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September 2006

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Assessment of New Calculation Method for Toxicological Sums-of-Fractions for Hanford Tank Farm Wastes

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September 2006

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Summary

The toxicological source terms used for potential accident assessment in the Tank Farms DSA are based on toxicological sums-of-fractions (SOFs) that were calculated in fiscal year 2002 and fiscal year 2003 based on the Best Basis Inventory (BBI) from May 2002, using the method described by Cowley et al. (2003). The present report describes a modified SOF-calculation method that is to be used in future toxicological updates and assessments and compares its results (for the 2002 BBI) to those of the old method.

In the old method, the Environmental Simulation Program, ESP[1], a chemical thermodynamic simulator, was employed on a tank-by-tank basis to determine the identities and the liquid- and dry-solid-phase concentrations of the chemicals in which the BBI analytes would be present at chemical equilibrium. The concentrations used as ESP input were the average composition of the waste in the tank, as calculated from BBI data, in effect assuming that all layers were completely mixed together. The composition predicted by ESP was used as the basis for the toxicological source term.

The new method does not process the BBI data through ESP. It uses the analyte concentrations and phases given in BBI for each layer[2] in the tank waste and assigns a chemically plausible compound to each analyte, based largely on the prevalent compounds predicted by ESP in the old method for the 2002 BBI. Each analyte is assigned the same compound in all tanks; therefore, the new methodology does not include the whole set of compounds in which an analyte might appear. To the extent that different compounds appear in different tanks and that these compounds have different toxicities, any given analyte may be represented in a more or less toxic fashion than in the old method. To conservatively account for variation in composition within a tank and to match the method used in radiological calculations, the SOFs that are used to represent each tank are the maximum SOFs over all the layers (liquid or wet bulk solids).

This study focuses on the replacement of ESP modeling by the direct use of BBI data. The method comparison therefore considered only the handling of the primary BBI analytes that were originally modeled using the ESP code (Ag, Al, Bi, Ca, Cl, Cr, F, Fe, Hg, K, La, Mn, Na, Ni, NO_2, NO_3, free OH, Pb, PO_4, Si, SO_4, Sr, TOC, U, and Zr), not the "trace" analytes. The discussion of the contributions of "trace" analytes is deferred to another document (Meacham et al. 2006). The new and old methods were compared on the basis of the same inventory (May 2002 BBI) and the same chemical toxicity data (Rev. 21A of TEEL-1, TEEL-2, and TEEL-3), ensuring that all differences in results were caused by method changes alone.

In 50 to 60% of the Hanford tanks, the new-method SOFs were within ±20% of the old method, while 15 to 20% of the tanks showed a difference of more than ±50%. The SOFs were increased by the new method more often than they were decreased. These statements hold for both the liquid and wet bulk solids SOFs. Thus, less than 10% of the tanks had SOFs that decreased (and therefore are possibly nonconservative) by more than 50%. For perspective, an uncertainty of 20% in analyte concentrations is a reasonable expectation for compositions based on sample measurements, considering the uncertainties

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[1] The Environmental Simulation Program (ESP) is a registered trademark of OLI Systems, Inc., Morris Plains, New Jersey.

[2] Here "layers" has the same meaning as the word "components" that is used in BBI terminology.

in sample concentration and density analyses and the variability of concentration within the waste. The overall uncertainty might be considerably greater in tanks that have not been sampled.

A detailed though semi-quantitative study was made to learn the reasons for method-related changes in SOFs at TEEL-3. This TEEL level was chosen because new-method SOFs differed from old-method values somewhat more than at the other TEEL levels. Three aspects of the change in SOF calculation method were the causes of significant changes (those exceeding 30%) in liquid-phase SOFs for TEEL-3:

- In 16 of the 24 tanks in which significant increases occurred, the primary cause was differences between the ESP-predicted and BBI solubilities of analytes (most often NO_3, NO_2, OH, and Al). This was also the primary cause of the major decreases in liquid SOFs, which occurred in 14 tanks.

- In 3 of the tanks in which significant increases occurred, the primary cause was the use of analyte concentrations from the maximum-SOF layer instead of the tank-average waste.

- In 5 of the tanks in which significant increases occurred, the primary cause was the increase in the effective toxicity of TOC that resulted from using oxalate to represent all TOC.

Several aspects of the change in SOF calculation method were the causes of significant changes (those exceeding 30%) in wet bulk solid SOFs for TEEL-3:

- In 37 of the 45 tanks in which significant increases occurred, the primary cause was the use of the concentrations of the layer that had the maximum SOF in the tank instead of the tank-average waste.

- In all 5 of the tanks in which significant decreases occurred and in one of the tanks that showed an increase, the primary cause was solubility changes (ESP versus BBI).

- In 4 of the tanks in which significant increases occurred, the primary cause was an increase in the effective toxicity of lead because of its assignment to the compound lead hydroxide.

- In 2 of the tanks in which significant increases occurred, the primary cause was an increase in the effective toxicity of TOC because of its assignment to oxalate.

- In one of the tanks in which significant increases occurred, the primary cause was adjustments made to the ESP compositions in the old method.

Taking the results for liquid and wet bulk solids SOFs together, it is clear that the use of the maximum-layer approach was the dominant reason why the new method calculated different (in particular, larger) SOFs than the old. This maximum-layer approach was chosen to be consistent with the approach used in calculating ULDs for radiological assessments, and led to a change in the direction of conservatism. Differences between ESP and BBI solubilities were the next most common reason for differences between new and old SOFs, particularly in the liquid phase. The solubility-related changes in SOF were roughly equally distributed between increases and decreases. Changes in the effective toxicities of TOC and lead were the third most common reason. These toxicity changes increased SOFs and so were in a conservative direction.

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Acronyms and Abbreviations

BBI	Best Basis Inventory
BBI-S	Best Basis Inventory – Supplemental
DST	Double-shell tank
EDTA	Ethylenediaminetetraacetate
HEDTA	Hydroxyethylethylenediaminetriacetate
SOF	Sum of fractions
SST	Single-shell tank
TCD	Tank Characterization Database
TEEL	Temporary Emergency Exposure Limit
TIC	Total inorganic carbon
TOC	Total organic carbon
ULD	Unit liter dose

1.0   Introduction

The toxicological source terms used for potential accident assessment in the Tank Farms DSA is based on toxicological sums-of-fractions (SOFs) that were calculated in FY02 and FY03 based on the Best Basis Inventory (BBI) from May 2002, using the method described by Cowley et al. (2003). The present report describes a modified SOF-calculation method that is to be used in future toxicological updates and assessments, gives its basis, and compares its results (for the 2002 BBI) to those calculated by the old method.

In the old method, the Environmental Simulation Program, ESP[1], a chemical thermodynamic simulator, was employed on a tank-by-tank basis to determine the identities and the liquid- and dry-solid-phase concentrations of the chemicals in which the BBI analytes would be present at chemical equilibrium. The concentrations used as ESP input were the average composition of the waste in the tank, as calculated from BBI data, in effect assuming that all layers were completely mixed together. ESP predicted concentrations of chemicals in the solid and liquid phases, and drew no distinction between supernatant and interstitial liquids. SOFs derived from ESP solids were consequently for dry solid, not wet bulk solids (which incorporate interstitial liquid). The liquid and dry-solid concentrations of ESP-predicted compounds then were input to the "SOF Program," which converted ions into compounds as necessary and paired the chemical composition data with toxicological parameters to obtain the toxicological source terms. The toxicological parameter chosen in RPP-8369 is the Temporary Emergency Exposure Limit (TEEL), developed and periodically updated by DOE Subcommittee on Consequence Assessment and Protective Actions (SCAPA).[2] There are four TEEL levels, TEEL-0, -1, -2 and -3, defined as the airborne concentrations of a chemical that could be expected to have certain human health consequences. The SOF is simply the sum over all chemicals of the dimensionless ratio of concentration divided by the appropriate TEEL. Revision 19 of the TEELs was used by Cowley et al. (2003).

The new method does not process the BBI data through ESP. It uses the analyte concentrations and phases given in BBI for each layer[3] in the tank waste and assigns chemically plausible compounds to each analyte, based largely on the most prevalent compounds predicted by ESP in the old method for the 2002 BBI. The compound assignments are the same for all tanks. The new methodology includes, not the whole set of compounds in which an analyte might appear, but only the commonest compounds or those that are toxicologically representative of a group of compounds that contain a common analyte. In the new method the basis for the solid phase has been changed to wet bulk solids, a basis that is consistent with BBI usage and with the radiological source term used in the DSA. The SOFs that are used to represent each tank are the maximum SOFs over all the layers (of the appropriate phase) that are present.

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[1]   The Environmental Simulation Program (ESP) is a registered trademark of OLI Systems, Inc., Morris Plains, New Jersey.

[2]   TEELs set the maximum allowable airborne concentrations of compounds (DOE 2006). TEEL-0 is the concentration at or below which it is believed that nearly all individuals could be exposed without experiencing other than mild transient adverse health effects or perceiving a clearly defined, objectionable odor. At the other end, TEEL-3 is the concentration below which it is believed that nearly all individuals could be exposed without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.   The TEEL level that is appropriate in evaluating accident consequences is selected based on the probability of the accident. There is some ambiguity regarding the name of the current version of TEELs. They were obtained from a website that calls them "Revision 21" but the spreadsheet of TEELs is called "TEELs_Rev21A_publ.xls". In this report this set of TEELs is referred to as Rev. 21A.

[3]   Here "layers" has the same meaning as the word "components" that is used in BBI terminology.

The object of this report is to provide a detailed description of the new method that is to be used for the 2006 BBI, compare the SOF predictions to those made by the old method, and explain the reasons for the differences. The report focuses on the replacement of ESP modeling by phase data available in the BBI and a simplified, reasonably universal set of chemical equations. This report is limited to those chemicals, primarily the 25 BBI constituents, that were previously addressed by ESP in the old method. Trace constituents, defined here to be any chemical not considered a primary waste constituent in the BBI, are not addressed here. Two exceptions to this are silver and hydroxide; the former because its solid/liquid distribution was determined by ESP in the old method (though it is not a primary BBI constituent), and the latter because it is an extremely important factor in the waste chemistry and its toxicity.

Section 2 of this report describes the old and new methods in more detail. The important differences between the methods are detailed in Section 3. In Section 4, the results given by the two methods are compared. Section 5 contains the conclusions and Section 6 the references. The chemical equations used by the new method are in Appendix A, together with an explanation of them. Appendix B provides the rationale for the choice of compounds to be assigned to each analyte in the new method. Appendixes C and D contain tabulations of OH^- and NO_2^- concentrations and of solid volume fractions in wet bulk solids.

2.0   Overviews of Old and New Methods

2.1   Overview of Old Method

The study done by Cowley et al. (2003) used the tank-average Best Basis Inventory (BBI) concentrations of major analytes, with ESP modeling of the most significant analytes, to produce SOFs for the liquid and dry solid phases. Figure 2.1 is a flowchart of the old method.

The concentration inputs used by the old method were the following:

- The calculation details files of the May 2002 BBI provided the tank-average concentrations of the major analytes in each tank's waste (TWINS 2002). These included the non-radioactive species in the BBI (Al, Bi, Ca, Cl, Cr, F, Fe, Hg, K, La, Mn, Na, Ni, NO_2, NO_3, Pb, PO_4, Si, SO_4, Sr, U, and Zr) as well as Ag and Cs (the latter being based on Cs-137). Hydroxide was not taken from any BBI data; rather, it was calculated by the ESP model as part of the charge and mass balance.

- Trace analytes (including a number of other inorganic species, organic anions, and organic compounds) were obtained from one of three sources, in decreasing order of preference:

  - The calculation details files of the supplemental May 2002 BBI (BBI-S);

  - tank characterization database (TCD) consolidated sample analysis results available from TWINS in May 2002; and

  - default concentrations that were established for the three tank classes (DSTs, 100-series SSTs, and 200-series SSTs) by taking the maximum concentrations found in BBI-S or TCD for any member of the tank class.

Spreadsheets were used to set up the inputs to the ESP chemical thermodynamic simulator. In these spreadsheets, the soluble concentration of Cr was used to calculate the split of Cr between the more toxic and more soluble Cr(VI) and the less toxic and less soluble Cr(III). The soluble concentration of TOC was used to calculate the split of TOC between soluble acetate and much less soluble oxalate.

The BBI-based tank-average concentrations of major analytes (in $\mu g/g$) and the BBI-derived splits for Cr and TOC supplied the input to the ESP model, which predicted the phase concentrations of the numerous compounds and ions that would be formed by the analytes at chemical equilibrium. (Note that oxidation states were frozen; i.e., redox equilibrium was not modeled.) The phases for which ESP provided output were the dry solid (containing no interstitial liquid) and the liquid. ESP also calculated the OH ion concentration in the liquid and the amounts and densities of each phase that were chemically consistent with the average waste composition. In some cases, where the predicted OH/pH differed substantially from the expected or measured value, the charge balance in the ESP inputs was adjusted iteratively, by spreadsheet calculations, to make the model predictions match the measurements more closely. Trace analytes were not modeled by ESP.

When ESP modeling was complete, the Visual Basic software "SOF Program" (version 1.2) converted the ESP-predicted compounds and ions to the most chemically similar compounds for which toxicological parameters were available. This conversion used a large set of stoichiometric chemical equations that maintained the species mass balances. (These equations can be found in Tables C.3 and C.4 of Cowley et al. [2003]) Because ESP tended to underpredict the solubility of NO_2 (putting some of it into the solid

```
                    ┌─────────────────────┐
                    │     BBI data:       │
                    │   Major analytes    │
                    └─────────────────────┘
                              │
                              ▼
          ┌───────────────────────────────────────┐
          │       Preprocessing Spreadsheet       │
          │ Generate inventory-average concentrations; │
          │     Convert Cr to Cr(III) and Cr(VI);  │
          │    Convert TOC to oxalate and acetate; │
          │          Initial charge balance;       │
          │   Format concentration data as ESP input │
          └───────────────────────────────────────┘
                              │
                              ▼
     ┌──────────────────────────────────────┐   ┌──────────────────────────┐
     │             ESP Simulator            │   │ Inorganic and organic trace │
     │  Balance charges, defining OH concentration; │ │ concentrations for liquid and │
     │  Balance mass, defining water concentration; │ │   solid phases based on     │
     │ Determine concentrations of complexes and │ │      BBI-S, TCD, and        │
     │  compounds in the liquid and solid phases │ │    tank-class maxima        │
     └──────────────────────────────────────┘   └──────────────────────────┘
```

Preprocessing Spreadsheet
Generate inventory-average concentrations;
Convert Cr to Cr(III) and Cr(VI);
Convert TOC to oxalate and acetate;
Initial charge balance;
Format concentration data as ESP input

ESP Simulator
Balance charges, defining OH concentration;
Balance mass, defining water concentration;
Determine concentrations of complexes and
compounds in the liquid and solid phases

Inorganic and organic trace
concentrations for liquid and
solid phases based on
BBI-S, TCD, and
tank-class maxima

Control inputs:
Long set of chemical equations;
TEELs;
tank ID

SOFProgram

Outputs:
SOFs;
Concentrations of compounds;
Documentation of inputs

Figure 2.1. Flowchart of Old SOF Calculation Method

phase) and overpredict the solubility of Hg (putting too much into the liquid phase), the SOF Program chemical equation inputs were also used to put all NO_2 in the liquid phase and all Hg in the solid phase. SOF Program also drew upon spreadsheet-based inputs of the trace analyte concentrations and converted these into appropriate compounds, based on chemical equations in the SOF Program inputs.

Finally, SOF Program used all the converted compound concentrations to calculate the SOFs in each phase for each tank and produced a summary table of the SOFs for the average dry-solid and aqueous liquid phases in all tanks.

For completeness, it should be noted that Cowley et al. also calculated SOFs for separated organic liquid layers in tanks 241-C-103, C-106, and AY-102 based on information from several sources. Headspace vapor SOFs were determined as well, based on data from the TCD. These did not involve ESP (nor was the SOF Program used to calculate these SOFs) and they are not considered further in this report.

2.2   Overview of New Method

The new method starts from the Best Basis Inventory (BBI) concentrations of major analytes in each layer, assigns each analyte to the compound considered most likely to contain it (taking chemical plausibility and toxicological conservatism into account), calculates SOFs for all the layers in the tank, and then selects the maximum layer SOFs to represent the liquid and wet bulk solid phases. Figure 2.2 is a flowchart of the new method.

The concentration inputs used by the new method are the following:

- The calculation details files of the current BBI and BBI-S provide the concentrations of analytes in each layer of the tank waste. (Note the original method used *tank-average* concentrations.)

- When free OH and certain trace metal concentration data are not available in the BBI-S, the following substitute data sources are used as defaults:

    – In liquid layers, the concentration of free OH is taken from the ESP output for each tank;

    – in wet bulk solids layers, the concentration of free OH is calculated by scaling the ESP-output liquid-phase concentration of free OH by a ratio of the BBI-derived inventory-maximum NO_2 concentration for the wet bulk solids phase to the ESP-output NO_2 concentration for the liquid phase;

    – for the fourteen trace metals Ag, As, Be, Cd, Co, Pd, Rh, Se, Sn, Te, Th, Tl, W, and Zn, default concentrations are specified for liquid, saltcake, and sludge types of layers based on BBI protocols.

An Excel spreadsheet was used to acquire the BBI data, make units conversions, and calculate a Cr(VI)/Cr(III) split. All Cr in the liquid layers was considered to be Cr(VI). In the wet bulk solid layers, the water wash factor from the BBI database was used to calculate the Cr(VI)/Cr(III) split. The wash factor times the Cr gave the Cr(VI) concentration, with the remainder being assigned to Cr(III). TOC was treated as being 100% oxalate. The same spreadsheet also drew on the default concentration data for free OH and the fourteen trace metals as needed.

The concentrations became the input to another Excel spreadsheet that converted all the input analytes to the most plausible compounds for which toxicological data were available. This conversion used a set of stoichiometric chemical equations that maintained the species mass balances; there were fewer equations than in the old method because each analyte was assigned to a smaller number of compounds (in many cases, only to one).

Finally, the spreadsheet used all the converted compound concentrations to calculate the SOFs in each layer for each tank. The output from all runs was gathered to create the summary all-layer table. Finally the maximum layer SOF was selected to represent each phase in the tank. The layer that supplied the maximum SOF could differ for different TEEL levels.

```
┌─────────────────────────┐          ┌─────────────────────────┐
│  Phase-specific default OH│         │      **BBI data:**       │
│   and trace metal        │          │  BBI layer compositions; │
│ concentrations for each tank│       │     Cr wash factors;     │
│                          │          │      layer densities     │
└───────────┬─────────────┘          └───────────┬─────────────┘
            │                                    │
            ▼                                    ▼
┌───────────────────────────────────────────────────────────────┐
│           Convert units of layer concentrations;               │
│      Use default OH/trace metals if BBI data lacking;          │
│            Convert Cr to Cr(III) and Cr(VI)                     │
└───────────────────────────────────────┬───────────────────────┘
                                         │
┌─────────────────────────┐             │
│      **Other data:**     │             │
│ Short set of chemical equations;│      │
│          TEELs;          │             │
│          tank ID         │             │
└───────────┬─────────────┘             │
            │                           │
            ▼                           ▼
┌───────────────────────────────────────────────┐
│        **Apply chemical equations and**        │
│        **calculate SOFs for each layer;**      │
│        **find layer with maximum SOF**         │
└───────────────────────┬───────────────────────┘
                        │
                        ▼
┌───────────────────────────────────────────────┐
│                  **Outputs:**                  │
│                 SOFs by layer;                 │
│             Maximum SOFs by tank               │
│        Concentrations of compounds by layer    │
└───────────────────────────────────────────────┘
```

Figure 2.2. Flowchart of New SOF Calculation Method

3.0   Details of the New Method

For the purpose of this comparison, the important changes from the old method to the new method fall into three broad categories:

1. assignment of compounds to analytes on a generic basis, making the SOF calculations less tank-specific but avoiding the resource-intensive use of the ESP model;

2. using a wet-bulk-solids phase instead of a dry-solid phase, thereby putting the toxicological source term on the same phase basis as the radiological source term; and

3. changes in the phase concentrations of analytes, which arise from

    –   choosing layer concentrations instead of tank-average concentrations;

    –   deriving the phase distributions of analytes directly from BBI data instead of thermodynamically calculating them with ESP;

    –   using the chromium wash factor to calculate Cr(VI)/Cr(III) splits;

    –   obtaining the OH concentration from the ESP outputs used by Cowley et al. (2003), in cases where no data are available from the BBI;

    –   charge balance effects on the concentrations of certain significant sodium compounds;

    –   and using different phase densities to convert mass-basis concentrations to volumetric concentrations, and vice versa.

The three categories of changes are discussed in the remainder of this section.

3.1   Change in Assignment of Compounds to Analytes

In the old calculations, the ESP model used equilibrium thermodynamic principles to calculate, on a tank-by-tank basis, which compounds or complexes were formed from the major analytes. For example, ESP could potentially predict that Pb would be present as $Pb(NO_2)_2$, $Pb(NO_2)_3^{-1}$, $PbNO_2^{+1}$, Pb^{+2}, $Pb(CH_3CO_2)_3^{-1}$, $Pb(OH)_2$, $HPbO_2^{-1}$, $PbOH^{+1}$, $Pb_3(PO_4)_2$, PbC_2O_4, and/or PbO in the liquid phase, and as $Pb(OH)_2$, $Pb_3(PO_4)_2$, and/or $PbCO_3$ in the dry-solid phase. ESP estimated concentrations for each of these Pb compounds and complexes based on the pH and the counter-ion concentrations that were present in each individual tank.

