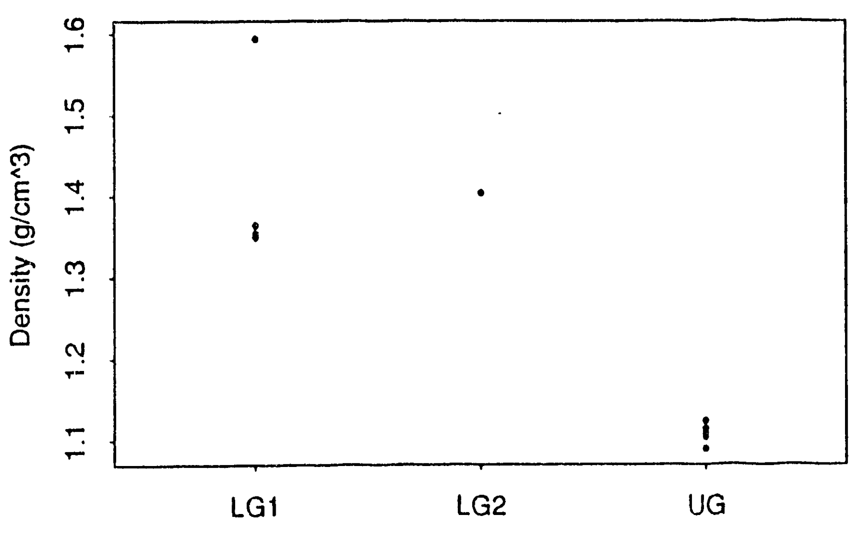


Figure 5. Density Measurements by Group

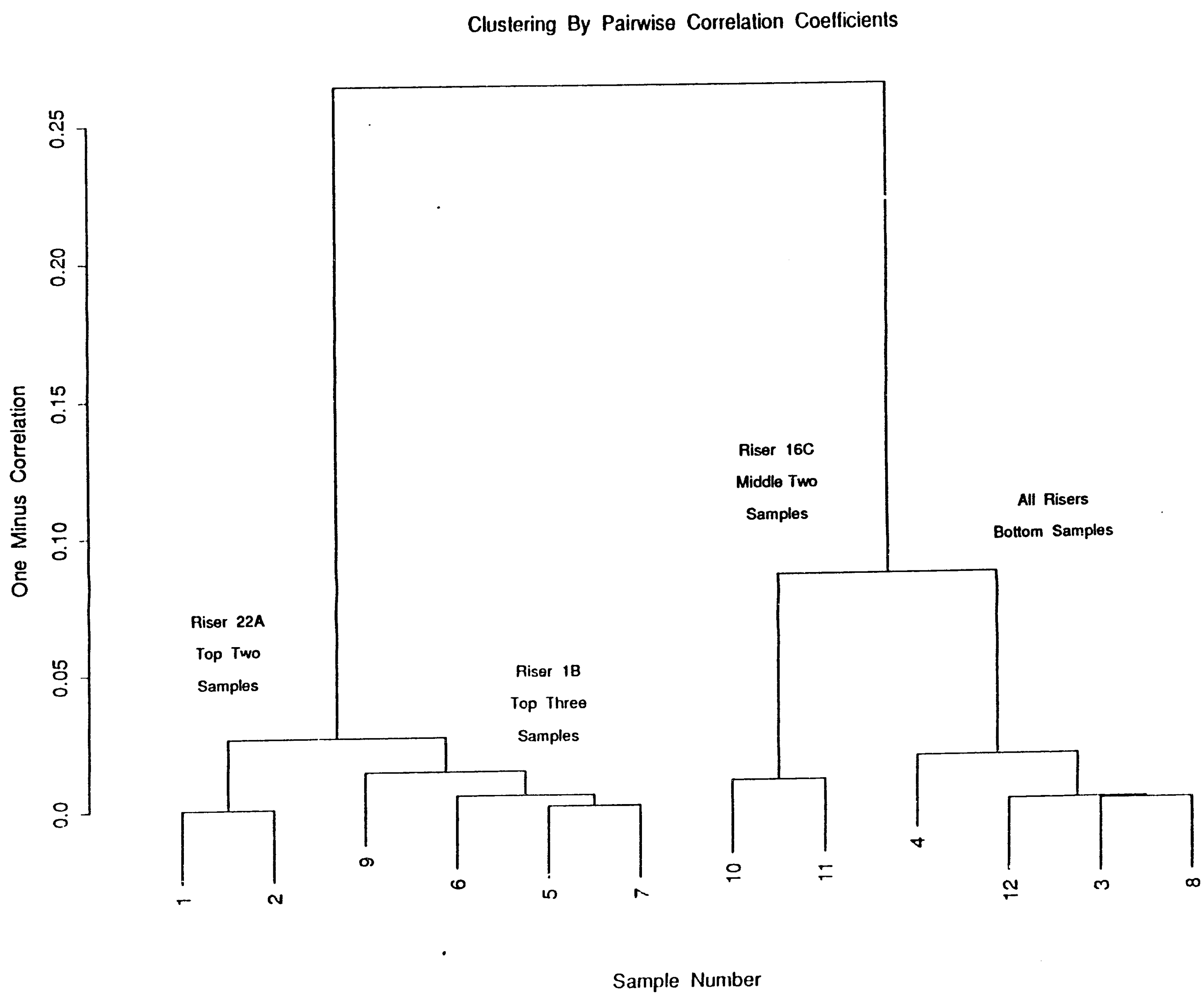


Figure 6. Sample Clustering Across Concentration Constituents

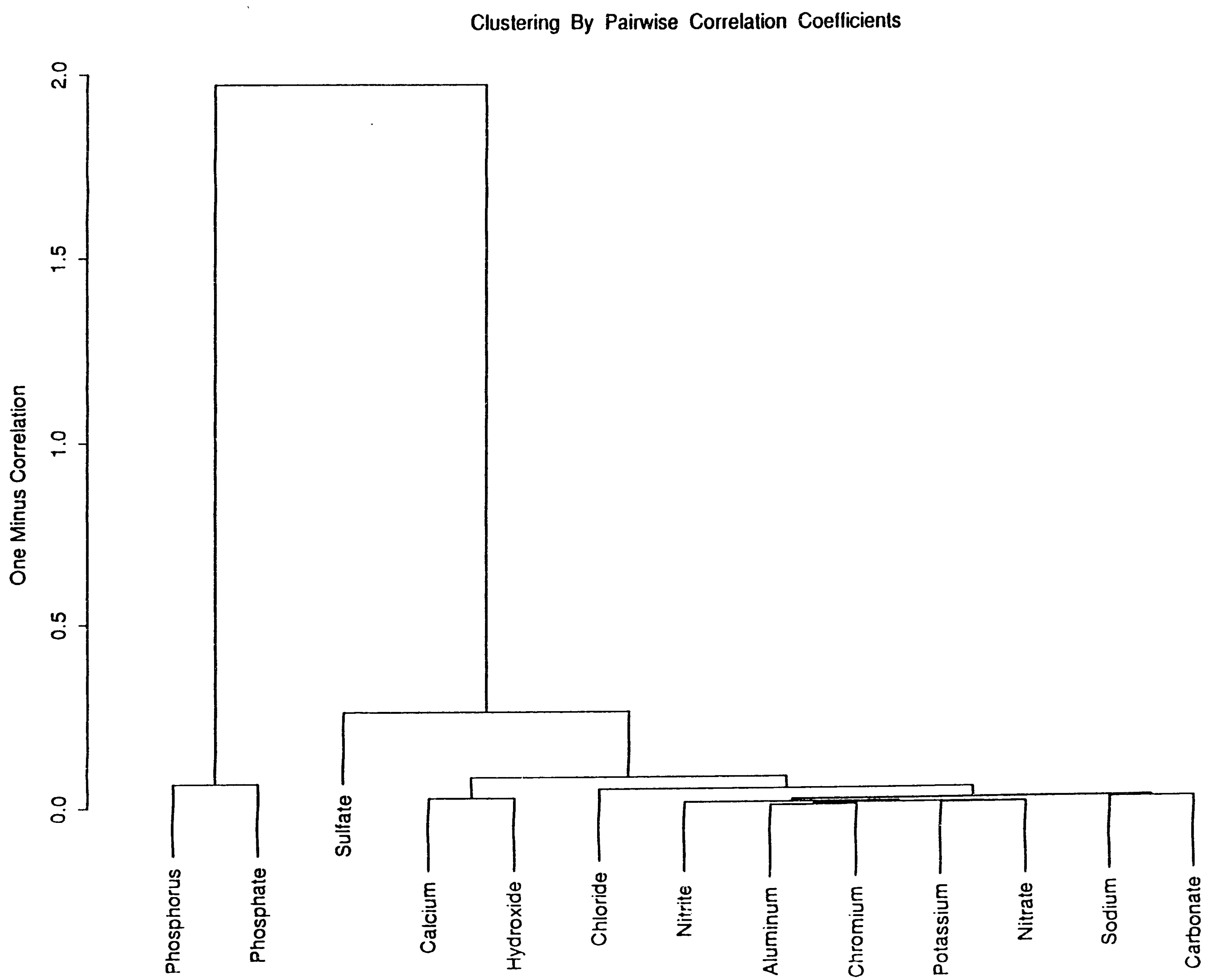


Figure 7. Constituent Clustering Across Samples

quite differently from all others: high concentrations of C1 constituents correspond with low concentrations of others with nearly perfect (negative) correlation.

