Estimation of Alkali Metal Mole Percent and Weight of Calcined Solids for ICPP Calcine

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ABSTRACT

An updated method is given for estimation of the weight of calcined solids and volume reduction factor for calcine, and mole percent sodium plus potassium in calcine produced from radioactive waste in a fluidized-bed calciner at the Idaho Chemical Processing Plant (ICPP). It incorporates new information on a calcine chemistry from a study by K. N. Brewer and G. F. Kessinger in which they determined the compounds formed during calcination by both high temperature thermodynamic equilibrium calculations and by analyses of pilot-plant calcines. An explanation of the assumptions made in the calculations, along with several example calculations and comparisons with the previous calculation methods are included. This method allows calculation of the heat generation rate and sodium content of the calcine, which are used to determine the suitability of the calcine for storage in the ICPP bin sets. Although this method accurately predicts the weight of calcine and mole percent Na+K for its intended purpose, the compounds predicted should only be used as a first approximation for other purposes since the calculation does not incorporate all of the compounds, such as mixed-metal oxides, which may form during calcination.

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SUMMARY

An updated method is given for estimation of the weight of calcined solids and volume reduction factor for calcine, and mole percent sodium plus potassium in calcine produced from radioactive waste in a fluidized bed calciner at the Idaho Chemical Processing Plant. This method is a simplification of the complex chemical reactions which occur during calcination and allows calculation of the heat generation rate and sodium content of the calcine, which are used to determine the suitability of the calcine for storage in the ICPP Calcined Solids Storage Facilities (CSSFs). Although this method accurately predicts the weight of calcine, weight percent of elements in the calcine, and mole percent of Na+K in calcine for its intended purpose, the compounds predicted should only be used as a first approximation for other purposes since the calculation does not incorporate all of the compounds, such as bimetallic oxides, which may form during calcination.

The previous method for calculating the weight of calcined solids from the feed composition was primarily designed for use with raffinates from fuel dissolution and was inadequate for blends where there is insufficient fluoride to form Na_3AlF_6 , such as in cold aluminum nitrate/sodium waste blends. In addition, the previous method for calculating the sodium plus potassium mole percent in calcine did not use all of the feed components used in the solids calculation, and also did not account for the nitrate present in the calcine. These previous methods had been used to verify suitability of calcine for storage in Calcined Solids Storage Facilities 5 and 6 while the updated method will be used for calcine stored in CSSF 6 and future Calcined Solids Storage Facilities (CSSFs) after NWCF campaign H-3.

The updated method assumes the same compounds are formed for both calculation of weight of calcined solids and sodium plus potassium mole percent of calcine. It incorporates new information on calcine chemistry from a study by K. N. Brewer and G. F. Kessinger in which they determined the compounds formed during calcination by both high temperature thermodynamic equilibrium calculations and by analyses of pilot plant calcines. An explanation of the assumptions made in the calculations, along with several example calculations and comparisons of calculated values with values using the previous calculation methods are attached.

ACKNOWLEDGEMENTS

This work combines new information from a study by K. N. Brewer and G. F. Kessinger with earlier work by a number of people, principle among them being B. J. Newby, W. B. Palmer, and J. R. Berreth. The author would especially like to thank K. N. Brewer for his assistance and helpful comments.

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1. INTRODUCTION

The weight of solids produced during calcination is needed to predict the volume of calcine which will be produced for calcine storage. The calcined solids weight, along with its specific volume, are also needed to predict the heat generation rate of the calcine to ensure that temperatures in the Calcined Solids Storage Facilities (CSSFs) do not exceed the temperature at which the calcine will cake. In addition, the caking tendency of calcine is dependent on the alkali metal content of the calcine. A method for estimating the compounds formed during calcination is necessary to determine the weight of solids produced during calcination and the alkali metal content of the calcine.

The previous method for calculating the weight of solids produced during calcination (Reference 1) assumed that the sodium and potassium in the calcine formed fluoaluminates (Na_3AlF_6 and K_3AlF_6); however, this assumption is not applicable in cases where insufficient fluoride is available, such as in aluminum nitrate/sodium waste blends. In addition, the method for calculating alkali metal (sodium plus potassium) mole percent in calcine (Reference 2) assumed slightly different compounds were formed than Reference 1, did not use all the feed components used in the calcined solids calculation method of Reference 1, and also did not account for nitrate formation in the calcine. An updated calculation method which uses the same chemistry and compounds formed for calculating both the calcined solids produced and mole percent alkali metals in the calcine, and which incorporates information from a new study of calcination chemistry, has been developed.

The updated method incorporates information from a comprehensive study of calcination chemistry by K. N. Brewer and G. F. Kessinger (References 3 and 4) in which calcination chemistry was determined by both thermodynamic equilibrium calculations and analysis of pilot-plant calcine using SEM, x-ray diffraction, and elemental analysis.

The methods in References 1 and 2 have been used to verify compliance of New Waste Calcining Facility (NWCF) feed blends with the Technical Specifications for calcine storage in CSSF 5 and 6. The updated method will be used to verify compliance of future NWCF waste blends, particularly high sodium content blends of aluminum nitrate and sodium waste, with the operating limits in the new revisions of the technical standards for calcine storage in CSSFs 6 and 7. In addition, the values for weight of calcined solids and associated volume reduction factors are used by operations

personnel to estimate the volume of calcine transferred to the CSSFs from the amount of feed processed at the NWCF. Although this method accurately predicts the weight of calcine and mole percent Na+K for its intended purpose, the compounds predicted should only be used as a first approximation for other purposes such as prediction of ceramic forms in the calcine since the calculation does not incorporate all of the compounds, such as bimetallic oxides, which may form during calcination. For example, sodium oxide (Na_2O) is very reactive and would be expected to exist in the calcine as sodium aluminate ($\text{Na}_2\text{O} \cdot x\text{Al}_2\text{O}_3$) or another more thermodynamically favorable bi- or tri-metallic oxide (Reference 5). In addition, the compounds formed are to some extent dependent on the feed composition.

The method can be used to predict weight percents of individual elements in the calcine such as calcium and nitrate.

2. COMPOUNDS FORMED DURING CALCINATION

Calcination is a very complex chemical process due to the large number of chemical species and wide variation in chemical concentrations in the calciner feed. Crystalline compounds in calcine can be determined by x-ray diffraction methods; however, the majority of compounds in calcine are amorphous (non-crystalline) and usually the concentrations of only a few crystalline compounds are above the detection limits. A program which calculates the chemical equilibrium, such as the F*A*C*T EQUILIB program (Reference 6) used by K. N. Brewer and G. F. Kessinger, can be used to estimate the distribution of compounds formed at equilibrium. Unfortunately, the fluidized bed calciner is not an equilibrium process due to the finite residence time in the calciner, local temperature variations in the bed, and continuously changing operating conditions such as feed rate and fuel rate. For example, the thermodynamic calculations predicted that no nitrates would remain at equilibrium while analyses of calcine have shown that nitrates are present.

A brief description of the assumptions and simplifications used in the calculation method are listed below. These assumptions are based primarily on the work of K. N. Brewer and G. F. Kessinger (References 3 and 4), and on an examination of the free energies and heats of formation for potential compounds. K. N. Brewer and G. F. Kessinger determined calcine composition by thermodynamic

equilibrium calculations using the F*A*C*T EQUILIB program, and compared the results with analyses of pilot plant calcines.

For the purposes of the calculation, nitrates are assumed to form first, followed by phosphates, fluorides, sulfates, chlorides, and then oxides. This assumption is a simplification that allows the calculation to be made in a non-iterative fashion.

2.1 Nitrates

A fixed mole fraction of the sodium and potassium is assumed to form nitrates in the calcine. For pilot plant calcine, this value was calculated to be an average of 0.66 ± 0.05 moles of nitrate per mole of sodium plus potassium (Reference 7), and this mole ratio is used to calculate nitrate in the calcine. The remaining nitrate present in the feed is conservatively assumed to volatilize. The nitrate content of calcine varies inversely with calcination temperature for the same feed composition (Reference 8); however, the calciner pilot plant and NWCF operating temperatures do not vary significantly from 500°C. Reducing agents have been successfully tested in pilot plant calciners to reduce the amount of nitrates in the calcine (Reference 9). The average value of 0.66 moles nitrate per mole of sodium is not applicable for instances where reducing agents such as sugar have been used to destroy the nitrates in the calciner feed; however, these types of feed additives are not currently used at the NWCF. If reducing agents or other chemicals expected to affect the nitrate content of the calcine are to be used, then pilot plant or plant data for that feed composition and additives should be used to estimate the nitrate content of the calcine for the calculation.

The previous method for calculation of sodium plus potassium content (Reference 2) neglected nitrate formation, while the method for calculation of calcined solids (Reference 1) assumed that 10% of the sodium and potassium and 50% of the excess calcium existed as nitrates. The new value of 66% of the sodium plus potassium existing as nitrates is based on pilot plant data and should be more accurate than the old value of 10%. For calcium nitrate, the thermodynamic equilibrium calculations performed by Brewer and Kessinger (References 3 and 4) did not predict that calcium nitrate would form, and in addition, the nitrate content of pilot plant calcines does not show a strong correlation with the excess calcium (Reference 7). Therefore, all the excess calcium (after formation of phosphates, fluorides, sulfates, and chlorides) was assumed to form oxides in the updated calculation method.

2.2 Phosphates

Calcium phosphate is assumed to form first, followed by sodium and potassium phosphate, based on the equilibrium calculations. If there is insufficient calcium, sodium and potassium, the remaining phosphate is conservatively assumed to volatilize.

The previous calculation of sodium plus potassium content (Reference 2) neglected phosphate since the measured phosphate in tank farm wastes is small. Historically, the phosphate content in tank farm wastes has never exceeded 0.028 M (Reference 10). The previous calculation method for calcined solids (Reference 1) assumed that 50% of the phosphate volatilized; however, in pilot plant tests which burned tri-butyl-phosphate-containing process solvent as fuel the majority of the phosphate stayed in the calcine solids and less than 1% volatilized as determined by analyses of the acid scrub and off-gas (Reference 11). Brewer's equilibrium calculations (Reference 4) indicated that sodium and potassium phosphate could form, but only if there was insufficient calcium.

2.3 Fluorides

Calcium fluoride (CaF_2) is assumed to preferentially form, followed by NaF and KF, based on equilibrium calculations (Reference 3). If insufficient calcium, sodium and fluoride are available for these compounds, the excess fluoride is conservatively assumed to volatilize.

In both of the previous calculations (References 1 and 2), Na_3AlF_6 and K_3AlF_6 were assumed to form preferentially to CaF_2 ; however, K. N. Brewer's equilibrium calculations and analyses indicated that most of the fluoride forms CaF_2 , with only small amounts of NaF and KF, and no Na_3AlF_6 or K_3AlF_6 .

Fluoride volatility is routinely measured during pilot plant tests and only flowsheets which have fluoride volatility of less than 1% are recommended for operation at NWCF. For Fluorinel/Sodium waste blends and Aluminum/Fluorinel/Sodium blends in the Enclosed 30-cm Calciner Pilot Plant, the fluoride volatility ranged from 0.1 to 0.5 % (Reference 12). Therefore, the assumption that all fluoride is tied up by Ca, Na, and K is reasonable, especially since a calcium to fluoride ratio of 0.55 or greater is required for NWCF operation with fluoride blends (Reference 13) and because the sodium concentration in current sodium wastes is much greater than the fluoride concentrations in those wastes.

2.4 Sulfates

Potassium sulfate is assumed to form, followed by sodium sulfate, calcium sulfate, and then cadmium sulfate. If insufficient K, Na, Ca and Cd is available for sulfate formation, then any excess sulfate is conservatively assumed to volatilize.

The previous methods assumed that cadmium sulfate would form first, but the free energy for cadmium sulfate is less favorable than that for potassium, sodium, or calcium sulfate. The thermodynamic equilibrium calculations also favored potassium, sodium and calcium over cadmium sulfate, but the lab analyses of pilot plant calcine by x-ray diffraction in the K. N. Brewer's study indicated the presence of CdS. It is unlikely that SO_4 in the feed would dissociate. It is possible the sulfur could be from the small amount of sulfur (< 0.04 wt%) present in the kerosene used as fuel in the calciners. If CdS does form from the sulfur present in the kerosene instead of CdO, the total number of elemental moles in the calcine and hence the mole % sodium plus potassium would be unchanged. Since the molecular weight of CdO is less than CdS, the assumption that CdO is formed will give a lower calculated weight of calcined solids and will provide a conservatively high calculated volume reduction factor in corresponding calcine heat generation rate.

2.5 Chlorides

Potassium chloride and sodium chloride are assumed to form before calcium chloride based on the thermodynamic equilibrium calculations. If there is not enough potassium, sodium, and calcium, the excess chloride is conservatively assumed to volatilize. The previous methods assumed that only CaCl_2 was formed.

2.6 Oxides

Sodium and potassium are assumed to form NaAlO_2 if there is enough aluminum. Any remaining sodium, potassium, and other metals are treated as their respective metal oxides. Many of the metals, including sodium and especially potassium, probably exist in calcine as mixed metal oxides such as KBO_2 , NaBO_2 , NaCrO_2 , $3\text{CaO}\cdot\text{B}_2\text{O}_3$ and $\text{CdO}\cdot\text{Al}_2\text{O}_3$; however, the oxides are treated as separate

compounds in the calculations since: 1) this does not affect the total moles of metals and oxygen present, and 2) the exact oxide compounds which form can change based on the relative mole ratios in the feed. While the use of individual oxides is adequate for the above mentioned purposes, it does not provide the exact compounds formed during calcination in all cases, and as such should only be used as a first approximation if such information is desired. For a more detailed discussion of mixed metal oxides which may form, see References 3 and 5.