Taking the concentrations of this mixture of Pb-containing chemicals as inputs, the old-method SOF Program applied user-specified mass-balanced chemical equations (as indicated in Figure 2.1) to convert all the chemicals that ESP predicted into chemically-related neutral compounds for which TEELs were available. This permitted the SOF contributions to be calculated. In the case of Pb, the following equations were applied:

Liquid Phase

$\mathbf{[Pb(NO_2)_2]}$ = $[Pb(NO_2)_2]$ + $[Pb(NO_2)_3^{-1}]$ + $[PbNO_2^{+1}]$ + $NO_2Ratio*([Pb^{+2}]$ + $[Pb(CH_3CO_2)_3^{-1}])$

$\mathbf{[Pb(NO_3)_2]}$ = $NO_3Ratio*([Pb^{+2}]$ + $[Pb(CH_3CO_2)_3^{-1}])$

[Pb(OH)₂] = [Pb(OH)₂] + [HPbO₂⁻¹] + [PbOH⁺¹] + OHRatio*([Pb⁺²] + [Pb(CH₃CO₂)₃⁻¹])

[Pb₃(PO₄)₂] = [Pb₃(PO₄)₂]

[PbC₂O₄] = [PbC₂O₄]

[PbO] = [PbO]

Dry-Solid Phase

[Pb(OH)₂] = [Pb(OH)₂]

[Pb₃(PO₄)₂] = [Pb₃(PO₄)₂]

[PbCO₃] = [PbCO₃]
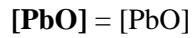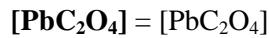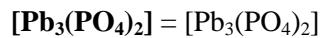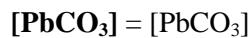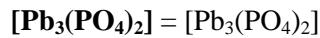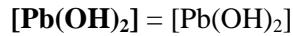
These equations represent the concentrations as molarities. The bold-face concentrations on the left of the equal signs are the output of the SOF Program conversion, in other words the values used for SOF calculation. The ones on the right are the ESP output concentrations, the inputs to SOF Program. The variables OHRatio, NO₂Ratio, and NO₃Ratio are used to split the Pb in some of the ESP species between OH⁻, NO₂⁻, and NO₃⁻, in proportion to the concentrations of these major anions.

The chemical equations used in the old SOF calculations can be seen in Tables C.3 and C.4 of Cowley et al. (2003). Appendix C of that document should be referred to for a more complete understanding of the equations and their basis.

In the new method a smaller set of chemical formulas are used for each analyte, and the analyte concentrations from the BBI are used directly as input to the formulas without any intermediary thermodynamic equilibrium calculations. The result is that there is much less tank-to-tank variation between the compounds in which any given analyte is found. However, some variation does arise from the differences in OH⁻, NO₂⁻, and NO₃⁻ concentrations, which change the associated ratios and therefore change the splits of those analytes to which the ratios are applied. The overall toxicity of an analyte, which depends on which compounds it is found in, tends to be more constant from tank to tank in the new method than in the old.

Continuing the example, the analyte Pb has the following equations applied to it in the new method:

Liquid Phase

[NaHPbO₂] = NaRatio* [Pb]

[KHPbO₂] = KRatio* [Pb]

Wet bulk solid Phase

[Pb(OH)₂] = [Pb]
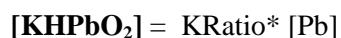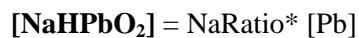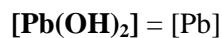
In the liquid phase, the variables KRatio and NaRatio are used to split the HPbO₂⁻ anion between K and Na, in proportion to the concentrations of these major cations. Note that as a result of the change several

Pb compounds that were considered by Cowley et al. (2003) are no longer considered: $Pb_3(PO_4)_2$, PbC_2O_4, PbO, and $PbCO_3$. This decrease in the number of applicable compounds is typical of many of the analytes. The complete set of chemical formulas used in the new method's SOF calculations can be seen in Appendix A.

The net effect of the change in assignment of compounds is to make the overall toxicity of any given analyte (average over all compounds that are present) somewhat different from its old value. The rationale for the new method's choice of compounds is given in Appendix B. Generally speaking, chemical plausibility, prevalence in the Hanford wastes, and reasonable toxicological conservatism were all considered in choosing the simplified set of compounds. On occasion there were trade-offs between these factors, so some engineering judgment was required to make the choices of compounds.

3.2   Change in the Basis of the Solid Phase

Because ESP made predictions of chemical concentrations in terms of liquid and dry solid phases, the solid-phase SOFs calculated by the old method were based only on precipitated compounds for the major species. The solid-phase concentrations of the trace analytes, however, were based directly on BBI or TCD data and therefore were on the basis of wet bulk solids. In the new method all analyte concentrations are taken directly from BBI or TCD data and are therefore on a wet bulk solids basis. As a result, the solid phase now includes chemicals that are part of the interstitial liquid in the bulk solids. This causes two kinds of changes in the SOFs.

To the extent that the interstitial liquid in the wet bulk solids contains lower concentrations of toxic analytes than does the dry solid, the SOFs for wet bulk solids (new method) will be lower than for the dry solid phase (old method) that is part of the bulk. Because the SOFs are measures of toxicity per unit volume of solid, the added volume of water in wet bulk solids dilutes the toxicity and decreases the SOF relative to the dry solid phase. This could produce a factor of 5 to 10 reduction in solid-phase SOF in some wastes (e.g., sludges, which have dilute interstitial liquid and low volume fractions of solids).

However, dilution by water is not the only effect of using a wet bulk solids basis. The interstitial liquid in the wet bulk solids contains toxic analytes whose effect is included in the new-method SOFs. These species (NO_2, free OH, and Cr(VI) as particular examples) were not present in as great a volumetric concentration in the dry-solid SOFs calculated by the old method. To the extent the interstitial liquid contains species that are more toxic than those found in the dry solid—which is likeliest to be true for saltcake liquids, which have high NO_2, free OH, and NO_3—the solid SOF in the new method can be higher than in the old method.

Because the effects of dilution and soluble toxic chemicals act in opposite directions, the solid-phase SOFs calculated by the new method may be less or greater than those from the old method. It depends on the concentrations and TEELs of the chemicals that are present.

The basis of the solid-phase SOFs was changed because the radionuclide source term calculations are based on wet bulk solids and it is preferable to put the toxic source term on the same basis. From the point of view of accident analysis, making a toxicological distinction between the liquid and the dry solid that are contained in bulk solids requires one of two assumptions: (1) an accident could physically separate the solid from the interstitial liquid, or (2) the liquid and solid volume fractions in the bulk solids must be assumed. Physical separation of the two phases is unlikely, since the liquid in the bulk solid

phase (as defined by the BBI) is not drainable. With respect to the second assumption, the volume fractions of solid and liquid are frequently not known. The bulk-wet-solid basis for the solid-phase SOFs is therefore a reasonable and useful representation of the solid part of the accident source term.

In addition, unless the ESP model is used (a resource-intensive effort) there is no consistent method for distributing species between liquid and dry solid phases. The BBI and TCD data might support such calculations for some well-characterized tanks but not for all.

3.3   Changes in Phase Concentrations of Analytes

Several different features of the new method caused changes in the phase concentrations of the analytes, compared to the old method. Each feature will be discussed in its own subsection.

3.3.1   Use of Layer Concentrations and Maximum-Layer SOFs

The old-method SOF calculations were based on the whole-tank average concentrations of analytes. These were used as inputs to the ESP model, which calculated the equilibrium compositions of each of the phases. The new-method calculations are based on the concentrations of analytes in individual waste layers. The SOFs are calculated for each layer. Then the maximum SOF over all liquid layers in the tank is used to represent the liquid in the tank and the maximum SOF over all wet bulk solids layers is used to represent the solid in the tank.

The maximum-layer SOFs were preferred to SOFs based on the average composition because of concerns that the average did not conservatively represent the concentration variation within a tank's waste. An accident might involve only a portion of the waste in a tank, rather than the whole inventory, and that portion could come from a layer of waste that is more toxic than the average. Thus the maximum-layer SOFs are a more appropriate safety basis than were the averages.

3.3.2   Using Analyte Phase Concentrations Taken Directly From the BBI

In the old study, the concentrations of analytes in the liquid and dry-solid phases were determined by the ESP model. The predicted concentrations in the liquid did not always match the measured concentrations, where measurements were available. Concentrations in the dry solid could not be compared to measurements because the latter were always on a bulk-solids basis. However, the presence of differences between predicted and measured concentrations in the liquid suggests that there would also be differences in the dry-solid phase.

The new method uses the concentrations found in the BBI, back-calculating them from total inventory in a layer and the density and volume of the layer. These concentrations may be based from sample analyses, process knowledge, engineering templates, or other estimates, depending on how complete the data set is for the analyte. No chemical model is applied to modify the concentrations from those given in the BBI.

In some cases, the concentrations found in the BBI would be considered the better estimates to use for SOF calculation. This would be the case when the BBI concentration in both the bulk-solids and liquid phases is based directly on sample measurements and those measurements were above the minimum detection limit (MDL) for the analyte. In other cases, the ESP prediction could be the better estimate.

This would apply to a liquid concentration derived from an MDL, since the MDL overestimates the true concentration. It would also apply when the concentration in one or both of the phases is based on an estimate. The ESP prediction of the concentration in the liquid would be thermodynamically consistent with the concentration in the bulk solids, whereas this would not necessarily be true of an estimated concentration.

For example, some B-Farm tanks contain sludge whose bulk solids NO_2 concentration (estimated or measured) is said by the BBI to be much higher than the concentration in the liquid (estimated). This relationship implies a NO_2 concentration difference between the sludge and supernate phases that could not be sustained over the period that the tank has been inactive. In these cases the old liquid-phase SOFs, for which ESP predicted higher NO_2^- liquid-phase concentrations than were given in the BBI estimates, are probably closer to the in-tank conditions than the new SOFs.

Although the phase concentrations found in the BBI are not necessarily completely chemically consistent with each other, they are in a certain sense preferable to the more consistent concentrations that can be produced by chemical modeling based on BBI data. The Best Basis Inventory has been approved as the single tank-waste basis for safety and other calculations. In this regard it makes sense to use the BBI concentration data directly, rather than using re-interpretations of the concentrations that come from chemical modeling.

3.3.3 Basing the Cr(VI)/Cr(III) Split on the BBI Wash Factor for Chromium

The toxicity of the chromium in the Hanford tank waste depend strongly on whether its oxidation state is three or six, the latter being more toxic and far more soluble. In the old method, the split between the two oxidation states was determined by one of several methods, depending on what information was available. Where both liquid and bulk composition data were available in the BBI, a liquid tracer analyte (NO_2, Cl, K, or Cs-137) was used to estimate the average liquid volume fraction in the waste.[1] This information allowed a calculation of the fraction of Cr that was present in the liquid. The soluble fraction of the Cr was assigned to Cr(VI) and the remainder to Cr(III), and this split was used as input to ESP. For the few tank wastes where hexavalent chromium measurements were included in the Tank Characterization Database (TCD), they were used for the split instead of the soluble fraction. In cases where bulk but not liquid composition data were available in the BBI, no soluble fraction could be calculated. For these tank wastes, the Cr was conservatively assumed to be 100% Cr(VI), that being the more toxic oxidation state.

In the new SOF calculation method, the BBI water wash factor defined for Cr in each tank was used to split the solid-phase Cr between soluble Cr, which was assigned to Cr(VI), and insoluble Cr, which was assigned to Cr(III). All Cr in the liquid phase was treated as Cr(VI).

> In the solids, Cr(III) = (1-washfactor)*Cr, and Cr(VI) = washfactor*Cr
> In the liquid, Cr(III) = 0, and Cr(VI) = Cr   (3.1)

The water wash factor in the BBI reflects the fraction of an analyte that can be removed from bulk waste by water washing of the waste. For Cr, this fraction approximates the in-situ Cr(VI) fraction, or could possibly overestimate it if the experiment that obtained the water wash factor caused any Cr(III) to become oxidized to Cr(VI).

The change in method was made in order to have a consistent Cr split method for all tanks. The contribution of Cr to the solid SOF could increase or decrease in the new method, compared to the old, depending on the value of the wash factor. Cr(VI) has been found to constitute nearly all the liquid-phase Cr in those liquid samples where both Cr and Cr(VI) have been measured, so assigning all the dissolved Cr to Cr(VI) would produce only a slight increase in the new-method liquid SOF, compared to the old method.

3.3.4   Use of the ESP-Modeled Hydroxide Concentrations as Defaults

In the old method, ESP calculated the OH ion concentration in the liquid that was chemically consistent with the average waste composition. In some cases, where the predicted OH/pH differed substantially from the expected or measured value, the charge balance in the ESP inputs was adjusted iteratively, by spreadsheet calculations, to make the model predictions match the measurements more closely.

The new method calculates free OH default concentrations based on the liquid-phase free OH^- concentrations that were predicted by ESP for the year-2002 average tank waste in the study by Cowley et al. (2003). These default concentrations are used only when the BBIS does not provide any free OH^- concentration information for a layer.

The ESP-based liquid-phase free OH was assumed to include both the OH^- ion, as predicted by the ESP model, and one mole of OH from each mole of $Al(OH)_4^-$ complex predicted by ESP. This summation is consistent with the way in which free OH is measured during sample analysis.[2] The free OH concentrations from Cowley et al. (2003) are whole-tank averages; therefore all of a tank's liquid layers that lack BBI-S free OH data are given the same default free OH concentration.

In the new method, when a wet bulk solids layer does not have a BBI-S free OH value, the default concentration of free OH is estimated by multiplying the current BBI concentration of NO2 in the layer by the free OH/NO_2^- ratio that was predicted by ESP in 2002 for the average liquid in the tank.

Appendix C contains the default free OH concentrations to be used for the liquid phase in any Hanford tank waste layer for which there is no BBI free OH data. The appendix also includes the liquid-phase NO_2^- ion concentrations predicted by the ESP model in 2002. The ESP-based liquid-phase NO_2^- concentration includes the predicted NO_2^- ion itself, the predicted $NaNO_2$ complex in solution, and the $NaNO_2$ solid that ESP mispredicted to exist in some tanks and that belonged in the liquid phase. (As noted in Section 2.1, ESP underestimated the solubility of $NaNO_2$ under some conditions, hence the recalculation of liquid NO_2^- concentration as including the $NaNO_2$ that ESP put into solid phase.)

The predicted NO_2^- is used as a liquid tracer to calculate the default free OH^- in bulk solids phases where no BBI-S data are available. The equation used is

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[1] Liquid tracer species are expected to be completely soluble (at their actual concentrations in the waste) and are used to estimate the amount of liquid in a wet solid.

[2] In the liquid portion of tank waste sample, aluminum is present almost entirely as $Al(OH)_4^-$ complex. The aluminum in a sample is precipitated as neutral $Al(OH)_3$ during the preparation of the sample for hydroxide measurement, causing one mole of OH^- to be freed from the complex. Thus, the measured free OH includes both the in-situ free OH and a contribution from hydroxide that was originally part of the Al complex. Other metals may also be found in solution as hydroxide complexes, potentially contributing to the analyzed free hydroxide, but these contributions are relatively small and are neglected.

$$\textit{Wet Bulk Solids OH} = \left(\textit{ESP liquid OH}\right) \frac{\textit{Wet Bulk Solids NO}_2 \textit{ from BBI}}{\textit{ESP liquid NO}_2} \qquad (3.2)$$

It is assumed that free OH and NO_2^- are both present only in the liquid phase, and that the ratio between them is the same in the waste liquid in every layer of the tank as it was in the tank average liquid in 2002. The ratio is based on NO_2^- because the BBI provides an estimate for NO_2^- in all waste layers (the layer data needed are available) and NO_2^- is never present at high enough concentrations to bias the ratio by precipitation (nor are nitrite solids present that could dissolve and bias the free-OH/NO_2^- ratio in the bulk solids layer). Because NO_2 is a major analyte, meaning that it is always included in the BBI for every layer in every tank, the method outlined above can provide a free OH estimate for both phases in every tank.

Any discrepancies between the 2002 hydroxide calculations and the currently existing hydroxide will be of concern only for those waste layers for which the BBI does not include free OH inventories. As of May 2006, free OH inventories in one or more liquid phases are included in the BBI for at least some layers in

- all the DSTs;

- A-101 through A-103, AX-101, BY-103, BY-105, BY-106, C-106;

- S-101, S-103, S-104, S-106, S-108, S-109, S-111, SX-101 through SX-106, T-101, T-102, TX-112, TX-113, TX-115, TX-116, TX-118, TY-102, TY-103, U-102, U-103, U-105 through U-109, U-111; and

- the four U-200 tanks.

Free OH inventories in the wet bulk solid phases are present in the May 2006 BBI for at least some layers in

- AN-102 through AN-107, AP-102, AP-105, AW-101, AW-103, AW-105, AW-106, AZ-101, AZ-102, SY-102, and SY-103;

- S-101, S-102, S-103, S-107, S-108, S-109, S-111, S-111, S-112, SX-102, SX-103, SX-105, SX-106, TY-102, TY-103, TY-105, U-103, U-109, and U-111.

Perhaps arguably, this list of cases where the default free OH concentration data will not be needed includes most of the tanks in which activity requiring specific safety analyses is likely to occur. The free OH data for these and other tanks will be updated as a result of compatibility requirements as new operations are planned, which will update the concentrations in the BBI that will be used instead of the defaults. The use of OH^- and NO_2^- data from Cowley et al. (2003) is therefore considered an acceptable approximation.

3.3.5   Charge Balance Effects

The old method provided a charge-balanced combination of ESP-modeled (major) analytes. The trace analytes were then included in this composition in the form of compounds, which frequently were sodium and potassium salts. This additional Na and K was offset by reducing the major sodium salts NaOH, $NaNO_2$, and $NaNO_3$, a step that tended to reduce the old-method SOF (as is detailed below).

The trace compounds were neutral compounds and therefore inherently charge-balanced, but their addition tended to increase the concentrations of sodium and potassium in the waste composition above the BBI values. To reduce the excess of sodium and potassium in the liquid phase, the Na and K that were associated with two of the trace analytes (HEDTA and EDTA) were subtracted from the total liquid-phase Na and K given in the ESP output. The result was to decrease the amount of sodium and potassium that were available to be assigned to sodium nitrite, nitrate, and hydroxide and to potassium nitrite, nitrate, and hydroxide.

Taking sodium as an example, the process followed by the old method was this:

TempNa = $[Na^+]$ + [sum of assorted contributions of Na from species predicted by the ESP model]
– [sum of Na needed by anionic species that are split between Na and K using NaRatio]
– 4*NaRatio*[EDTA] – 3* NaRatio* [HEDTA]

Here, TempNa was an intermediate Na concentration variable that included the effects of mass-balance accounting on Na, [Na+] was the molar concentration of sodium ion in solution predicted by ESP, and [EDTA] and [HEDTA] were the molar concentrations of the two trace analytes. The concentrations of $NaNO_2$, $NaNO_3$, and NaOH were then calculated as

[NaNO$_2$] = [$NaNO_2$ complex in solution] + TempNa * ([NO_2^- in solution]/[NO_2^- + NO_3^- + OH^-])

[NaNO$_3$] = [$NaNO_3$ complex in solution] + TempNa * ([NO_3^- in solution]/[NO_2^- + NO_3^- + OH^-])

[NaOH] = TempNa * ([OH^- in solution]/[NO_2^- + NO_3^- + OH^-])

The equation has been somewhat simplified to clarify the effect of the Na consumption caused by the trace analytes. The sodium that was subtracted from TempNa was made unavailable for sodium nitrate, nitrite, and hydroxide. This often decreased the SOF by reducing the concentration of the three anions' salts, in that the toxicity of EDTA and HEDTA salts was less than that of sodium nitrite and hydroxide.

The new method does not include the organic salts in question (Section 3.1) and therefore, all other factors being equal, the SOFs calculated by the new method are likely to be higher.

3.3.6   Different Choice of Phase Densities

When converting concentrations from μg/g to μg/mL or vice versa, the old method used the ESP-calculated densities for the liquid and dry-solid phases of the average waste in a tank. The new method, being based directly on BBI data, uses the densities that are part of the BBI database for each layer (also known as a component). The difference in the basis densities can affect the concentrations used for SOF calculation.

The first step in units conversion is made during the generation of SOFProgram concentration input. The analyte concentrations that come from the BBI are converted to SOFProgram concentration inputs as described in Section 3.3.1: the layer (component) densities and volumes are used to convert the inventories in each solid layer to μg/g concentrations, and the layer volumes are used to convert the inventories in each liquid layer to μg/mL concentrations. The analyte concentrations that come from the trace metal and OH default concentration input are already in the input units required by SOFProgram,

μg/g for solids layers and μg/mL for liquid layers. For default concentrations, therefore, no unit conversion is needed at this step.

In the final units conversion step, the component density input is used within SOFProgram to convert the solid-phase concentration inputs from the received units of μg/g to the units required for SOF calculation, mg/m^3.

The use of BBI-based rather than ESP-predicted densities is unavoidable, if BBI concentrations are to be used directly.

4.0 Comparison of Results for New and Old Methods

As discussed in Section 3, the several ways in which the new SOF calculation method was changed compared to the old method can be expected to affect the SOFs in various ways. The overall effect may be either an increase or decrease for any particular tank, phase, and TEEL level; the direction cannot be predicted *a priori*. Therefore, a systematic comparison of the SOFs calculated by the new and old methods is needed in order to evaluate the effects of the method change.