The results in Figure 7 have some important implications with respect to the design of formulation studies for 241-AN-106 wastes. Specifically, the results indicate that it is not necessary to treat C3 constituents separately. Consequently, it is sufficient to fix their concentration ratios at average concentrations, as given in Table -4.1, and then vary the dilution factor. A similar argument can be made for C1 constituents. Of course, this design strategy is inappropriate for other constituents that do not exhibit such high correlations, and it should not be used for other tanks or waste types without verification.

4.2 CHARACTERIZATION OF TANK 241-AN-106 WASTE

The results of a statistical analysis to address the question in Section 1.0 concerning characterization are presented in this section. These results differ from those in Welsh (1991) in that we have explicitly

Table 4.1. Characterization and Performance Results for Tank 241-AN-106

Constituent	Mean Conc. (mg/L)	95% LCL (mg/L)	95% UCL (mg/L)	Acceptance Limit (mg/L)	Sig. Level (mg/L) One-Sided	Risk
Aluminum	9580	6470	12700	20300	0.9934	0.0066
Calcium	77	59	96	573	0.9996	0.0004
Chromium	569	410	727	21000	0.9999	0.0001
Phosphorus	6262	5340	7190	NA	NA	NA
Potassium	1020	876	1170	11500	0.9999	0.0001
Sodium	89300	86400	92200	122000	>0.9999	<0.0001
Carbonate	21000	18500	23500	22920	0.9520	0.0480
Chloride	2505	2220	2790	5360	>0.9999	<0.0001
Hydroxide	8230	6870	9590	34850	>0.9999	<0.0001
Nitrite	27700	22800	32600	38250	0.9909	0.0091
Nitrate	74800	66300	83300	186000	>0.9999	<0.0001
Phosphate	17900	13900	21800	18430	0.7651	0.2349
Sulphate	2570	2360	2790	5100	>0.9999	<0.0001
Cesium-137	211000	139000	284000	371800	0.9892	0.0108
Density	1.26	1.23	1.29	1.4	>0.9999	0.0001

calculated an estimate of analytical error while WHC did not. This difference does not affect the estimate of variability that was used to compute the confidence intervals. The difference in approach does affect the degrees of freedom used to find the t value for the intervals, but differences are generally negligible.

Figure 8 shows the average concentration for each constituent, together with the corresponding upper 95% confidence limits. The solid dots in Figure 8 show the acceptance limits (converted to suitable units) given in Table 8-3 of Hendrickson (1991). Acceptance criteria are met--at the specified confidence level--for those constituents where the upper confidence limit is less than the corresponding acceptance limit. The results shown in Figure 8 are given in tabular form in first four columns of Table 4.1.

The confidence intervals shown in Figure 8 and given in Table 4.1 provide a "characterization" of 241-AN-106 wastes in the sense that they have a specified high probability of containing the true constituent concentrations. However, the intervals are not based on any criteria that specify the degree of characterization required. One example of such a criterion is a rule that specifies a maximum interval width, such as "the width of the interval must not exceed 25% of the mean." While such rules are better than none at all, it would be far better if the degree of characterization were tied to meaningful performance criteria. Given that the sampling of 241-AN-106 waste was not closely tied to a set of performance criteria, it is perhaps fortuitous that the performance results reported below turned out so favorably. This point is discussed further in Section 5.0.

4.3 PERFORMANCE OF TANK 241-AN-106 WASTE

For each 241-AN-106 waste constituent identified above, the last column of Table 4.1 contains significance levels calculated as described in Section 2.2. For each constituent, a t-value is obtained by computing the number of standard deviations between its sample average, $\bar{x}$, and its performance limit, L:

$$t = (L - \bar{x})/s$$

The significance level, α, corresponding to the resulting value of t is then determined. If α is large, then there is a high probability that the constituent will satisfy the performance limit. Equivalently, the risk, $(1 - \alpha)$, is low that the performance criteria will not be met. From Table 4.1, we can see that, except for phosphate and carbonate, there is little risk that any of the sampled constituents will violate the performance limits specified in Table 8-3 of Hendrickson (1991).

The analysis of the 241-AN-106 sampling data reveals that the wastes in this tank form at least two regions in which measured constituents have considerably different concentrations. It might be argued, therefore, that a

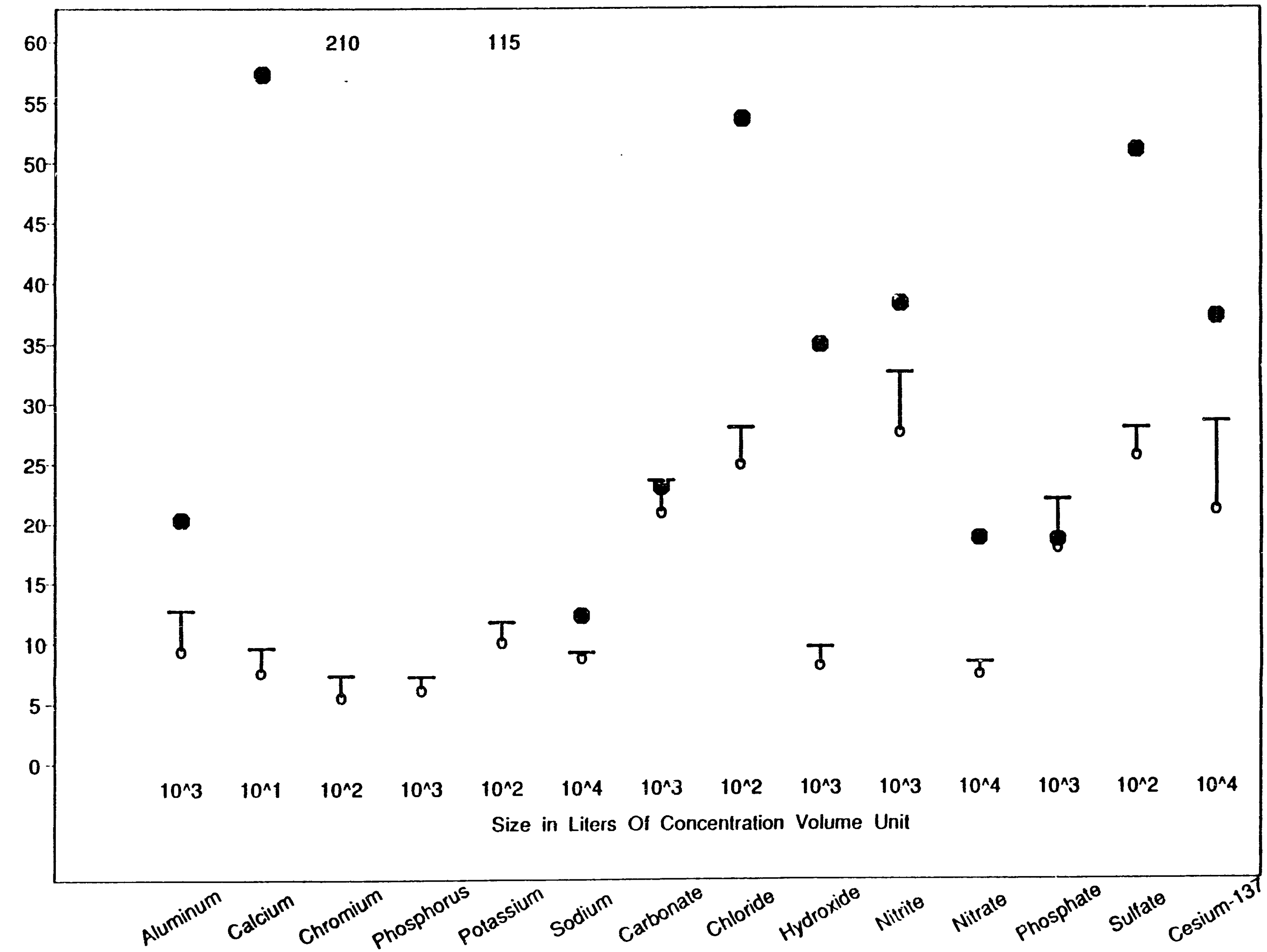


Figure 8. 95% Confidence Intervals for Tank 241-AN-106

volume-weighted average of observed concentrations should be used to assess performance. (The results in Figure 8 and Table 4.1 are for unweighted averages.) This calculation requires estimates of the volume of waste in each region, so uncertainty in volume estimates becomes a factor in the assessment. The sensitivity of performance measures to volume uncertainty was assessed, and results of that assessment are shown in Figures 9a and 9b. Figure 9a is similar to Figure 8, except that calculations were done under the assumption that 40% of the waste is in the lower layer (samples 3, 4, 8, 10, 11, 12) and 60% is in the upper layer (samples, 1, 2, 5, 6, 7, 9). For this weighting, performance criteria are met for all constituents, except phosphate. Figure 9b is similar to Figure 9a, except that the volume percentages assigned to the two layers are reversed. For this weighting, performance criteria are met for all constituents except carbonate, nitrite, and phosphate. These results indicate that characterization results for phosphate, carbonate and nitrite are sensitive to uncertainties in estimates of volume in each layer. Based on the pumping history for 241-AN-106, which indicated that 58.85% of the waste is in the bottom layer, carefully calculated volume-weighted concentration estimates are expect to be quite close to those given in Figure 9b.

4.4 CHARACTERIZATION OF TANK 241-AP-102 WASTE

Appendix A of WHC-SD-WM-TP-136 contains calculated estimates of the concentrations of approximately 80 constituents of the wastes in 241-AP-102. Actual measurements of these constituents were made for the phosphate-sulfate wastes, and selected constituents were measured for the PUREX additions (see Section 3.2). Minimal direct measurements of constituents in the grout leachate were made to comply with then current SDT tank requirements. In WHC-SD-WM-TP-136, all non-measured concentrations are assumed to be the same as those measured in the phosphate-sulfate waste. In all cases, measurements below detection limits have been replaced by the detection limit. Under these circumstances, the calculated concentration estimates can be regarded as upper limits on corresponding actual concentrations.