2.7 Undissolved Solids

The undissolved solids (UDS) in the feed are assumed to remain solid in the calcine and are added to the weight of calcine produced, but are not used for calculation of the sodium plus potassium content. This assumption is the same as that used in the previous calculation methods.

2.8 Minor Feed Components

Over 99% of mercury in the feed volatilizes during calcination at 500°C (Reference 15), so mercury is not included in the calculations. As a cautionary note, a significant portion of mercury did remain in the calcine during early calcination at ICPP when indirect heating and calcination temperatures of 400°C were used.

Minor feed components with concentrations less than 0.5 g/L are neglected. This is conservative since neglecting feed components (other than sodium and potassium) reduces the total weight and total moles for calcine produced. This results in a conservatively low weight of calcined solids with a corresponding conservatively high calcine heat generation rate, and a conservatively high sodium plus potassium mole percent. If the concentration of a feed component is known to exceed 0.5 g/L in the feed blend, then it can be included by assuming that its oxidation state in the calcine is the same as that in the feed and that it forms an oxide. Although they are usually less than 0.5 g/L in calciner feed, the toxic metals cadmium, chromium, and lead, and also uranium are included in the calculation because their content in calcine is usually desired for waste management purposes.

3. CALCULATION METHODS

3.1 Detailed Method

The detailed method for calculating sodium plus potassium mole percent in calcine, the weight of solids produced per liter of feed, and the volume reduction factor are given in Appendix A, along with a sample calculation. A list of the compounds which are assumed to be formed, and the order of preference for formation is also listed in Appendix A.

In Appendix A, the moles of each individual compound are calculated, and then the oxygen in oxides is summed to determine the total moles of oxygen in the calcined solids. The moles and weights of each element or species in the calcine, including oxides and nitrates, are then summed to determine the total moles in the calcine and the total weight of calcine, respectively. Amounts of elements which were calculated to volatilize are subtracted from the sums.

3.2 Simplified Method

An alternate method, which has been used previously (Reference 5), and is simpler than calculating the moles of each individual compound, is to calculate the moles of oxygen in oxides from the sum of the moles of the other elements in the calcine times their oxidation states. The sum of the oxidation states for all the elements in the calcine must sum to zero, otherwise the calcine would be ionically charged. The amounts of each element which remain after formation of nitrates, phosphates, fluorides, sulfates, and chlorides are assumed to form oxides and for the sum of charges to balance, with oxygen having an oxidation state of (-2), then:

$$(-2) \text{ moles}_{\text{Oxygen}} + \sum_{i=1}^{\text{Components}} ((\text{Oxidation State}_i)(\text{moles}_i)) = 0 \quad (1)$$

Thus, the moles of oxygen in the calcine can be calculated without having to determine the moles of each individual compound formed. Solving for moles of oxygen, equation (1) rearranges to:

$$\text{moles}_{\text{Oxygen}} = \frac{1}{2} \left(\sum_{i=1}^{\text{Components}} ((\text{Oxidation State}_i)(\text{moles}_i)) \right) \quad (2)$$

For the elements used in the calculation in Appendix A, equation 2 becomes:

$$\text{moles}_{\text{Oxygen}} = \frac{1}{2} \left(\begin{aligned} &3Al + Na + (-1)(X_{\text{NO}_3} Na) + K + (-1)(X_{\text{NO}_3} K) + 2Ca \\ &+ (-3)(PO_4 - PO_{4,\text{volatilized}}) + (-2)(SO_4 - SO_{4,\text{volatilized}}) \\ &+ (-1)(F - F_{\text{volatilized}}) + (-1)(Cl - Cl_{\text{volatilized}}) \\ &+ 4Zr + 3B + 3Fe + 2Cd + 3Cr + 2Pb + 6U \end{aligned} \right) \quad (3)$$

where: Al, Na, K, etc. are the moles of each component per liter of feed.

X_{NO_3} is the mole fraction of sodium and potassium that forms nitrates in the calcine.

To determine the amounts of species which volatilize, the moles of each individual compound must be determined, as in Appendix A. However, if there is sufficient calcium, sodium, and potassium to tie up all the phosphate, fluoride, sulfate, and chloride, then the amounts of these species which volatilize will be zero. For this to be true, then there must be sufficient calcium, sodium, and potassium for all the phosphate, fluoride, sulfate, and chloride:

$$[2Ca + (1 - X_{\text{NO}_3})(Na + K)] \geq (3PO_4 + F + 2SO_4 + Cl) \quad (4)$$

If equation (4) is true, then there will be sufficient Na, K, and Ca to form sulfates, so there will be no sulfate available to form cadmium sulfate.

If equations (4) is not true for a given feed composition, then some species will possibly volatilize, in which case the detailed method in Appendix A must be used instead of the simplified method. If equations (4) is true, then there is enough Na, K, and Ca to combine with all the PO_4 , F, SO_4 , and Cl, and none of them will volatilize. Equation (3) then becomes:

$$moles_{Oxygen} = \frac{1}{2} \left(\begin{array}{l} 3Al + Na + (-1)(X_{NO_3} Na) + K + (-1)(X_{NO_3} K) + 2Ca \\ + (-3)PO_4 + (-2)SO_4 \\ + (-1)F + (-1)Cl \\ + 4Zr + 3B + 3Fe + 2Cd + 3Cr + 2Pb + 6U \end{array} \right) \quad (5)$$

It can be shown that for all cases where equation (4) is true that the calculation method in Appendix A and equation (5) result in the same value for moles of oxygen. Appendix B shows the derivation of equation (5) from the calculation method in Appendix A for several cases. If equation (4) is not all true, then it is uncertain whether any PO_4 , F , SO_4 , or Cl will volatilize, and the method in Appendix A must be used to determine the moles of oxygen in the calcine.

Once the total moles of oxygen is calculated using equation (5), then the moles and weights of each element in the calcine can be summed to determine the total moles and the total weight of calcine, respectively.

3.3 Summary of Calculation Method

In summary, to determine mole percent sodium plus potassium and weight of calcined solids:

1. Determine if equations (4) is true.
2. If equation (4) is true, then use equation (5) to calculate moles of oxygen, otherwise use the method in Appendix A.
3. Calculate the mole percent sodium plus potassium by dividing the moles of sodium plus potassium by the sum of moles in the calcine, including oxides and nitrates. Moles of nitrate, phosphate, and sulfate are used in the calculation of total moles rather than the moles of individual elements for these species.
4. Calculate the weight of calcined solids either by summing the molecular weight times the moles of individual elements and species, including the weight of oxygen and nitrate, or alternatively by summing the molecular weights times moles for all the compounds formed.
5. Obtain the bulk density of calcine product from either plant or pilot plant data from

calcination of a similar feed.

6. Estimate the bulk density of the product and fines mixture as a percentage of the product bulk density based on the expected product-to-fines ratio from pilot plant tests. For most cases, use 95% of the product bulk density. If the product-to-fines ratio is less than 2, use 90% of the product bulk density. See figure G-1 in ENICO-1100 (Reference 1).
7. From the bulk density and weight of solids produced, calculate the volume reduction factor as volume of calciner feed to volume of calcine produced.
8. Since cold chemicals such as aluminum nitrate are not normally included in the volume reduction factor, adjust the volume reduction factor to be the ratio of tank farm solution volume to volume of calcine produced.
9.
 - a. Determine the heat generation rate for the liquid feed blend (see Appendix E), then apply the volume reduction factor from step 7 to determine the heat generation rate for the calcined solids.
 - or b. Determine the heat generation rates for the tank farm liquid (see Appendix E), then apply the volume reduction factor from step 8 to determine the heat generation rate for the calcined solids.

Example calculations of sodium plus potassium content, weight of calcined solids, volume reduction factor, and calcine heat generation for several typical feed compositions are given in Appendix C. Calculation of liquid and calcine heat generation rates is given in Appendix E.

4. COMPARISON OF CALCULATED VALUES WITH PREVIOUS METHODS

B. J. Newby used a 5:1 blend of 'typical' Fluorinel and Sodium wastes as the first example calculation of mole percent sodium plus potassium in Reference 2. The value for mole percent sodium plus potassium for this blend the updated method is 4.75 mole % (see Appendix D) while B. J. Newby's method gives a slightly higher value of 4.84 mole %. This is a relative difference of 2.0%. The value calculated by the updated method is lower because the total moles is increased by the addition of nitrates and other species such as iron and chloride which B. J. Newby assumed were negligible.

Since values of mole percent sodium plus potassium calculated using B. J. Newby's method are available for previous blends, it is useful to have a quick way to convert from the Newby value to the new method value. If the Fe, Cr, Pb, Cl, U and PO_4 in the feed are small, then the mole percent sodium plus potassium can be approximated from the Newby value by:

$$\text{Molpcnt}_{\text{NaK}_{\text{approximate}}} = \frac{\text{Molpcnt}_{\text{NaK}_{\text{Newby}}}}{100 + \text{Molpcnt}_{\text{NaK}_{\text{Newby}}} \left[\frac{1}{2} X_{\text{NO}_3} \right]} (100\%) \quad (6)$$

Derivation of equation (6) is shown in Appendix D. For Newby's 5:1 'typical' Fluorinel/Sodium blend, the approximate value is in error by only +0.44 relative %. Equation (6) should only be used to convert or compare previously reported mole% Na+K values to updated method values and should not be used for the NWCF feed blend calculations which are used for operational Run Plans..

The weight of calcined solids is also calculated for the 5:1 Fluorinel/Sodium blend used Newby's letter on mole percent calculation (Reference 2) and compared with the value calculated using the method in ENICO-1100 (Reference 1). For this feed blend, the value calculated using the new method (190.8 gm calcine per liter of feed) differs from the value calculated using the old method (216.7 gm calcine per liter of feed) by 13.6%. The main reason for the difference is that, when a large excess of calcium (Ca/F ratio of 0.7) is used to suppress chloride volatility, the assumptions made in the old method that 1) Na_3AlF_6 and K_3AlF_6 form before CaF_2 and 2) 50% of the excess calcium becomes nitrate, result in an overestimate of the amount of nitrates in the calcine.

For Newby's test case, the old method assumptions result in a calculated nitrate content of 19.5 wt% while the new method gives a nitrate content of 6.5 wt%. By comparison, the nitrate content was 8.3 wt% for calcine from Enclosed 30-cm Calciner Pilot Plant Run 10 (Reference 12), which calcined a Fluorinel/Sodium blend having a sodium plus potassium content similar to Newby's test case.

5. EFFECTS OF NEGLECTING TRACE OR UNKNOWN CONCENTRATIONS OF FEED COMPONENTS

Concentrations of minor feed components, such as phosphate, lead, and chromium, are often

unavailable and must be assumed to be zero for the calculations. Neglecting trace metals such as lead and chromium, will reduce the moles of oxygen and total moles in the calcine, and will result in: 1) a conservative (higher) value for sodium plus potassium mole percent, 2) a lower weight of calcined solids, 3) a higher volume reduction factor, and 4) a conservatively higher heat generation rate. Neglecting phosphate will also provide: 1) a lower weight of calcined solids, 2) a higher volume reduction factor, and 3) a conservatively higher heat generation rate but will provide a negligibly lower (non-conservative) calculated mole % Na+K.

In most cases the phosphate in the feed is unknown since it is difficult to analyze for in high nitric acid solutions. If phosphate is neglected, calcium which would have formed $\text{Ca}_3(\text{PO}_4)_2$ would instead be assumed in the calculation to form CaO, or every 2/3 mole of phosphate would be replaced by 1 mole of oxide. Therefore, assuming the amount of phosphate is negligible would overestimate the total moles by 1/3 of the actual phosphate concentration. This means the calculation would give a non-conservatively low sodium plus potassium value. The maximum phosphate concentration in the tank farm wastes is currently only 0.02 M, and has never exceeded 0.028 M (Reference 14), so in general, assuming that the phosphate concentration is negligible will only introduce a very small non-conservative error (0.1 relative %) to the calculated sodium plus potassium content. This is very small compared to the overall error for the calculations. In addition, this will be more than offset by the moles of other minor components such as cesium and strontium, which are neglected in the calculation.

6. CALCULATIONAL ERROR

The standard error associated with the calculated values (e.g. from sample analyses and solids bulk density data) is being estimated by J. J. Jacobson, and will be provided in a separate letter.

The population standard deviation has been determined by J. J. Jacobsen to be less than 8% ($\sigma < 0.08$, References 16 and 17) for heat generation rates calculated using the method described in this report for the volume reduction factor. The population standard deviation for the mole percent Na+K calculated using the updated method in this report was determined to be 5.5 relative % ($\sigma < 0.055$, Reference 17). Factors for standard normal distribution should be used to determine confidence levels ('z test') for determining confidence limits rather than 't test' values since Jacobsen used a very large

population sample (10000 samples). For 95% confidence limits, the range is:

$$X_{95\% \text{ C.L.}} = \left(1 \pm 1.645 \frac{\sigma}{\sqrt{n}} \right) X_n \quad (7)$$

where: σ = population standard deviation , 0.08 for heat generation rate or 0.055 for mole percent sodium plus potassium

X_n = Mean heat generation rate or mole percent sodium plus potassium for calcine for n samples

n = Number of data samples

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Appendix A
Sample Detailed Calculation of Sodium Plus Potassium Content
and Weight of Calcined Solids

Appendix A

Sample Detailed Calculation of Sodium Plus Potassium Content and Weight of Calcined Solids

Wanted: Mole percent of sodium plus potassium in the calcine and the weight of solid calcine produced per liter of feed based on the calciner feed solution composition.