This report focuses on the replacement of ESP modeling by the direct use of BBI data. The method comparison therefore considers only the handling of those "non-trace" analytes that were originally modeled using the ESP code, as defined in Section 2.1, not the "trace" analytes that were included in the SOF in a different manner. The discussion of the contributions of "trace" analytes is deferred to another document (Meacham et al. 2006).

4.1 Basis for Method Comparison

The new and old methods cannot be compared unless both are applied on the same basis. Because the old method depended on BBI data as of May 2002, the new-method inputs were derived from that inventory. In addition, the old method SOF Program runs were redone with the same TEELs (Rev. 21A) used in the new method. This ensured that all differences in results were caused by method changes alone.

The change from dry-solid basis, in the old method, to wet bulk solids basis, in the new method, causes some difficulty in comparing solid-phase results. To improve comparability, the old method's solid SOF results were converted to a wet bulk solid basis. The volume fraction of dry solid phase in the average wet bulk solids in a tank was calculated using the following equation:

$$\phi_S = \frac{V\phi_{ESP}}{V - V_{DL}} \tag{4.1}$$

where ϕ_S =   dry-solid volume fraction in wet bulk solids
   ϕ_{ESP} =   ESP-predicted dry-solid fraction, average of all the waste in the tank
   V =   The total waste volume in the tank as defined by the BBI
   V_{DL} =   The total volume of liquid that the BBI explicitly defines as being liquid, separate from the liquid that is present only implicitly as part of the bulk solids; V_{DL} is the sum of supernatant, drainable sludge liquid, and drainable saltcake liquid

The numerator of the fraction is the interstitial liquid volume in the wet bulk solids and the denominator is the total wet bulk solid volume. The solid volume fraction calculated by the above equation is approximate because of uncertainty in the parameters and because retained gas volume is not accounted for. The combination of ESP-predicted total liquid in the tank with independently-estimated volumes also adds an uncertainty. Table D.1 in Appendix D shows the solid fractions that were used.

Wet bulk solid SOFs are calculated from the old method's dry-solid and liquid SOFs as the volume-weighted average:

Wet Bulk Solid SOF $= \phi_S *$ *Dry Solid SOF* $+ (1 - \phi_S) *$ *Liquid SOF* $\tag{4.2}$

Because there are inherent differences between the ESP-based solid fraction, ϕ_S, of Eq. (4.2) and the unspecified value for solid fraction in the BBI, the comparison between new and old methods for the wet bulk solid phase SOFs is less exact than the comparison of the liquid phase SOFs.

4.2 Overall Comparison of Major-Analyte SOFs Calculated by Old and New Methods

As already noted, this report considers only the major (non-trace) analytes. Accordingly the SOFs discussed here are the sums of the contributions made by major-analyte compounds alone. Trace contributions are not included and the TEELs have been updated; therefore the old-method SOFs shown in this report are not the same as those given by Cowley et al. (2003).

Figure 4.1 shows old and new liquid-phase SOFs for each of the three TEEL levels of concern, TEEL-1, TEEL-2, and TEEL-3. The figure includes SOFs for all 177 tanks, grouped by DSTs (left), 100-SSTs (center), and 200-SSTs (right). The tanks are arranged along the x-axis in order of increasing old-method SOF, within the tank group. Note that the tanks are not in the same sequence for all three TEELs, so a location on the x-axis does not indicate the same tank on all three plots.

The y-axis is the SOF value. (In the y-axis label, "SOF-1", "SOF-2", "SOF-3" are abbreviations for the SOF based on TEEL-1, TEEL-2, or TEEL-3, respectively) The solid lines in the figures represent the old-method tank SOFs; the hollow boxes are the new-method SOFs for the corresponding tanks. For tanks where the BBI does not define any liquid phase, there are no new-method points. The 100-SST and 200-SST that had the bounding SOF-1 and SOF-2 values, according to the old method, are among those that have no new-method point because there is no BBI-defined liquid phase.

Certain features of the change in method can be seen in Figure 4.1. The differences between old and new SOFs are generally smaller for the DSTs than for the other groups of tanks, although many of the tanks at the high-SOF end of the 100-SST range also have old and new-method SOFs that are very similar. The differences generally become more positive as the TEEL level increases; the resulting increase in scatter (in the absolute magnitude of the change) is evident, based on comparing the TEEL-3 figure to those for TEEL-1 or TEEL-2. A discussion of the causes of the differences is deferred to a later section.

Table 4.1 lists how many of the tanks in each group are found in different parts of the difference range. In the table, the percent difference is expressed in terms of (new – old)/old.
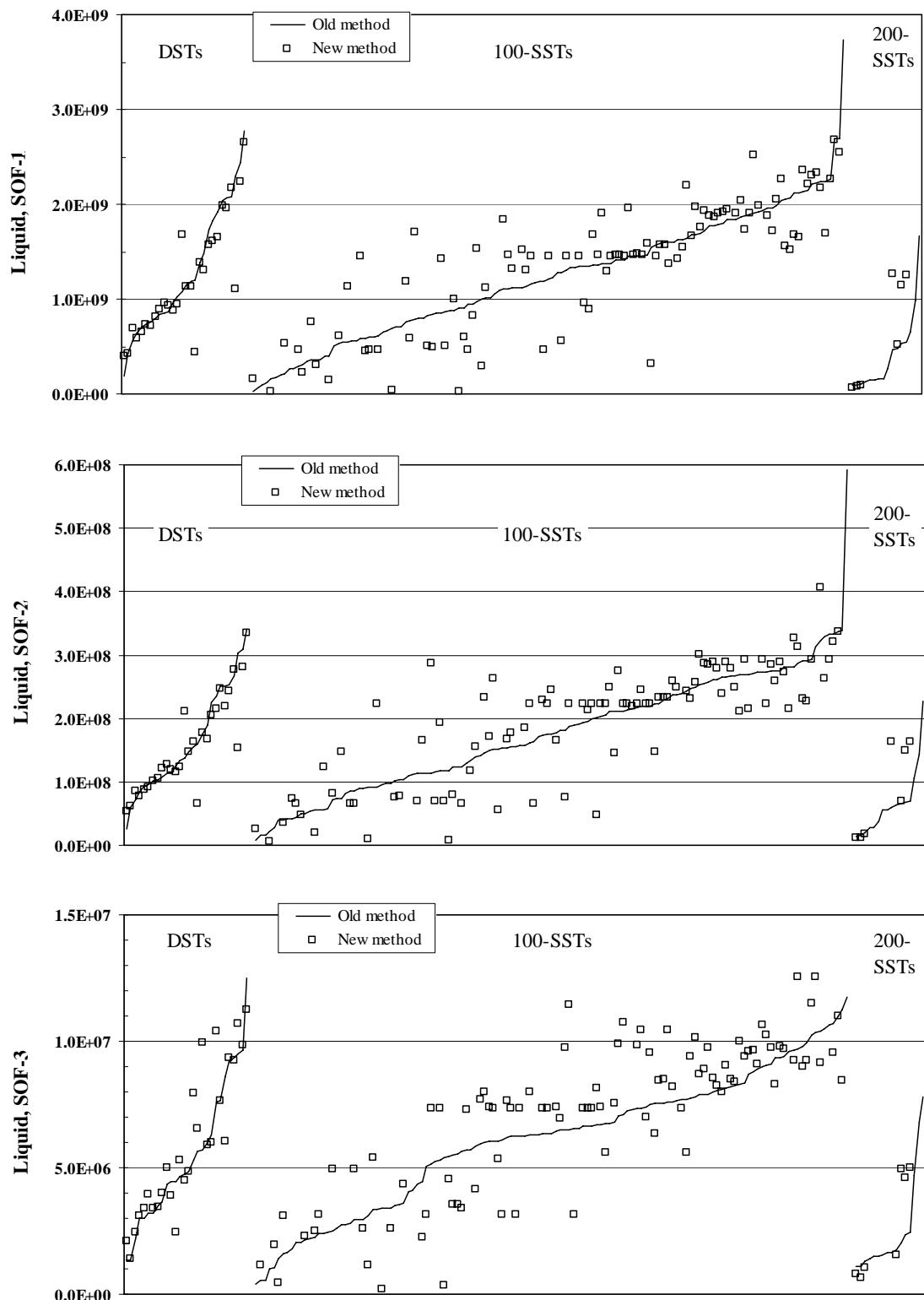
Figure 4.1. Comparison of Old and New Liquid-Phase SOFs for TEEL-1, -2, and -3

Table 4.1. Differences Between Old and New Liquid-Phase SOFs for TEEL-1, -2, and -3

(New-Old)/Old	DST		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	2	1	0
-50% to -20%	0	1	2
-20% to 0%	16	14	7
0% to +20%	7	10	14
+20% to +50%	1	0	3
+50% to +100%	1	1	2
> +100%	1	1	0
(New-Old)/Old	**100-SST**		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	8	8	5
-50% to -20%	17	15	11
-20% to 0%	17	15	14
0% to +20%	35	41	35
+20% to +50%	8	7	23
+50% to +100%	5	6	7
> +100%	6	4	1
(New-Old)/Old	**200-SST**		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	0	0	0
-50% to -20%	1	2	2
-20% to 0%	2	1	2
0% to +20%	1	1	0
+20% to +50%	0	0	0
+50% to +100%	0	0	1
> +100%	3	3	2

Table 4.2 and Figure 4.2 provide a similar overview of the differences in wet bulk solid SOF that are caused by the change in method. Figure 4.3 shows the wet bulk solids SOF-2 and SOF-3 values with an expanded y-axis that shows more details of the lower values. The trends are much the same for wet bulk solids as for liquid, except that the DSTs show more scatter (mostly upward) for solids than for liquid, while the SSTs show less. Relatively few tanks have a new-method SOF that is less than the old-method SOF by more than 20% of the old value.

Considering all three TEEL levels, 50 to 60% of the Hanford tanks had SOFs for which the new method is within ±20% of the old method, while 15 to 20% of the tanks show a difference of more than ±50%. The SOFs are increased by the new method more often than they are decreased. These statements hold for both the liquid and wet bulk solids SOFs. Thus, less than ten percent of the tanks had SOFs that decreased by more than 50%. For perspective, an uncertainty of 20% in analyte concentrations is a reasonable expectation for compositions based on sample measurements, considering the uncertainties in sample concentration and density analyses and the variability of concentration within the waste. The overall uncertainty might be considerably greater in tanks that have not been sampled, for which the composition is based on process knowledge or a template (Place and Higley 2005).

Table 4.2. Differences Between Old and New Wet Bulk Solids SOFs for TEEL-1, -2, and -3

(New-Old)/Old	DST		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	1	0	0
-50% to -20%	1	1	3
-20% to 0%	4	5	9
0% to +20%	5	5	4
+20% to +50%	4	6	4
+50% to +100%	4	3	0
> +100%	1	0	0
(New-Old)/Old	100-SST		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	0	0	0
-50% to -20%	3	2	0
-20% to 0%	41	39	29
0% to +20%	51	44	54
+20% to +50%	19	32	25
+50% to +100%	13	8	13
> +100%	6	8	12
(New-Old)/Old	200-SST		
	TEEL-1	**TEEL-2**	**TEEL-3**
-100% to -50%	0	0	0
-50% to -20%	2	5	2
-20% to 0%	9	3	4
0% to +20%	5	3	8
+20% to +50%	0	4	0
+50% to +100%	0	0	1
> +100%	0	1	1
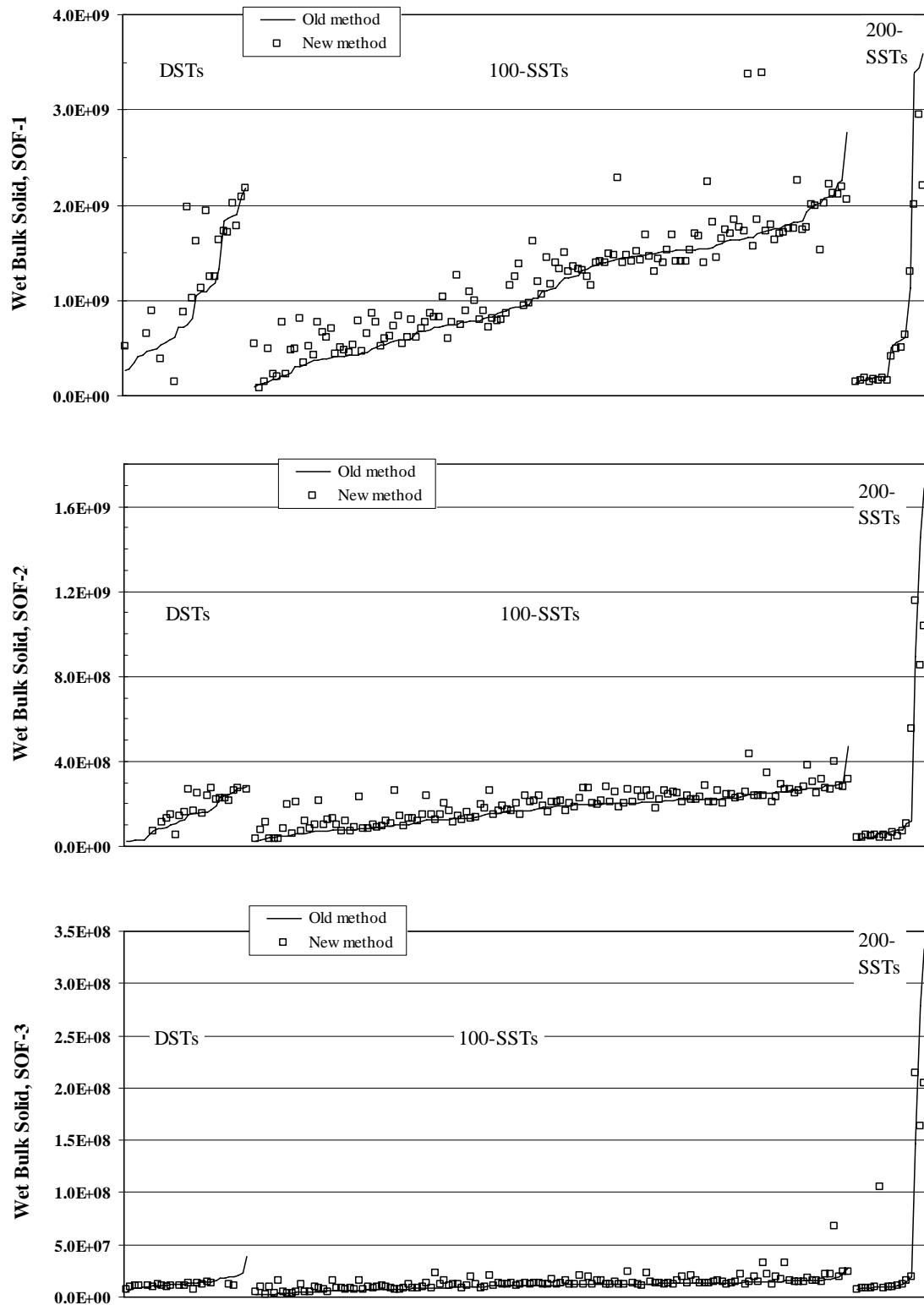
Figure 4.2. Comparison of Old and New Wet Bulk Solids SOFs for TEEL-1, -2, and -3
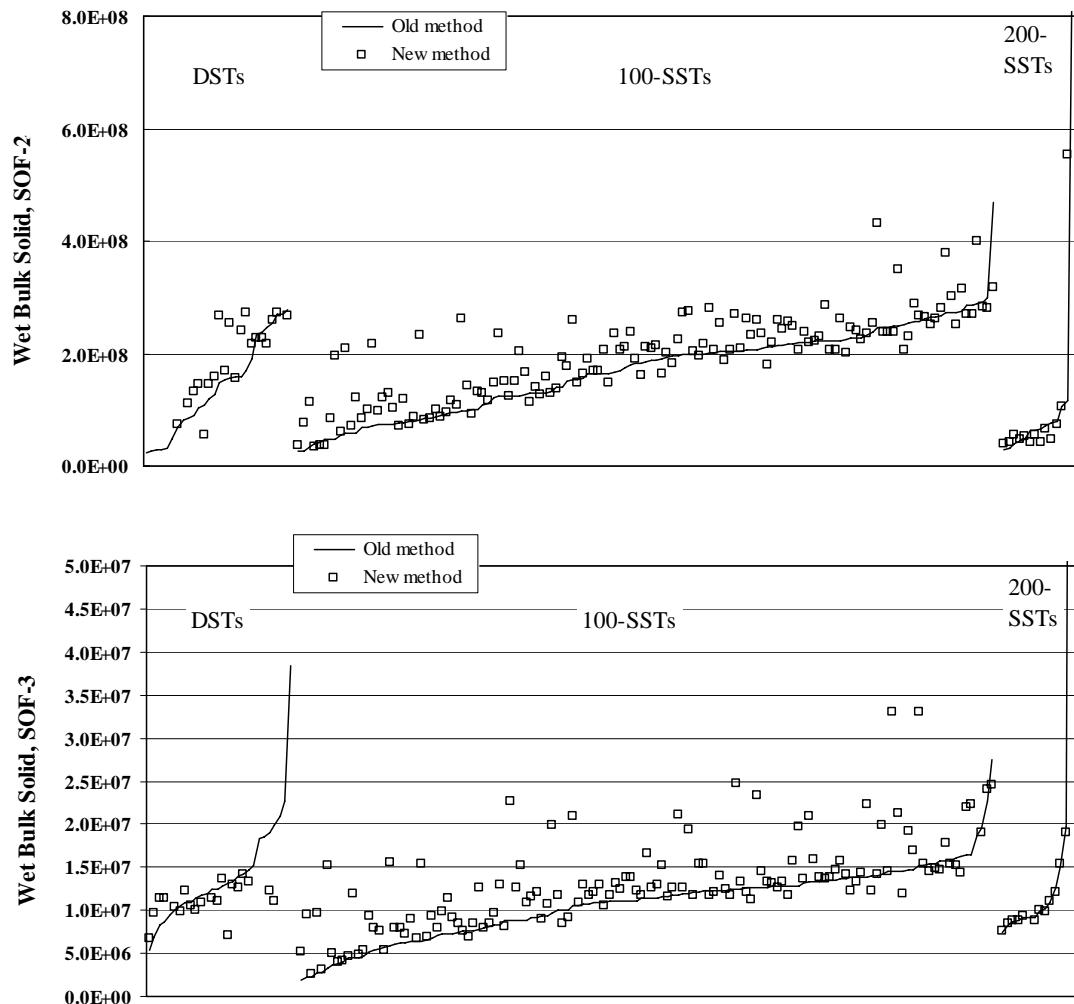
Figure 4.3. Comparison of Old and New Wet Bulk Solids SOFs for TEEL-2 and -3 (y-axis expanded, compared to Figure 4.2)

4.3   Detailed Evaluation of Changes in Major-Analyte Liquid-Phase SOFs

Because the SOF-3 values showed greater difference between old and new methods, they were used as the basis for a detailed investigation of the causes of the differences produced by the change in methods. In each case where the liquid-phase SOF-3 change was relatively large, defined as an increase or decrease of more than 30% — that is, a change rounding to 31% or more — the analytes were identified that jointly produced 80% or more of the overall change in the SOF. Every analyte that contributed more than 10% of a large change was considered.

For each selected analyte, three ratios were calculated:

- new-method analyte contribution to the SOF-3 / old-method contribution;
- new-method analyte concentration in the liquid / old-method concentration;
- new-method analyte effective TEEL-3 value / old-method value.

The effective TEEL by dividing the total analyte concentration by the total analyte SOF contribution). Because an analyte may be distributed into more than one compound, each of which has its own TEEL, the effective TEEL is needed as a measure of the weighted average toxicity of the analyte, accounting for all the compounds in which it is present. As is the case for the compound TEELs, a lower effective TEEL indicates higher toxicity and vice versa.

The ratio of new to old contributions shows how much the analyte's contribution to the TEEL-3 liquid SOF changed because of the change in method. The ratio of concentrations and the ratio of effective TEELs allow a distinction to be made between those contribution changes that result from concentration changes (for example, different estimates of solubility) and those that arise from toxicity changes (different assigned compounds). The method changes described in Section 3.1 produce toxicity changes. Those described in Sections 3.2 and 3.3 produce concentration changes.

Table 4.3 (located at the end of this subsection) assembles the information related to liquid-phase SOF decreases of more than 30%. For each of the 14 tanks for which such a decrease occurred, the table shows the old and new SOF-3 values and their ratio, as well as data for the significant analytes. "Significant analytes" were those that individually caused 10% or more of the change in SOF-3. For each of these significant analytes, the table shows the ratio of new to old contributions ("New/Old Contrib-3 ratio"), the ratio of new to old concentrations, the ratio of new to old effective TEELs. Some ratios are stated as "undefined" because the concentration in the old or new method was zero (giving a divide-by-zero error). The table also includes the fraction of the SOF decrease that comes from each analyte (the fractions do not sum to 100% because only the significant analytes are included). This last number is negative when the analyte's contribution increased (i.e., a negative decrease). The reason for the change in the analyte contribution is also listed.

In all cases, the major decreases in the liquid SOF-3 were caused by differences between the ESP-predicted analyte solubilities and those implied by the liquid-phase concentrations in the BBI. The differences in predicted and BBI liquid concentrations were observed by comparing the ESP output liquid concentrations to BBI values averaged over all liquid layers. As discussed in Section 3.3.2, it is not possible to make a general statement about whether the ESP prediction or the BBI is more accurate. In the cases of B-111 and B-110 (the B-Farm tanks mentioned in Section 3.3.2), there seems to have been an inconsistency between the NO_3 and NO_2 concentrations in the liquid, which were estimates, and the measurement-based bulk-solid concentrations in the year-2002 BBI. In other cases, such as C-110 and B-204, the 2002 BBI was based on measured concentrations; this suggests that ESP's thermodynamic database did not describe the tank's chemistry well.