The magnitudes of 241-AP-102 constituent concentrations, relative to 241-AN-106 concentrations, are important for determining whether the combined wastes from these two tanks will meet acceptance criteria. For constituents identified in Section 4.1, Table 4.2 contains their concentrations in both 241-AN-106 and 241-AP-102 wastes. It is clear from this table that 241-AP-102 wastes are much more dilute than those in 241-AN-106 for every constituent listed except phosphorus and phosphate. For these two constituents, the mean concentration in 241-AN-106 waste will be close to that in the final grout feed. For the remaining constituents, these that meet acceptance criteria at their 241-AN-106 concentrations will meet acceptance criteria at the dilute concentrations expected in the combined 241-AN-106/241-AP-102 waste that will be grouted. More precise estimates of constituent concentrations in the combined 241-AN-106/241-AP-102 waste are given in the next section.

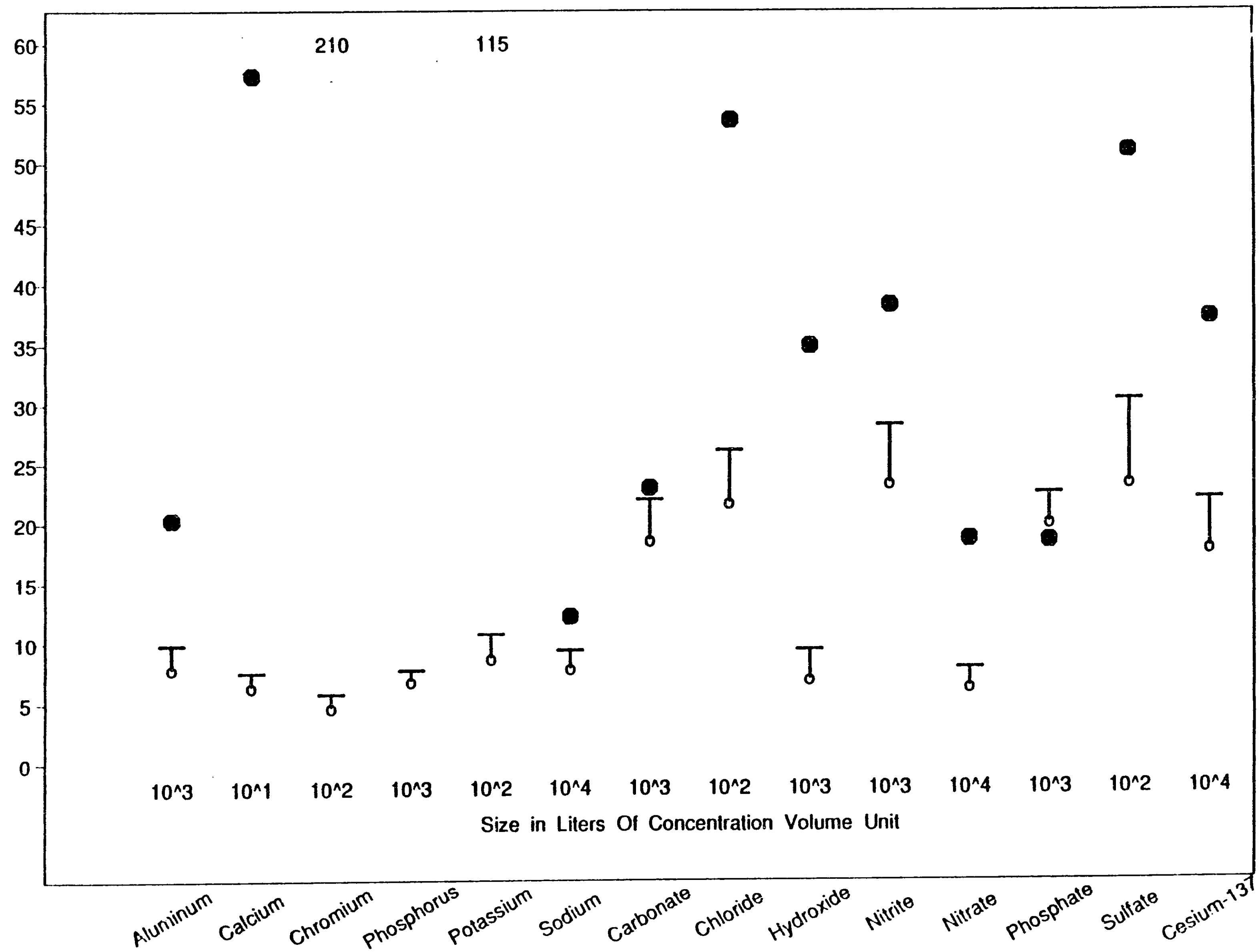


Figure 9a. 95% Confidence Intervals for Tank 241-AN-106 (40% B/60% T)

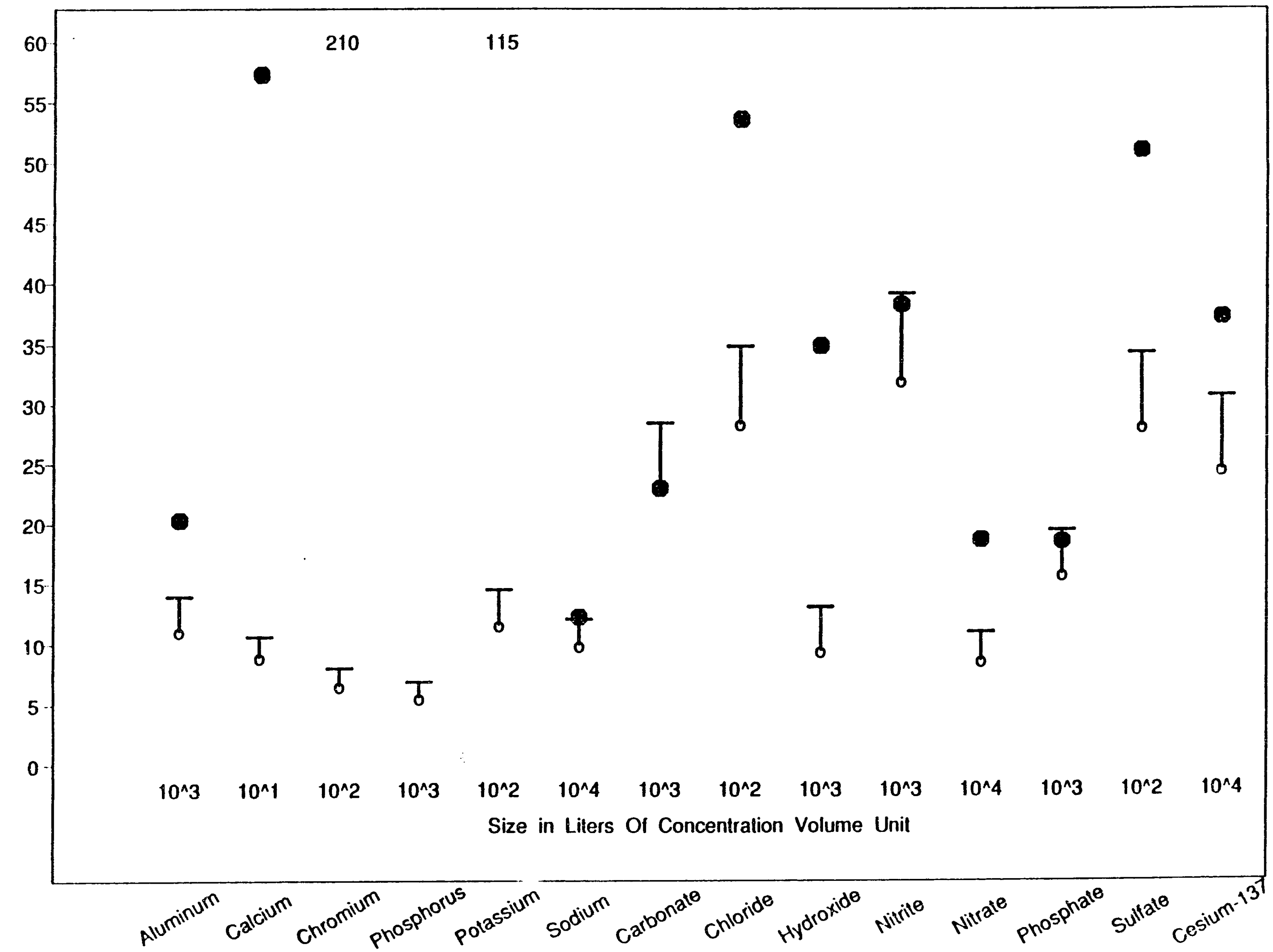


Figure 9b. 95% Confidence Intervals for Tank 241-AN-106 (60% B/40% T)

4.5 CHARACTERIZATION OF COMBINED TANK 241-AN-106 AND 241-AP-102 WASTES

The waste that must eventually prove acceptable is a mixture of 241-AN-106 and the heel that is currently contained in 241-AP-102. Based on the information contained in Sections 4.2 through 4.4, an estimate of the overall concentration of this final waste feed is provided in this section. Tank 241-AP-102 currently contains 136,000 gallons of waste. Approximately 985,000 gallons of 241-AN-106 waste will be added to 241-AP-102 to produce a total waste volume of 112,000 gallons. Tank 241-AP-102 contains a dilute mixed phosphate-sulphate waste similar to that in 241-AN-106. Thus, transferring waste from 241-AN-106 to 241-AP-102 will produce in the latter a dilute waste similar to that presently in 241-AN-106. The resulting mixed waste will be composed of 88% 241-AN-106 waste and 12% 241-AP-102 waste.