- Method:**
1. Make assumptions of the compounds formed and preference order during calcination.
 2. Calculate moles of each compound formed to determine the moles of species which will volatilize and the moles of compounds which contain oxygen.
 3. Calculate moles of oxygen in oxides
 4. Mole percent Na+K= (Moles Na+K)/(oxygen in oxides + moles of non-volatile elements)
 5. Weight of calcine = weight of non-volatile elements from feed + weight of oxygen in oxides

Given:

Solution Content for 1 liter of Solution- Test Case is a theoretical Fluoride/Sodium Waste blend (used for the sample calculation):

F := 2·mole	Al := .5·mole	Ca := 1.4·mole	Cr := 0.0001·mole
SO ₄ := 0.1·mole	Zr := 0.25·mole	B := 0.15·mole	Pb := 0.0001·mole
Cl := 0.01·mole	Na := 0.25·mole	Fe := 0.1·mole	U := 0.0001·mole
PO ₄ := 0.001·mole	K := 0.05·mole	Cd := 0.1·mole	UDS := 1·gm

(Nitrate and acid concentrations in feed are not used in the calculation, but are given here for completeness)

NO₃ := 5·mole Acid := 1.5·mole

Estimated calcine product bulk density for theoretical blend: $\rho_{b_p} := 1.7 \cdot \frac{\text{gm}}{\text{cm}^3}$ (typical value for a Fluorinel/Na blend)
(bulk density is usually obtained from plant or pilot plant data)

Molecular Weights and Atomic Weights (from the CRC Handbook of Chemistry and Physics, 62nd ed):

$W_{Al} = 26.98154 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_F = 18.9984 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_P = 30.9738 \cdot \text{gm} \cdot \text{mole}^{-1}$
$W_B = 10.81 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_{Fe} = 55.847 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_{Pb} = 207.19 \cdot \text{gm} \cdot \text{mole}^{-1}$
$W_{Ca} = 40.08 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_K = 39.0983 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_S = 32.064 \cdot \text{gm} \cdot \text{mole}^{-1}$
$W_{Cd} = 112.41 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_N = 14.0067 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_U = 235 \cdot \text{gm} \cdot \text{mole}^{-1}$
$W_{Cl} = 35.453 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_{Na} = 22.98977 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_{Zr} = 91.22 \cdot \text{gm} \cdot \text{mole}^{-1}$
$W_{Cr} = 51.996 \cdot \text{gm} \cdot \text{mole}^{-1}$	$W_O = 15.9994 \cdot \text{gm} \cdot \text{mole}^{-1}$	
$W_{NO_3} = (W_N + 3 \cdot W_O)$	$W_{NO_3} = 62.005 \cdot \text{gm} \cdot \text{mole}^{-1}$	
$W_{PO_4} = (W_P + 4 \cdot W_O)$	$W_{PO_4} = 94.971 \cdot \text{gm} \cdot \text{mole}^{-1}$	
$W_{SO_4} = (W_S + 4 \cdot W_O)$	$W_{SO_4} = 96.062 \cdot \text{gm} \cdot \text{mole}^{-1}$	

Assumptions:

Compounds Assumed to be Formed During ICPP Waste Calcination:

Components -> Products (Molecular Weight), listed in order of preference for formation

1. NO_3 (62.067) -> $\text{NaNO}_3 + \text{KNO}_3$... Nitrates are assumed proportional to Na+K
2. PO_4 (94.971) -> $\text{Ca}_3(\text{PO}_4)_2$ (310.18) + $\text{Na}_3\text{PO}_4 + \text{K}_3\text{PO}_4$
3. F (18.9984) -> CaF_2 (78.08) + $\text{Na}_3\text{AlF}_6 + \text{KF}$
4. SO_4 (96.058) -> K_2SO_4 (174.27) + Na_2SO_4 (142.04) + CaSO_4 (132.14) + CdSO_4 (208.47)
5. Cl (35.453) -> KCl (74.56) + NaCl (58.443) + CaCl_2 (110.99)
6. Na (22.98977) -> NaNO_3 (84.99) + Na_2SO_4 (142.04) + NaCl (58.443) + $\text{NaAlO}_2 + \text{Na}_2\text{O}$ (81.97)*
7. K (39.0983) -> KNO_3 (101.11) + K_2SO_4 (174.27) + KCl (74.56) + $\text{KAlO}_2 + \text{K}_2\text{O}$ (94.20)*
8. Al (26.98154) -> $\text{NaAlO}_2 + \text{KAlO}_2 + \text{Al}_2\text{O}_3$ (101.96)
9. Ca (40.08) -> $\text{Ca}_3(\text{PO}_4)_2$ (310.18) + CaF_2 (78.08) + CaSO_4 (132.14) + CaCl_2 (110.99)
+ CaO (56.08)
10. Cd (112.41) -> CdSO_4 (208.47) + CdO (128.41)
11. Zr (91.22) -> ZrO_2 (123.22)
12. B (10.81) -> B_2O_3 (69.92)
13. Fe (55.847) -> Fe_2O_3 (159.69)
14. Cr (51.996) -> Cr_2O_3 (151.99)
15. Pb (207.19) -> PbO (223.19)
16. U (235) -> UO_3 (283.00) -> use average uranium isotopic weight instead of 235 if known
17. Undissolved Solids, UDS -> UDS weight added to weight of calcine solids
18. Other:
 - Hg (200.59) -> Assume most volatilizes and HgO remaining is negligible
 - Ag, As, Sb, Cs, Ce, Ni, Mn, Mo, Nb, Sn, Gd ... -> Assume negligible since concentrations in most tank farm wastes are <0.5 g/L. If the concentration of a metal is known and is >0.5 g/L in the feed blend, then assume it forms an oxide of the same oxidation state as the metal in solution.

NOTES:

- * Na and K oxides will exist primarily as mixed metal oxides with other metals such as Al and B.
- ** Although they are usually less than 0.5 g/L in calciner feed, the toxic metals cadmium, chromium, and lead, and also uranium are included in the calculation because their content in calcine is usually desired for other purposes.

Calculations:

NOTES:

1. In equations that follow, equations along the left side with ":= " or "≡" operators are equation definitions, while the values preceded by "=" along the right side are values calculated using the test case solution composition.
2. Syntax for "if" statements is: "x:=if(a≥b,c,d)" is equivalent to "If a is greater than or equal to b, then set x equal to c, otherwise set x equal to d."

1. Nitrate Solids:

Average Mole fraction of Na and K as nitrates in calcine based on analyses of calcine:

$$X_{NO_3} \equiv 0.66 \frac{\text{mole} \cdot NO_3}{\text{mole} \cdot (Na + K)} \quad (0.66 \pm 0.05 \text{ based on analyses of pilot plant calcine without reducing agents, Reference 7. Use pilot plant calcine data for } NO_3/(Na+K) \text{ ratios if reducing agents such as sugar are used.})$$

$$NaNO_3 := X_{NO_3} \cdot Na$$

$$NaNO_3 = 0.165 \cdot \text{mole}$$

$$KNO_3 := X_{NO_3} \cdot K$$

$$KNO_3 = 0.033 \cdot \text{mole}$$

2. Phosphate solids:

If enough Ca for Phosphate, then all phosphate forms $Ca_3(PO_4)_2$:

$$Ca_3PO_4_2 := \text{if} \left(Ca \geq \frac{3}{2} \cdot PO_4, \frac{PO_4}{2}, \frac{Ca}{3} \right)$$

Check value of inequality (=0 for false, 1 for true):

$$\left(Ca \geq \frac{3}{2} \cdot PO_4 \right) = 1$$

$$Ca_3PO_4_2 = 5 \cdot 10^{-4} \cdot \text{mole}$$

If not enough Ca for $Ca_3(PO_4)_2$, then

If enough Na is available then remaining phosphate forms Na_3PO_4

else all remaining Na forms Na_3PO_4 :

$$PO_4_{rem} := PO_4 - 2 \cdot Ca_3PO_4_2$$

$$PO_4_{rem} = 0 \cdot \text{mole}$$

$$Na_3PO_4 := \text{if} \left[PO_4_{rem} \geq \frac{(1 - X_{NO_3}) \cdot Na}{3}, \frac{(1 - X_{NO_3}) \cdot Na}{3}, PO_4_{rem} \right] \quad Na_3PO_4 = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left[PO_4_{rem} \geq \frac{(1 - X_{NO_3}) \cdot Na}{3} \right] = 0$$

2. Phosphate solids (cont.):

If not enough Na, then

If enough K is available then remaining phosphate forms K₃PO₄

else all remaining K forms K₃PO₄:

$$PO4_{rem_b} := PO4 - 2 \cdot Ca_3PO4_2 - Na_3PO4$$

$$PO4_{rem_b} = 0 \cdot \text{mole}$$

$$K_3PO4 := \text{if} \left[PO4_{rem_b} \geq \frac{(1 - X_{NO3}) \cdot K}{3}, \frac{(1 - X_{NO3}) \cdot K}{3}, PO4_{rem_b} \right] \quad K_3PO4 = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left[PO4_{rem_b} \geq \frac{(1 - X_{NO3}) \cdot K}{3} \right] = 0$$

If not enough Ca, Na, or K available, assume remaining phosphate volatilizes:

$$PO4_{volat} := PO4 - 2 \cdot Ca_3PO4_2 - Na_3PO4 - K_3PO4$$

$$PO4_{volat} = 0 \cdot \text{mole}$$

3. Fluoride Solids:

If sufficient Ca after phosphate is formed, all F forms CaF₂, else all remaining Ca forms CaF₂:

$$Ca_{avail3} := Ca - 3 \cdot Ca_3PO4_2$$

$$Ca_{avail3} = 1.398 \cdot \text{mole}$$

$$CaF_2 := \text{if} \left(\frac{F}{2} \geq Ca_{avail3}, Ca_{avail3}, \frac{F}{2} \right)$$

Check value of inequality (=0 for false, 1 for true):

$$\left(\frac{F}{2} \geq Ca_{avail3} \right) = 0$$

$$CaF_2 = 1 \cdot \text{mole}$$

If not enough Ca available for CaF₂, then

If enough Na is left after NaNO₃ and Na₃PO₄ formation to form NaF then all remaining F forms NaF

else all Na left forms NaF:

$$F_{rem} := F - 2 \cdot CaF_2$$

$$F_{rem} = 0 \cdot \text{mole}$$

$$Na_{avail3} := Na - NaNO_3 - 3 \cdot Na_3PO_4$$

$$Na_{avail3} = 0.085 \cdot \text{mole}$$

$$NaF := \text{if} (F_{rem} \geq Na_{avail3}, Na_{avail3}, F_{rem}) \quad \text{Check value of inequality (=0 for false, 1 for true):}$$

$$(F_{rem} \geq Na_{avail3}) = 0$$

$$NaF = 0 \cdot \text{mole}$$

3. Fluoride Solids (cont.):

If not enough Ca for CaF₂ and not enough Na or Al for NaF, then

If enough K is available after KNO₃ formation for KF then all remaining F forms KF

Else if not enough K not as KNO₃ for KF then all remaining K forms KF:

$$F_{\text{rem}_b} := (F - 2 \cdot \text{CaF}_2 - \text{NaF})$$

$$F_{\text{rem}_b} = 0$$

$$K_{\text{avail3}} := K - \text{KNO}_3 - 3 \cdot \text{K}_3\text{PO}_4$$

$$K_{\text{avail3}} = 0.017 \cdot \text{mole}$$

$$\text{KF} := \text{if}(F_{\text{rem}_b} \geq K_{\text{avail3}}, K_{\text{avail3}}, F_{\text{rem}_b})$$

$$\text{KF} = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$(F_{\text{rem}_b} \geq K_{\text{avail3}}) = 0$$

Any remaining F not forming compounds with Ca, Na and K is conservatively assumed to volatilize:

$$F_{\text{volat}} := F - 2 \cdot \text{CaF}_2 - \text{NaF} - \text{KF}$$

$$F_{\text{volat}} = 0 \cdot \text{mole}$$

4. Sulfate (SO₄) Solids:

Potassium not as nitrate, phosphate, or fluoride:

$$K_{\text{avail4}} := K - \text{KNO}_3 - 3 \cdot \text{K}_3\text{PO}_4 - \text{KF}$$

$$K_{\text{avail4}} = 0.017 \cdot \text{mole}$$

If sulfate is greater than remaining K, then all remaining K forms K₂SO₄,

Otherwise, all sulfate forms K₂SO₄:

$$\text{K}_2\text{SO}_4 := \text{if}\left(\text{SO}_4 \geq \frac{K_{\text{avail4}}}{2}, \frac{K_{\text{avail4}}}{2}, \text{SO}_4\right)$$

$$\text{K}_2\text{SO}_4 = 0.009 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left(\text{SO}_4 \geq \frac{K_{\text{avail4}}}{2}\right) = 1$$

$$\text{SO}_4_{\text{rem}_a} := \text{SO}_4 - \text{K}_2\text{SO}_4$$

$$\text{SO}_4_{\text{rem}_a} = 0.091 \cdot \text{mole}$$

4. Sulfate (SO4) Solids (cont.):

If there is any sulfate remaining, it forms Na₂SO₄ if there is enough Na available.