It can be argued that in some tanks – for example, B-110 and B-111 – SOF calculations would be more accurate if the ESP model were used, because of apparent inconsistencies between the compositions of the liquid and bulk-solids phases as given by the estimates used in the BBI. However, the same uncertainties and approximations that cause the inter-phase inconsistencies also affect the accuracy of the inputs to the ESP model. This being the case, it is not clear how much improvement the additional step of thermodynamic equilibrium calculation would provide.

Table 4.4 contains the information related to liquid-phase SOF increases of more than 30%. Three aspects of the change in SOF calculation method are the causes of the major increases in liquid-phase SOFs:

- In 16 tanks, the differences in SOFs were primarily due to differences between the ESP-predicted and BBI solubilities of analytes (most often NO_3, NO_2, OH, and Al), as was also the case for the major decreases in liquid SOFs;

- In 3 tanks, the differences were primarily due to the use of analyte concentrations from the maximum-SOF layer, as discussed in Section 3.3.1; and

- In 5 tanks, the differences were primarily due to an increase in the effective toxicity of one analyte (TOC), as discussed in Section 3.1.

In some cases, the concentration of an analyte changed because of both solubility differences and the use of maximum-SOF layer concentrations. The effect of solubility difference was judged by comparing the ESP-predicted concentration with the average concentration over all liquid layers in the BBI, while the effect of maximum-layer concentrations was evaluated by comparing the layer concentration to the average liquid concentration. If the latter effect produced a greater increase than the former, then the maximum-layer concentration was given in the table as the reason for the change.

A complicating factor appears in tanks S-109 and BY-101. When these two tanks were modeled in 2002 with ESP, the model could not be made to converge on the BBI-average composition. Convergence was obtained by diluting the waste composition with water. Thus, for these two tanks part of the difference between ESP and BBI solubility came from the waste dilution used for ESP, which would have increased the amount of liquid and decreased the concentrations of completely-dissolved analytes such as Cr(VI), free OH, and NO_2. This effect accounts for a portion of the increase in SOF from the old to the new method, and in these cases the new method more accurately reflect the waste compositions.

The increase in the effective toxicity of TOC resulted from assigning sodium and potassium oxalate as the TOC compounds. In the ESP runs, the TOC concentration in the BBI was split into a dissolved fraction, which was input to ESP as acetate, and a precipitated fraction, which was input as oxalate. In most tanks, the TOC in the liquid was predicted to consist primarily of acetate. In the new method, all TOC is oxalate, including that in the liquid. Because oxalate is a more toxic form of TOC than acetate, the effective toxicity of the TOC (particularly of TOC in the liquid) was increased by the new method. Section B.22 in Appendix B contains more information on the selection of oxalate salts as the assigned TOC compounds.

4.4   Detailed Evaluation of Changes in Major-Analyte Wet Bulk Solids SOFs

The largest changes in the wet bulk solids SOF-3s were analyzed in the same manner as the liquid-phase SOF-3s, defining a change of 30% or more as a major change. Tables 4.5 and 4.6 show the old and new SOF-3 values, their ratios, and data for the significant analytes. Table 4.5 contains information for the tanks in which the SOF-3 decreased by more than 30% and Table 4.6 describes the tanks that had SOF-3 increases of more than 30%. Five tanks fell into the "decrease" category and forty-five into the "increase" category.

Several aspects of the change in SOF calculation method are the causes of the major changes in bulk wet solids SOFs:

- In 37 of the major increases, the primary cause was the use of the concentrations of the maximum-SOF layer;

Table 4.3. Causes of Method-Related Liquid-Phase SOF-3 Decreases of More Than 30%

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF decrease from this analyte	Comments
B-111	0.059	2.0E+05	3.4E+06	NO_3	0.087	0.087	1.00	44%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				NO_2	0.018	0.018	1.00	48%	
B-110	0.060	3.3E+05	5.4E+06	NO_3	0.030	0.030	1.00	86%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
T-110	0.34	4.7E+05	1.4E+06	TOC	0.046	0.044	0.96	11%	Difference between ESP and BBI solubility. BBI was measured.
				U	0.049	0.048	0.99	12%	
				NO_2	0.010	0.010	1.00	16%	Difference between ESP and BBI solubility. BBI used estimate for solids.
				NO_3	0.29	0.29	1.00	67%	
C-110	0.37	1.1E+06	3.1E+06	NO_3	0.33	0.33	1.00	87%	Difference between ESP and BBI solubility. BBI was measured.
TX-117	0.48	3.2E+06	6.6E+06	NO_2	0.29	0.29	1.00	33%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				NO_3	0.58	0.58	1.00	51%	
TY-104	0.51	2.2E+06	4.4E+06	NO_3	4.5	4.5	1.00	-48%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				NO_2	0.15	0.15	1.00	74%	
				U	0.0021	0.0019	0.93	80%	
TY-101	0.51	3.2E+06	6.2E+06	NO_2	0.53	0.54	1.00	13%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				NO_3	0.45	0.45	1.00	93%	
B-104	0.52	3.2E+06	6.1E+06	NO_2	3.9	3.9	1.00	-11%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				U	0.019	0.019	0.99	12%	
				NO_3	0.46	0.46	1.00	97%	

Table 4.3. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF decrease from this analyte	Comments
AN-106	0.55	2.5E+06	4.5E+06	TOC	8.9	1.2	0.13	-10%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				NO_3	0.58	0.60	1.03	35%	Difference between ESP and BBI solubility. BBI used estimate for solids.
				NO_2	0.30	0.31	1.04	70%	
B-204	0.59	6.6E+05	1.1E+06	TOC	1.35E-05	8.51E-06	0.63	12%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				F	0.62	0.63	1.02	17%	Difference between ESP and BBI solubility. BBI was measured.
				NO_3	0.58	0.58	0.99	68%	
B-102	0.60	3.4E+06	5.7E+06	NO_2	0.56	0.56	1.00	16%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				NO_3	0.58	0.58	1.00	76%	
B-106	0.62	3.2E+06	5.1E+06	NO_3	0.53	0.53	1.00	112%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
B-103	0.64	3.5E+06	5.6E+06	NO_2	0.50	0.50	1.00	23%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				NO_3	0.65	0.64	1.00	64%	
T-108	0.65	3.6E+06	5.5E+06	CO_3	0.13	0.13	1.00	15%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				NO_2	0.54	0.54	1.00	20%	
				NO_3	0.66	0.66	1.00	64%	

Table 4.4. Causes of Method-Related Liquid-Phase SOF-3 Increases of More Than 30%

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
T-109	1.33	3.17E+06	2.38E+06	CO_3	0.24	0.24	1.00	-19%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solid.
				U	0.048	0.047	0.99	-17%	
				NO_2	1.9	1.9	1.00	28%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				NO_3	1.5	1.5	1.00	103%	Difference between ESP and BBI solubility. BBI was measured.
B-108	1.34	8.01E+06	5.98E+06	NO_2	0.86	0.86	1.00	-10%	Difference between ESP and BBI solubility. BBI was measured.
				SO_4	0.17	0.17	1.00	-10%	
				NO_3	2.2	2.2	1.00	137%	
BX-111	1.34	9.85E+06	7.36E+06	Al	2.2	2.2	1.00	25%	Difference between ESP and BBI solubility. BBI was measured.
				NO_2	1.5	1.5	1.01	33%	
				NO_3	1.6	1.6	1.00	38%	
AN-102	1.36	1.04E+07	7.62E+06	NO_2	0.80	0.81	1.00	-21%	Difference between ESP and BBI solubility. BBI used estimate for solids.
				NO_3	1.20	1.20	1.00	24%	
				TOC	14	0.90	0.063	92%	Increase is the result of toxicity change (by assigning oxalate), not concentration change.
BX-110	1.38	1.05E+07	7.59E+06	NO_2	0.57	0.56	1.00	-35%	Difference between ESP and BBI solubility. BBI was measured.
				TOC	14	0.88	0.064	33%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				NO_3	2.6	2.6	0.99	120%	Difference between ESP and BBI solubility. BBI was measured.

Table 4.4. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
TX-118	1.39	7.34E+06	5.29E+06	NO_3	0.71	0.71	1.00	-45%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				NO_2	1.5	1.5	1.00	41%	
				Al	34417	34417	1.00	42%	
				TOC	12	0.96	0.077	54%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
U-102	1.40	9.91E+06	7.06E+06	NO_3	0.67	0.67	1.00	-47%	Difference between ESP and BBI solubility. BBI was measured.
				Al	192	192	1.00	27%	
				NO_2	1.4	1.4	1.01	38%	
				TOC	18	1.3	0.069	41%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				OH	77	77	1.00	48%	Difference between ESP and BBI solubility. BBI was measured.
S-106	1.42	1.04E+07	7.36E+06	NO_3	1.21	1.21	1.00	18%	Difference between ESP and BBI solubility. BBI was measured.
				Al	3.5	3.5	1.00	20%	
				NO_2	1.3	1.4	1.00	22%	
				OH	2.0	2.0	1.00	42%	
TX-113	1.42	7.34E+06	5.17E+06	NO_3	0.63	0.63	1.00	-62%	Difference between ESP and BBI solubility. BBI used estimate for liquid.
				PO_4	0.11	0.10	0.87	-18%	
				Al	undefined	undefined	undefined	40%	
				TOC	94	5.8	0.062	55%	Increase is the result of toxicity change (assigning oxalate); also difference between ESP and BBI solubility.
				NO_2	5.8	5.8	1.00	91%	Difference between ESP and BBI solubility. BBI used estimate for liquid.

Table 4.4. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
S-109	1.50	9.73E+06	6.50E+06	NO$_3$	0.77	0.77	1.00	-16%	Difference between ESP and BBI solubility. BBI was measured; ESP was diluted for convergence.
				Cr(VI)	4.3	4.3	1.00	17%	
				Al	2.6	2.6	1.00	20%	
				OH	1.3	1.3	1.00	29%	
				NO$_2$	4.4	4.4	1.00	50%	
AW-104	1.50	7.95E+06	5.28E+06	TOC	8.2	0.58	0.071	13%	Increase is the result of toxicity change (assigning oxalate); there is also a difference between ESP and BBI solubility. BBI was measured.
				OH	1.2	1.2	1.00	14%	Use of concentration from maximum-SOF layer.
				Al	2.9	2.9	1.00	17%	
				NO$_3$	1.6	1.6	1.01	27%	
				NO$_2$	1.6	1.6	1.01	33%	
BY-101	1.51	1.07E+07	7.11E+06	Al	1.8	1.8	1.00	12%	Difference between ESP and BBI solubility. BBI was measured; ESP was diluted for convergence.
				NO$_3$	1.3	1.3	0.99	14%	
				TOC	31	2.0	0.065	28%	Increase is the result of toxicity change (assigning oxalate) and concentration change
				NO$_2$	2.1	2.1	0.99	36%	Difference between ESP and BBI solubility. BBI was measured; ESP was diluted for convergence.
AW-105	1.56	2.09E+06	1.33E+06	TOC	0.00027	0.000088	0.32	-14%	Use of concentration from maximum-SOF layer.
				Al	6.9	6.9	1.00	11%	
				OH	1.6	1.5	0.98	20%	
				NO$_3$	1.5	1.5	0.98	31%	
				NO$_2$	2.7	2.7	0.98	45%	

Table 4.4. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
S-107	1.61	5.39E+06	3.35E+06	NO$_3$	1.3	1.3	1.00	18%	Difference between ESP and BBI solubility. BBI was measured.
				NO$_2$	1.5	1.5	1.00	30%	
				OH	2.6	2.6	1.00	42%	
B-107	1.69	4.97E+06	2.94E+06	F	0.024	0.024	1.00	-45%	Difference between ESP and BBI solubility. BBI was measured.
				SO$_4$	0.16	0.16	1.00	-21%	
				NO$_3$	3.5	3.5	1.00	159%	
AN-107	1.74	9.95E+06	5.71E+06	TOC	15	0.91	0.062	100%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
U-106	1.76	1.15E+07	6.50E+06	TOC	18	1.1	0.063	90%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
C-103	1.88	1.96E+06	1.04E+06	NO$_2$	0.73	0.72	0.98	-17%	Difference between ESP and BBI solubility. BBI was measured.
				U	44	40	0.92	55%	Difference between ESP and BBI solubility. BBI liquid was measured but solids were estimate.
				TOC	3.2	0.40	0.13	56%	Increase is the result of toxicity change (assigning oxalate); also difference between ESP and BBI solubility. BBI was measured.
U-202	1.95	4.62E+06	2.37E+06	NO$_3$	1.5	1.5	1.00	14%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
				Al	16	16	1.00	36%	
				NO$_2$	2.4	2.4	1.00	51%	
T-103	1.96	3.09E+06	1.58E+06	Al	944	944	1.00	19%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
				NO$_3$	1.9	1.9	1.00	37%	Use of concentration from maximum-SOF layer. BBI used estimates for liquid and solids.
				NO$_2$	2.2	2.2	1.00	45%	

Table 4.4. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
BX-105	2.00	4.95E+06	2.48E+06	NO_3	1.7	1.7	1.00	26%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
				TOC	39	2.4	0.062	41%	Increase is the result of toxicity change (assigning oxalate) and difference between ESP and BBI solubility.
				NO_2	2.2	2.2	1.00	43%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
U-201	2.04	4.99E+06	2.44E+06	NO_3	1.6	1.6	1.00	15%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
				Al	17	17	1.00	35%	
				NO_2	2.5	2.5	1.00	51%	
C-106	2.20	1.16E+06	5.26E+05	U	8.7	8.0	0.92	12%	Difference between ESP and BBI solubility. BBI was measured.
				TOC	3.5	1.1	0.32	39%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				NO_2	7.5	7.5	1.00	43%	Difference between ESP and BBI solubility. BBI was measured.
U-203	2.42	4.96E+06	2.05E+06	NO_3	2.0	2.0	1.00	17%	Difference between ESP and BBI solubility. BBI used estimates for liquid and solids.
				Al	22	22	1.00	32%	
				NO_2	3.0	3.0	1.00	50%	

Table 4.5. Causes of Method-Related Wet Bulk Solids SOF-3 Decreases of More Than 30%

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF decrease from this analyte	Comments
AP-105	0.55	7.14E+06	1.31E+07	NO$_2$	undefined	undefined	undefined	-20%	Artifact of using an estimated solid fraction (1.0) to convert old method from dry-solids basis to bulk wet solids. For Al, CO$_3$, and F there was also a difference in the ESP and BBI solubilities; the BBI used a estimate for the liquid.
				TOC	4.4	4.4	1.00	-13%	
				F	0.52	0.52	1.00	15%	
				CO$_3$	0.25	0.25	1.00	21%	
				Al	0.055	0.056	1.02	89%	
AW-102	0.56	1.11E+07	1.99E+07	Al	0.36	0.38	1.06	93%	Artifact of using an estimated solid fraction (0.93) to convert old method from dry-solids basis to bulk wet solids; also a difference in ESP and BBI solubilities. The BBI used a estimate for liquid and solids.
C-203	0.59	1.63E+08	2.78E+08	Pb	0.58	0.58	1.00	94%	Artifact of using an estimated solid fraction (0.38) to convert old method from dry-solids basis to bulk wet solids.
C-201	0.61	2.05E+08	3.34E+08	Pb	0.61	0.61	1.00	93%	Artifact of using an estimated solid fraction (0.56) to convert old method from dry-solids basis to bulk wet solids.
AN-102	0.65	1.24E+07	1.90E+07	NO$_2$	4.3	4.3	1.00	-28%	Artifact of using an estimated solid fraction (0.81) to convert old method from dry-solids basis to bulk wet solids. For TOC there was also a toxicity change (by assigning oxalate).
				TOC	1.3	1.1	0.85	-14%	
				Pb	0.082	0.082	1.00	17%	
				Al	0.17	0.18	1.06	31%	
				NO$_3$	0.39	0.40	1.01	85%	

Table 4.6. Causes of Method-Related Wet Bulk Solids SOF-3 Increases of More Than 30%

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
U-106	1.31	1.21E+07	9.22E+06	TOC	5.4	0.89	0.17	109%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
B-107	1.31	7.88E+06	6.01E+06	Al	1.8	1.4	0.79	16%	Use of concentration from maximum-SOF layer; toxicity increase (by assigning aluminum hydroxide instead of sodium aluminum carbonate hydroxide)
				NO$_3$	1.5	1.5	1.00	87%	Use of concentration from maximum-SOF layer
TX-108	1.31	1.53E+07	1.16E+07	NO$_3$	0.13	0.13	1.02	-196%	Use of concentration from maximum-SOF layer. In the case of Al, there is also a toxicity decrease (because Al is generated by assigning Si to NaAlSiO$_4$)
				Al	0.053	0.10	1.92	-17%	
				Pb	3.0	3.0	1.00	15%	
				U	35	35	1.00	314%	
AW-104	1.32	1.14E+07	8.66E+06	U	0.041	0.041	1.00	-35%	Use of concentration from maximum-SOF layer
				NO$_3$	1.4	1.5	1.11	16%	
				F	1.4	1.4	1.00	21%	
				TOC	2.4	1.0	0.43	23%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				NO$_2$	1.7	1.6	0.98	33%	Use of concentration from maximum-SOF layer
				OH	1.7	1.6	0.98	40%	Same reason as NO$_2$ (default scaled using NO$_2$)

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
BY-105	1.34	2.20E+07	1.64E+07	NO$_3$	0.33	0.33	1.01	-143%	Use of concentration from maximum-SOF layer
				Ca	0.30	1.9	6.2	-10%	Primarily toxicity change (by assigning calcium phosphate hydroxide instead of calcium carbonate); also use of concentration from maximum-SOF layer
				NO$_2$	2.1	2.1	1.00	11%	Use of concentration from maximum-SOF layer. In the case of TOC, there is also an increase in toxicity (by assigning oxalate).
				Ni	8.2	8.2	1.00	27%	
				OH	22	22	0.99	36%	
				Sr	9.2	9.2	1.00	42%	
				TOC	10	5.5	0.54	50%	
				U	8.7	8.7	1.00	78%	
BY-108	1.36	2.23E+07	1.65E+07	NO$_3$	0.34	0.35	1.03	-57%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO$_2$. In the case of TOC, there is a toxicity decrease (by assigning oxalate)
				Al	0.26	0.27	1.05	-38%	
				Ni	3.0	3.0	1.00	16%	
				OH	1.4	1.4	0.99	16%	
				TOC	3.4	1.9	0.55	21%	
				Pb	3.1	3.1	1.00	21%	
				Sr	3.9	3.9	1.00	31%	
				U	3.8	3.8	1.00	82%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
BX-103	1.36	9.28E+06	6.80E+06	Al	0.033	0.033	1.01	-79%	Use of concentration from maximum-SOF layer
				Pb	0.52	0.52	1.00	-23%	
				PO$_4$	3.4	3.4	0.99	13%	
				NO$_2$	1.9	1.9	1.00	13%	
				TOC	1.6	1.1	0.69	24%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				U	3.0	3.0	1.00	39%	Use of concentration from maximum-SOF layer
				NO$_3$	3.5	3.5	1.00	110%	
S-107	1.37	9.93E+06	7.24E+06	F	1.4	1.4	1.00	10%	Use of concentration from maximum-SOF layer
				Zr	1.4	1.4	1.00	10%	
				U	1.4	1.4	1.00	12%	
				NO$_2$	1.4	1.4	1.00	16%	
				NO$_3$	1.4	1.4	1.01	16%	
				Al	1.3	1.3	1.00	19%	
SX-115	1.37	7.70E+06	5.60E+06	Fe	0.56	0.56	1.00	-16%	In old method, ESP input concentration was increased for charge balance
				TOC	2.2	1.1	0.51	6%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				Al	1.1	1.1	1.01	8%	Difference in ESP and BBI bulk density
				NO$_3$	2.6	2.6	0.99	88%	In old method, ESP input concentration was decreased for charge balance

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
AN-107	1.38	1.14E+07	8.25E+06	Pb	0.26	0.26	1.00	-38%	Artifact of using an estimated solid fraction (0.13) to convert old method from dry-solids basis to bulk wet solids; also a difference in the ESP and BBI solubilities. BBI is measured.
				F	0.33	0.33	1.00	-15%	
				Al	2.0	0.94	0.46	13%	Increase is the result of toxicity change (by assigning aluminum hydroxide, not sodium aluminum carbonate dihydroxide), not concentration change
				TOC	17.3	1.1	0.061	140%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
AN-106	1.38	9.60E+06	6.94E+06	CO$_3$	1.6	1.6	1.01	7%	Artifact of using an estimated solid fraction (0.13) to convert old method from dry-solids basis to bulk wet solids; also a difference in the ESP and BBI solubilities. BBI uses estimate for solids.
				NO$_3$	1.6	1.6	1.01	30%	
				NO$_2$	1.9	1.9	0.97	61%	
B-111	1.39	5.00E+06	3.61E+06	Pb	82	0.89	0.011	103%	Increase is the result of toxicity change (by assigning lead hydroxide rather than lead carbonate), not concentration change
C-108	1.41	8.98E+06	6.38E+06	Pb	3.4	3.4	1.00	88%	Use of concentration from maximum-SOF layer
C-111	1.41	2.00E+07	1.41E+07	NO$_3$	1.5	1.5	0.99	7%	Use of concentration from maximum-SOF layer. In addition, in the old method the NO$_3$ input to ESP was adjusted down to reach charge balance.
				NO$_2$	1.7	1.7	0.98	14%	
				Pb	2.4	1.1	0.45	64%	Toxicity change (by assigning lead hydroxide in the solid instead of part lead hydroxide and part lead phosphate)