To obtain an estimate and 95% confidence interval for constituents in the final waste feed, several assumptions had to be made. First, it was assumed for each constituent that the ratio of standard deviation to the mean is the same for both tanks. Second, the estimates for Tank 241-AP-102 were assumed to be mean concentrations. With these assumptions, it is possible to obtain an estimate of a mean and standard deviation for each constituent for each tank. A weighted mean concentration for the final waste feed was then obtained by weighing the respective tank means by the percentage of overall volume; i.e., the mean for Tank 241-AN-106 had a weight of 985,000/112,000 (0.88) and the mean for Tank 241-AP-102 had a weight of 136,000/112,000 (0.12). An appropriate standard deviation was estimated and a 95% confidence interval was calculated. The results of this analysis are presented in Table 4.3.

Table 4.3 represents our best estimate of the final concentration of the waste feed. Carbonate and phosphate are the constituents that have upper 95% confidence limits that exceed the acceptance limit.

Table 4.2. Constituent Concentrations for 241-AN-106 and 241-AP-102 Wastes

Constituent	Concentration 241-AN-106 (Measured)	241-AP-102 (Computed)	241-AP-102 (Converted)
Aluminum	9580 mg/L	0.947 ppm	0.947 mg/L
Calcium	77 mg/L	0.853 ppm	0.853 mg/L
Chromium	569 mg/L	1.610 ppm	1.610 mg/L
Phosphorus	6262 mg/L	5021 ppm	5021 mg/L
Potassium	1020 mg/L	9.473 ppm	9.473 mg/L
Sodium	89300 mg/L	11370 ppm	11370 mg/L
Carbonate	21000 mg/L	0.031 M	1876 mg/L
Chloride	2505 mg/L	0.001 M	34.6 mg/L
Hydroxide	8230 mg/L	0.106 M	1794 mg/L
Nitrate	74800 mg/L	0.002 M	119 mg/L
Nitrite	27700 mg/L	0.011 M	501 mg/L
Phosphate	17900 mg/L	0.163 M	15479 mg/L
Sulfate	2570 mg/L	0.017 M	1591 mg/L
Cesium-137	211000 μCi/L	4.63E-07 Ci/L	0.463 μCi/L

Table 4.3. Estimated Upper 95% Confidence Limits for Combined Waste from Tanks 241-AN-106 and Tank 241-AP-102

Constituents	Units	Mean (106)	UCL (106)	Mean (102)	UCL (Comb)	Acc Limit
Aluminum	mg/l	11168	13943	0.974	12140	20300
Calcium	mg/l	90	106	0.853	93	573
Chromium	mg/l	659	802	1.610	699	21000
Phosphorus	mg/l	5624	6859	5021.000	6604	
Potassium	mg/l	1162	1449	9.473	1263	11500
Sodium	mg/l	99211	120537	11370.00	106445	122000
Carbonate	mg/l	23372	28396	1876.00	24985	22920
Chloride	mg/l	2837	3483	34.600	3041	5360
Hydroxide	mg/l	9463	13034	1794.000	11537	34850
Nitrite	mg/l	31962	39171	119.000	34147	38250
Nitrate	mg/l	86230	109649	501.000	95456	186000
Phosphate	mg/l	15748	19378	15479.000	18807	18430
Sulfate	mg/l	2811	3427	1591.000	3201	5100
Cesium-137	uCl/l	244405	306396	0.463	266720	371800

5.0 ADEQUACY OF CHARACTERIZATION DATA

The confidence we can place in the conclusions reached in Section 4.0 depend on a number of factors. These include how well the acceptance criteria have been defined and applied, the validity of the sampling plan, and the quality of the data. Each of these factors will be discussed in this section.

5.1 ACCEPTANCE CRITERIA

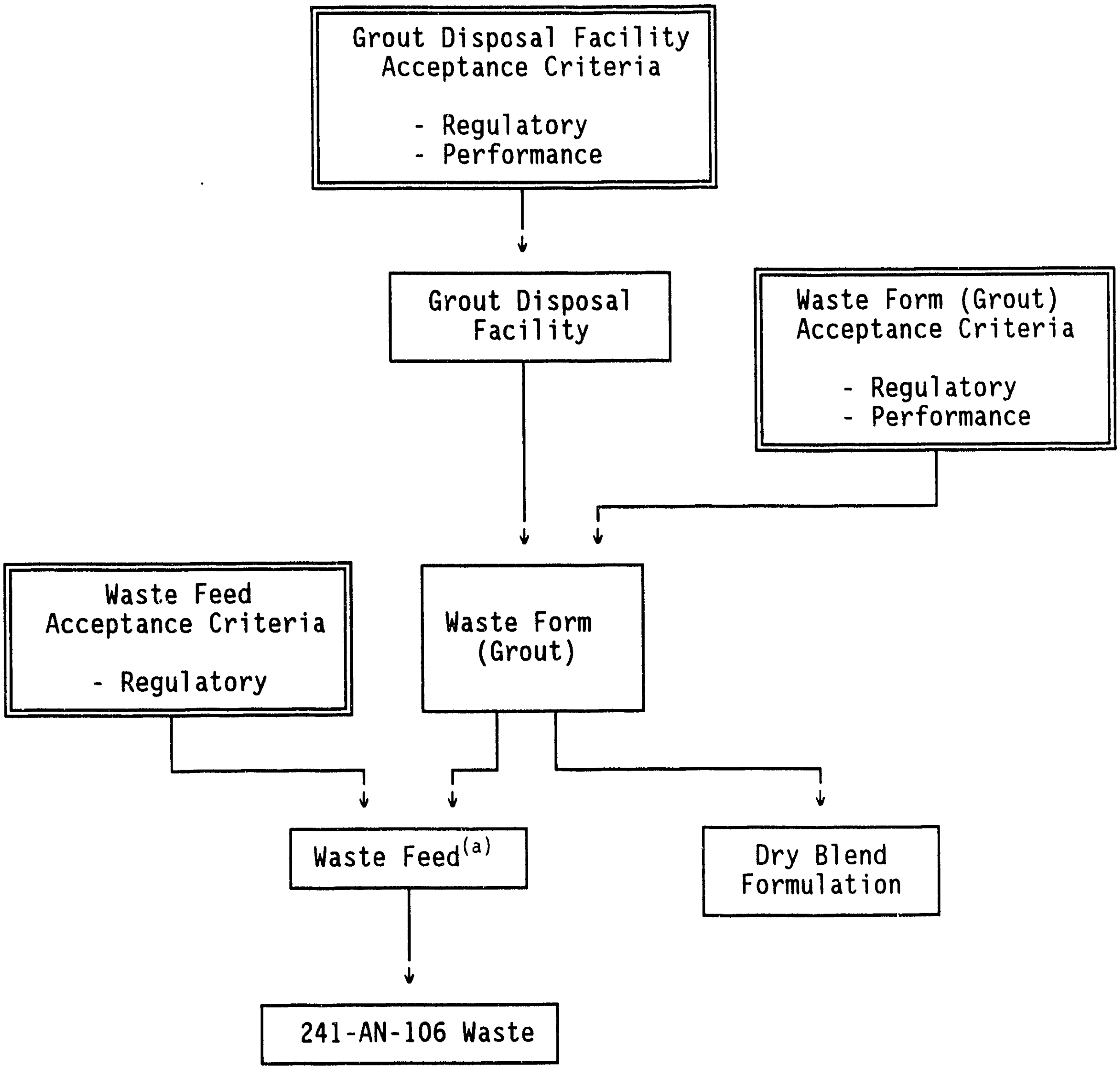
Established acceptance criteria must serve as the basis for evaluating characterization results for 241-AN-106 wastes, as measured by the width of confidence intervals for constituent concentrations (see Section 2.0). Suitable acceptance criteria must specify not only key waste constituents and grout performance but also quantitative limits for each.

5.1.1 Sources of Criteria

Acceptance criteria that apply to the wastes in 241-AN-106 grout waste disposal process are derived from several sources. Regulatory limits are imposed on the waste feed, the waste form (grout) and the disposal facility (vault) to ensure health and safety. Performance limits are imposed on the waste form and disposal facility to ensure that process requirements are met and that the final grout product has certain physicochemical properties. One set of constraints may not be independent of others, and the constraints do not all apply at the same point in the grout formulation process.

Our interpretation of where regulatory and performance requirements apply in the grout formulation process, and how they relate to the contents of 241-AN-106, are shown in Figure 10. Both regulatory and performance (processing) requirements are imposed on the waste disposal facility. These requirements on the waste disposal facility, in turn, impose requirements on the grout. Additional acceptance requirements may be imposed directly on the grout. These requirements are, in turn, translated into requirements on the dry blend formulation and waste feed streams. (The waste feed is the combined contents of 241-AN-106 and 241-AP-102.) As with the grout, the waste feed stream is subjected to directly-imposed regulatory requirements. Finally, by considering the percentage of wastes contributed by each of 241-AN-106 and 241-AP-102, requirements imposed on the waste feed are translated into concentration limits on waste constituents in 241-AN-106.