Available Na not as nitrate, phosphate or fluoride:

$$\text{Na}_{\text{avail4}} := \text{Na} - \text{NaNO}_3 - 3 \cdot \text{Na}_3\text{PO}_4 - \text{NaF}$$

$$\text{Na}_{\text{avail4}} = 0.085 \cdot \text{mole}$$

$$\text{Na}_2\text{SO}_4 := \text{if} \left(\text{SO}_4_{\text{rem}_a} \geq \frac{\text{Na}_{\text{avail4}}}{2}, \frac{\text{Na}_{\text{avail4}}}{2}, \text{SO}_4_{\text{rem}_a} \right)$$

$$\text{Na}_2\text{SO}_4 = 0.042 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left(\text{SO}_4_{\text{rem}_a} \geq \frac{\text{Na}_{\text{avail4}}}{2} \right) = 1$$

$$\text{SO}_4_{\text{rem}_b} := \text{SO}_4 - \text{K}_2\text{SO}_4 - \text{Na}_2\text{SO}_4$$

$$\text{SO}_4_{\text{rem}_b} = 0.049 \cdot \text{mole}$$

If there is any sulfate remaining, it forms CaSO₄:

$$\text{Ca}_{\text{avail4}} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4_2 - \text{CaF}_2$$

$$\text{Ca}_{\text{avail4}} = 0.398 \cdot \text{mole}$$

$$\text{CaSO}_4 := \text{if} \left(\text{SO}_4_{\text{rem}_b} \geq \text{Ca}_{\text{avail4}}, \text{Ca}_{\text{avail4}}, \text{SO}_4_{\text{rem}_b} \right)$$

$$\text{CaSO}_4 = 0.049 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left(\text{SO}_4_{\text{rem}_b} \geq \text{Ca}_{\text{avail4}} \right) = 0$$

$$\text{SO}_4_{\text{rem}_c} := \text{SO}_4 - \text{K}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{CaSO}_4$$

$$\text{SO}_4_{\text{rem}_c} = 0 \cdot \text{mole}$$

If there is any sulfate remaining, it forms CdSO₄, otherwise it is conservatively assumed to volatilize:

$$\text{CdSO}_4 := \text{if} \left(\text{SO}_4_{\text{rem}_c} \geq \text{Cd}, \text{Cd}, \text{SO}_4_{\text{rem}_c} \right)$$

$$\text{CdSO}_4 = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left(\text{SO}_4_{\text{rem}_c} \geq \text{Cd} \right) = 0$$

$$\text{SO}_4_{\text{volat}} := \text{SO}_4 - \text{K}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{CaSO}_4 - \text{CdSO}_4$$

$$\text{SO}_4_{\text{volat}} = 0 \cdot \text{mole}$$

5. Chloride Solids:

If enough K, then form KCl:

$$K_{\text{avail5}} := K - KNO_3 - KF - 2 \cdot K_2SO_4$$

$$K_{\text{avail5}} = 0 \cdot \text{mole}$$

$$KCl := \text{if}(Cl \geq K_{\text{avail5}}, K_{\text{avail5}}, Cl)$$

$$KCl = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$(Cl \geq K_{\text{avail5}}) = 1$$

$$Cl_{\text{rem_a}} := Cl - KCl$$

$$Cl_{\text{rem_a}} = 0.01 \cdot \text{mole}$$

Form NaCl if any Cl remains:

$$Na_{\text{avail5}} := Na - NaNO_3 - NaF - 2 \cdot Na_2SO_4$$

$$Na_{\text{avail5}} = 0 \cdot \text{mole}$$

$$NaCl := \text{if}(Cl_{\text{rem_a}} \geq Na_{\text{avail5}}, Na_{\text{avail5}}, Cl_{\text{rem_a}})$$

$$NaCl = 0 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$(Cl_{\text{rem_a}} \geq Na_{\text{avail5}}) = 1$$

$$Cl_{\text{rem_b}} := Cl - KCl - NaCl$$

$$Cl_{\text{rem_b}} = 0.01 \cdot \text{mole}$$

Form CaCl₂ if any Cl remains:

$$Ca_{\text{avail5}} := Ca - 3 \cdot Ca_3PO_4 \cdot 2 - CaF_2 - CaSO_4$$

$$Ca_{\text{avail5}} = 0.349 \cdot \text{mole}$$

$$CaCl_2 := \text{if}\left(\frac{1}{2} \cdot Cl_{\text{rem_b}} \geq Ca_{\text{avail5}}, Ca_{\text{avail5}}, \frac{Cl_{\text{rem_b}}}{2}\right)$$

$$CaCl_2 = 0.005 \cdot \text{mole}$$

Check value of inequality (=0 for false, 1 for true):

$$\left(Cl_{\text{rem_b}} \geq \frac{1}{2} \cdot Ca_{\text{avail5}}\right) = 0$$

Any remaining Cl volatilizes:

$$Cl_{\text{volat}} := Cl - KCl - NaCl - 2 \cdot CaCl_2$$

$$Cl_{\text{volat}} = 0 \cdot \text{mole}$$

6. Sodium Solids:

Any remaining Na forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$\text{Na}_{\text{avail6}} := \text{Na} - \text{NaNO}_3 - 2 \cdot \text{Na}_2\text{SO}_4 - \text{NaCl} - \text{NaF}$$

$$\text{Na}_{\text{avail6}} = 0 \cdot \text{mole}$$

$$\text{NaAlO}_2 := \text{if}(\text{Al} > \text{Na}_{\text{avail6}}, \text{Na}_{\text{avail6}}, \text{Al})$$

Check value of inequality (=0 for false, 1 for true):

$$(\text{Al} > \text{Na}_{\text{avail6}}) = 1$$

$$\text{NaAlO}_2 = 0 \cdot \text{mole}$$

$$\text{Na}_2\text{O} := \frac{1}{2} \cdot (\text{Na}_{\text{avail6}} - \text{NaAlO}_2)$$

$$\text{Na}_2\text{O} = 0 \cdot \text{mole}$$

7. Potassium Solids:

Any remaining K forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$\text{K}_{\text{avail7}} := \text{K} - \text{KNO}_3 - 2 \cdot \text{K}_2\text{SO}_4 - \text{KCl} - \text{KF}$$

$$\text{K}_{\text{avail7}} = 0 \cdot \text{mole}$$

$$\text{KAlO}_2 := \text{if}(\text{Al} - \text{NaAlO}_2 > \text{K}_{\text{avail7}}, \text{K}_{\text{avail7}}, \text{Al} - \text{NaAlO}_2)$$

Check value of inequality (=0 for false, 1 for true):

$$(\text{Al} - \text{NaAlO}_2 > \text{K}_{\text{avail7}}) = 1$$

$$\text{KAlO}_2 = 0 \cdot \text{mole}$$

$$\text{K}_2\text{O} := \frac{1}{2} \cdot (\text{K}_{\text{avail7}} - \text{KAlO}_2)$$

$$\text{K}_2\text{O} = 0 \cdot \text{mole}$$

6. Aluminum Solids:

Aluminum oxide:

$$\text{Al}_2\text{O}_3 := \frac{1}{2} \cdot (\text{Al} - \text{NaAlO}_2 - \text{KAlO}_2)$$

$$\text{Al}_2\text{O}_3 = 0.25 \cdot \text{mole}$$

9. Calcium Solids:

Any remaining Calcium forms oxide:

$$\text{CaO} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4\text{ _2} - \text{CaF}_2 - \text{CaSO}_4 - \text{CaCl}_2$$

$$\text{CaO} = 0.344 \cdot \text{mole}$$

10. Cadmium Solids:

Any remaining Cadmium forms oxide:

$$\text{CdO} := \text{Cd} - \text{CdSO}_4$$

$$\text{CdO} = 0.1 \cdot \text{mole}$$

CALCULATE SODIUM PLUS POTASSIUM MOLE PERCENT

Moles of oxygen in compounds with cations Al, Na, K, Ca and Cd:

$$O_a := 2 \cdot \text{NaAlO}_2 + 2 \cdot \text{KAlO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + 3 \cdot \text{Al}_2\text{O}_3 + \text{CaO} + \text{CdO} \quad O_a = 1.194 \cdot \text{mole}$$

Moles of oxygen for feed components which are assumed to form only oxides:

$$O_b := 2 \cdot \text{Zr} + \frac{3}{2} \cdot \text{B} + \frac{3}{2} \cdot \text{Fe} + \frac{3}{2} \cdot \text{Cr} + \text{Pb} + 3 \cdot \text{U}$$

$$O_b = 0.876 \cdot \text{mole}$$

$$O_{\text{tot}} := O_a + O_b$$

$$O_{\text{tot}} = 2.07 \cdot \text{mole}$$

Total Moles is sum of moles of oxygen + nitrate + feed components - volatilized components:

$$\begin{aligned} \text{Mol}_{\text{tot}} := & O_{\text{tot}} + \text{Al} + (1 + X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) + \text{Ca} \dots \quad (\text{Note that } X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) \text{ is the moles of nitrate}) \\ & + (\text{PO}_4 - \text{PO}_4_{\text{volat}}) + (\text{F} - \text{F}_{\text{volat}}) \dots \\ & + (\text{SO}_4 - \text{SO}_4_{\text{volat}}) + (\text{Cl} - \text{Cl}_{\text{volat}}) \dots \\ & + \text{Zr} + \text{B} + \text{Fe} + \text{Cd} + \text{Cr} + \text{Pb} + \text{U} \end{aligned}$$

$$X_{\text{NO}_3} = 0.66 \frac{\text{mole} \cdot \text{NO}_3}{\text{mole} \cdot (\text{Na} + \text{K})}$$

$$\text{Mol}_{\text{tot}} = 7.179 \cdot \text{mole}$$

$$\text{Mol\% NaK} := \frac{\text{Na} + \text{K}}{\text{Mol}_{\text{tot}}} \cdot 100\%$$

$$\text{Mol\% NaK} = 4.179\%$$

CALCULATE WEIGHT OF CALCINED SOLIDS

Total calcine weight is the sum of (MW x moles):

(Note: For Uranium, use average isotopic weight for uranium instead of 235, or weight conc (in g/L) of uranium instead of "235 U", if available)

$$\begin{aligned} \text{Calcine_Wt}_{\text{tot}} := & W_O \cdot O_{\text{tot}} + W_{\text{Al}} \cdot \text{Al} + W_{\text{NO}_3} \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) \dots \\ & + W_{\text{Na}} \cdot \text{Na} + W_{\text{K}} \cdot \text{K} + W_{\text{Ca}} \cdot \text{Ca} \dots \\ & + W_{\text{PO}_4} \cdot (\text{PO}_4 - \text{PO}_4_{\text{volat}}) + W_{\text{F}} \cdot (\text{F} - \text{F}_{\text{volat}}) \dots \\ & + W_{\text{SO}_4} \cdot (\text{SO}_4 - \text{SO}_4_{\text{volat}}) + W_{\text{Cl}} \cdot (\text{Cl} - \text{Cl}_{\text{volat}}) \dots \\ & + W_{\text{Zr}} \cdot \text{Zr} + W_{\text{B}} \cdot \text{B} + W_{\text{Fe}} \cdot \text{Fe} + W_{\text{Cd}} \cdot \text{Cd} + W_{\text{Cr}} \cdot \text{Cr} + W_{\text{Pb}} \cdot \text{Pb} \dots \\ & + W_{\text{U}} \cdot \text{U} + \text{UDS} \end{aligned}$$

Substituting for molecular/atomic weights:

$$\begin{aligned} \text{Calcine_Wt}_{\text{tot}} := & 15.9994 \cdot O_{\text{tot}} + 26.98154 \cdot \text{Al} + 62.005 \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) \dots \\ & + 22.98977 \cdot \text{Na} + 39.0983 \cdot \text{K} + 40.08 \cdot \text{Ca} \dots \\ & + 94.971 \cdot (\text{PO}_4 - \text{PO}_4_{\text{volat}}) + 18.9984 \cdot (\text{F} - \text{F}_{\text{volat}}) \dots \\ & + 96.062 \cdot (\text{SO}_4 - \text{SO}_4_{\text{volat}}) + 35.453 \cdot (\text{Cl} - \text{Cl}_{\text{volat}}) \dots \\ & + 91.22 \cdot \text{Zr} + 10.81 \cdot \text{B} + 55.847 \cdot \text{Fe} + 112.41 \cdot \text{Cd} + 51.996 \cdot \text{Cr} \dots \\ & + 207.19 \cdot \text{Pb} + 235 \cdot \text{U} + \text{UDS} \end{aligned}$$

$$\text{Calcine_Wt}_{\text{tot}} = 213.1 \cdot \text{gm} \quad (\text{per liter of solution})$$

CALCULATE VOLUME REDUCTION FACTOR OF CALCINED SOLIDS

(after Appendix G of ENICO-1100):

1. Estimate bulk density of calcined solids product and fines from plant or pilot plant data:

(value for a typical Fluorinel/Na blend is)

$$\rho_{b_p} = 1.7 \cdot \frac{\text{gm}}{\text{cm}^3}$$

2. Estimate density of product and fines mixture based on expected product to fines ratio using the method in ENICO-1100. Use 95% of product bulk density in most cases. Use 90% of product bulk density if P/F ratio is less than 2. Using a higher density will generally result in a higher, and more conservative, calculated heat generation rate for the calcine.