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
U-112	1.43	1.26E+07	8.82E+06	Pb	2.8	2.8	1.00	47%	Use of concentration from maximum-SOF layer
				Al	1.5	1.4	0.98	60%	
U-105	1.45	2.12E+07	1.46E+07	NO_3	0.47	0.47	1.00	-64%	Use of concentration from maximum-SOF layer
				NO_2	0.46	0.46	0.99	-15%	
				TOC	2.4	0.53	0.22	17%	Increase is the result of toxicity change (by assigning oxalate), not concentration change
				Al	4.5	4.5	0.99	71%	Use of concentration from maximum-SOF layer
				U	7.2	7.2	1.00	97%	
C-202	1.46	2.14E+08	1.47E+08	Pb	1.6	0.80	0.50	109%	Toxicity change (by assigning lead hydroxide in the solid instead of part lead hydroxide and part lead carbonate)
BY-112	1.46	1.66E+07	1.14E+07	TOC	0.074	0.072	0.98	-31%	Use of concentration from maximum-SOF layer. In the case of Al, there is also a toxicity decrease (because Al is generated by assigning Si to $NaAlSiO_4$)
				Cr(III)	0.081	0.081	1.00	-21%	
				CO_3	0.089	0.089	1.00	-20%	
				NO_3	0.52	0.53	1.02	-18%	
				Al	0.043	0.088	2.1	-15%	
				Pb	5.1	5.1	1.00	12%	
				U	63	63	1.00	223%	
T-105	1.47	8.01E+06	5.45E+06	Pb	0.54	0.54	1.00	-16%	Use of concentration from maximum-SOF layer. In the case of TOC, there is also a toxicity increase (by assigning oxalate)
				U	2.4	2.4	1.00	15%	
				TOC	3.3	1.7	0.53	18%	
				Al	2.7	2.4	0.91	85%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
BY-104	1.52	1.96E+07	1.29E+07	NO$_3$	0.51	0.53	1.02	-39%	Use of concentration from maximum-SOF layer. In the case of TOC, there is also a toxicity increase (by assigning oxalate)
				Pb	3.4	3.4	1.00	12%	
				Al	1.7	1.8	1.02	14%	
				TOC	2.4	1.5	0.63	18%	
				Ni	5.4	5.4	1.00	18%	
				Sr	5.6	5.6	1.00	28%	
				U	5.6	5.6	1.00	52%	
BY-109	1.56	1.29E+07	8.27E+06	F	0.022	0.022	1.00	-36%	Use of concentration from maximum-SOF layer. In the case of TOC, there is also a toxicity increase (by assigning oxalate)
				TOC	0.18	0.15	0.82	-15%	
				Al	5.8	5.5	0.95	163%	
U-110	1.57	1.14E+07	7.26E+06	OH	2.0	2.0	0.99	11%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO$_2$.
				NO$_3$	1.8	1.8	1.01	12%	
				Pb	1.7	1.7	1.00	13%	
				U	1.5	1.5	1.00	23%	
				Al	1.4	1.4	1.00	25%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
A-101	1.58	2.10E+07	1.33E+07	NO_3	0.25	0.25	1.00	-44%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO_2. In the case of Al, there is a toxicity decrease (because part of the Al is in $NaAlSiO_4$, which is the compound assigned to Si)
				NO_2	0.026	0.026	0.99	-40%	
				OH	0.027	0.026	0.99	-25%	
				TOC	0	0	undefined	-12%	
				La	21	21	1.00	15%	
				Ni	44	44	1.00	18%	
				Al	4.7	5.9	1.3	49%	
				Pb	28	28	1.00	132%	
S-109	1.60	2.22E+07	1.39E+07	NO_3	0.22	0.22	1.01	-109%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO_2. A further increase because, in the old method, the inputs to ESP were diluted by 20% to make the model converge.
				NO_2	7.1	7.1	1.00	17%	
				Al	29	29	1.01	67%	
				OH	7.1	7.1	1.00	106%	
B-108	1.62	1.26E+07	7.80E+06	F	0.54	0.54	1.00	-14%	Use of concentration from maximum-SOF layer. A further increase because, in the old method, the inputs to ESP were diluted by 10% to make the model converge.
				NO_2	2.4	2.4	0.99	7%	
				Pb	2.5	2.5	1.00	31%	
				Al	2.6	2.6	1.00	72%	
BY-101	1.63	1.95E+07	1.19E+07	NO_3	0.15	0.15	1.01	-86%	Use of concentration from maximum-SOF layer. A further increase because, in the old method, the inputs to ESP were diluted by 10% to make the model converge.
				NO_2	7.2	7.1	0.99	20%	
				Ni	9.3	9.3	1.00	25%	
				Pb	7.3	7.3	1.00	36%	
				U	9.1	9.1	1.00	52%	
				OH	6.3	6.2	0.99	53%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
T-103	1.72	1.53E+07	8.90E+06	Al	0.0083	0.017	2.1	-66%	Use of concentration from maximum-SOF layer. In the case of Al, there is a toxicity decrease (because the Al is generated as part of NaAlSiO$_4$, which is the compound assigned to Si)
				Pb	0.36	0.36	1.00	-22%	
				U	17	17	1.00	175%	
BY-107	1.79	2.11E+07	1.18E+07	NO$_3$	0.50	0.51	1.03	-24%	Use of concentration from maximum-SOF layer.
				TOC	2.3	2.1	0.93	10%	
				Sr	16	16	1.00	16%	
				Ni	16	16	1.00	16%	
				Pb	9.5	9.5	1.00	20%	
				U	12	12	1.00	51%	
TX-118	1.82	9.42E+06	5.16E+06	NO$_3$	0.26	0.27	1.03	-14%	Use of concentration from maximum-SOF layer. In addition, Cr(VI) is increased because the Cr wash fraction used to estimate Cr(VI) by the new method is greater than the Cr(VI)/Cr split used in the old. In the case of TOC, there is a toxicity increase (by assigning oxalate).
				U	2.8	2.8	1.00	8%	
				Cr(VI)	7.9	7.9	1.00	12%	
				Pb	3.1	3.1	1.00	19%	
				TOC	3.6	2.9	0.79	69%	
C-107	1.85	2.34E+07	1.26E+07	Al	3.3	3.2	0.98	28%	Use of concentration from maximum-SOF layer.
				Pb	1.9	1.9	1.00	63%	
BY-106	1.99	2.47E+07	1.24E+07	NO$_3$	0.32	0.33	1.03	-38%	Use of concentration from maximum-SOF layer. In the case of TOC, there is also a toxicity increase (by assigning oxalate)
				Sr	13	13	1.00	13%	
				Pb	7.8	7.8	1.00	14%	
				TOC	8.4	5.3	0.63	27%	
				U	12	12	1.00	32%	
				Ni	13	13	1.00	39%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
BY-110	2.00	2.10E+07	1.05E+07	TOC	3.3	1.5	0.47	12%	Increase is primarily the result of toxicity change (by assigning oxalate), not concentration change
				Sr	6.9	6.9	1.00	13%	Use of concentration from maximum-SOF layer.
				Ni	4.8	4.8	1.00	13%	
				Pb	4.7	4.7	1.00	24%	
				U	6.2	6.2	1.00	37%	
AX-103	2.05	2.00E+07	9.76E+06	NO$_2$	0.035	0.034	0.99	-27%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO$_2$.
				OH	0.036	0.035	0.99	-13%	
				Ni	10	10	1.00	8%	
				La	9.7	9.7	1.00	13%	
				Pb	9.7	9.7	1.00	114%	
S-112	2.16	3.30E+07	1.53E+07	NO$_3$	0.23	0.23	1.01	-48%	Use of concentration from maximum-SOF layer.
				Al	16	15	0.92	30%	
				OH	15	15	1.00	111%	
SX-114	2.27	3.31E+07	1.46E+07	NO$_3$	0.46	0.47	1.01	-16%	Use of concentration from maximum-SOF layer.
				Al	1.5	1.5	1.00	10%	
				OH	9.5	9.5	1.00	102%	
BX-105	2.40	1.55E+07	6.45E+06	U	5.9	5.9	1.00	109%	Use of concentration from maximum-SOF layer.
A-104	2.58	2.26E+07	8.78E+06	OH	0.14	0.14	1.00	-18%	Use of concentration from maximum-SOF layer. OH is default, scaled from NO$_2$.
				NO$_3$	25	25	1.01	10%	
				La	25	25	1.00	10%	
				Pb	24	24	1.00	89%	

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
SX-113	2.62	5.18E+06	1.98E+06	Si	0	0	undefined	-29%	Zeroed because all Si was assigned to NaAlSiO$_4$, which is credited to Al for the purpose of this table
				U	4.3	4.3	1.00	7%	Use of concentration from maximum-SOF layer.
				NO$_2$	undefined	undefined	undefined	23%	In old method, charge balance in postprocessing caused this concentration to be zeroed
				NO$_3$	undefined	undefined	undefined	34%	In old method, charge balance in postprocessing caused this concentration to be zeroed
				Al	5.7	2.6	0.46	64%	Use of concentration from maximum-SOF layer; toxicity increased because Al was present in NaAlSiO$_4$ in old method, but was assigned to Al(OH)$_3$ in new method.
B-103	2.66	1.56E+07	5.86E+06	Al	0.026	0.056	2.1	-14%	In the maximum-SOF layer, the only Al comes as part of NaAlSiO$_4$ (the compound assigned to Si). The toxicity decrease is based on the difference between the old Al(OH)$_3$ and the new NaAlSiO$_4$.
				U	22	22	1.00	116%	Use of concentration from maximum-SOF layer.
U-104	2.68	1.20E+07	4.47E+06	NO$_2$	1.7	1.7	1.00	9%	Use of concentration from maximum-SOF layer.
				NO$_3$	1.6	1.6	1.00	13%	
				Al	5.6	3.5	0.62	63%	Use of concentration from maximum-SOF layer. The toxicity increase in Al appears because part of the Al in the old method was NaAlSiO$_4$, but in the new method is Al(OH)$_3$.
BX-102	3.61	9.70E+06	2.69E+06	NO$_3$	4.3	4.3	1.02	6%	Use of concentration from maximum-SOF layer.
				Pb	213	2.4	0.011	32%	Toxicity change (by assigning lead hydroxide); also use of concentration from max.-SOF layer.
				Al	2.9	2.4	0.83	47%	Use of concentration from maximum-SOF layer.

Table 4.6. (contd.)

Tank	New/Old SOF-3 Ratio	New SOF-3	Old SOF-3	Analyte	New/Old Contrib-3 Ratio	New/Old Conc. Ratio	New/Old Effective TEEL-3 Ratio	Fraction of SOF increase from this analyte	Comments
U-108	3.65	6.80E+07	1.86E+07	NO$_3$	0.079	0.080	1.00	-13%	Use of concentration from maximum-SOF layer.
				U	11	11	1.00	19%	
				Pb	11	11	1.00	97%	
T-110	4.22	9.57E+06	2.27E+06	La	37	37	1.00	101%	Use of concentration from maximum-SOF layer.
C-102	4.52	1.52E+07	3.37E+06	U	25	26	1.01	96%	Use of concentration from maximum-SOF layer.
C-204	11.51	1.06E+08	9.18E+06	Pb	288	0.96	0.0033	100%	Toxicity change (by assigning lead hydroxide in the solid instead of lead carbonate)

- In all 5 of the major decreases and one of the increases, the primary cause was a combination of solubility changes (ESP versus BBI) with inaccuracies in the estimation method for the old-method solid volume fraction;

- In 4 of the increases, the primary cause was an increase in the toxicity of Pb;

- In 2 of the increases, the primary cause was an increase in the toxicity of TOC; and

- In one of the increases, the primary cause was charge-balance adjustments made to the ESP output composition in the old method.

The above list makes it appear that differences between ESP and BBI solubilities are not as important for wet bulk solids as they were for liquids. This is partly true; bulk solids contain both liquid and dry solid and the effect of solubility changes alone is offset by the presence of solid. Nevertheless, the apparent lack of effect of solubility is somewhat misleading.

Suppose, for example, the ESP model predicted lower solubility for an analyte than was seen in the BBI. This solubility difference would tend to increase the old-method analyte concentration in the dry-solid phase and decrease it in the liquid phase, compared to the BBI values used in the new method. Next consider the effect of the solid volume fraction used to combine the dry-solid and liquid concentrations into a wet bulk solids concentration. This solid fraction was estimated from BBI and ESP information (Equation 4.1 in Section 4.1). If the fraction is consistent with that in the BBI's wet bulk solid phase, then the old-method SOF will be higher or lower than the new one depending only on whether the solid or liquid phase dominates. If the old-method solid fraction is an overestimate (as it seems to be in AP-105, for one example) the old-method SOF is somewhat likelier to exceed the new one. If the old-method solid fraction is an underestimate, the opposite is true. As another complication, the old method density for the wet bulk solids may differ from the density given in the BBI. Thus the uncertainty in the estimated solid volume fraction is folded together with differences in solubility and density, and it is very difficult to determine the "real" cause of concentration changes.

The following general rules were used in assessing the causes of changes in the wet bulk solids SOF-3 values (as shown in Tables 4.5 and 4.6):

1. If a comparison of the original ESP output and the BBI showed that both sources showed about the same solubility for an analyte (i.e., its liquid-phase concentration), solubility differences were ruled out as the cause of SOF changes from the old to the new method.

2. If the BBI contained more than one bulk-solids layer and the one used for the tank SOF had distinctly different concentrations for the pertinent analytes, compared to the other solids layers, the SOF changes were considered to be the effect of selecting the maximum-SOF layer. Note that the maximum-SOF layer could have lower concentrations of some analytes than other layers, but higher concentrations of other analytes. Therefore, for layer-selection to be the reason for SOF changes, the layer concentrations had to be different from those in the rest of the tank in the correct direction.

3. When neither layer-selection nor solubility differences explained a change in an analyte concentration, an inaccuracy in the estimated solid volume fraction for the old method was considered to be the cause.

The process of deciding on a cause for concentration changes was only partly quantitative, as can be seen. On the other hand, the variation of analyte concentration from one layer to another in a tank was often so

significant that layer-selection was definitely the reason for the concentration change from old to new method. Even considering contributions from solid-fraction error and solubility changes, the use of maximum-SOF layer concentrations appears to have much more effect on wet bulk solids SOFs than any other aspect of the method change.

The next most common cause of changes in SOF-3 values for wet bulk solids was toxicity change in either TOC or lead. Changes in the effective toxicity of calcium and aluminum also appear in the table, but are not primary causes of the SOF-3 change; they consistently account for less than 20% of the change.

The use of oxalate to represent TOC was the primary cause of the SOF-3 increase in only 2 of 45 tanks, for wet bulk solids, although it was primary in 5 out of 24 tanks for liquids. The choice of oxalate had less effect on wet bulk solids SOFs than on liquids because most of the TOC in solids was already being assigned to oxalate in the old method. The increased toxicity of lead, which is the primary cause of the SOF-3 increase in 4 tanks, resulted from the choice of lead hydroxide as the solid compound for lead. In the old method, ESP had predicted lead carbonate and lead phosphate, which are less toxic than lead hydroxide, to be the precipitated forms of lead in a number of sludge tanks.

A few of the SOF increases had other causes. In some tanks (e.g., TX-108) the selected maximum-SOF wet bulk solids layer contained little or no aluminum, based on the BBI composition. However, the layer did contain silicon, which in the new method was assigned to the compound $NaAlSiO_4$. (See the discussion in Sections B.2 and B.18 of Appendix B.) Because this compound contains aluminum as well as silicon, the new method in effect "generated" aluminum in greater-than-BBI quantities to match the number of moles of silicon. In many cases (including TX-108) this results in a decreased concentration of aluminum, compared to the old tank-average value that included higher- aluminum layers in the average. In other cases (such as A-101) the aluminum concentration increases from the old-method value. SX-113 was the only tank in which the "generation" of Al contributed to a significant increase in the tank SOF-3, compared to the old method. The increase came about because a layer of Sludge/DE contained a high Si concentration; when the Si was represented as $NaAlSiO_4$, the resulting Al concentration exceeded the BBI value.

In a few cases the inputs to the ESP model, or the model outputs, had been adjusted in some manner in the old method.

- SX-115 and C-111: the composition input had to be modified from that of the tank-average waste to achieve the charge balance that the ESP model requires in its inputs. As a result nitrate was underestimated in the old method. The new method did not require this type of charge balance.

- S-109, B-108, and BY-101: the ESP model could not be made to converge on the BBI-average composition. Convergence was obtained by diluting the waste composition with water. As a result the concentrations and SOFs were underestimated in the old method, contributing (though not as a primary cause) to the increase shown under the new method. Note that this dilution also affected the old-method liquid SOF-3 values in S-109 and BY-101.

- SX-113: The charge balance carried out on ESP outputs in the old method to offset the organic complexant anions (which were added into the composition after ESP modeling) caused hydroxide, nitrate, and nitrite to be zeroed. (See Section 3.3.5 for a complete discussion.) As a result, the SOFs calculated by the old method were underestimated, contributing to an increase in SOF under the new method.

5.0   Conclusions

A new method of calculation for the toxicological SOFs of Hanford tank waste was compared to the old method that had been applied in 2002 and 2003 (Cowley et al. [2003]). The comparison was based on the SOFs for the major tank waste constituents (Al, Bi, Ca, Cl, Cr, F, Fe, Hg, K, La, Mn, Na, Ni, NO_2, NO_3, Pb, PO_4, Si, SO_4, Sr, TOC, U, and Zr) as well as Ag. The May 2002 BBI was the basis for waste compositions. The liquid-phase and wet bulk solids SOFs for TEEL-1, TEEL-2, and TEEL-3 were included.

It was found that 50 to 60% of the Hanford tanks had SOFs for which the new method is within ±20% of the old method, while 15 to 20% of the tanks show a difference of more than ±50%. The SOFs are increased by the new method more often than they are decreased. These statements hold for both the liquid and wet bulk solids SOFs. Thus, less than 10% of the tanks had SOFs that decreased (and therefore were possibly nonconservative) by more than 50%. For perspective, an uncertainty of 20% in analyte concentrations is a reasonable expectation for compositions based on sample measurements, considering the uncertainties in sample concentration and density analyses and the variability of concentration within the waste. The overall uncertainty could be considerably greater in tanks that have not been sampled, for which the composition is based on process knowledge or a template (Place and Higley 2005).

A detailed semi-quantitative study was made to learn the reasons for method-related changes in SOFs at TEEL-3. This TEEL level was chosen because its new-method SOFs differed from old-method values somewhat more than at the other TEEL levels. Three aspects of the change in SOF calculation method were identified as the causes of significant changes (those exceeding 30%) in liquid-phase SOFs for TEEL-3:

- In 16 of the 24 tanks in which significant increases occurred, the primary cause was a difference between the ESP-predicted and BBI solubility of one or more analytes (most often NO_3, NO_2, OH, and Al). This was also the primary cause of the major decreases in all 14 liquid SOFs that had more than a 30% decrease. Section 3.3.2 contains a general discussion of this point.

- In 3 of the tanks in which significant increases occurred, the primary cause was the use of analyte concentrations from the maximum-SOF layer instead of the tank-average waste, as discussed in Section 3.3.1.

- In 5 of the tanks in which significant increases occurred, the primary cause was the increase in the effective toxicity of TOC that resulted from using oxalate to represent all TOC. (Detailed discussion can be found in Sections 3.1 and C.22.)

Several aspects of the change in SOF calculation method were the causes of significant changes (those exceeding 30%) in wet bulk solid SOFs for TEEL-3:

- In 37 of the 45 tanks in which significant increases occurred, the primary cause was the use of the concentrations of the layer that had the maximum SOF in the tank instead of the tank-average waste.

- In all 5 of the tanks in which significant decreases occurred and in one of the tanks that showed an increase, the primary cause was a combination of solubility changes (ESP versus BBI) with differences in the calculated solid volume fraction used to put the old-method SOFs on the basis of wet bulk solids instead of dry solids. Section 4.1 discusses the uncertainty involved in making this basis change.

- In 4 of the tanks in which significant increases occurred, the primary cause was an increase in the effective toxicity of lead because of its assignment to the compound lead hydroxide.

- In 2 of the tanks in which significant increases occurred, the primary cause was an increase in the effective toxicity of TOC because of its assignment to oxalate.

- In one of the tanks in which significant increases occurred, the primary cause was charge-balance adjustments made to the ESP output in the old method. Section 3.3.5 discusses this effect.

The above list makes it appear that differences between ESP and BBI solubilities are not as important for wet bulk solids as they were for liquids. It is difficult to sort out the mingled effects of maximum-layer concentrations, solubility difference, solid fraction uncertainty, and (to a lesser extent) density differences. On the other hand, the variation of analyte concentration from one layer to another in a tank was often significant enough to make it clear that layer-selection was the reason for the concentration change from old to new method.

Taking the results for liquid and wet bulk solids SOFs together, it is clear that the use of the maximum-layer approach is the dominant reason why the new method calculates different (generally larger) SOFs than the old. This maximum-layer approach was chosen to be consistent with the approach used in calculating ULDs for radiological assessments, and led to a change in the direction of conservatism. Differences between ESP and BBI solubilities were the next most common reason for differences between new and old SOFs, particularly in the liquid phase. The solubility-related changes in SOF were roughly equally distributed between increases and decreases. Changes in the effective toxicities of TOC and lead were the third most common reason. These toxicity changes increased SOFs and so were in a conservative direction.