Hendrickson (1991) contains the most comprehensive evaluation of grout waste feed acceptance criteria available. Table 8-3 of that document summarizes limits for pH, total solids, heat generators, density, TOC and specific organic compounds, 35 cations/metals, 10 anions, and 21 radionuclides. The criteria are synthesized from an evaluation of grout disposal regulatory requirements, consideration of the types of Hanford waste, and heat generation requirements for the waste feed stream. Requirements pertaining to the classification and disposal of radioactive wastes, for example, are derived from NRC and DOE regulations. Requirements from a number of sources apply to



(a) Contains the combined wastes of 241-AN-106 and 241-AP-102.

Figure 10. Points at Which Acceptance Criteria are Imposed in the Grout Waste Disposal Process

the grout disposal facility. These include (but are not limited to) Resource Conservation and Recovery Act (RCRA) requirements found in Title 40 of the Code of Federal Regulations (40 CFR 161, 40 CFR 261, 40 CFR 268) and Chapters 173-303 of the Washington Administrative Code, as well as regulations pursuant to the Clean Air Act and the maintenance of groundwater quality. Table 8-3 of

Hendrickson (1991) also reflects limitations due to variability in the physical characteristics and the chemical composition of the waste feed. Finally, limits on TRU content are required to ensure that the peak temperature during processing does not exceed 90°C.

The grout product acceptance criteria is contained in Riebling et al. (1991). This document provides limits for leachability, toxicity, hazard classes, free-standing liquid, unconfined compressive strength, and grout homogeneity as criteria required for technical and environmental reasons. These criteria are synthesized from an evaluation of NRC recommendations, the Washington Administrative Code for Ecology, the Grout Treatment Facility Dangerous Waste Permit Application, and 10 CFR 61.56. In addition, limits for critical flow rate, ten-minute gel strength, frictional pressure drop, and adiabatic heat hydration temperature rise have been identified as processing criteria required to prepare and place the grout safely and economically within the vault. These criteria are not directly tied to any regulatory documents. Limits for time/temperature effects, irradiation, immersion, thermal conductivity, slurry cure time, and grout expansion/contraction have been specified as limits that are necessary either to yield acceptable product or to improve processing.

5.1.2 Concerns About Criteria

A number of concerns remain about the acceptance criteria developed by WHC to evaluate characterization adequacy. These are addressed below.

Relationships Among Criteria. From this review, it is clear that regulatory and performance limits arise from many sources and that these limits apply at various points in the grout formation process shown in Figure 10. What is not clear is how the requirements are interrelated. How, for example:

- do regulatory criteria that apply to the waste form (grout), for example, take into account criteria that apply to the grout disposal facility (vault)?
- are regulatory criteria imposed on the waste feed related to those that apply to the waste form (grout) or the grout disposal facility (vault)?
- are grout performance criteria based on applicable regulations, or are they derived solely from process considerations?

These questions must be answered so we can ensure that all criteria are met. If relationships among criteria exist that have not been identified, characterization and process decisions could unknowingly result in violation of an acceptance limit at some future time in the process.

Basis for Acceptance Limits. A second concern is the basis for a number of the published acceptance limits. This concern pertains especially to those derived from process or performance considerations. We cite as an example the limit on TRU content required to ensure that the peak temperature during processing does not exceed 90°C and the limit specified for phosphate.

It is clear that peak temperature is a concern, but to be defensible, the performance limit for temperature must be based on relevant experiments that take process variability into account. We find the link between the peak temperature limit of 90°C and the supporting experimental results to be weak. Next consider phosphate; the analysis in Section 4.0 indicates that phosphate has a high probability of exceeding its acceptance limit, but no remediation has been proposed by WHC. It is possible that there is little negative consequence in exceeding the limit for phosphate, but this adds to concerns about the original basis for the acceptance limit.

While we have demonstrated this concern with two examples, we do not consider this an exhaustive list. There may be other limits that lack strong experimental support or that are not defensible.

All the limits need to be believable. This can be accomplished both through appropriate experimentation and through programmatic action if a limit is violated. If justification is weak for even a few of the acceptance limits, there is a danger that the justification for all the limits will be considered weak.

Formulation of Grout. A third concern is potentially the most serious. It is not clear that the combined effect of variability in the waste feed and the dry blend formulations on the resulting grout product has been adequately taken into account in setting acceptance limits.

Experimental evidence relevant to this issue is sparse and inconclusive. Experiments done to date have involved either variability in the waste feed composition, with the dry blend formulation held constant, or vice versa. No experiments have been completed in which both the waste feed composition and the dry blend formulation have been varied simultaneously. (See Section 6.0 for further discussion of relevant experiments.)

If the combined effect of variability has not been taken into account in experimentation, then the acceptance criteria that have been developed from the experiments may be inappropriately specified and/or impossible to meet.

Accessibility of WHC Criteria. The acceptance criteria developed by WHC stem from a variety of regulatory agencies and apply at various points in the grout formulation process. We appreciate the large effort that has gone into developing this rather extensive catalog of criteria.

Nevertheless, the results are not easily accessible, even to those who are familiar with the grout program. In particular, the criteria and related documentation do not provide a sense of which of the many constituents are of greatest concern. We believe that it would be very helpful to have a "short list" of key constituent for which violation of acceptance limits is an important programmatic issue.

For example, it is clear that temperature and CS-137 would appear on this "short" list as would some concentrations of organics, but it is not clear what other analytes might appear.

This concern is important from a programmatic standpoint: project decision makers should have easy access to a list of acknowledged key constituents.

Application of Acceptance Criteria. We have emphasized that the adequacy of characterization results for 241-AN-106 is directly related to acceptance criteria for the waste, the grout, and the disposal facility. We have also emphasized that a sampling plan for characterization must be driven by clearly defined acceptance limits to ensure that results will be adequate.

For purposes of this report, we have used the WHC criteria as presented in Hendrickson (1991) and Riebling (1991) to evaluate 241-AN-106 characterization results. There are, however, some difficulties associated with this application of criteria to assess 241-AN-106 characterization.

First, these criteria did not exist when the sampling plan for 241-AN-106 was developed. To meet the need for a way to evaluate characterization results, the criteria were developed by WHC after the fact. Thus, the sampling plan was not--indeed, could not have been--designed to ensure that sampling results would provide adequate characterization. Rather the reverse occurred: the sampling results were used to develop acceptance criteria.

A more important difficulty is that the acceptance criteria developed by WHC have not been formally accepted by DOE and are therefore subject to change. Until these or other acceptance criteria are formally adopted, any evaluation of characterization adequacy must be regarded as preliminary and programmatic progress is stifled.

5.2 SAMPLING PLAN

The 241-AN-106 data analyzed for this report were collected according to the sampling plan in Hammitt et al. (1989). Salient features of that plan are described in Section 4.0.

5.2.1 Plan for 241-AN-106

The 241-AN-106 sampling plan called for 12 samples of waste from 241-AN-106 for the purpose of characterizing these wastes. Three of the 10 available risers were randomly selected for sampling, and four samples were taken from each riser. The exact locations of the four samples at each riser were determined as follows:

- The waste was divided into four layers (strata) of equal height.
- For each riser, a sampling location (height) was determined randomly within each layer.

The resulting sampling locations are shown in Figure 2.

Stratification was employed because it was believed that 241-AN-106 wastes were layered. The waste was divided into four layers tank to ensure reasonable vertical coverage. It was assumed that the wastes were homogeneous within layers. Under this assumption, it is appropriate to determine sampling locations randomly within the selected strata. In summary, the sampling plan is appropriate, given the information available at the time it was developed.

The sampling results presented in Section 4.0 indicate that the stated assumption are reasonable: the cluster analysis did identify several concentration regions. Although these regions do not appear to be as horizontally distinct as one would like, sampling results do not present serious contradictions of the underlying assumptions. Thus it is reasonable to conclude that the twelve samples are representative.[a]

The basic problem with the 241-AN-106 sampling plan is that it was not driven by any clearly focused objective. The plan was not designed to meet quantitative requirements on how well concentrations should be measured. Indeed, the basis for choosing an initial sample size of 12 was not motivated either by performance criteria or statistical considerations. The best justification we have found is that 12 samples were required (each sample contains 100 mL of waste) to produce the total volume of material (1200 mL) needed to perform all the planned chemical analyses. With this approach it was impossible to tell *a priori* how well a given constituent would be characterized.

The power of using statistical criteria to determine sample size is that the criteria can be used to control the precision of estimates. For example, sample sizes can be determined to ensure that some criterion such as "the width of the confidence interval must not exceed 25% of the mean" is satisfied. Such rules are better than none at all, but it would be far better if the degree of characterization was tied to meaningful performance criteria with sufficiently high probability. Unless a sampling plan is driven by clearly specified statistical or performance criteria, it is impossible to devise a plan that yield characterization measurements with a specified precision, i.e., that produced confidence intervals of a specified width.

Despite the lack of performance criteria to drive the sampling plan, the characterization results for 241-AN-106 turn out, perhaps fortuitously, to be reasonably adequate. Relatively little information is to be gained by additional sampling of 241-AN-106 wastes before they are transferred to 241-AP-102.

(a) A good design is closely tied to its underlying assumptions. Had sampling results been inconsistent with the underlying assumptions, we would have concluded that the sampling was not adequate.

5.2.2 Plan for 241-AP-102

We have been unable to find information on the plan for sampling of the residual phosphate-sulfate wastes in 241-AP-102. The waste in that tank represents only 12% (see Section 4.5) of the total volume of waste in question, and is considerably more dilute than that in 241-AN-106. Therefore, in our analysis we considered the details of the sampling plan for this tank to be less important than that for 241-AN-106. This plan was not further analyzed.