(P/F ratio for a FI/Na blend is 3 to 4 kg product per kg fines)

so use 95% in this case: $\rho_{b_m} := .95 \cdot \rho_{b_p}$

$$\rho_{b_m} = 1.615 \cdot \frac{\text{gm}}{\text{cm}^3}$$

3. Volume reduction factor = ratio of volume of liquid feed to volume of calcine solid produced:

$$\text{VRF} := \frac{\rho_{b_m} \cdot 1000 \cdot \frac{\text{cm}^3}{\text{liter}}}{\text{Calcine_Wt}_{\text{tot}} \cdot \text{liter}^{-1}}$$

$$\text{VRF} = 7.58 \frac{\text{liter_feed}}{\text{liter_calcine}}$$

4. The VRF used by operations is usually the the ratio of tank farm waste volume to calcine volume, and not the total volume of waste and feed additives such as aluminum nitrate, calcium nitrate and boric acid. This allows a direct calculation of bin volumes from tank farm depletion from the volume reduction factor.

The calcined solids calculation gave the amount of solids based on a solution volume of 1 liter):

$$V_{\text{total}} := 1 \cdot \text{liter}$$

For Fluorine/Na blends, only calcium nitrate is added. For simplicity in the example, assume solid calcium nitrate was added directly to the feed and did not increase the solution volume:

$$V_{\text{feed_additives}} := 0 \cdot \text{liter}$$

The volume of tank farm waste in the feed blend is then:

$$V_{\text{tankfarm_waste}} := V_{\text{total}} - V_{\text{feed_additives}}$$

$$V_{\text{tankfarm_waste}} = 1 \cdot \text{liter}$$

$$\text{VRF}_{\text{TF}} := \text{VRF} \cdot \left(\frac{V_{\text{total}} - V_{\text{feed_additives}}}{V_{\text{total}}} \right)$$

$$\text{VRF}_{\text{TF}} = 7.58 \frac{\text{liter_tank_farm_waste}}{\text{liter_calcine}}$$

Appendix B
Verification of Simplified Equation for Moles of Oxygen

APPENDIX B VERIFICATION OF SIMPLIFIED EQUATION FOR MOLES OF OXYGEN

If no phosphate, fluoride, sulfate, or chloride volatilize, then it can be shown for all cases that the total moles of oxygen can be determined from the sum of oxidation states of the other elements in the feed:

$$\text{moles_O_tot} := \frac{1}{2} \cdot \left(\sum_i \text{oxidation_states_moles_of_element}_i \right) \quad (\text{Oxygen has a -2 oxidation state})$$

This works since any elements remaining after formation of phosphates, fluorides, sulfates and chlorides are assumed to form oxides, and the oxidation states for all elements in the compounds formed must balance.

This method is less involved than that listed in Appendix A, since it does not require the calculation of the moles of each individual compound formed.

DERIVATION OF SIMPLIFIED EQUATION FOR MOLES OF OXYGEN Example Case #1-High Calcium and Potassium

Wanted: Express oxygen moles in terms of elemental concentrations in feed by combining terms in equations for compounds formed.

Basis: 1 liter of solution

- Method:**
1. Determine equations for moles of each compound formed for the case given in terms of elemental/molar concentrations in feed.
 2. Sum up moles of oxygen and substitute equations for oxides in terms of elemental compositions.
 3. Collect terms to verify that moles of oxygen equals $0.5 \times (\text{sum of (oxidation states} \times \text{elements)})$.

Given:

Case #1-High calcium and potassium (enough calcium to react with phosphate and fluoride, and enough potassium to react with sulfate and chloride) or:

$$\text{Ca} \geq \frac{3}{2} \cdot \text{PO}_4 \quad \text{and} \quad \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 \geq \frac{\text{F}}{2} \quad \text{and} \quad (1 - X_{\text{NO}_3}) \cdot \text{K} \geq 2 \cdot \text{SO}_4 \quad \text{and} \quad (1 - X_{\text{NO}_3}) \cdot \text{K} - 2 \cdot \text{K}_2\text{SO}_4 \geq \text{Cl}$$

Test Solution Content for 1 liter of Solution-Case #1(High calcium and potassium):

F := 1·mole	Al := 1·mole	Ca := .8·mole	Cr := .0001·mole
SO4 := .01·mole	Zr := 1·mole	B := .1·mole	Pb := .0001·mole
Cl := .01·mole	Na := .75·mole	Fe := .1·mole	Hg := .0001·mole
PO4 := .001·mole	K := .4·mole	Cd := .1·mole	U := .000·mole
NO3 := 5·mole	Acid := 2·mole	UDS := 1·gm	

Calculations:

Verify there is enough Ca, Na, and K, to react with all PO₄, F, SO₄, and Cl so that none of the PO₄, F, SO₄, and Cl volatilize:

$$\left[\left[2 \cdot \text{Ca} + (1 - X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) \right] \geq (3 \cdot \text{PO}_4 + \text{F} + 2 \cdot \text{SO}_4 + \text{Cl}) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

∴ True, therefore, there is sufficient Ca, Na, and K for all non-oxides assumed to form.

1. Nitrate Solids:

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{\text{NO}_3} = 0.66 \frac{\text{mole} \cdot \text{NO}_3}{\text{mole} \cdot (\text{Na} + \text{K})} \quad (0.66 \pm 0.05 \text{ based on analyses of pilot plant calcine, Reference 7})$$

$$\text{NaNO}_3 := X_{\text{NO}_3} \cdot \text{Na}$$

$$\text{KNO}_3 := X_{\text{NO}_3} \cdot \text{K}$$

2. Phosphate solids:

All goes to Calcium Phosphate since there is enough calcium:

$$\text{Ca} \geq \frac{3}{2} \cdot \text{PO}_4 = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

$$\text{Ca}_3\text{PO}_4_2 := \frac{\text{PO}_4}{2}$$

No phosphate to combine with Na and K so: $\text{Na}_3\text{PO}_4 := 0 \cdot \text{mole}$ $\text{K}_3\text{PO}_4 := 0 \cdot \text{mole}$

Check to make sure none volatilizes:

$$\text{PO}_4_{\text{volat}} := \text{PO}_4 - 2 \cdot \text{Ca}_3\text{PO}_4_2 \quad \text{PO}_4_{\text{volat}} = 0$$

3. Fluoride Solids:

Since there is sufficient Ca not as phosphate, all F goes to CaF₂:

$$\text{Ca}_{\text{rem}} := \text{Ca} - \frac{3}{2} \cdot \text{PO}_4$$

$$\text{Ca}_{\text{rem}} \geq \frac{\text{F}}{2} = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

$$\text{CaF}_2 := \frac{\text{F}}{2} \quad \text{All F goes to CaF}_2$$

$$\text{NaF} := 0 \cdot \text{mole} \quad \text{KF} := 0 \cdot \text{mole}$$

Check to make sure none volatilizes:

$$\text{F}_{\text{volat}} := \text{F} - 2 \cdot \text{CaF}_2 - \text{NaF} - \text{KF} \quad \text{F}_{\text{volat}} = 0$$

4. Sulfate (SO4) Solids:

Potassium not as nitrate or fluoride:

$$K_{rem4} := K - X_{NO3} \cdot K - KF$$

If sulfate is greater than remaining K, then all remaining K goes to sulfate,
Else all sulfate goes to K2SO4:

$$SO4 \geq \frac{K_{rem4}}{2} = 0 \quad (=0 \text{ for false, so sulfate is not greater than remaining K):$$

$$K2SO4 := SO4 \quad \text{All SO4 goes to K2SO4}$$

$$SO4_{rem} := SO4 - K2SO4$$

$$SO4_{rem} = 0 \cdot \text{mole}$$

$$Na2SO4 := 0 \cdot \text{mole}$$

$$CaSO4 := 0 \cdot \text{mole}$$

$$CdSO4 := 0 \cdot \text{mole}$$

Check to make sure none volatilizes:

$$SO4_{volat} := SO4 - K2SO4 - Na2SO4 - CaSO4 - CdSO4$$

$$SO4_{volat} = 0$$

5. Chloride Solids:

If enough K, then form KCl:

$$K_{rem5} := K - X_{NO3} \cdot K - KF - 2 \cdot K2SO4$$

$$Cl \geq K_{rem5} = 0 \quad (=0 \text{ for false, so Cl is not greater than remaining K):$$

$$KCl := Cl$$

$$Cl_{rem} := Cl - KCl$$

$$Cl_{rem} = 0$$

$$NaCl := 0 \cdot \text{mole}$$

$$CaCl2 := 0 \cdot \text{mole}$$

Check to make sure none volatilizes:

$$Cl_{volat} := Cl - KCl - NaCl - 2 \cdot CaCl2$$

$$Cl_{volat} = 0$$

6. Sodium Solids:

Any remaining Na forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$\text{Na}_{\text{avail6}} := \text{Na} - \text{NaNO}_3 - 3 \cdot \text{Na}_3\text{PO}_4 - 2 \cdot \text{Na}_2\text{SO}_4 - \text{NaCl} - \text{NaF}$$

$$\text{and } \text{NaF} = 0 \quad \text{Na}_3\text{PO}_4 = 0 \quad \text{Na}_2\text{SO}_4 = 0 \quad \text{NaCl} = 0$$

$$\text{so: } \text{Na}_{\text{avail6}} := (\text{Na} - \text{NaNO}_3)$$

Substituting for NaNO₃:

$$\text{Na}_{\text{avail6}} := (\text{Na} - X_{\text{NO}_3} \cdot \text{Na})$$

$$\text{NaAlO}_2 := \text{if}(\text{Al} > \text{Na}_{\text{avail6}}, \text{Na}_{\text{avail6}}, \text{Al}) \quad \text{and} \quad (\text{Al} > \text{Na}_{\text{avail6}}) = 1 \quad \text{so:}$$

$$\text{NaAlO}_2 := \text{Na}_{\text{avail6}} \quad \text{or:} \quad \text{NaAlO}_2 := (\text{Na} - X_{\text{NO}_3} \cdot \text{Na})$$

$$\text{Na}_2\text{O} := \frac{1}{2} (\text{Na}_{\text{avail6}} - \text{NaAlO}_2) \quad \text{but there is no Na left so: } \text{Na}_2\text{O} = 0 \cdot \text{mole}$$

7. Potassium Solids:

Any remaining K forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$\text{K}_{\text{avail7}} := \text{K} - \text{KNO}_3 - 3 \cdot \text{K}_3\text{PO}_4 - 2 \cdot \text{K}_2\text{SO}_4 - \text{KCl} - \text{KF}$$

$$\text{and } \text{KF} = 0 \quad \text{K}_3\text{PO}_4 = 0$$

$$\text{so: } \text{K}_{\text{avail7}} := \text{K} - \text{KNO}_3 - 2 \cdot \text{K}_2\text{SO}_4 - \text{KCl}$$

Substituting for KNO₃, K₂SO₄, and KCl:

$$\text{K}_{\text{avail7}} := \text{K} - X_{\text{NO}_3} \cdot \text{K} - 2 \cdot \text{SO}_4 - \text{Cl}$$

$$\text{KAlO}_2 := \text{if}(\text{Al} - \text{NaAlO}_2 > \text{K}_{\text{avail7}}, \text{K}_{\text{avail7}}, \text{Al}) \quad \text{and} \quad (\text{Al} - \text{NaAlO}_2 > \text{K}_{\text{avail7}}) = 1$$

so there is enough Al for all K and: $\text{KAlO}_2 := \text{K}_{\text{avail7}}$

$$\text{substituting gives: } \text{KAlO}_2 := \text{K} - X_{\text{NO}_3} \cdot \text{K} - 2 \cdot \text{SO}_4 - \text{Cl}$$

$$\text{K}_2\text{O} := \frac{1}{2} (\text{K}_{\text{avail7}} - \text{KAlO}_2) \quad \text{so: } \text{K}_2\text{O} = 0 \cdot \text{mole}$$

8. Aluminum Solids (other than NaAlO₂ and KAlO₂):

Aluminum oxide:

$$\text{Al}_2\text{O}_3 := \frac{1}{2} (\text{Al} - \text{NaAlO}_2 - \text{KAlO}_2)$$

Substituting for NaAlO₂ and KAlO₂ gives:

$$\text{Al}_2\text{O}_3 := \frac{1}{2} [\text{Al} - (\text{Na} - X_{\text{NO}_3} \cdot \text{Na}) - (\text{K} - X_{\text{NO}_3} \cdot \text{K} - 2 \cdot \text{SO}_4 - \text{Cl})]$$

9. Calcium Solids:

Any remaining Calcium goes to oxide:

$$\text{CaO} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4_2 - \text{CaF}_2 - \text{CaSO}_4 - \text{CaCl}_2$$

$$\text{CaSO}_4 = 0 \quad \text{and} \quad \text{CaCl}_2 = 0 \quad \text{so:}$$

$$\text{CaO} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4_2 - \text{CaF}_2$$

Substituting for Ca_3PO_4_2 and CaF_2

$$\text{CaO} := \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F}$$

10. Cadmium Solids:

Any remaining Cadmium goes to oxide:

$$\text{CdO} := \text{Cd} - \text{CdSO}_4 \quad \text{and} \quad \text{CdSO}_4 := 0 \quad \text{so:}$$

$$\text{CdO} := \text{Cd}$$

CALCULATE MOLES OF OXYGEN

Moles of oxygen in compounds with Al, Na, K, and Ca:

$$O_a := 2 \cdot NaAlO_2 + 2 \cdot KAlO_2 + Na_2O + K_2O + 3 \cdot Al_2O_3 + CaO + CdO$$