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Appendix A – User-Specified Chemical Equations Used by New Method in Comparison of New and Old Methods

Appendix A
User-Specified Chemical Equations Used by New Method in Comparison of New and Old Methods

This appendix lists and explains the chemical equations used to assign compounds to analytes in the new SOF calculation method. The justification of the choices of compounds is separately discussed in Appendix B.

A.1   New Chemical Equations

Table A.1 (located at the end of this appendix) contains all the chemical equations that are used for compound assignment in the new method. Several points should be noted. All the concentrations in the equations are notated in square brackets. Other entries (such as TempNa) are intermediate concentration variables. All have units of molarity. The concentrations that are never found on the left of an equals sign are the input analyte concentrations, which are based on BBI or default values. All others are compound concentrations, which are outputs.

For documentation purposes, the equations are given in a form that can be used for input to SOF Program. The intermediate concentration variables are calculated first, and the variables can refer to each other (though the references cannot be circular). The compound concentrations are calculated last, and the equation for one compound concentration cannot include a reference to any other compound concentration. Only analyte concentrations and variables can appear in the compound concentration equations.

The SOF Program software treats concentrations differently than intermediate concentration variables. The intermediate variables are allowed to take on negative values. The output (compound) concentrations are not; negative concentrations are automatically set to zero. This feature of SOF Program has required the use of workarounds in the intermediate variables, as is described in Section A.2. Workarounds have also been devised to avoid divide-by-zero errors.

The equations in Table A.1 use the same analytes that were among the ESP inputs used by Cowley et al. (2003), the major analytes and silver (Ag). Trace analyte equations are excluded in this comparison study, although they are included in the general form of the new method.

A.2   Liquid-Phase Equations

Analytes in the liquid phase fall into several categories:

1. Assigned to hydroxide compounds (e.g., Al, Bi, etc.);

2. Cations (e.g., Sr) that are charge-balanced by part of the dominant anions;

3. Assigned to compounds with analytes other than hydroxide (e.g., Ag, Ca, U);

4. Assigned to anions that form potassium and sodium salts (e.g., F);

5. Dominant anions (NO_2, NO_3, OH).

As an example of the first category, consider the analyte Al. Its compound assignment equation is

$[Al(OH)_3] = [Al]$

The assignment of Al to $Al(OH)_3$ does not affect any other analyte. The hydroxide in the compound is not free hydroxide, but bound to the metal in a hydroxide complex in solution. It therefore does not need to be subtracted from the [OH] concentration input to maintain a mass-balance on the OH analyte (which by definition is free OH).

By contrast, the analytes in the second category, of which the only example is Sr, do consume hydroxide as well as other analytes. The analyte Sr is present in solution as an uncomplexed cation, Sr^{+2}. Its main counterions would be the dominant anions, OH^-, NO_2^-, and NO_3^-. It is therefore assigned to $Sr(OH)_2$, $Sr(NO_2)_2$, and $Sr(NO_3)_2$.

$[Sr(NO_2)_2]$ $= NO_2Ratio*[Sr]$

$[Sr(NO_3)_2]$ $= NO_3Ratio*[Sr]$

$[Sr(OH)_2]$ $= OHRatio*[Sr]$

The amounts of these three anions that are consumed by Sr must be accounted for in the mass balances. The accounting is performed in Temp2OH, TempNO_2, and TempNO_3 (the equations have been simplified from the form in the table to support the current explanation).

Temp2OH $= [OH] – OHRatio*(2*[Sr])$

TempNO_2 $= [NO_2] – NO_2Ratio*(2*[Sr])$

TempNO_3 $= [NO_3] – NO_3Ratio*(2*[Sr])$

The ratios in the equations serve the purpose of splitting Sr among the compounds in proportion to the relative amounts of the dominant anions.

Analytes in the third category also consume other analytes, but do not consume the dominant anions. For example, Ag tends to form chloride complexes in solution, is assigned to AgCl, and therefore consumes Cl in the equations:

$[AgCl]$ $= [Ag]$

All of the Cl that is taken up by Ag must be removed to maintain the mass balance on Cl (again, this equation is simplified):

TempCl $= [Cl] - [Ag]$

The only condition under which the mass balance on Cl is not maintained is when [Ag] exceeds [Cl]. To prevent TempCl from being negative, the absolute-value function ABS() is used, as seen in the unsimplified version of the equation:

TempCl $= 0.5 * ([Cl] - [Ag] + ABS([Cl] - [Ag]))$

This equation sets TempCl to zero if the difference ([Cl]-[Ag]) is negative; in this circumstance Cl is in effect "generated" to match the amount of Ag in solution. The analytes Ca and Si, and U and CO_3, have the same kind of relationship as Ag and Cl.

Anionic analytes (other than the dominant anions) fall into the fourth category. These analytes, such as F and Cr(VI), are present in solution as the anions F^- and CrO_4^{-2}, which are countered by the dominant cations, Na^+ and K^+. The fourth-category analytes are therefore assigned to sodium and potassium salts in proportion to the relative amounts of Na and K. For example, the equations for the analyte F are

[KF] = KRatio*[F]

[NaF] = NaRatio*[F]

The fourth-category analytes consume the analytes Na and K, which is accounted for in the variables TempNa and TempK:

TempNa = [Na] - NaRatio*(TempCl + [TOC] + 2*TempCO$_3$ + 2*[CrVI] + [F] + 3*[PO$_4$] + 2*[SO$_4$] + 2*TempSi + [Pb])

TempK = [K] - KRatio*(TempCl + [TOC] + 2* TempCO$_3$ + 2*[CrVI] + [F] + 3*[PO$_4$] + 2*[SO$_4$] + 2*TempSi + [Pb])

All the fourth-category anions are included in these equations, which carry out mass-balance accounting for [Na] and [K]. Some of these anions – Cl^-, CO_3^{-2}, and SiO_3^{-2} (representing the analyte Si) – have already been partially or perhaps completely consumed by category-three analytes. Only the remaining portions of these anions (which may be zero) are assigned to sodium and potassium salts.

Note that TempCl, for example, is used as a term in the equations (to represent the portion of the Cl that is assigned to NaCl and KCl) instead of using the difference expression ([Cl] – [Ag]). The two expressions are not equivalent. TempCl can only be zero or positive. The difference ([Cl] – [Ag]) can be zero, positive, or negative. Of the two expressions, TempCl is the one that is required in the mass balance in order to maintain consistency with the NaCl and KCl equations. Using it ensures that [NaCl] and [KCl] are zeroed whenever [Ag] exceeds [Cl].

The only analytes in the fifth category, dominant anions, are OH (free OH), NO_2, and NO_3. These anions are treated as being counter-balanced by Na and K. They are split between Na and K in proportion to the relative amounts of the Na and K that are left over after all the other anions have been accounted for.

In summary, the liquid-phase compound assignment process in the new method begins by assigning compounds to analytes in the first three categories. Then the fourth-category anions (including the Cl, CO_3, and Si already partially consumed by Ag, U, and Ca) are assigned to sodium and potassium salts. Finally the dominant anions (free OH^-, NO_2^-, and NO_3^-) are split among Na and K.

Most of the liquid-phase chemical equations in Table B.1 carry out compound assignments, as just described. A few, however, carry out operations that are intended to avoid divide-by-zero errors in the calculation of ratios.

It is possible, in very dilute waste liquids, for [Na] and [K] both to be zero, in which case NaRatio and KRatio incur a divide-by-zero error. The variable TempXNa is used to avoid this:

TempXNa $= 0.000000001 + 0.5 * ([Na] + ABS([Na]))$

TempXNa will be given a value only negligibly different from [Na], so long as [Na] is non-zero. If [Na] is zero, TempXNa is given a value of 1E-09. This variable is used only in calculating NaRatio and KRatio:

NaRatio $= TempXNa / ([K] + TempXNa)$

KRatio $= 1 - NaRatio$

If [Na] is not zero, TempXNa is insignificant and NaRatio is [Na]/([K]+[Na]). If [Na] is zero and [K] is non-zero, NaRatio will be essentially equal to 1E-09/[K] and KRatio will be very close to unity. And if both [Na] and [K] equal zero, NaRatio is unity and KRatio is zero; all the anions are treated as forming sodium salts.

The variables TempXNO3, Temp2Na, and Temp2K provide the same type of protection against divide-by-zero errors in NO$_2$Ratio, NO$_3$Ratio, OHRatio and the final calculation of [NaNO$_3$], [NaNO$_2$], [NaOH], [KNO$_3$], [KNO$_2$], and [KOH].

A.3   Wet Bulk Solids Equations

The new-method chemical equations for the wet bulk solids phase are simpler than those for the liquid phase. Because potassium is not a major contributor to the dry solids, all the anionic analytes are treated as sodium salts (except that K is assigned to KNO$_3$). This approach eliminates the Na/K salt split carried out by ratios in the liquid phase. No divide-by-zero protections are needed.

In the wet bulk solids phase, several analytes are assigned in a manner that consumes other analytes, just as Ag consumed Cl in the liquid phase:

- Ag is assigned to Ag$_2$CO$_3$, consuming CO$_3$;

- Ca is assigned to Ca$_5$OH(PO$_4$)$_3$, consuming PO$_4$ (the OH is not derived from free OH);

- K is assigned to KNO$_3$, consuming NO$_3$;

- La is assigned to LaPO$_4$, consuming PO$_4$;

- Si is assigned to NaAlSiO$_4$, consuming Al; and

- Sr is assigned to SrCO$_3$, consuming CO$_3$.

The mass-balances on the consumed analytes are carried out as for the liquid phase. It is possible (as in the liquid) for the consumed analytes to have a higher concentration in the final mixture of compounds than in the BBI-based inputs. For example, if [Si] exceeds [Al], then enough NaAlSiO$_4$ will be formed to represent all the Si, which will over-represent the Al. As a result, the concentration [Al(OH)$_3$] will equal zero because SOF Program will set the negative difference ([Al] – [Si]) to zero.

Table A.1. Basis for Calculating Compounds of Major Analytes in the New SOF Calculation Method

Species in the Liquid
$TempXNa$ = 0.000000001 + 0.5 * ([Na] + ABS([Na]))
$NaRatio$ = TempXNa / ([K] + TempXNa)
$KRatio$ = 1 - NaRatio
$TempXNO_3$ = 0.000000001 + 0.5 * ([NO$_3$] + ABS([NO$_3$]))
NO_2Ratio = [NO$_2$] /([NO$_2$] + TempXNO$_3$ + [OH])
NO_3Ratio = TempXNO$_3$ /([NO$_2$] + TempXNO$_3$ + [OH])
$OHRatio$ = [OH] /([NO$_2$] + TempXNO$_3$ + [OH])
$TempCO_3$ = 0.5 * ([CO$_3$] - [U] + ABS([CO$_3$] - [U]))
$TempSi$ = 0.5 * ([Si] - [Ca] + ABS([Si] - [Ca]))
$TempCl$ = 0.5 * ([Cl] - [Ag] + ABS([Cl] - [Ag]))
$TempNa$ = [Na] - NaRatio*(TempCl + [TOC] + 2*TempCO$_3$ + 2*[CrVI] + [F] + 3*[PO$_4$] + 2*[SO$_4$] + 2*TempSi + [Pb])
$TempK$ = [K] - KRatio*(TempCl + [TOC] + 2* TempCO$_3$ + 2*[CrVI] + [F] + 3*[PO$_4$] + 2*[SO$_4$] + 2* TempSi + [Pb])
$Temp2Na$ = 0.000000001 + 0.5 * (TempNa + ABS(TempNa))
$Temp2K$ = 0.5 * (TempK + ABS(TempK))
$Temp2OH$ = 0.5 * ([OH] - OHRatio*(2*[Sr]) + ABS([OH] - OHRatio*(2*[Sr])))
$TempNO_2$ = 0.5 * ([NO$_2$] - NO$_2$Ratio*(2*[Sr]) + ABS([NO$_2$] - NO$_2$Ratio*(2*[Sr])))
$TempNO_3$ = 0.5 * ([NO$_3$] - NO$_3$Ratio*(2*[Sr]) + ABS([NO$_3$] - NO$_3$Ratio*(2*[Sr])))
[AgCl] = [Ag]
[Al(OH)$_3$] = [Al]
[Bi(OH)$_3$] = [Bi]
[CaSiO$_3$] = [Ca]
[Cr(OH)$_3$] = [CrIII]
[Fe(OH)$_3$] = [Fe]
[Hg(OH)$_2$] = [Hg]
[KHPbO$_2$] = KRatio*[Pb]
[K$_2$C$_2$O$_4$] = KRatio*0.5*[TOC]
[K$_2$CO$_3$] = KRatio*TempCO$_3$
[K$_2$CrO$_4$] = KRatio*[CrVI]
[K$_2$SiO$_3$] = KRatio*TempSi
[K$_2$SO$_4$] = KRatio*[SO$_4$]
[K$_3$PO$_4$] = KRatio*[PO$_4$]
[KCl] = KRatio*TempCl
[KF] = KRatio*[F]
[KNO$_2$] = TempNO$_2$*Temp2K/(Temp2K + Temp2Na)
[KNO$_3$] = TempNO$_3$*Temp2K/(Temp2K + Temp2Na)
[KOH] = Temp2OH*Temp2K/(Temp2K + Temp2Na)

Species in the Liquid
[La(OH)$_3$] = [La]
[Mn(OH)$_2$] = [Mn]
[NaHPbO$_2$] = NaRatio*[Pb]
[Na$_2$C$_2$O$_4$] = NaRatio*0.5*[TOC]
[Na$_2$CO$_3$] = NaRatio*TempCO$_3$
[Na$_2$CrO$_4$] = NaRatio*[CrVI]
[Na$_2$SiO$_3$] = NaRatio*TempSi
[Na$_2$SO$_4$] = NaRatio*[SO$_4$]
[Na$_3$PO$_4$] = NaRatio*[PO$_4$]
[NaCl] = NaRatio*TempCl
[NaF] = NaRatio*[F]
[NaNO$_2$] = TempNO$_2$*Temp2Na/(Temp2K + Temp2Na)
[NaNO$_3$] = TempNO$_3$*Temp2Na/(Temp2K + Temp2Na)
[NaOH] = Temp2OH*Temp2Na/(Temp2K + Temp2Na)
[Ni(OH)$_2$] = [Ni]
[Sr(NO$_2$)$_2$] = NO$_2$Ratio*[Sr]
[Sr(NO$_3$)$_2$] = NO$_3$Ratio*[Sr]
[Sr(OH)$_2$] = OHRatio*[Sr]
[UO$_2$CO$_3$] = [U]
[Zr(OH)$_4$] = [Zr]
Species in the Wet bulk solids
[Ag$_2$CO$_3$]s = 0.5*[Ag]s
[Al(OH)$_3$]s = [Al]s – [Si]s
[Bi$_2$O$_3$]s = 0.5*[Bi]s
[Na$_2$C$_2$O$_4$]s = 0.5*[TOC]s
[Na$_2$CO$_3$]s = [CO$_3$]s – 0.5*[Ag]s – [Sr]s
[Ca$_5$OH(PO$_4$)$_3$]s = 0.2*[Ca]s
[NaCl]s = [Cl]s
[CrOOH]s = [CrIII]s
[Na$_2$CrO$_4$]s = [CrVI]s
[NaF]s = [F]s
[FeOOH]s = [Fe]s
[HgO]s = [Hg]s
[KNO$_3$]s = [K]s
[LaPO$_4$]s = [La]s
[Mn(OH)$_2$]s = [Mn]s
[Ni(OH)$_2$]s = [Ni]s
[NaNO$_2$]s = [NO$_2$]s

Species in the Liquid
[NaNO$_3$]s = [NO$_3$]s - [K]s
[NaOH]s = [OH]s
[Na$_3$PO$_4$]s = [PO$_4$]s – 0.6*[Ca]s – [La]s
[Pb(OH)$_2$]s = [Pb]s
[Na$_2$SO$_4$]s = [SO$_4$]s
[NaAlSiO$_4$]s = [Si]s
[SrCO$_3$]s = [Sr]s
[Na$_2$U$_2$O$_7$]s = 0.5*[U]s
[ZrO$_2$]s = [Zr]s
All concentrations (items in square brackets) and variables (such as TempNa) are in units of molarity.

Appendix B – Basis for Assignment of Major Compounds in the New SOF Calculation Method

Appendix B – Basis for Assignment of Major Compounds in the New SOF Calculation Method

Compared to the old method, the one used for and described by Cowley et al. (2003), the new method of SOF calculation relies on a smaller and less tank-specific set of chemical compounds to represent each of the analytes in the Best Basis Inventory. In the old method, the ESP chemical thermodynamic model was used to predict the compounds in which each analyte would be present in each tank, based on the overall chemical composition of that tank's waste. The ESP output was post-processed, using the chemical equations in Tables C.3 and C.4 of the study done by Cowley et al., to convert ionic complexes, double salts, and hydrates (for example) to neutral compounds for which TEELs were available, that information being requisite to SOF calculation. The new method uses a smaller set of chemical equations (Appendix A of this report) to convert the BBI analytes directly to compounds. Table B.1 expresses all concentrations (items in square brackets) and variables (such as TempNa) in units of molarity. Boldface items are either output compound concentrations or intermediate (placeholder) concentration variables. The concentrations that are not in boldface are the input analyte concentrations.

The net effect of the change in assignment of compounds is to make the overall toxicity of any given analyte different from its value under the old method. Generally speaking, ESP-predicted prevalence in the Hanford wastes was the main consideration in choosing the simplified set of compounds; chemical plausibility and reasonable toxicological conservatism were also considered. On occasion there were trade-offs between these factors, so some engineering judgment was required to make the choices of compounds.

The purpose of this appendix is to justify the choices of compounds. Most of the attention is directed to the metals (other than sodium and potassium) and their compounds. The metals each have a wide range of possible counter-ions; they could hypothetically appear as oxides, hydroxides, oxyhydroxides, chlorides, sulfates, carbonates, with these compounds potentially having different toxicities, so that ESP modeling results for complexing and precipitation must be considered to justify which compound is chosen. The compounds used to represent the anions (Cl^-, F^-, NO_2^-, NO_3^-, free OH^-, CO_3^{-2}, PO_4^{-3}, SO_4^{-2}, and TOC anions) require less justification. The only significant counter-ions for the anions are sodium and potassium. For this reason, the assignment of anions to sodium and potassium salts is not discussed in detail, unlike the assignment of metal compounds.

Table B.1, which gives the information pertinent to silver, is an example of the systematic approach that was used to assign compounds to metals. On the left, the table lists the moles of the silver-containing neutral compounds and ionic complexes that ESP predicted to exist in all 177 tanks, based on the May 2002 BBI. On the right, the table lists the values of TEEL-1, -2, and -3 for the same compounds. The TEELs are expressed not in the conventional units of mg compound/m^3, but as mmol Ag/m^3. (Lower TEELs indicate greater toxicity.) These units allow comparison of Ag-containing species in terms of the toxicity that is attributed to Ag. Charged complexes by definition do not have TEELs, and there are a few compounds for which TEELs were not obtained. In some cases, such as the nitrite, the toxicity may derive more from the anion than from the silver; however, for the purpose of compound assignment only the silver is considered.

The remainder of this appendix discusses the rationale for compound selection on an analyte-by-analyte basis.

B.1 Silver (Ag)

In the new method, silver is defined as AgCl in the liquid phase. In the wet bulk solid phase, silver is assigned to silver carbonate, Ag_2CO_3. The chemical equations that make these assignments can be seen in Table A.1. Table B.1 shows the information relevant to the assignment of compounds.

The predominant form of Ag in solution was silver chloride complexes, with silver hydroxide complexes coming a distant second. In the wet bulk solid the prevalent compound was silver carbonate. The assignment of Ag to AgCl means that, in cases where the molar concentration of Ag exceeds that of Cl, chloride in excess of that given by the BBI will be "generated" to fill out the AgCl. In addition, because all the chloride is taken up by AgCl, none will be left over to form liquid-phase NaCl. This effect is unavoidable if liquid-phase Ag is to be appropriately represented. Similar statements can be made for carbonate in the solid phase because of the assignment of solid-phase Ag to Ag_2CO_3.

Table B.1. Prevalence and Toxicity of Silver Compounds

| Analyte: Silver | Total over all tanks, 2002 ESP Prediction | | TEELs expressed in mmol analyte/m^3 | | |
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Silver carbonate	0	3.62E+04	0.00029	0.00044	0.091
Silver chloride and complexes	2.28E+04	0	0.00028	0.00042	0.087
Silver hydroxide and complexes	8.92E+02	0	0.00028	0.00048	0.080
Silver nitrate	4.21E-03	0	0.00026	0.00044	0.088
Silver nitrite and complexes	7.42E+01	0	0.00026	0.00039	0.081
Potassium argentate	0	0	0.00028	0.00041	0.083
Sodium argentate	0	0	0.00024	0.00045	0.091
Ag^+	1.12E-02	0			
Ag acetate and complexes	1.34E-03	0			
Ag oxalate and complexes	1.69E-02	0			
Ag fluoride and complexes	1.01E-03	0			
Ag sulfate and complexes	1.88E-03	0			

B.2 Aluminum (Al)

The new method defines aluminum as being present only as $Al(OH)_3$ in the liquid phase and primarily as $Al(OH)_3$ in the wet bulk solid phase. Some aluminum may also be present as sodium aluminosilicate, $NaAlSiO_4$, if silicon (Si) is present in the solids. The basis for this assignment of compounds can be seen in Table B.2.