5.3 DATA QUALITY

Three major components of the data acquisition process that affect the quality or reliability of 241-AN-106 sampling data are 1) sample handling, 2) chemical analysis of the samples, and 3) statistical analysis. All three affect the confidence we can place in the sampling results reported in Section 4.0. Each is discussed in the following.

5.3.1 Sample Handling

The sample handling procedures for 241-AN-106 are specified in Hammitt et al. (1989). These are used to ensure that the sample is properly labeled, safely transported to the laboratory, and correctly submitted for analysis. An inconsistency or error in these procedures could result in unreliable characterization data. For example, it is suspected that two samples taken from 241-AN-106 were switched when they were packed into pigs and loaded onto the sample truck (see Section 5.3.3). This suspicion stems from the observation that one sample had a lower density than samples taken at higher levels, contrary to the pattern in samples from other risers (see Section 4.1). However, there is no corroborating evidence to support this conjecture, so the data are used as reported. Other than this one example of suspect sample handling, all other evidence seems to show that the samples were labeled, transported, and submitted appropriately.

Waste samples were obtained from each riser of 241-AN-106 by means of a sampling method commonly called "Bottle On A String." With this method, a sample is obtained by the following sequence of steps. A stoppered sample bottle is lowered to the specified location within the tank, the stopper is removed (remotely), the bottle is allowed to fill, and the bottle is retrieved after a specified time.

With this type of sample retrieval method, questions are often raised about the representativeness of the sample. Specifically, there is a concern that solids that may be present in the waste could either fail to enter the bottle due to the size of the bottle opening and/or block the bottle opening so that only a partial sample would be retrieved. These concerns can only be addressed if there is an underlying knowledge about the consistency of the waste. Certainly, they would have to be answered on a tank by tank basis.

For 241-AN-106, the physical description of the waste indicates that no solids were present in the samples until the waste cooled to room temperature. Also the viscosity of the waste is similar to water, so there is little concern (for this tank) about partial filling of the samples.

Therefore, from the perspective of sample acquisition, the samples can be considered representative of the liquid wastes in 241-AN-106.

5.3.2 Chemical Analysis

The chemical analysis component of the data acquisition process presents two basic technical concerns: one for the temperature of the tank contents and the other for the quality of data on organics.

The concern for the temperature of the contents relates to 1) whether precipitates (crystals) form because of temperature differences between the tank and the analyzed samples and 2) whether the precipitates are appropriately accounted for in the chemical analysis. For 241-AN-106, precipitate (crystals) did appear when temperature decreased after sampling. When the sample was heated to 35° - 40° and agitated, the precipitates redissolved. This heated sample was then submitted for analysis. There was no evidence of undissolved solids in the samples that were analyzed.

Our concern about organic constituents in 241-AN-106 wastes is that there is not enough information to characterize them. Analytical procedures called for WHC to analyze the composite sample (only) for total organic carbon (TOC). If TOC was greater than 2 g/L, then a sample was to be submitted to the PNL laboratory in the 300 Area for additional analysis. When the samples were taken in 1989, the measured value (a mean of two subsamples) of TOC for 241-AN-106 was 3.26 g/L, so a 500 ml sample was subsequently sent to PNL. Only 4 organic compounds were detected in the sample during the PNL analysis. There is, however, concern that delay in analyzing the samples may have affected these results, even though we have no documentation that addresses the PNL delay in conducting the analysis and/or its effect on the organic analyses.

Additional concern is generated because acceptance criteria exist (see, for example, Table 8-3 in Hendrickson (1991) for many organic compounds for which there is no sampling data. Likewise, analyses have been performed for constituents that have no criteria. Finally, the data that do exist cannot be used to compute reliable confidence limits for measured compounds, because composite samples yield no information about in-tank variability and little information (1 degree of freedom) about analytical variability.

There is another, fundamental, concern about the organics that underlies this entire discussion. The concern has been raised about the appropriateness of the specific chemical procedure used in 1989 to analyze the samples for organics. The contention is that the analytical results we have are not representative of the organics that are currently in 241-AN-106. This highly technical chemistry issue is not addressed in this report.

5.3.3 Statistical Analysis

A statistical analysis of the 241-AN-106 sampling data is presented in Welsh (1991). Although we prefer a multivariate treatment of the sampling data, the overall analysis is adequate. Outliers and missing values were treated in a reasonable manner.

In the analysis, the wastes in 241-AN-106 were found to be layered and the data were stratified accordingly. Average concentrations and their corresponding variance estimates were calculated using methods that take this stratification into account. The calculations are consistent with the underlying sampling plan, which involved stratification to ensure that suspected waste layers were adequately sampled. Because the data confirm the underlying assumptions of the sampling plan (or at least do not show significant discrepancies in them), there is no reason to question the validity of the results.

Confidence intervals for constituent concentrations are presented in Welsh (1991): Each constituent was treated independently from all others. Confidence intervals presented in this report were also computed separately for each constituent, but intervals for all constituents are displayed together in a single plot. Although the methods used to calculate confidence intervals presented in this report differ from those used in Welsh (1991), the resulting differences in corresponding confidence intervals are small and do not lead to different conclusions.

For the profile plots and cluster analysis presented in Section 4.0, sampling data for all constituents were treated jointly. We believe that a multivariate approach offers certain advantages over a univariable approach. A multivariate treatment of the data is not only more comprehensive but makes it possible to present results in a more easily understood format.

Statistical analyses of the sampling data revealed the possibility that successive samples out of one riser (Riser 1B) may have been mislabeled. It is possible that the samples were switched when they were packed into pigs and loaded onto the sample truck (see Section 4.0). This suspicion stems from the observation that one sample had a lower density than samples taken at higher levels in the tank, contrary to the pattern in samples from other risers. There is no corroborating evidence to support this conjecture. It was the judgement of the grout team at the time the data were analyzed that this uncertainty did not have a significant effect on characterization results. We concur with that judgment.

6.0 GROUT FORMULATION

Of all the factors we have investigated, the greatest uncertainty by far involves the composition of the final grout waste form, which includes the dry blend formulation and the waste feed, and the properties it must possess. There must be sufficient experimental evidence that the current dry blend formulation will produce a grout with acceptable waste form properties when mixed with the waste feed. Studies that have been conducted in order to provide this evidence are summarized below.

6.1 EARLY EXPERIMENTS

A number of tests were conducted early in the grout program to ensure that the final grout product would possess certain "desirable" properties. Note that these experiments were carried out before formal acceptance criteria were developed. Some of these experiments are described in Section 6.0 of Hendrickson (1991). One was a laboratory-scale study to 1) characterize the ability of phosphate-sulfate grout to resist leaching of waste constituents to groundwater and 2) identify mechanisms that control leach rates and adsorption potential (Serne et al. 1987). The study used actual N-reactor phosphate wastes and simulated sulfate wastes in a 3:2 ratio. The dry blend formulation was composed of portland Type I and II cement (41 wt%), Class F fly ash (40 wt%), attapulgite clay (11 wt%), and indian red pottery clay (8 wt%).

A pilot-scale study was conducted in July 1986 to evaluate grout properties that will affect processability and to provide a preliminary indication of "large" scale grout properties such as leachability, compressive strength, and drainable liquids (Fow et al. 1987, Lokken et al. 1988). Equal volumes of phosphate and sulfate wastes were used in the study. The dry blend formulation was composed of portland cement (41%), Class F fly ash (40%), attapulgite clay (11%), and illitic clay (8%). This study provided information on the flow characteristics (acceptable) and density (1.3-1.4 Kg/L) of the unsolidified grout mixture as well as results of TCLP leachate analysis (within limits) and compressive strength measurements (258-441 psi) of the cured grout. Drainable liquid ranged from 3.6 to 16.4 percent (by volume).

A laboratory study of the leaching characteristics of 14 constituents of 241-AN-106 wastes was conducted in 1989 (Serne et al. 1989). For this study, the dry blend formulation was composed of portland type I-II cement (5 wt%), class C fly ash from Centralia, Washington (47.5 wt%), and ground blast furnace slag (47.5 wt%). Similar studies for simulated DSSF wastes (Serne 1990, Lokken et al. 1989[a]) were conducted with a dry blend formulation composed of type I-II portland cement (6 wt%), fly ash (47 wt%), and blast furnace slag (47 wt%).

(a) Draft report, Lokken, R.O., P.F.C. Martin, J.W. Shade, 1989, Characterization of DSSF Grout Produced in a Pilot-Scale Test, Pacific Northwest Laboratory, Richland, Washington

In both tests, grouts exceeded waste form leachability criteria. Leachability, toxicity, and compressive strength (phosphate-sulfate waste only) tests were conducted on solidified grout made from phosphate-sulfate, 241-AN-106, and simulated DSSF wastes. Results exceeded suggested NRC criteria.

It is noteworthy that no two of these studies used the same dry blend or the same waste composition. While these studies provided useful preliminary information, they are unrelated to each other, and therefore do not provide defensible evidence that important grout properties will be obtained at acceptable levels.

6.2 HEAT GENERATION

It is claimed (Fow et al. 1987) that grout will have acceptable properties when the peak cure temperature is kept below 100°C. Consequently, WHC set their peak temperature criterion at 90°C, giving a 10°C safety margin. No basis for this choice is given.

The main source of heat are hydration and radiolytic decay. Variations in concentration of waste feed constituents (e.g., aluminum) lead to variations in the rate of hydration, which in turn produce uncertainties in the peak cure temperature. Thermal conductivity and thickness of the grout and vault material also affect the peak temperature; indeed, the thermal conductivity of the grout may be the most critical factor affecting the rate of cooling and hence the peak temperature.