Substituting for moles of NaAlO₂ and KAlO₂, Na₂O and K₂O, Al₂O₃, CaO, CdO:

$$\begin{aligned} O_a := & 2 \cdot \left((Na - X_{NO_3} \cdot Na) \right) + 2 \cdot \left(K - X_{NO_3} \cdot K - 2 \cdot SO_4 - Cl \right) \dots \\ & + 0 \cdot \text{mole} + 0 \cdot \text{mole} \dots \\ & + 3 \cdot \left[\frac{1}{2} \cdot \left[Al - (Na - X_{NO_3} \cdot Na) - (K - X_{NO_3} \cdot K - 2 \cdot SO_4 - Cl) \right] \right] \dots \\ & + \left(Ca - \frac{3}{2} \cdot PO_4 - \frac{1}{2} \cdot F \right) \dots \\ & + Cd \end{aligned}$$

simplifies to

$$O_a := \frac{1}{2} \cdot Na - \frac{1}{2} \cdot X_{NO_3} \cdot Na + \frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO_3} \cdot K - SO_4 - \frac{1}{2} \cdot Cl + \frac{3}{2} \cdot Al + Ca - \frac{3}{2} \cdot PO_4 - \frac{1}{2} \cdot F + Cd$$

rearranges to

$$O_a := \frac{1}{2} \cdot (3 \cdot Al + Na + K + 2 \cdot Ca - X_{NO_3} \cdot Na - X_{NO_3} \cdot K - 2 \cdot SO_4 - Cl - 3 \cdot PO_4 - F + 2 \cdot Cd)$$

or, collecting terms for Na and K:

$$O_a := \frac{1}{2} \cdot [3 \cdot Al + (1 - X_{NO_3}) \cdot Na + (1 - X_{NO_3}) \cdot K + 2 \cdot Ca + -2 \cdot SO_4 + -1 \cdot Cl + -3 \cdot PO_4 + -1 \cdot F + 2 \cdot Cd]$$

which can be represented as

$$O_a := \frac{1}{2} \cdot \left[\sum_{\text{elements}} ((\text{oxidation_state}) \cdot (\text{moles_of_element})) \right]$$

This is also true for elements assumed to form only oxides:

$$O_b := 2 \cdot Zr + \frac{3}{2} \cdot B + \frac{3}{2} \cdot Fe + \frac{3}{2} \cdot Cr + Pb + 3 \cdot U$$

rearranges to

$$O_b := \frac{1}{2} \cdot (4 \cdot Zr + 3 \cdot B + 3 \cdot Fe + 3 \cdot Cr + 2 \cdot Pb + 6 \cdot U)$$

Which is also the based on the sum of oxidation times concentration:

$$O_b := \frac{1}{2} \cdot \left[\sum_{\text{elements}} ((\text{oxidation_state}) \cdot (\text{moles_of_element})) \right]$$

∴ Therefore, the moles of oxygen the calcine can be determined from the sum of oxidation states of the other elements in the feed for this example.

Derive Simplified Equation for Moles of Oxygen
Example Case #2 - High Calcium, But Not Enough Potassium for Sulfate

Wanted: Express moles of oxygen in calcine in terms of elements in feed by combining terms in equations for compounds formed.

Basis: 1 liter of solution

- Method:** 1. Determine equations for moles of each compound formed for the case given in terms of elemental/molar concentrations in feed.
 2. Sum up moles of oxygen and substitute equations for oxides in terms of elemental compositions.
 3. Collect terms to verify that moles of oxygen = $0.5 \times (\text{sum of (oxidation states} \times \text{elements)})$.

Given:

Case #2 - Not enough potassium to form sulfate, enough Ca and Na for remainder.

Basis: 1 liter of solution

Test Case Solution Content for 1 liter of Solution-Case #2 (Not enough potassium to form sulfate, but enough Ca and Na for remainder)

F := 1·mole	Al := 1·mole	Ca := .8·mole	Cr := .0001·mole
SO4 := .1·mole	Zr := 1·mole	B := .1·mole	Pb := .0001·mole
Cl := .01·mole	Na := .5·mole	Fe := .1·mole	Hg := .0001·mole
PO4 := .001·mole	K := .1·mole	Cd := .1·mole	U := .000·mole
NO3 := 5·mole	Acid _{Na} := 2·mole	UDS := 1·gm	

Calculations:

Verify there is enough Ca, Na, and K, to react with all PO4, F, SO4, and Cl so that none of the PO4, F, SO4, and Cl volatilize:

$$\left[\left[2 \cdot \text{Ca} + (1 - X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) \right] \geq (3 \cdot \text{PO}_4 + \text{F} + 2 \cdot \text{SO}_4 + \text{Cl}) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

∴ True, therefore, there is sufficient Ca, Na, and K for all non-oxides assumed to form.

(This is somewhat conservative since it doesn't account for possible CdSO4)

1. Nitrate Solids:

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{\text{NO}_3} := 0.66 \frac{\text{mole} \cdot \text{NO}_3}{\text{mole} \cdot (\text{Na} + \text{K})}$$

$$\text{NaNO}_3 := X_{\text{NO}_3} \cdot \text{Na}$$

$$\text{KNO}_3 := X_{\text{NO}_3} \cdot \text{K}$$

2. Phosphate solids:

All goes to Calcium Phosphate,

If not enough Ca for Phosphate, then excess phosphate volatilizes:

$$\text{Ca} \geq \frac{3}{2} \cdot \text{PO}_4 = 1 \quad (= 1 \text{ for true, so there is enough calcium})$$

$$\text{Ca}_3\text{PO}_4_2 := \frac{\text{PO}_4}{2}$$

No phosphate to combine with Na and K so: $\text{Na}_3\text{PO}_4 := 0 \cdot \text{mole}$ $\text{K}_3\text{PO}_4 := 0 \cdot \text{mole}$

Check to make sure none volatilizes:

$$\text{PO}_4_{\text{volat}} := \text{PO}_4 - 2 \cdot \text{Ca}_3\text{PO}_4_2 - \text{Na}_3\text{PO}_4 - \text{K}_3\text{PO}_4$$

$$\text{PO}_4_{\text{volat}} = 0$$

3. Fluoride Solids:

If sufficient Ca not as phosphate, all F goes to CaF_2 , else all Ca goes to CaF_2 :

$$\text{Ca}_{\text{avail}3} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4_2$$

$$\frac{\text{F}}{2} \geq \text{Ca}_{\text{avail}3} = 0 \quad \rightarrow = 0 \text{ for false, so all F goes to } \text{CaF}_2$$

$$\text{CaF}_2 := \frac{\text{F}}{2}$$

$$\text{F}_{\text{rem}} := \text{F} - 2 \cdot \text{CaF}_2 \quad \text{F}_{\text{rem}} = 0$$

No fluoride left to combine with Na and K so:

$$\text{NaF} := 0 \cdot \text{mole} \quad \text{KF} := 0 \cdot \text{mole}$$

Check to make sure none volatilizes:

$$\text{F}_{\text{volat}} := \text{F} - 2 \cdot \text{CaF}_2 - \text{NaF} - \text{KF} \quad \text{F}_{\text{volat}} = 0$$

4. Sulfate (SO4) Solids:

Potassium not as nitrate or fluoride:

$$K_{avail4} := K - X_{NO3} \cdot K - 3 \cdot K3PO4 - KF$$

$$SO4 \geq \frac{K_{avail4}}{2} = 1 \quad \rightarrow \text{Not enough K to tie up all sulfate}$$

$$K2SO4 := \frac{K_{avail4}}{2} \quad \rightarrow \text{All available K goes to K2SO4}$$

by substitution, yields

$$K2SO4 := \frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO3} \cdot K - \frac{1}{2} \cdot 0 \cdot \text{mole} - \frac{1}{2} \cdot (3 \cdot 0 \cdot \text{mole})$$

simplifies to

$$K2SO4 := \frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO3} \cdot K$$

$$SO4_{rem_a} := SO4 - K2SO4$$

If there is any sulfate left, it forms Na2SO4, CaSO4, and CdSO4

Na not as nitrate or fluoride:

$$Na_{avail4} := Na - X_{NO3} \cdot Na - 3 \cdot Na3PO4 - NaF$$

$$SO4_{rem_a} \geq \frac{Na_{avail4}}{2} = 0 \quad \rightarrow \text{All remaining SO4 goes to Na2SO4}$$

$$Na2SO4 := SO4_{rem_a}$$

by substitution yields,

$$Na2SO4 := SO4 - K2SO4 \quad \text{or} \quad Na2SO4 := SO4 - \left(\frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO3} \cdot K \right)$$

No sulfate left for Ca and Cd:

$$SO4_{rem_b} := SO4 - K2SO4 - Na2SO4 \quad SO4_{rem_b} = 0$$

$$CaSO4 := SO4_{rem_b} \quad CaSO4 = 0$$

$$SO4_{rem_c} := SO4 - K2SO4 - Na2SO4 - CaSO4 \quad SO4_{rem_c} = 0$$

$$CdSO4 := SO4_{rem_c} \quad CdSO4 = 0$$

Verify nothing volatilizes

$$SO4_{volat} := SO4 - K2SO4 - Na2SO4 - CaSO4 - CdSO4$$

$$SO4_{volat} = 0$$

5. Chloride Solids:

If enough K, then form KCl:

$$K_{\text{avail5}} := K - X_{\text{NO3}} \cdot K - 3 \cdot K_3\text{PO4} - KF - 2 \cdot K_2\text{SO4} \quad K_{\text{avail5}} = 0$$

$$KCl := K_{\text{avail5}} \quad KCl = 0$$

Else form NaCl:

$$Cl_{\text{rem_a}} := Cl - KCl$$

$$Cl_{\text{rem_a}} := Cl$$

$$Na_{\text{avail5}} := Na - X_{\text{NO3}} \cdot Na - 3 \cdot Na_3\text{PO4} - NaF - 2 \cdot Na_2\text{SO4}$$

$$Cl_{\text{rem_a}} \geq Na_{\text{avail5}} = 1 \quad \rightarrow \text{Enough Na, so all Cl goes to NaCl}$$

$$NaCl := Cl_{\text{rem_a}}$$

$$NaCl := Cl$$

Else form CaCl2:

$$Cl_{\text{rem_b}} := Cl - KCl - NaCl \quad Cl_{\text{rem_b}} = 0$$

$$CaCl_2 := \frac{Cl_{\text{rem_b}}}{2} \quad CaCl_2 = 0$$

Check to make sure no Cl volatilizes:

$$Cl_{\text{volat}} := Cl - KCl - NaCl - 2 \cdot CaCl_2$$

$$Cl_{\text{volat}} = 0$$

6. Sodium Solids:

Any remaining Na forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$Na_{avail6} := (Na - NaNO_3 - 3 \cdot Na_3PO_4 - 2 \cdot Na_2SO_4 - NaCl - NaF)$$

$$NaF = 0 \quad \text{and} \quad Na_3PO_4 = 0 \quad \text{so:}$$

$$Na_{avail6} := (Na - NaNO_3 - 2 \cdot Na_2SO_4 - NaCl)$$

Substituting for NaNO₃, Na₂SO₄, and NaCl:

$$Na_{avail6} := \left[Na - X_{NO_3} \cdot Na - 2 \cdot \left[SO_4 - \left(\frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO_3} \cdot K \right) \right] - Cl \right]$$

$$NaAlO_2 := \text{if}(Al > Na_{avail6}, Na_{avail6}, Al) \quad \text{and} \quad (Al > Na_{avail6}) = 1 \quad \text{so:}$$

$$NaAlO_2 := Na_{avail6} \quad \text{or:} \quad NaAlO_2 := \left[Na - X_{NO_3} \cdot Na - 2 \cdot \left[SO_4 - \left(\frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO_3} \cdot K \right) \right] - Cl \right]$$

$$Na_2O := \frac{1}{2} \cdot (Na_{avail6} - NaAlO_2) \quad \text{leaving} \quad Na_2O = 0 \cdot \text{mole}$$

7. Potassium Solids:

Any remaining K forms oxides which may or may not exist as complexes with other oxide compounds such as Aluminum oxide:

$$K_{avail7} := (K - KNO_3 - 3 \cdot K_3PO_4 - 2 \cdot K_2SO_4 - KCl - KF)$$

$$K_{avail7} = 0 \cdot \text{mole} \quad \text{no potassium left}$$

$$KAlO_2 := \text{if}(Al - NaAlO_2 > K_{avail7}, K_{avail7}, Al) \quad \text{and} \quad (Al - NaAlO_2 > K_{avail7}) = 1$$

so there is enough Al for all K and: $KAlO_2 := K_{avail7}$

substituting gives: $KAlO_2 = 0 \cdot \text{mole}$

$$K_2O := \frac{1}{2} \cdot (K_{avail7} - KAlO_2) \quad \text{so:} \quad K_2O = 0 \cdot \text{mole}$$

8. Aluminum Solids (other than NaAlO₂ and KAlO₂):

Aluminum oxide:

$$Al_2O_3 := \frac{1}{2} \cdot (Al - NaAlO_2 - KAlO_2)$$

Substituting for NaAlO₂ and KAlO₂ gives:

$$Al_2O_3 := \frac{1}{2} \cdot \left[Al - \left[Na - X_{NO_3} \cdot Na - 2 \cdot \left[SO_4 - \left(\frac{1}{2} \cdot K - \frac{1}{2} \cdot X_{NO_3} \cdot K \right) \right] - Cl \right] \right]$$