The overwhelmingly predominant form of Al in solution was the $Al(OH)_4^-$ ionic complex, which is considered to be toxicologically equivalent to $Al(OH)_3$. This equivalence is consistent with the assumptions made in the old method.

Table B.2. Prevalence and Toxicity of Aluminum Compounds

Analyte: Aluminum	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m³		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Aluminum hydroxide and most OH complexes	5.11E-01	1.85E+08	0.058	1.6	1.6
Aluminum nitrite	0	0	0.27	0.45	3.0
Aluminum nitrate	0	0	0.21	0.35	2.3
Sodium aluminate	0	1.26E+05	0.073	0.12	6.1
Monopotassium aluminum hydroxide	0	0	0.056	0.093	3.7
Potassium aluminate	0	0	0.20	0.36	1.5
Potassium alumino-silicate	0	4.90E+05	0.19	0.32	3.2
Sodium aluminosilicate	0	2.00E+07	0.070	0.11	3.5
Sodium aluminum carbonate dihydroxide	0	1.39E+07	0.069	1.0	3.5
Al^{+3}	2.44E-13	0			
$Al(OH)_4^-$	8.11E+07	0			
Al fluoride and complexes	8.38E+02	0			
Al acetate and complexes	4.02E-14	0			
Al sulfate and complexes	2.25E-12	0			

Aluminum hydroxide, $Al(OH)_3$, also predominated in the dry solid phase in the predicted total inventory of 2002. However, there were competing forms of aluminum solids. The major competitor was $NaAlSiO_4$, a compound whose toxicity could be assigned to either Al or Si. In the new model all wet-solid-phase Si is assigned to the aluminosilicate; an amount of Al that is equal to the Si is also assigned to $NaAlSiO_4$, and any Al in excess of that is assigned to $Al(OH)_3$ in the solids. In tanks where the Si concentration exceeds the Al, this approach will produce an Al concentration in the solids that exceeds the BBI value, in effect "generating" Al, and will assign all Al to the aluminosilicate and none to aluminum hydroxide. These effects are unavoidable if Si is to be represented in a reasonably conservative way.

B.3   Bismuth (Bi)

The new method defines bismuth as being present only as $Bi(OH)_3$ in the liquid phase and only as Bi_2O_3 in the wet bulk solid phase. Table B.3 shows that these assignments are in accord with the predominant species in the liquid and dry solid phases, as predicted by the ESP model for all 177 tanks in May 2002.

Table B.3. Prevalence and Toxicity of Bismuth Compounds

Analyte: Bismuth	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Bismuth hydroxide and complexes	1.83E+04	0	0.0038	0.012	0.38
Bismuth nitrate and complexes	1.34E-14	0	0.010	0.063	1.3
Bismuth oxychloride	0	2.44E+05	0.96	1.9	1.9
Bismuth sesquioxide	0	2.44E+06	0.26	1.7	2.1
Monopotassium bismuth hydroxide	0	0	0.013	0.079	0.63
Monosodium bismuth hydroxide	0	0	0.017	0.12	0.50
Bi^{+3}	1.19E-16	0			
Bi acetate and complexes	3.55E-18	0			
Bi chloride and complexes	7.17E-15	0			

B.4 Calcium (Ca)

In the new method, calcium is defined as calcium metasilicate, $CaSiO_3$, in the liquid phase. In the wet bulk solid phase calcium is assigned to calcium hydroxyapatite, $Ca_5OH(PO_4)_3$. Table B.4 shows the available information.

Table B.4. Prevalence and Toxicity of Calcium Compounds

Analyte: Calcium	Total over all tanks, 2002 ESP Prediction		Rev. 21A TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Calcium carbonate and complexes	3.58E+01	2.50E+05	0.15	0.15	0.15
Calcium fluoride and complexes	1.10E-02	8.21E+05	0.19	0.32	6.4
Calcium hydroxide and complexes	5.79E+01	3.91E+04	0.20	0.34	6.7
Calcium hydroxyapatite	0	5.17E+06	0.35	0.60	5.0
Calcium metasilicate	0	0	0.26	0.43	2.2
Calcium oxide	0	0	0.089	0.089	0.45
Calcium phosphate and complexes	4.51E+02	0	0.19	0.34	3.4
Calcium sulfate and complexes	9.83E+00	0	0.22	0.37	1.8
Calcium nitrate and complexes	1.10E+02	0	0.021	0.15	0.76
Calcium nitrite and complexes	0	0	0.00057	0.0045	0.38
Calcium oxalate and complexes	2.55E+00	2.38E+03	0.12	0.39	0.39
Ca^{+2}	8.79E+02	0			
Calcium hydrogen metasilicate ion	1.76E+02	0			
Calcium dihydrogen silicate	3.59E+03	0			
Ca acetate and complexes	9.62E+00	0			

The predominant form of Ca in solution was calcium dihydrogen silicate, for which there is no TEEL. There is, however, a TEEL for a closely related compound, calcium metasilicate. This compound is used to represent calcium in the liquid phase. The assignment of Ca to $CaSiO_3$ means that, in cases where the molar concentration of Ca exceeds that of Si, silicon in excess of that given by the BBI will be "generated" to fill out the $CaSiO_3$. In addition, because all the silicon is taken up by $CaSiO_3$, none will be left over to form liquid-phase sodium and potassium metasilicates. This effect is unavoidable if liquid-phase Ca is to be appropriately represented.

$Ca_5OH(PO_4)_3$ predominated by about a factor of 5 in the dry solid phase in the predicted total inventory of 2002. It was therefore assigned to Ca as the solid-phase compound. It does not conservatively represent the toxicity of all the solid-phase Ca compounds, which on the average are a factor of 2 more toxic. However, because it is predicted to be about 5 times more prevalent, the assumption that all Ca is $Ca_5OH(PO_4)_3$ is considered reasonably conservative.

B.5   Chloride (Cl)

In the new method, as in the old, chloride was split between NaCl and KCl in the liquid and was assigned to NaCl in the solid (Table A.1). The liquid-phase chloride that was included in silver chloride (Section B.1) was not part of that which was split between NaCl and KCl. In a tank where dissolved Ag exceeds dissolved Cl, the method would indicate that there was no NaCl or KCl and would produce Cl concentrations greater than the BBI value. This effect is unavoidable if liquid-phase Ag is to be appropriately represented.

B.6   Chromium (Cr)

The new method assigns Cr(III) to $Cr(OH)_3$ in the liquid and to chromium oxyhydroxide (CrOOH) in the wet bulk solid. As shown in Table B.5a, the basis for the assignment of Cr(III) compounds was prevalence in the ESP-predicted 177-tank inventory.

Table B.5a. Prevalence and Toxicity of Chromium (III) Compounds

| Analyte: Chromium (III) | Total over all tanks, 2002 ESP Prediction | | TEELs expressed in mmol analyte/m³ | | |
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Chromic oxide Cr_2O_3	0	0	0.030	0.049	0.46
Chromium III hydroxide and complexes	3.84E-04	0	0.015	0.049	0.49
Chromium oxyhydroxide	0	8.14E+06	0.012	0.044	0.47
Chromium(III) nitrate and complexes	3.11E-15	0	0.025	0.042	0.42
Cr^{+3}	4.83E-17	0			
Cr fluoride and complexes	7.09E-11	0			
Cr chloride and complexes	5.38E-18	0			
Cr phosphate and complexes	3.80E-09	0			
Cr sulfate and complexes	3.29E-13	0			

In the new method, as in the old, Cr(VI) in the liquid was assigned to Na_2CrO_4 and K_2CrO_4. All Cr(VI) in the wet bulk solid phase is assigned to sodium chromate, Na_2CrO_4. Table B.5b shows the basis for this choice; chromium (VI) hydroxide and dichromate ion are negligible in Hanford tank waste, according to the 2002 ESP predictions.

Table B.5b. Prevalence and Toxicity of Chromium (VI) Compounds

Analyte: Chromium (VI)	Total over all tanks, 2002 ESP Prediction		Rev. 21A TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Chromium(VI) hydroxide	0	0	0.00019	0.00065	0.097
Sodium chromate	0	0	0.0019	0.0019	0.25
Potassium chromate(VI)	0	0	0.0018	0.018	0.26
Cr^{+6}	0	0			
Chromate ion CrO_4^{-2} and hydrogen chromate ion	4.04E+06	0			
Dichromate ion $Cr_2O_7^{-2}$	1.34E-02	0			

B.7 Fluoride (F)

In the new method, fluoride was split between NaF and KF in the liquid and was assigned to NaF in the wet bulk solid (Table A.1). This was essentially the same approach as was used in the old method. The fluoride double salts predicted by the ESP model were split into single salts for the purpose of toxicological assessment; that separation, in effect, assigned all solid fluoride to NaF.

B.8 Iron (Fe)

The new method assigns iron to $Fe(OH)_3$ in the liquid and goethite (FeOOH) in the wet bulk solid. As shown in Table B.6, the basis for the assignment of Fe compounds was prevalence in the ESP-predicted 177-tank inventory.

Table B.6. Prevalence and Toxicity of Iron Compounds

Analyte: Iron	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
FeOOH (goethite)	0	2.35E+07	0.56	0.84	3.9
Iron III hydroxide (and complexes)	1.72E+02	0	0.094	0.70	3.7
Ferric oxide	0	0	0.25	0.44	6.3
Fe^{+3}	3.79E-19	0			
Fe oxalate and complexes	3.88E-06	0			
Fe chloride and complexes	7.97E-22	0			
Fe fluoride and complexes	1.65E-15	0			
Fe phosphate and complexes	8.26E-14	0			
Fe nitrate and complexes	6.74E-21	0			
Fe sulfate and complexes	3.69E-20	0			

B.9 Mercury (Hg)

The new method assigns mercury to $Hg(OH)_2$ in the liquid and to mercuric oxide (HgO) in the wet bulk solid. As shown in Table B.7, the basis for the assignment of Hg compounds is consistent with prevalence.

Table B.7. Prevalence and Toxicity of Mercury Compounds

Analyte: Mercury	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Mercury hydroxide (and complexes)	4.17E+03	0	0.00043	0.00043	0.043
Mercury nitrate	0	0	0.00046	0.00046	0.046
Mercury nitrite	0	0	0.00021	0.0014	0.0068
Mercury(II) chloride (and complexes)	1.58E+01	0	0.00046	0.046	0.046
Mercury(II) oxide	0	5.45E+03	0.00046	0.0046	0.046
Hg^{+2}	2.75E-09	0			
Hg acetate and complexes	2.11E-06	0			
Hg oxalate and complexes	3.16E-03	0			
Hg fluoride and complexes	1.86E-10	0			

B.10 Potassium (K)

In the liquid, potassium is used as a counter-ion for anion analytes, providing a charge balance (together with Na). Therefore no liquid-phase compounds are assigned specifically to K. In the wet bulk solids, the new method assigns potassium to potassium nitrate (KNO_3), nitrate being the most plausible counter-ion. Because K is used to supply the charge balance, its output concentration typically differs from the BBI value.

B.11 Lanthanum (La)

The new method assigns lanthanum to $La(OH)_3$ in the liquid phase and $LaPO_4$ in the wet bulk solids phase. As shown in Table B.8, the assignment of lanthanum compounds in the liquid phase was based on prevalence.

Table B.8. Prevalence and Toxicity of Lanthanum Compounds

| Analyte: Lanthanum | Total over all tanks, 2002 ESP Prediction | | TEELs expressed in mmol analyte/m³ | | |
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Lanthanum fluoride (and complexes)	3.83E-07	0	0.038	0.19	1.3
Lanthanum hydroxide (and complexes)	9.47E-03	1.16E+04	0.0039	0.011	0.013
Lanthanum nitrate (and complexes)	9.43E-15	0	0.0038	0.023	1.5
Lanthanum phosphate (and complexes)	1.26E-24	2.63E+05	0.0032	0.013	0.013
La^{+3}	5.18E-14	0			
La acetate and complexes	3.43E-15	0			
La chloride and complexes	2.64E-16	0			
La carbonate and complexes	6.49E-11	0			
La sulfate and complexes	8.01E-16	0			

B.12 Manganese (Mn)

In the new method, manganese is assigned to $Mn(OH)_2$ in both the liquid phase and the wet bulk solid phase. Table B.9 shows the available information. Manganese hydroxide is the prevalent compound in both phases.

Table B.9. Prevalence and Toxicity of Manganese Compounds

| Analyte: Manganese | Total over all tanks, 2002 ESP Prediction | | TEELs expressed in mmol analyte/m³ | | |
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Manganese carbonate	0	1.90E+05	0.052	0.087	4.3
Manganese dioxide	0	0	0.046	0.86	5.8
Manganese hydroxide (and complexes)	3.38E+05	1.97E+06	0.056	0.084	5.6
Manganese nitrite	0	0	0.051	0.085	3.4
Manganese oxalate (and complexes)	5.19E+02	0	0.052	0.087	3.5
Manganese oxide	0	0	0.0098	0.79	6.6
Manganese phosphate	0	5.56E+05	0.051	0.085	4.2
Manganese(II) nitrate (and complexes)	3.37E+00	0	0.056	0.084	2.8
Manganous sulfate	1.84E-01	0	0.050	0.083	3.3
Mn^{+2}	3.83E+00	0			
Mn acetate and complexes	4.68E-01	0			
Mn chloride and complexes	4.28E-02	0			

B.13 Sodium (Na)

In the liquid, sodium is used as a counter-ion for anionic analytes, providing a charge balance (together with K). In the wet bulk solids, Na is used as the only counter-ion for the anionic analytes. Therefore no compounds are assigned specifically to Na.

Because Na is used to supply the charge balance, its output concentration typically differs from the BBI value.

B.14 Nickel (Ni)

The new method defines nickel as being $Ni(OH)_2$ in both the liquid phase and the wet bulk solid phase. Table B.10 shows the available information.

The predominant form of Ni in solution was nickel hydroxide complexes. Nickel oxalate complexes came a distant second. Nickel hydroxide predominated by about a factor of 40 in the dry solid phase in the predicted total inventory of 2002. Based on prevalence, the hydroxide was therefore assigned to Ni as the liquid-phase and solid-phase compound.

Table B.10. Prevalence and Toxicity of Nickel Compounds

Analyte: Nickel	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m³		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Nickel oxalate and complexes (liquids)	2.86E+02	n/a	0.0051	0.0085	0.17
Nickel oxalate (solids)	n/a	3.24E+04	0.010	0.017	0.17
Nickel(II) hydroxide and complexes	7.89E+03	2.04E+06	0.0081	0.016	0.16
Nickel(II) nitrate and complexes	2.46E+00	0	0.016	0.016	0.16
Nickel(II) nitrite	0	0	0.0020	0.0033	0.066
Nickel(II) phosphate	0	2.17E+04	0.0049	0.0082	0.082
Potassium nickelate (Liquids)	0	0	0.0049	0.0073	0.17
Potassium nickelate (Solids)	0	0	0.010	0.017	0.17
Sodium nickelate (Liquids)	0	0	0.0043	0.0087	0.17
Sodium nickelate (Solids)	0	0	0.0087	0.017	0.17
Ni^{+2}	7.26E+00	0			
Ni acetate and complexes	1.97E-02	0			
Ni chloride and complexes	4.89E-04	0			
Ni fluoride and complexes	8.79E-03	0			
Ni sulfate and complexes	3.96E-01	0			

B.15 Nitrate, Nitrite, and Hydroxide (NO_3, NO_2, and OH)

The major anions in Hanford tank waste, nitrate, nitrite, and hydroxide, are assigned to compounds in a two-step process.

First, certain metals are assigned these anions as counter-ions. In the liquid phase, Sr is split between hydroxide, nitrate, and nitrite according to the relative concentrations of the three anions in the liquid. (See the equations for the metals and for NO_2Ratio, NO_3Ratio, and OHRatio in Table A.1.)

In the second step, the amounts of anion consumed by the listed metals are then subtracted from the input anions. (See the equations for Temp2OH, TempNO$_2$, and TempNO$_3$ in Table A.1.) The remaining anion concentrations are split between Na and K compounds ($NaNO_3$, $NaNO_2$, NaOH, KNO_3, KNO_2, and KOH) as can be seen in the equations for these compounds in Table B.1.

In the wet bulk solid phase less accounting is necessary because there are no three-way splits of metals between the anions. All NO_2 is allotted to $NaNO_2$ and all OH to NaOH. The NO_3 that remains after assigning part of it to K (for KNO_3) is allotted to $NaNO_3$.

Note that the hydroxide in such neutral species as $Al(OH)_3$, $Bi(OH)_3$, $Hg(OH)_2$, and many other hydroxides does not need to be subtracted from the input OH. The input OH is composed only of free hydroxide, and measurements of free OH do not include the hydroxide that is bound into neutral compounds and complexes. Therefore only the part of the OH^- that is used as a counterion for those metal cations that are predicted to be mostly uncomplexed (Sr, for example) is subtracted from the input hydroxide to give Temp2OH.

A similar process was followed in the old method, though it was complicated by the presence of more metals and complexes that needed to be included in the mass-balance accounting.

B.16 Lead (Pb)

The new method defines lead as being split between $NaHPbO_2$ and $KHPbO_2$ in the liquid phase. In the wet bulk solid phase lead is assigned to lead hydroxide, $Pb(OH)_2$. Table B.11 shows the available information.

The predominant form of Pb in solution was $HPbO_2^{-1}$, hydrogen lead hydroxide ion. The available TEELs were for sodium and potassium salts of the ion.

$Pb(OH)_2$ predominated by a factor of more than 10 over other Pb compounds in the dry solid phase in the predicted total inventory of 2002. It was therefore assigned to Pb as the solid-phase compound. Note that it conservatively represents the toxicity of other solid-phase Pb compounds.

Table B.11. Prevalence and Toxicity of Lead Compounds

	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m³		
Analyte: Lead	**Moles analyte in liquid in this form**	**Moles analyte in dry solid in this form**	**TEEL-1**	**TEEL-2**	**TEEL-3**
Lead carbonate	0	1.87E+04	0.00075	0.011	1.9
Lead hydroxide and complexes	1.54E-03	3.92E+05	0.00062	0.0012	0.0062
Lead nitrate and complexes	2.70E-03	0	0.00068	0.0011	0.45
Lead nitrite and complexes	1.03E+02	0	0.00067	0.0012	0.0050
Lead oxalate	5.41E-01	0	0.00068	0.0012	0.0051
Lead oxide	2.09E-01	0	0.00022	0.00022	0.45
Lead phosphate and complexes	9.73E-05	1.26E+04	0.00074	0.11	0.55
Potassium hydrogen lead oxide	0	0	0.00021	0.00021	0.45
Sodium hydrogen lead oxide	0	0	0.00023	0.00023	0.47
Pb^{+2}	9.82E-04	0			
PbO_2^{-2} and complexes	1.49E+03	0			
Pb acetate and complexes	1.55E-03	0			
Pb chloride and complexes	6.00E-05	0			
Pb fluoride and complexes	1.06E-04	0			

B.17 Phosphate (PO_4)

In the new method, the liquid-phase phosphate was split between Na_3PO_4 and K_3PO_4. In the wet bulk solid phase, phosphate was first allotted to Ca, La, and Zn to form phosphate compounds with those metals. The remaining phosphate was assigned to Na_3PO_4 (Table A.1). This approach was consistent with the old method. If the moles of phosphate that are required to form the Ca, La, and Zn phosphate compounds are in excess of the moles given by the BBI, then no sodium phosphate will be formed and the output phosphate concentration will exceed the BBI value.

B.18 Silicon (Si)

The new method defines silicon as being represented by disodium and dipotassium metasilicate (Na_2SiO_3 and K_2SiO_3) in the liquid phase and by $NaAlSiO_4$ in the wet bulk solid phase. Table B.12 shows the available information.

Table B.12. Prevalence and Toxicity of Silicon Compounds

Analyte: Silicon	Total over all tanks, 2002 ESP Prediction		Rev. 21A TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Silica	7.32E+03	2.60E+06	0.50	0.83	8.3
Silicic acid	0	0	0.13	0.64	5.1
Sodium aluminosilicate	0	2.00E+07	0.070	0.11	3.5
Calcium metasilicate	0	0	0.26	0.43	2.2
Sodium metasilicate	0	0	1.2	2.0	4.1
Potassium alumino-silicate	0	4.90E+05	0.19	0.32	3.2
Potassium hydrogen silicate	0	0	0.26	0.43	2.2
Potassium trihydrogen silicate	0	0	0.22	0.37	1.9
Dipotassium dihydrogen silicate	0	0	0.17	0.29	1.5
Dipotassium metasilicate	0	0	0.097	0.81	3.2
Disodium dihydrogen silicate	0	0	0.21	0.36	1.8
Disodium metasilicate	0	0	0.10	0.61	4.1
Sodium hydrogen metasilicate	4.71E+06	0	0.12	0.75	4.0
Sodium trihydrogen silicate	0	0	0.25	0.42	2.1
SiO_4^{-4} (silicate) and complexes	1.07E+06	0			
Si fluoride and complexes	9.84E-14	0			
Calcium hydrogen metasilicate ion	1.76E+02	0			
Calcium dihydrogen silicate	3.59E+03	0			

In the liquid phase, the dominant silicon compound is sodium hydrogen metasilicate ($NaHSiO_3$). Because no TEEL was available for potassium hydrogen metasilicate, the metasilicates (Na_2SiO_3 and K_2SiO_3) were assigned instead. These compounds are a good match for the prevalent ones both chemically and toxicologically. Only the portion of the liquid-phase silicon that exceeds the moles of calcium in the liquid is assigned to the metasilicates. Section B.4 discusses this constraint more completely.