It is stated in Hendrickson (1991) that the isotopic mix in the waste stream must be controlled to ensure that the peak temperature will not be exceeded. A similar statement is made about the total concentration of alpha-emitting radionuclides. Relative to the heat of hydration, it is not clear to us what effect these constituent have on the curing rate and peak temperature.

6.3 STATISTICALLY DESIGNED EXPERIMENTS

Several statistically designed experiments have been completed using simulated 241-AN-106 waste to determine the acceptability of the grout product properties. We believe the simulated waste used in these experiments has been formulated at concentrations expected in the combined waste from 241-AN-106 and the heel of the grout feed tank, 241-AP-102. We have not found any documentation to support this statement. Each of the experiments is described below, with important limitations.

Westinghouse Factorial Experiment. A factorial experiment was designed by Westinghouse in 1990 to determine the effects of the variability of the waste feed on grout properties. The dry blend formulation used for this experiment consisted of 40% limestone, 28% slag, 28% fly ash, and 4% cement. Five constituents of the waste were identified as being important to the grout product, and these were varied in a factorial design to cover expected variations in the waste stream. The remaining waste constituents were held constant throughout the experiment. The dry blend formulation was not varied.

The results from this experiment have not been formally released. However, the results are of questionable utility because the current dry blend formulation has been modified so that limestone is no longer a candidate material. This change is expected to alter the properties of the final grout product, so the results of this experiment will not be representative of the 241-AN-106 campaign. At best, an extrapolation of the results from this experiment to the 241-AN-106 campaign would be questionable.

Mixture Experiment at Oak Ridge National Laboratory (ORNL). A mixture experiment approach was taken by Oak Ridge National Laboratory staff (this work was paid for by WHC and supported by PNL) to determine a dry blend formulation for the 241-AN-106 campaign. The idea was to use a constant simulated 241-AN-106 waste while the levels of four dry blend materials (cement, fly ash, slag, and attapulgite clay) were varied. Levels of the dry blend materials that produce and acceptable grout were identified in experimental results and modeled to determine a region of acceptable dry blend formulations.

The results from this experiment are currently in review at WHC. The results indicate there are several dry blend formulations that will produce acceptable grout product properties according to the product criteria as they are currently interpreted. One of these formulations has been chosen as the final 241-AN-106 dry blend formulation. The limiting factor for these experiments appeared to be the leachability index. One drawback of this experiment is that it used a cure temperature of 90°C. This temperature is thought to be too high to get reliable results for leachability and compressive strength. Again, any direct interpretation of these results should be done with great care.

Pilot-Scale Run. A pilot-scale test was conducted at PNL under the direction of WHC to determine the effect on grout properties of the variability inherent in large-scale processing. A formal design was not used for this pilot-scale run. The final dry blend formulation from the mixture experiment above was used with simulated 241-AN-106 waste. The dry blend formulation was adjusted part way through the run because of pumping problems that resulted from a high critical flow rate. The resulting formulation was still in the range for acceptable grout from the mixture experiment.

Cores from the grout product from the pilot-scale run have been sent to the laboratory for analysis. These analyses have not yet been completed. This data, when obtained, can be used to determine if the grout has properties that meet the specified criteria.

Formulation Verification at PNL. A factorial experiment is being conducted at PNL to test the final dry blend formulation for 241-AN-106 waste. Dry blend compositions are being varied over small ranges and the dilution factor for the simulated waste is being varied over +/-15%. Moreover, the curing temperature problem from the ORNL experiment was corrected. This experiment is meant to be a final check of the dry blend formulation over the expected range of variability due to processing. In a limited way, this experiment addresses the effects of varying both the dry blend formulation and waste concentrations.

Preliminary results from this experiment have been submitted to Westinghouse. The result of greatest interest is the wide variability in compressive strength that seems to be directly tied to the dilution factor of the simulated waste. Formal analysis of the data has not been completed. Leachability data have not yet been obtained for this experiment. Final results of this experiment should provide a good indication of the viability of the grout product properties over the range of variability expected in waste feed stream and in the dry blend mix.

In summary, these experiments do not provide sufficient statistical evidence that an acceptable grout product can be made with the current dry blend formulation, given the expected variability in the waste and the dry blend. There are, however, several sources of data (not yet formally analyzed) that can be used to decide whether a viable grout product can be made during the 241-AN-106 campaign. It is the professional opinion of many scientists associated with the grout project that an acceptable grout can be made with the current formulation, but we do not yet have solid statistical evidence to support this opinion.

7.0 CONCLUSIONS AND RECOMMENDATIONS

This section contains a summary of major conclusions, together with recommendations for dealing with unresolved issues.

7.1 CHARACTERIZATION

Acceptability is defined in terms of performance criteria for the final grout product. These criteria must be translated into feed acceptance criteria which, in turn, determine the degree of characterization that is required for 241-AN-106 wastes. Because 241-AP-102 wastes are more dilute than those in Tank 241-AN-106, it is conservative to apply acceptance limits directly to the wastes in 241-AN-106. The results of Section 4.0 reveal that the following 241-AN-106 waste constituents meet the acceptance criteria given in Table 8-3 of Hendrickson (1991): aluminum, calcium, chromium, phosphorus (no limit given), potassium, sodium, chloride, hydroxide, nitrate, sulfate, and cesium-137. Comparisons are unclear for carbonate, nitrite, and phosphate. When the relative volumes of the wastes in the two tanks are taken into account, it appears that only carbonate and phosphate exceed waste feed acceptance criteria.

The characterization of 241-AN-106 wastes is generally adequate, provided that we assume that the final feed acceptance criteria will not be materially different from those in Hendrickson (1991). We conclude, therefore, that there is little to be gained from additional efforts to characterize 241-AN-106 wastes. This conclusion is based solely on the constituents analyzed in Section 4.0 and not on the entire suite of analytes identified in Hendrickson (1991) as having regulatory or performance significance. The implicit assumption is that both unsampled constituents and sampled constituents whose concentrations fell below detection limits can be ignored.

It was pointed out in Section 5.2 that the sampling plan for characterizing 241-AN-106 wastes was not driven by any well-defined criteria (such as measurement precision) or data quality requirements and that acceptance criteria were derived from sampling results rather than vice versa. With this approach, it is impossible to tell *a priori* how well a given constituent will be characterized. It is fortuitous that the characterization results for 241-AN-106 came out so well. However, for future tanks, characterization sampling should be driven by requirements to guard against (ensure appropriate characterization) the possibility of a less fortunate outcome.

It is not clear to us how important organics are in the grout process. There is some feeling that small concentrations of organics can have a significant effect on the performance properties of the final grout product. However, the attention paid to organics in the characterization of 241-AN-106 is not consistent with this concern. The importance of characterizing for organics generally, and for specific organics in particular, should be resolved.

7.2 TRANSFER

There are several issues related to the transfer of 214-AN-106 wastes to 241-AP-102. One concern is the formation of solids, either during transfer operations or during initial stages of mixing in 241-AP-102. A more serious concern is whether the 241-AN-106 wastes, when transferred and mixed with those in 214-AP-102, will form an adequate grout.

Formation of Solids. Formation of crystallization gels during the transfer of 241-AN-106 wastes is a concern because of the possible formation of gels that resist movement, thereby limiting resuspension and subsequent dissolution of the material. Indeed, because of the problems with the formation of solids in the evaporation process, the amount of evaporation of 241-AN-106 wastes was limited. Therefore, the wastes in 214-AN-106 are actually more dilute than those in tanks that contain slurry feed wastes. In laboratory samples of 241-AN-106 wastes, solids were observed at temperatures below approximately 35°C. When samples were heated to 35°-40° and agitated, the solids redissolved.

A plan has been developed by WHC to transfer material [illegible] 241-AN-106 to 241-AP-102 that preserves the existing layering and minimizes mixing (and therefore the potential for crystallization) during transfer. The idea is to transfer the wastes off the floor of 241-AN-106 so that the lower (sulfate layer) is transferred first. Because of density differences in the two waste layers, this strategy is expected to largely maintain their relative positions in 241-AP-102.

To avoid crystallization problems after transfer, a plan has been developed to heat the wastes in 241-AN-102 with a deep-well jet mixing pump. At 150 hp (381,372 BTU/hr), the pump is capable of increasing the temperature of 1 megagallon of water by 0.61°C/day (=1.1°F/day). The high velocity and floor sweeping actions of the mixer pump are expected to adequately suspend the gel particles until temperatures become high enough for the solids to redissolve. The main concern with the use of the mixer is how long it will continue to work, particularly if it is damaged by crystallization in the mixed wastes. A replacement pump has been ordered as a backup, but it is not yet available.

Grout Adequacy. It is highly undesirable to transfer the contents of 241-AN-106 until we are confident that they will form an acceptable grout. Target properties have been defined for the final grout waste product Reibling and Fadeff (1991). However, the relationships that link these properties to waste feed acceptance criteria to ensure that formulation requirements are met have not been adequately developed. Consequently, there is some risk that the 241-AN-106 wastes will prove inadequate for making an acceptable grout.

There are two alternatives in case the combined wastes of 241-AN-106 and 241-AP-102 do not set up in tests of grout adequacy. One is to treat the wastes in some manner (e.g., by dilution, for example[(a)]) to make it acceptable. The alternative is that the material in the feed tank (241-AP-102) will have to be transferred to another tank. This alternative will obviously require more tank-related operations, such as pumping and flushing. We have not addressed the costs or potential safety issues associated with these operations. This alternative is not desirable, but it does not appear to pose major technical difficulties.