9. Calcium Solids:

Any remaining Calcium goes to oxides:

$$\text{CaO} := \text{Ca} - 3 \cdot \text{Ca}_3\text{PO}_4\text{--}_2 - \text{CaF}_2 - \text{CaSO}_4 - \text{CaCl}_2$$

by substitution for $\text{Ca}_3\text{PO}_4\text{--}_2$, CaF_2 , CaSO_4 , and CaCl_2 , yields

$$\text{CaO} := \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F}$$

simplifies to

$$\text{CaO} := \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F}$$

10. Cadmium Solids:

Any remaining Cadmium goes to oxide:

$$\text{CdO} := \text{Cd} - \text{CdSO}_4 \quad \text{CdSO}_4 = 0$$

$$\text{CdO} := \text{Cd}$$

CALCULATE SODIUM PLUS POTASSIUM MOLE PERCENT

Moles of oxygen in compounds with Al, Na, K, and Ca:

$$O_a := 2 \cdot \text{NaAlO}_2 + 2 \cdot \text{KAlO}_2 + \text{Na}_2\text{O} + \text{K}_2\text{O} + 3 \cdot \text{Al}_2\text{O}_3 + \text{CaO} + \text{CdO}$$

Substituting for moles of NaAlO₂ and KAlO₂, Na₂O and K₂O, Al₂O₃, CaO, CdO:

$$\begin{aligned} O_a := & 2 \cdot \left[\text{Na} - X_{\text{NO}_3} \cdot \text{Na} - 2 \cdot \left[\text{SO}_4 - \left(\frac{1}{2} \cdot \text{K} - \frac{1}{2} \cdot X_{\text{NO}_3} \cdot \text{K} \right) \right] - \text{Cl} \right] \dots \\ & + 3 \cdot \left[\frac{1}{2} \cdot \left[\text{Al} - \left[\text{Na} - X_{\text{NO}_3} \cdot \text{Na} - 2 \cdot \left[\text{SO}_4 - \left(\frac{1}{2} \cdot \text{K} - \frac{1}{2} \cdot X_{\text{NO}_3} \cdot \text{K} \right) \right] - \text{Cl} \right] \right] \right] \dots \\ & + \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F} + \text{Cd} \end{aligned}$$

simplifies to

$$O_a := \frac{1}{2} \cdot \text{Na} - \frac{1}{2} \cdot X_{\text{NO}_3} \cdot \text{Na} + \frac{1}{2} \cdot \text{K} - \frac{1}{2} \cdot X_{\text{NO}_3} \cdot \text{K} - \text{SO}_4 - \frac{1}{2} \cdot \text{Cl} + \frac{3}{2} \cdot \text{Al} + \text{Ca} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F} + \text{Cd}$$

rearranges to

$$O_a := \frac{1}{2} \cdot \left[3 \cdot \text{Al} + (1 - X_{\text{NO}_3}) \cdot \text{Na} + (1 - X_{\text{NO}_3}) \cdot \text{K} + 2 \cdot \text{Ca} - 2 \cdot \text{SO}_4 - \text{Cl} - 3 \cdot \text{PO}_4 - \text{F} + 2 \cdot \text{Cd} \right]$$

which can be represented as

$$O_a := \frac{1}{2} \cdot \left[\sum_{\text{elements}} ((\text{oxidation_state}) \cdot (\text{moles_of_element})) \right]$$

This is also true for elements assumed to form only oxides:

$$O_b := 2 \cdot \text{Zr} + \frac{3}{2} \cdot \text{B} + \frac{3}{2} \cdot \text{Fe} + \frac{3}{2} \cdot \text{Cr} + \text{Pb} + 3 \cdot \text{U}$$

rearranges to

$$O_b := \frac{1}{2} \cdot (4 \cdot \text{Zr} + 3 \cdot \text{B} + 3 \cdot \text{Fe} + 3 \cdot \text{Cr} + 2 \cdot \text{Pb} + 6 \cdot \text{U})$$

Which is also based on the sum of oxidation times concentration

$$O_b := \frac{1}{2} \cdot \left[\sum_{\text{elements}} ((\text{oxidation_state}) \cdot (\text{moles_of_element})) \right]$$

∴ Therefore, the moles of oxygen the calcine can be determined from the sum of oxidation states of the other elements in the feed for this example.

Appendix C
Example Calculations

EXAMPLE CALCULATION #1 **CASE Nby#1**

Test Case Solution Content for 1 liter of Solution-Case Nby1 (Values from letter Nby-08-90, case 1):

Solution is a 5:1 blend of Typical Fluorinel and Na waste.

$$\begin{aligned}
 F &:= \frac{5 \cdot 2.27 + 0.049}{6} \cdot \text{mole} & Al &:= \frac{5 \cdot 0.36 + .45}{6} \cdot \text{mole} & Ca &:= 0.7 \cdot F & Cr &:= .0 \cdot \text{mole} \\
 SO_4 &:= \frac{5 \cdot 0.079 + .048}{6} \cdot \text{mole} & Zr &:= \frac{5 \cdot 0.29 + 0}{6} \cdot \text{mole} & B &:= \frac{5 \cdot 0.17 + 0.024}{6} \cdot \text{mole} & Pb &:= 0 \cdot \text{mole} \\
 Cl &:= \frac{5 \cdot 0.0016 + 0.031}{6} \cdot \text{mole} & Na &:= \frac{5 \cdot 0.028 + 1.46}{6} \cdot \text{mole} & Fe &:= \frac{5 \cdot 0.0072 + 0.023}{6} \cdot \text{mole} & U &:= 0 \cdot \text{mole} \\
 PO_4 &:= .0 \cdot \text{mole} & K &:= \frac{5 \cdot 0.0028 + .21}{6} \cdot \text{mole} & Cd &:= \frac{5 \cdot 0.11 + 0}{6} \cdot \text{mole} & & \text{(Use ave isotopic weight for uranium if analyses is available)} \\
 NO_3 &:= \left(\frac{5 \cdot 2.37 + 4.47}{6} \right) \cdot \text{mole} + 2 \cdot Ca & \text{Acid}_{Na} &:= \frac{5 \cdot 2.04 + 1.69}{6} \cdot \text{mole} & UDS &:= \frac{5 \cdot 2 + 1}{6} \cdot \text{gm}
 \end{aligned}$$

Calculated concentrations for 5:1 blend:

$$\begin{aligned}
 F &= 1.9 \cdot \text{mole} & Al &= 0.375 \cdot \text{mole} & Ca &= 1.33 \cdot \text{mole} & Cr &= 0 \cdot \text{mole} \\
 SO_4 &= 0.074 \cdot \text{mole} & Zr &= 0.242 \cdot \text{mole} & B &= 0.146 \cdot \text{mole} & Pb &= 0 \cdot \text{mole} \\
 Cl &= 0.006 \cdot \text{mole} & Na &= 0.267 \cdot \text{mole} & Fe &= 0.01 & U &= 0 \cdot \text{mole} \\
 PO_4 &= 0 \cdot \text{mole} & K &= 0.037 \cdot \text{mole} & Cd &= 0.092 \cdot \text{mole} & UDS &= 1.833 \cdot \text{gm}
 \end{aligned}$$

(Nitrate and acid concentrations in feed are not used in the calculation, but are given here for completeness)

$$NO_3 = 5.38 \cdot \text{mole} \quad Na + K = 0.304 \cdot \text{mole} \quad \text{Acid}_{Na} = 1.982 \cdot \text{mole}$$

Estimated calcine product bulk density for Case #Nby1: $\rho_{b_p} := 1.7 \cdot \frac{\text{gm}}{\text{cm}^3}$ (value for a typical Fluorinel/Na blend)

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{NO_3} := 0.66 \frac{\text{mole} \cdot NO_3}{\text{mole} \cdot (Na + K)} \quad (0.66 \pm 0.05 \text{ based on analyses of pilot plant calcine without reducing agents, Reference 7. Use pilot plant calcine data for } NO_3/(Na+K) \text{ ratios if reducing agents such as sugar are used.})$$

Calculations:

1. Verify there is enough Ca, Na, and K, to react with all PO₄, F, SO₄, and Cl so that none of the PO₄, F, SO₄, and Cl volatilize:

$$\left[\left[2 \cdot Ca + (1 - X_{NO_3}) \cdot (Na + K) \right] \geq (3 \cdot PO_4 + F + 2 \cdot SO_4 + Cl) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

∴ **True, therefore, there is sufficient Ca, Na, and K for all non-oxides assumed to form.**

(This is somewhat conservative since it doesn't account for possible CdSO₄)

2. Calculate moles of oxygen:

There is enough Ca, Na, K, and Al, so the simplified equation for determining moles of oxygen is preferred to the detailed calculation of Appendix A:

Total moles of oxygen in oxides is therefore:

$$O_{tot} := \frac{3}{2} \cdot Al + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot Na + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot K + Ca - SO4 - \frac{1}{2} \cdot Cl - \frac{3}{2} \cdot PO4 - \frac{1}{2} \cdot F + Cd \dots$$

$$+ 2 \cdot Zr + \frac{3}{2} \cdot B + \frac{3}{2} \cdot Fe + \frac{3}{2} \cdot Cr + Pb + 3 \cdot U$$

$$O_{tot} = 1.725$$

Total Moles is sum of oxygen + nitrates + feed components:

$$Mol_{tot} := O_{tot} + Al + (1 + X_{NO3}) \cdot (Na + K) + Ca \dots$$

$$+ PO4 + F + SO4 + Cl + Zr + B + Fe + Cd + Cr + Pb + U$$

$$Mol_{tot} = 6.404$$

3. Calculate mole percent sodium plus potassium:

Mole % Na+K is:

$$Mol\%_{NaK} := \frac{(Na + K)}{Mol_{tot}} \cdot 100\%$$

$$Mol\%_{NaK} = 4.747\%$$

4. Calculate weight of calcined solids:

Total calcine weight is the sum of (MW x moles):

$$Calcine_Wt_{tot} := \left[\begin{array}{l} 15.9994 \cdot O_{tot} + 26.98154 \cdot Al + 62.005 \cdot X_{NO3} \cdot (Na + K) \dots \\ + 22.98977 \cdot Na + 39.0983 \cdot K + 40.08 \cdot Ca \dots \\ + 94.971 \cdot PO4 + 18.9984 \cdot F \dots \\ + 96.062 \cdot SO4 + 35.453 \cdot Cl \dots \\ + 91.22 \cdot Zr + 10.81 \cdot B + 55.847 \cdot Fe + 112.41 \cdot Cd + 51.996 \cdot Cr \dots \\ + 207.19 \cdot Pb + 235 \cdot U \end{array} \right] \cdot \frac{gm}{mole} + UDS$$

(Use average isotopic weight for uranium instead of 235, or weight conc (g/L) of uranium instead of "235 U", if available)

$$Calcine_Wt_{tot} = 190.8 \cdot gm \text{ (per liter of solution)}$$

5. Estimated bulk density of calcined solids product and fines from plant or pilot plant data:

$$\rho_{b_p} = 1.7 \cdot \frac{gm}{cm^3} \quad (\text{value given is for a typical Fluorinel/Na blend})$$

6. Conservatively estimate density of product and fines mixture based on expected product to fines ratio. Use 95% of product bulk density in most cases. Use 90% of product bulk density if P/F ratio is less than 2.

$$\rho_{b_m} := .95 \cdot \rho_{b_p}$$

$$\rho_{b_m} = 1.615 \cdot \frac{gm}{cm^3}$$

(P/F ratio for a FI/Na blend is about 3 to 4 kg product per kg fines so use 95% of product bulk density)

7. Volume reduction factor = ratio of volume of liquid feed to volume of calcine solid produced:

$$\text{VRF} := \frac{\rho_{b_m} \cdot 1000 \cdot \text{cm}^3 \cdot \text{liter}^{-1}}{\text{Calcine_Wt}_{\text{tot}} \cdot \text{liter}^{-1}} \quad \text{VRF} = 8.465 \frac{\text{liter_feed}}{\text{liter_calcine}}$$

8. The VRF is usually corrected for feed additives (such as Calcium nitrate and aluminum nitrate) to give the ratio of volume of tank farm waste to volume of calcine solid produced. This allows a direct calculation of bin volumes from tank farm depletion.