In the solid phase, the dominant compounds are aluminosilicates. In the new model all wet-solid-phase Si is assigned to the aluminosilicate; an amount of Al that is equal to the Si is also assigned to $NaAlSiO_4$, and any Al in excess of that is assigned to $Al(OH)_3$ in the solids. In tanks where the Si concentration exceeds the Al, this approach will produce an Al concentration in the solids that exceeds the BBI value and will assign all Al to the aluminosilicate and none to aluminum hydroxide. These effects are unavoidable if Si is to be represented in a reasonably conservative way.

B.19 Sulfate (SO_4)

In the new method, sulfate was split between Na_2SO_4 and K_2SO_4 in the liquid and was assigned to Na_2SO_4 in the wet bulk solid (Table A.1). This was essentially the same approach as was used in the old method. In the old method the sulfate double salts predicted by the ESP model were split into single salts for the purpose of toxicological assessment; this step in effect assigned all solid sulfate to Na_2SO_4.

B.20 Strontium (Sr)

In the new method, strontium is defined as being split between $Sr(OH)_2$, $Sr(NO_2)_2$, and $Sr(NO_3)_2$ in the liquid phase. In the wet bulk solid phase strontium is assigned to $SrCO_3$. See Table B.13 for the data.

The predominant form of Sr in solution was $Sr(OH)_2$ and related complexes, with Sr^{2+} ion (which is balanced chiefly by NO_2^-, NO_3^-, and OH-) and strontium nitrate complexes making contributions of similar magnitude. This being the case, Sr was split among the three major anions (hydroxide, nitrate, and nitrite) in the new method (Table A.1). The split is somewhat conservative toxicologically because it includes the nitrite with its high toxicity.

The two prevalent solids were strontium carbonate and phosphate. The carbonate was chosen because it outweighed the phosphate by a factor of nearly twenty and was toxicologically conservative.

Table B.13. Prevalence and Toxicity of Strontium Compounds

Analyte: Strontium	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m³		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Strontium carbonate	0	4.51E+05	0.14	0.14	0.14
Strontium hydroxide and complexes	3.67E+02	0	0.0062	0.16	0.62
Strontium nitrate and complexes	2.19E+02	0	0.14	0.24	2.4
Strontium nitrite	0	0	0.00056	0.0042	0.42
Strontium oxalate and complexes	3.55E+00	0	0.14	0.34	0.43
Strontium phosphate and complexes	8.98E+01	2.68E+04	0.20	3.3	3.3
Strontium sulfate	0	0	0.16	0.27	1.4
Potassium strontium phosphate	0	0	0.14	0.23	2.3
Sodium strontium phosphate	0	0	0.15	0.24	2.4
Sr^{+2}	2.40E+02	0			
Sr acetate and complexes	9.37E+00	0			
Sr fluoride and complexes	1.14E+00	0			

B.21 Total Inorganic Carbon as Carbonate (TIC as CO₃)

In the new method, carbonate was assigned to UO_2CO_3 in the liquid, which consumed as many moles of CO_3 as there were of U.   The remaining liquid-phase carbonate was split between Na_2CO_3 and K_2CO_3. In the wet bulk solid phase, carbonate was first allotted to Ag and Sr to form carbonate compounds with those metals. The remaining carbonate was assigned to Na_3CO_3 (Table A.1). This approach was consistent with the old method. If Ag and Sr are high compared to CO_3, the same type of mass-balance changes may occur for carbonate that were described for phosphate (Section B.19).

B.22 Total Organic Carbon (TOC)

In the old method, the TOC was split between oxalate and acetate according to the fraction of the carbon that was present in the liquid phase. (See Section 2.1.) In the new method all of the TOC is assigned to oxalate, whether it is in the wet bulk solids phase or the liquid phase.

Table B.14 gives the available information about TOC compounds. It can be seen that sodium oxalate is more toxic than, or approximately as toxic as, the other organic salts. It is also more toxic than most non-salt organic compounds. (Oxalic acid, though more toxic than sodium oxalate, was predicted to be present in such a small amount that even if it were all present in one tank, the effect on the overall waste toxicity would be negligible.) Sodium oxalate was chosen for use in the wet bulk solids in the new method because of its toxicity, as an attempt to represent all other trace organic anions and compounds in a way that is more often than not conservative.

Table B.14. Prevalence and Toxicity of TOC Salts

Analyte: TOC	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m³		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Sodium acetate	6.13E+07	0	0.98	7.3	12
Potassium acetate	2.27E+05	0	0.82	5.1	10
Sodium oxalate	0	3.50E+07	0.45	0.75	0.75
Acetic acid	2.51E+00	0	0.40	2.9	20
Oxalic acid	4.44E-10	0	0.044	0.11	11
Sodium formate	not in BBI	not in BBI	1.8	7.4	7.4
Sodium citrate	not in BBI	not in BBI	5.0	8.4	84
Tetrasodium ethylenediaminetetraacetate (EDTA)	not in BBI	not in BBI	0.11	0.79	3.9
Acetate ion	1.43E+07	0			
Oxalate ion	1.75E+06	0			

B.23 Uranium (U)

The new method assigns liquid-phase uranium to UO_2CO_3. The uranium in the wet bulk solids is assigned to sodium diuranate, $Na_2U_2O_7$. Table B.15 gives the available information.

Uranyl carbonate was essentially the only form of uranium that appeared in the liquid, and sodium diuranate was the only form predicted by the ESP model in the dry solid phase. The uranium compounds in Table B.15 all have about the same toxicity in terms of their uranium content, so the assigned species can be considered representative.

Table B.15. Prevalence and Toxicity of Uranium Compounds

Analyte: Uranium	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Uranyl hydroxide and complexes (liquid)	3.38E-05	n/a	0.0025	0.0041	0.041
Uranyl nitrate	0	0	0.0025	0.0038	0.038
Uranyl nitrite (liquid)	0	n/a	0.0021	0.0041	0.041
Sodium diuranate (solid)	n/a	2.42E+06	0.0024	0.0047	0.047
Uranyl carbonate (liquids)	0	n/a	0.0023	0.0038	0.038
UO_2^{+2}	4.09E-10	0			
Uranyl acetate and complexes	1.75E-09	0			
Uranyl oxalate and complexes	1.20E-04	0			
Uranyl chloride and complexes	9.18E-12	0			
Uranyl carbonate and complexes	1.06E+05	0			
Uranyl fluoride and complexes	1.03E-04	0			
Uranyl sulfate and complexes	1.04E-08	0			

B.24 Zirconium (Zr)

In the new method, all liquid-phase zirconium is assigned to $Zr(OH)_4$ and all the zirconium in the wet bulk solids is assigned to ZrO_2. As can be seen from Table B.16, this assignment is consistent with the prevalent compounds predicted by the ESP model for the 177 tanks based on their May 2002 inventories.

Table B.16. Prevalence and Toxicity of Zirconium Compounds

Analyte: Zirconium	Total over all tanks, 2002 ESP Prediction		TEELs expressed in mmol analyte/m^3		
	Moles analyte in liquid in this form	Moles analyte in dry solid in this form	TEEL-1	TEEL-2	TEEL-3
Zirconium dioxide	0	4.34E+06	0.10	0.10	0.28
Zirconium hydroxide and complexes	1.54E+04	0	0.094	0.094	0.25
Monopotassium zirconium(IV) hydroxide	0	0	0.12	0.12	0.58
Monosodium zirconium hydroxide	0	0	0.10	0.10	0.50
Potassium zirconate	0	0	0.11	0.11	0.28
Sodium zirconate	0	0	0.11	0.11	0.27
Zr^{+4}	0	0			
Zr oxalate and complexes	1.20E-15	0			
Zr fluoride and complexes	1.84E-09	0			

Appendix C – Default Free Hydroxide Concentration Inputs

Appendix C – Default Free Hydroxide Concentration Inputs

Table C.1. Concentrations Used in Calculating the Default Free
OH in the New SOF Calculation Method

Tank	μg/mL free OH in liquid	μg/mL NO$_2^-$ in liquid
241-A-101	62,602	180,419
241-A-102	19,813	101,974
241-A-103	48,218	149,496
241-A-104	82,094	38,887
241-A-105	89,717	5,025
241-A-106	95.1	283,966
241-AN-101	25,271	44,625
241-AN-102	14,831	117,543
241-AN-103	117,281	174,543
241-AN-104	88,689	124,301
241-AN-105	70922	124,969
241-AN-106	4,048	82,651
241-AN-107	13.8	70,430
241-AP-101	31,677	41,422
241-AP-102	18,856	36,852
241-AP-103	12,319	119,477
241-AP-104	20,862	73,140
241-AP-105	16,654	124,041
241-AP-106	16,104	41,985
241-AP-107	25,869	58,799
241-AP-108	13,479	51,683
241-AW-101	99,566	122,852
241-AW-102	29,311	54,314
241-AW-103	17,542	39,834
241-AW-104	40,896	62,226
241-AW-105	5,878	8,483
241-AW-106	29,010	153,828
241-AX-101	52,967	185,106
241-AX-102	456	74,732
241-AX-103	34,650	132,422
241-AX-104	22.5	6,864
241-AY-101	49,255	51,170
241-AY-102	16,828	40,267
241-AZ-101	8,738	59,393
241-AZ-102	664	32,398
241-B-101	38,548	150,475
241-B-102	4,742	33,449

Table C.1. (contd.)

Tank	µg/mL free OH in liquid	µg/mL NO_2^- in liquid
241-B-103	8,104	37,738
241-B-104	3.27	4,817
241-B-105	28,999	47,733
241-B-106	8.24	13,367
241-B-107	6.77	8,163
241-B-108	28,900	64,183
241-B-109	20,875	93,805
241-B-110	2,658	18,941
241-B-111	0.074	67,257
241-B-112	5,680	44,119
241-B-201	96.6	1,268
241-B-202	3,830	1,405
241-B-203	75.5	871
241-B-204	486	721
241-BX-101	107	29,505
241-BX-102	0.333	10,972
241-BX-103	88.4	20,268
241-BX-104	2,151	61,105
241-BX-105	3,770	39,953
241-BX-106	50.9	66,878
241-BX-107	6.15	16,374
241-BX-108	15.6	67,067
241-BX-109	32.1	32,446
241-BX-110	42,719	94,811
241-BX-111	69,267	74,128
241-BX-112	3,876	50,673
241-BY-101	70,001	48,200
241-BY-102	32,046	47,793
241-BY-103	34,945	43,451
241-BY-104	17,539	115,975
241-BY-105	5,359	57,950
241-BY-106	35,360	72,154
241-BY-107	60,139	99,707
241-BY-108	111,743	104,764
241-BY-109	33,190	70,125
241-BY-110	38,878	94,193
241-BY-111	73,048	65,907
241-BY-112	87,912	105,861
241-C-101	15.7	66,948
241-C-102	67.1	12,180

Table C.1. (contd.)

Tank	µg/mL free OH in liquid	µg/mL NO_2^- in liquid
241-C-103	245	36,033
241-C-104	33,369	41,615
241-C-105	18,054	40,768
241-C-106	675	11,976
241-C-107	162	43,946
241-C-108	63.1	49,591
241-C-109	62.9	89,904
241-C-110	71.1	13,346
241-C-111	0.934	81,078
241-C-112	5.53	79,220
241-C-201	1,954	38,780
241-C-202	0.217	116,812
241-C-203	0.390	67,691
241-C-204	1.04	19,182
241-S-101	62,111	109,213
241-S-102	15,989	104,245
241-S-103	28,062	138,536
241-S-104	22,118	63,477
241-S-105	29,925	138,503
241-S-106	29,500	79,041
241-S-107	12,937	50,514
241-S-108	23,451	138,969
241-S-109	64,359	19,845
241-S-110	31,707	92,358
241-S-111	56,869	87,130
241-S-112	80,887	73,743
241-SX-101	113,650	66,137
241-SX-102	29,740	143,609
241-SX-103	14,157	132,247
241-SX-104	34,497	117,274
241-SX-105	47,319	142,133
241-SX-106	42,106	150,208
241-SX-107	49,212	93,395
241-SX-108	35,205	45,254
241-SX-109	81,312	103,533
241-SX-110	62,254	94,467
241-SX-111	53,240	90,000
241-SX-112	55,393	98,123
241-SX-113	31.4	5,581
241-SX-114	69,838	94,111

Table C.1. (contd.)

Tank	µg/mL free OH in liquid	µg/mL NO_2^- in liquid
241-SX-115	180	4,031
241-SY-101	24,303	89,211
241-SY-102	35,533	91,921
241-SY-103	51,507	164,429
241-T-101	14,276	56,951
241-T-102	62.3	33,909
241-T-103	112	28,113
241-T-104	18.8	6,864
241-T-105	19,400	51,863
241-T-106	4.14	50,999
241-T-107	12.1	21,141
241-T-108	8,509	34,973
241-T-109	8.43	11,133
241-T-110	2.86	7,436
241-T-111	0.667	957
241-T-112	20,574	37,797
241-T-201	1,651	526
241-T-202	1,831	792
241-T-203	90	403
241-T-204	1727	356
241-TX-101	44,060	101,795
241-TX-102	4,412	88,028
241-TX-103	1,624	91,840
241-TX-104	4,096	76,746
241-TX-105	23,693	93,639
241-TX-106	1,767	88,875
241-TX-107	334	149,074
241-TX-108	350	85,259
241-TX-109	4,816	18,955
241-TX-110	298	75,742
241-TX-111	267	72,396
241-TX-112	411	88,049
241-TX-113	0.092	17,378
241-TX-114	358	79,820
241-TX-115	399	88,901
241-TX-116	0.718	36,485
241-TX-117	7.56	64,903
241-TX-118	4.61	64,989
241-TY-101	0.010	35,080
241-TY-102	0.146	65,212

Table C.1. (contd.)

Tank	μg/mL free OH in liquid	μg/mL NO_2^- in liquid
241-TY-103	16.0	87,701
241-TY-104	13.7	91,776
241-TY-105	39.9	61,481
241-TY-106	1.30	27,941
241-U-101	40,037	92,112
241-U-102	409	104,333
241-U-103	62,786	117,164
241-U-104	510	50,276
241-U-105	20,824	149,142
241-U-106	426	94,429
241-U-107	20,800	128,131
241-U-108	66,326	139,926
241-U-109	3,311	136,897
241-U-110	13,919	19,695
241-U-111	34,807	114,870
241-U-112	10.5	9,498
241-U-201	18,533	37,472
241-U-202	18,226	36,349
241-U-203	16,621	32,670
241-U-204	1,300	39,118

The predicted NO_2^- concentration, which is derived from the ESP runs supporting Cowley et al. (2003), is used solely as a liquid tracer to calculate the default free OH in bulk solids phases where no BBI data are available. It is not used to calculate any NO_2 concentrations.

Appendix D –
Estimated Dry-Solid Volume Fraction in Wet Bulk Solids

Appendix D –
Estimated Dry-Solid Volume Fraction in Wet Bulk Solids

Table D.1. Estimated Dry-Solid Volume Fraction in the Average
Wet Bulk Solids, Based on the 2002 BBI and ESP Predictions

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-A-101	0.279	0.446
241-A-102	0.122	0.712
241-A-103	0.190	0.742
241-A-104	0.211	1
241-A-105	0.239	1
241-A-106	0.313	1
241-AN-101[*]	1	0
241-AN-102	0.809	0.129
241-AN-103	0.393	0.449
241-AN-104	0.239	0.455
241-AN-105	0.199	0.424
241-AN-106	0.134	0.455
241-AN-107	0.133	0.237
241-AP-101[*]	1	0
241-AP-102[*]	1	0
241-AP-103[*]	1	0
241-AP-104[*]	1	0
241-AP-105	1.145 [**]	0.078
241-AP-106[*]	1	0
241-AP-107[*]	1	0
241-AP-108[*]	1	0
241-AW-101	0.324	0.329
241-AW-102	0.930	0.029
241-AW-103	0.163	0.284
241-AW-104	0.097	0.542
241-AW-105	0.105	0.448
241-AW-106	0.204	0.812
241-AX-101	0.305	0.536
241-AX-102	0.278	1
241-AX-103	0.095	0.768

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-AX-104	0.395	1
241-AY-101	0.339	0.447
241-AY-102	0.162	0.213
241-AZ-101	0.232	0.047
241-AZ-102	0.111	0.105
241-B-101	0.341	0.818
241-B-102	0.881	0.661
241-B-103	0.852	0.754
241-B-104	0.116	0.974
241-B-105	0.801	0.932
241-B-106	0.227	0.991
241-B-107	0.480	0.884
241-B-108	0.846	0.825
241-B-109	1.027 **	0.850
241-B-110	0.190	0.996
241-B-111	0.112	0.996
241-B-112	0.204	0.795
241-B-201	0.059	1
241-B-202	0.038	1
241-B-203	0.025	0.990
241-B-204	0.028	0.984
241-BX-101	0.278	1
241-BX-102	0.211	1
241-BX-103	0.205	0.848
241-BX-104	0.346	0.971
241-BX-105	0.315	0.934
241-BX-106	0.506	1
241-BX-107	0.302	1
241-BX-108	0.521	1
241-BX-109	0.156	1
241-BX-110	0.855	0.831
241-BX-111	0.636	0.913
241-BX-112	0.274	0.992

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-BY-101	0.791	0.949
241-BY-102	0.330	0.856
241-BY-103	0.647	0.864
241-BY-104	0.426	0.878
241-BY-105	0.602	0.865
241-BY-106	0.311	0.811
241-BY-107	0.329	0.855
241-BY-108	0.540	0.878
241-BY-109	0.433	0.861
241-BY-110	0.347	0.958
241-BY-111	0.594	0.941
241-BY-112	0.558	0.934
241-C-101	0.517	1
241-C-102	0.112	1
241-C-103	0.487	0.627
241-C-104	0.178	1
241-C-105	0.537	1
241-C-106	0.240	0.167
241-C-107	0.218	1
241-C-108	0.301	1
241-C-109	0.361	1
241-C-110	0.271	0.994
241-C-111	0.363	1
241-C-112	0.177	1
241-C-201	0.562	1
241-C-202	0.429	1
241-C-203	0.383	1
241-C-204	0.139	1
241-S-101	0.239	0.823
241-S-102	0.412	0.761
241-S-103	0.363	0.760
241-S-104	0.366	0.872
241-S-105	0.417	0.898

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-S-106	0.450	0.943
241-S-107	0.141	0.947
241-S-108	0.394	0.993
241-S-109	0.508	0.969
241-S-110	0.582	0.922
241-S-111	0.422	0.722
241-S-112	0.634	0.873
241-SX-101	0.350	0.861
241-SX-102	0.162	0.777
241-SX-103	0.306	0.899
241-SX-104	0.342	0.940
241-SX-105	0.191	0.886
241-SX-106	0.245	0.901
241-SX-107	0.275	0.958
241-SX-108	0.367	1
241-SX-109	0.387	1
241-SX-110	0.317	1
241-SX-111	0.254	0.915
241-SX-112	0.310	0.936
241-SX-113	0.244	1
241-SX-114	0.298	0.816
241-SX-115	0.185	1
241-SY-101	0.222	0.273
241-SY-102	0.368	0.096
241-SY-103	0.240	0.440
241-T-101	0.269	0.843
241-T-102	0.645	0.595
241-T-103	0.268	0.853
241-T-104	0.217	1
241-T-105	0.117	1
241-T-106	0.484	1
241-T-107	0.240	1
241-T-108	0.734	0.833

Table D.1. (contd.)

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-T-109	0.751	0.749
241-T-110	0.026	0.998
241-T-111	0.037	1
241-T-112	0.052	0.897
241-T-201	0.047	0.932
241-T-202	0.022	1
241-T-203	0.021	1
241-T-204	0.027	1
241-TX-101	0.372	0.953
241-TX-102	0.418	0.853
241-TX-103	0.450	0.874
241-TX-104	0.474	0.847
241-TX-105	0.470	0.951
241-TX-106	0.423	0.885
241-TX-107	0.625	0.750
241-TX-108	0.437	0.928
241-TX-109	0.326	1
241-TX-110	0.396	0.981
241-TX-111	0.388	0.991
241-TX-112	0.448	0.955
241-TX-113	0.543	0.991
241-TX-114	0.450	0.963
241-TX-115	0.434	0.951
241-TX-116	0.505	0.953
241-TX-117	0.488	0.984
241-TX-118	0.742	0.856
241-TY-101	0.366	0.996
241-TY-102	0.568	0.739
241-TY-103	0.228	0.935
241-TY-104	0.281	0.976
241-TY-105	0.448	1
241-TY-106	0.479	1
241-U-101	0.318	1

Table D.1. (contd.)

Tank	Solid volume fraction in wet bulk solids	Volume fraction of wet bulk solids in total waste
241-U-102	0.248	0.955
241-U-103	0.292	0.914
241-U-104	0.129	1
241-U-105	0.494	0.875
241-U-106	0.132	0.742
241-U-107	0.560	0.714
241-U-108	0.392	0.726
241-U-109	0.433	0.905
241-U-110	0.245	1
241-U-111	0.319	0.769
241-U-112	0.449	1
241-U-201	0.232	0.789
241-U-202	0.226	0.765
241-U-203	0.175	0.765
241-U-204	0.452	0.733

* According to the BBI there is no solid in these tanks.

** Owing to approximations, the dry solid volume fraction was calculated to be greater than 1, a physically unrealistic value. A value of 1 was substituted in the SOF calculations for wet bulk solids.

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