A concern was voiced to us that if, after transfer, it was discovered that 241-AN-106 wastes did not produce an acceptable grout, then the wastes would have to be pumped out of 241-AP-102 and that tank would have to be abandoned as a feed tank. We do not view this as a serious concern. Tank 241-AP-102 already contains 50,000 gallons of low level phosphate-sulfate wastes of the type in tank 241-AN-106. Thus, phosphate-sulfate wastes will be a factor in every future campaign conducted from 241-AP-102, regardless of the decision to transfer 241-AN-106 wastes.

We believe that process/procedural concerns (solids formation) are secondary to questions of grout adequacy. Based on comparisons of the characterization results presented in Section 4.0 with grout feed acceptance criteria given in Table 8.3 Hendrickson (1991) we believe that the risk is small that 241-AN-106 wastes will prove unacceptable for grout. Moreover, the relationships between grout formulation requirements and feed acceptability criteria (that determine the degree of characterization required) cannot be definitively tested until after the wastes have been transferred. In summary, we find no compelling reasons to hold up the transfer of the 241-AN-106 wastes to 241-AP-102. It is, therefore, our recommendation that the transfer proceed as planned.

7.3 ACCEPTANCE CRITERIA

Acceptance criteria have been developed by WHC for the grout waste form and the waste feed (Hendrickson [1991], Riebling et al. [1991]). These criteria have been established to ensure that the grout waste form possesses the necessary physical/chemical properties to meet applicable regulations. The criteria given in Hendrickson (1991) and Riebling et al. (1991) are used to reach the conclusions about the adequacy of 241-AN-106 waste characterization presented in this report. However, these criteria have not been formally adopted by DOE. Indeed, some are still subject to change pending the outcome of formulation experiments. Until all necessary (present or future)

(a) However, the practicality of this alternative may be severely limited by the capacity of tank 214-AP-102 . The maximum operating capacity of this tank is 1140 kgal and the after-transfer waste volume will be in excess of 1120 kgal.

formulations experiments have been completed and the criteria are formally adopted, any conclusion presented in this report or elsewhere must be considered subject to change.

We appreciate the extensive analysis that went into the preparation of acceptance criteria. However, in addition to the basic problem described above, some difficulties remain. First, the basis for many of the criteria is either weak or obscure. It is often unclear whether a particular limit is driven by performance or regulatory constraints. Such obscurities should be clarified.

Based on Fow et al. (1987), a limit of 90°C has been set for the peak cure temperature. The claim is that this limit gives a 10°C safety margin for developing acceptable grout. However, no quantitative basis is given for the limit. Moreover, the peak temperature can be controlled either by means of performance limits (e.g., limiting the isotopic content of the waste) or engineering practices (such as how the grout will be poured into the vault). The extent to which heat will be treated as a performance issue rather than an engineering issue should be resolved.

As shown in Figure 10, criteria may apply to either the disposal system (vault), the waste form (grout) or the waste feed (combined contents of 241-AN-106 and 241-AP-102). It is often unclear how criteria that apply at one point in the process are related to those that apply at other points. What is the effect, for example, on the concentration limit for a 241-AN-106 radionuclide of a limit imposed on the vault? Relationships among these groups of criteria should be clarified.

Other difficulties exist. There are discrepancies between the list of 241-AN-106 analytes and the list of constituents for which feed criteria are given. For example, limits are given for boron, but boron concentrations were not determined (see Hendrickson [1991] and Welsh [1991]). Such discrepancies should be resolved. If regulated constituents are not sampled, for example, the reasons should be documented and they should be eliminated from the list of performance criteria.

Because the consequences of not meeting regulatory criteria and performance criteria are certainly different, we recommend that performance and regulatory criteria be given separately, possibly in two tables. One table should contain the analytes and their process constraints; the other should contain the analytes and their regulatory limits. In preparing the recommended tables, the criteria should be ranked in terms of importance. At a minimum, analytes that are most sensitive or of greatest concern should be identified. These, together with corresponding acceptance limits, should be presented in a "short list" that distinguishes them from analytes of lesser concern.

We have noted that the basis for current acceptance criteria is weak. Ideally, grout performance criteria will be based on the results of well-defined experiments involving the target grout and waste feed compositions. These experiments should take into account processing variability in the waste feed and t[illegible] blend feed streams. No experiments have been conducted that deal jointly [illegible] variability in two feed streams. The lack of this vital information represents a serious weakness in the technical basis for performance criteria. A high priority should be place on conducting the experiments needed to provide this vital information.

As noted in Section 5.1.2, the sampling results from 241-AN-106 were used to drive the development of acceptance criteria, whereas ideally it should be the other way around. For other tanks, it should be a high-priority programmatic objective to establish acceptance criteria <u>before</u> characterization sampling is undertaken. The data quality objectives (DQO) process being developed by DOE/ERWM represents one promising way to develop adequate acceptance criteria. To be successful, the process must be guided by suitable formulation experiments.

7.4 GROUT FORMULATION

Of all the factors we have investigated, the greatest source of uncertainty in the grout program involves the formulation of the final grout waste form and the properties it must possess. Studies involving grout properties and grout formulation are summarized in Section 6.0.

Each of the experiments is limited in some way or another. Experiments that were conducted early in the grout program were used to demonstrate that the grout would possess "desirable" properties. It is noteworthy that no two of these studies used the same dry blend formulation or the same waste composition. None can provide defensible evidence that important grout properties will be obtained at acceptable levels.

Several statistically designed experiments have been completed using simulated 241-AN-106 wastes. In a Westinghouse designed factional experiment, the dry blend formulation (which is significantly different from the current reference formulation) was held constant while the effects of variability in the waste was determined. The results of that experiment are of questionable utility because of dry blend formulation. A mixture experiment conducted at ORNL used a constant waste stimulant and varied the dry blend materials. However, these results must be viewed with caution due to a high curing temperature.

To date, only one experiment has been conducted in which both the dry blend formulation and the waste feed were varied jointly (see Section 6.3, "Formulation Verification at PNL"). In this experiment, the dry blend is varied by ±5% of its target formulation and the waste composition is varied by ±15% of expected dilution. However, analysis of the results of this experiment has not yet been completed, and it has not been demonstrated that the range of experimental conditions will actually bracket the conditions expected in practice (although it should be close). In summary, these experiments do not provide sufficient evidence that an acceptable grout product can be made with the current dry blend formulation, given expected variability in the waste and the dry blend feed streams.

It is the professional opinion of many scientist associated with the grout project that an acceptable grout can be made with the current formulation, but we do not yet have solid statistical evidence to support this opinion. Until we acquire the experimental evidence necessary to support this opinion, other key aspects of the grout program, such as waste feed acceptance criteria, cannot be finalized.

We recommend that testing needed to resolve grout adequacy questions be undertaken as soon as 241-AN-106 waste is transferred to 241-AP-102. The tests should be statistically designed. Moreover, they should use the target dry blend formulation and expected waste feed composition, both of which are varied jointly over the compositional ranges expected during processing. Insofar as possible, these tests should be conducted under actual operating conditions.

7.5 OTHER

In addition to the major issues discussed in Sections 7.1-7.4, a number of secondary points are raised or reemphasized in this section.

Less-Than Values. In Welsh (1991), sampling results are given for 32 constituents of 241-AN-106 wastes. Many of these observations--in fact, a majority--are reported as "less than" values, meaning that the observed concentration fell below some detection limit. As a result, enough observations to carry out the analyses in Section 4.0 were available for only 14 constituents. Because only "less than" values were reported for all other observations, the potential information they contain is irretrievably lost. It must be understood that, even though individual observations may fall below detection limits, in aggregate they contain valuable information.

The practice of recording "less than" values for individual measurements should be abandoned. This practice contributes more to the loss of information and the increase in uncertainty than any other step in the analytical process. When data are truncated in this manner, it is impossible to obtain unbiased parameter estimates. Perhaps more serious is the fact that when "less than" values are replaced by their detection limit (a common practice), variances may be seriously underestimated. A practical consequence is that we may conclude that wastes are adequately characterized, when in fact they are not. In a forthcoming paper, Prof. Noel Cressie of Iowa State University, one of the world's foremost statisticians, gives a technical justification supporting this recommendation.[a]

Detection Limits versus Acceptance Limits. Samples of 241-AN-106 wastes were analyzed for 33 inorganic constituents. Of these, 19 were not observed at concentrations greater than detection limits. By omitting these 19 consti-

(a) N.A.C. Cressie. 1992. "Spatial Chemostatistics." Preprint Number 92-15, Iowa State University Department of Statistics, Ames Iowa. See especially Section 4.

tuents from the analysis, it is implicitly assumed that they are insignificant, both individually and in aggregate, for determining grout acceptability. This is true only if detection limits are significantly less than acceptance limits. The two limits should be compared for each constituent that is observed only at concentrations below its detection limit. Even when the comparison is made, however, there is no information to quantify the degree of significance unless actual values have been recorded.

Sampling Plans. A good and efficient (in terms of minimal sample size) statistical sampling plan is designed to answer a specific question. Moreover, sampling results are defensible only insofar as they relate to the sampling objective. Since no characterization criteria were used to design the 241-AN-106 sampling plan, it is fortuitous that the plan worked as well as it did. The value of experiments, such as those involving grout and waste properties, can be greatly improved if 1) sampling objectives are clearly spelled out before the experiment is conducted and 2) sound principles of statistical design are used to ensure that the experiment will meet the stated objectives. This point is especially relevant to the design of future formulation experiments that take into account expected variability in both the waste feed and grout feed.

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