(Calculation basis=1 liter) $V_{\text{totalfeed}} := 1 \cdot \text{liter}$

The calculated concentrations did not include volume due to additives, such as water in CaNO_3_2 , so:

$V_{\text{feed_additives}} := 0 \cdot \text{liter}$ for this case.

$$V_{\text{tankfarm_waste}} := V_{\text{totalfeed}} - V_{\text{feed_additives}}$$

$$V_{\text{tankfarm_waste}} = 1 \cdot \text{liter}$$

$$\text{VRF}_{\text{TF}} := \text{VRF} \cdot \left(\frac{V_{\text{totalfeed}} - V_{\text{feed_additives}}}{V_{\text{totalfeed}}} \right)$$

$$\text{VRF}_{\text{TF}} = 8.465 \frac{\text{liter_tank_farm_waste}}{\text{liter_calcine}}$$

9. Calculate heat generation rate of calcine from VRF and liquid heat generation rate:

$$Q_{\text{liq}} := 5 \cdot \frac{\text{watt}}{\text{m}^3} \quad (\text{see Appendix E for calculation of liquid heat generation}) \text{ Use an estimated value since no radiochem was listed in Nby-08-90.}$$

Calcine heat generation rate is then:

$$Q_{\text{calcine}} := Q_{\text{liq}} \cdot \text{VRF} \quad \text{if liquid heat generation was per volume of blend.}$$

or

$$Q_{\text{calcine}} := Q_{\text{liq}} \cdot \text{VRF}_{\text{TF}} \quad \text{if liquid heat generation was per volume of waste without cold additives.}$$

Which for this case is:

$$Q_{\text{calcine}} := Q_{\text{liq}} \cdot \text{VRF}_{\text{TF}}$$

$$Q_{\text{calcine}} = 42.327 \cdot \frac{\text{watt}}{\text{m}^3}$$

EXAMPLE CALCULATION #2

NWCF High Sodium Blended Feed of Evaporated WM-183/189 (mixed with WM-188 heel) With Aluminum Nitrate

Test Case Solution Content for 1 liter of Feed (without scrub recycle) (Values from letters RJR-05-94 and RJR-07-94, references 19 and 20) :

Solution is high sodium blend of Sodium Waste and Aluminum Nitrate:

$F := .1575 \cdot \text{mole}$	$Al := 1.2139 \cdot \text{mole}$	$Ca := .1099 \cdot \text{mole}$	$Cr := .0101 \cdot \text{mole}$
$SO_4 := .006 \cdot \text{mole}$	$Zr := .0172 \cdot \text{mole}$	$B := .0999 \cdot \text{mole}$	$Pb := \frac{.1911}{207.19} \cdot \text{mole}$
$Cl := .0041 \cdot \text{mole}$	$Na := .4708 \cdot \text{mole}$	$Fe := .0363 \cdot \text{mole}$	$U := \frac{.07897}{235} \cdot \text{mole}$
$PO_4 := \frac{.34505}{94.971} \cdot \text{mole}$	$K := .0666 \cdot \text{mole}$	$Cd := .0068 \cdot \text{mole}$	(Use ave isotopic weight for uranium if analyses is available)

(Nitrate and acid concentrations in feed are not used in the calculation, but are given here for completeness)

$NO_3 := 6.0659 \cdot \text{mole}$	$\text{Acid}_{Na} := 1.5573 \cdot \text{mole}$	$UDS := 3.8335 \cdot \text{gm}$
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Calculated concentrations:

$PO_4 = 0.004 \cdot \text{mole}$	$Pb = 9.223 \cdot 10^{-4} \cdot \text{mole}$	$U = 3.36 \cdot 10^{-4} \cdot \text{mole}$
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Estimated calcine product bulk density from RJR-05-94: $\rho_{b_p} := 1.5 \cdot \frac{\text{gm}}{\text{cm}^3}$

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{NO_3} := 0.66 \frac{\text{mole} \cdot NO_3}{\text{mole} \cdot (Na + K)} \quad (0.66 \pm 0.05 \text{ based on analyses of pilot plant calcine without reducing agents, Reference 7. Use pilot plant calcine data for } NO_3/(Na+K) \text{ ratios if reducing agents such as sugar are used.})$$

Calculations:

1. Verify there is enough Ca, Na, and K, to react with all PO_4 , F, SO_4 , and Cl so that none of the PO_4 , F, SO_4 , and Cl volatilize:

$$\left[\left[2 \cdot Ca + (1 - X_{NO_3}) \cdot (Na + K) \right] \geq (3 \cdot PO_4 + F + 2 \cdot SO_4 + Cl) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

∴ True, therefore, there is sufficient Ca, Na, and K for all non-oxides assumed to form.

(This is somewhat conservative since it doesn't account for possible $CdSO_4$)

2. Calculate moles of oxygen and total moles:

There is enough Ca, Na, K, and Al, so the simplified equation for determining moles of oxygen is preferred to the detailed calculation of Appendix A:

Total moles of oxygen in oxides is therefore:

$$O_{tot} := \frac{3}{2} \cdot Al + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot Na + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot K + Ca - SO4 - \frac{1}{2} \cdot Cl - \frac{3}{2} \cdot PO4 - \frac{1}{2} \cdot F + Cd \dots$$

$$+ 2 \cdot Zr + \frac{3}{2} \cdot B + \frac{3}{2} \cdot Fe + \frac{3}{2} \cdot Cr + Pb + 3 \cdot U$$

$$O_{tot} = 2.192$$

Total Moles is sum of oxygen + nitrates + feed components:

$$Mol_{tot} := O_{tot} + Al + (1 + X_{NO3}) \cdot (Na + K) + Ca \dots$$

$$+ PO4 + F + SO4 + Cl + Zr + B + Fe + Cd + Cr + Pb + U$$

$$Mol_{tot} = 4.751$$

3. Calculate mole percent sodium plus potassium:

Mole % Na+K is:

$$Mol\%_{NaK} := \frac{(Na + K)}{Mol_{tot}} \cdot 100\%$$

$$Mol\%_{NaK} = 11.31\%$$

4. Calculate weight of calcined solids:

Total calcine weight is the sum of (MW x moles):

$$Calcine_Wt_{tot} := \left[\begin{array}{l} 15.9994 \cdot O_{tot} + 26.98154 \cdot Al + 62.005 \cdot X_{NO3} \cdot (Na + K) \dots \\ + 22.98977 \cdot Na + 39.0983 \cdot K + 40.08 \cdot Ca \dots \\ + 94.971 \cdot PO4 + 18.9984 \cdot F \dots \\ + 96.062 \cdot SO4 + 35.453 \cdot Cl \dots \\ + 91.22 \cdot Zr + 10.81 \cdot B + 55.847 \cdot Fe + 112.41 \cdot Cd + 51.996 \cdot Cr \dots \\ + 207.19 \cdot Pb + 235 \cdot U \end{array} \right] \cdot \frac{gm}{mole} + UDS$$

(Use average isotopic weight for uranium instead of 235, or weight conc (g/L) of uranium instead of "235 U", if available)

$$Calcine_Wt_{tot} = 121.8 \cdot gm \text{ (per liter of solution)}$$

5. Estimated bulk density of calcined solids product and fines from plant or pilot plant data:

$$\rho_{b_p} = 1.5 \cdot \frac{gm}{cm^3}$$

6. Conservatively estimate density of product and fines mixture based on expected product to fines ratio. Use 95% of product bulk density in most cases. Use 90% of product bulk density if P/F ratio is less than 2.

$$\rho_{b_m} := .90 \cdot \rho_{b_p}$$

(P/F ratio for an ANN/Na Blend is about 1 kg product per kg fines so use 90% of product bulk density)

$$\rho_{b_m} = 1.35 \cdot \frac{gm}{cm^3}$$

7. Volume reduction factor = ratio of volume of liquid feed to volume of calcine solid produced:

$$\text{VRF} := \frac{\rho_{b_m} \cdot 1000 \cdot \text{cm}^3 \cdot \text{liter}^{-1}}{\text{Calcine_Wt}_{\text{tot}} \cdot \text{liter}^{-1}} \quad \text{VRF} = 11.085 \frac{\text{liter_feed}}{\text{liter_calcine}}$$

8. The VRF is usually corrected for feed additives (such as Calcium nitrate and aluminum nitrate) to give the ratio of volume of tank farm waste to volume of calcine solid produced. This allows a direct calculation of bin volumes from tank farm depletion.

(Calculation basis was 1 liter) $V_{\text{totalfeed}} := 1 \cdot \text{liter}$

The volumes of ANN, liquid $\text{Ca}(\text{NO}_3)_2$, and boric acid from RJR-05-94 (given as liters per liter of waste) are:

$$V_{\text{feed_additives}} := \frac{.611 + .018 + .197}{(1.0 + .611 + .018 + .197)} \cdot \text{liter per liter of total feed}$$

Volume of tank farm waste in the blend is then:

$$V_{\text{tankfarm_waste}} := V_{\text{totalfeed}} - V_{\text{feed_additives}}$$

$$V_{\text{tankfarm_waste}} = 0.548 \cdot \text{liter}$$

$$\text{VRF}_{\text{TF}} := \text{VRF} \cdot \left(\frac{V_{\text{totalfeed}} - V_{\text{feed_additives}}}{V_{\text{totalfeed}}} \right)$$

$$\text{VRF}_{\text{TF}} = 6.071 \frac{\text{liter_tank_farm_waste}}{\text{liter_calcine}} \quad \text{for the high sodium 188/183/189/ANN blended feed}$$

9. Calculate heat generation rate of calcine from VRF and liquid heat generation rate:

$$Q_{\text{liq}} := 2.350 \frac{\text{watt}}{\text{m}^3} \quad \text{for the 188/183/189/ANN high sodium blend (see Appendix E), concentrations are per liquid volume of the blended feed, not volume of tank farm waste.}$$

$$Q_{\text{calcine}} := Q_{\text{liq}} \cdot \text{VRF}$$

$$Q_{\text{calcine}} = 26.05 \frac{\text{watt}}{\text{m}^3}$$

EXAMPLE CALCULATION #3

10-cm Calciner Pilot Plant Run SBW4-46: Simulated High Sodium Blend of Aluminum Nitrate and Sodium Waste

Test Case Solution Content for 1 liter of Feed (without scrub recycle) (Values from test plan letter TJM-03-93, Reference 22). This run simulated a high sodium ANN/Na blend of ANN and WM-180:

F := 0.013-mole	Al := 1.686-mole	Ca := 0.036-mole	Cr := 0.0-mole
SO4 := 0.017-mole	Zr := 0.0-mole	B := 0.15-mole	Pb := 0.0-mole
Cl := 0.010-mole	Na := 0.623-mole	Fe := 0.005-mole	U := 0.0-mole
PO4 := 0.0-mole	K := 0.056-mole	Cd := 0.0-mole	(Use ave isotopic weight for uranium if analyses is available)

(Nitrate and acid concentrations in feed are not used in the calculation, but are given here for completeness)

NO3 := 5.65-mole	Acid _{Na} := 0.620-mole	UDS := 0.0-gm
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Calcine product bulk density from pilot plant run SBW4-46:

$$\rho_{b_p} := 1.75 \frac{\text{gm}}{\text{cm}^3}$$

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{\text{NO}_3} := 0.66 \frac{\text{mole-NO}_3}{\text{mole} \cdot (\text{Na} + \text{K})} \quad (0.66 \pm 0.05 \text{ based on analyses of pilot plant calcine without reducing agents, Reference 7. Use pilot plant calcine data for } \text{NO}_3/(\text{Na} + \text{K}) \text{ ratios if reducing agents such as sugar are used.})$$

Calculation:

1. Verify there is enough Ca, Na, and K, to react with all PO4, F, SO4, and Cl so that none of the PO4, F, SO4, and Cl volatilize:

$$\left[\left[2 \cdot \text{Ca} + (1 - X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) \right] \geq (3 \cdot \text{PO}_4 + \text{F} + 2 \cdot \text{SO}_4 + \text{Cl}) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

∴ True, therefore, there is sufficient Ca, Na, and K for all non-oxides assumed to form.
(This is somewhat conservative since it doesn't account for possible CdSO4)

2. Calculate moles of oxygen and total moles:

There is enough Ca, Na, K, and Al, so the simplified equation for determining moles of oxygen is preferred to the detailed calculation of Appendix A:

Total moles of oxygen in oxides is therefore:

$$O_{tot} := \frac{3}{2} \cdot Al + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot Na + \frac{1}{2} \cdot (1 - X_{NO3}) \cdot K + Ca - SO4 - \frac{1}{2} \cdot Cl - \frac{3}{2} \cdot PO4 - \frac{1}{2} \cdot F + Cd \dots$$

$$+ 2 \cdot Zr + \frac{3}{2} \cdot B + \frac{3}{2} \cdot Fe + \frac{3}{2} \cdot Cr + Pb + 3 \cdot U$$

$$O_{tot} = 2.884$$

Total Moles is sum of oxygen + nitrates + feed components:

$$Mol_{tot} := O_{tot} + Al + (1 + X_{NO3}) \cdot (Na + K) + Ca \dots$$

$$+ PO4 + F + SO4 + Cl + Zr + B + Fe + Cd + Cr + Pb + U$$

$$Mol_{tot} = 5.929$$

3. Calculate mole percent sodium plus potassium

Mole % Na+K is:

$$Mol\%_{NaK} := \frac{(Na + K)}{Mol_{tot}} \cdot 100\%$$

$$Mol\%_{NaK} = 11.45\%$$

4. Calculate weight of calcined solids:

Total calcine weight is the sum of (MW x moles):

$$Calcine_Wt_{tot} := \left[\begin{array}{l} 15.9994 \cdot O_{tot} + 26.98154 \cdot Al + 62.005 \cdot X_{NO3} \cdot (Na + K) \dots \\ + 22.98977 \cdot Na + 39.0983 \cdot K + 40.08 \cdot Ca \dots \\ + 94.971 \cdot PO4 + 18.9984 \cdot F \dots \\ + 96.062 \cdot SO4 + 35.453 \cdot Cl \dots \\ + 91.22 \cdot Zr + 10.81 \cdot B + 55.847 \cdot Fe + 112.41 \cdot Cd + 51.996 \cdot Cr \dots \\ + 207.19 \cdot Pb + 235 \cdot U \end{array} \right] \cdot \frac{gm}{mole} + UDS$$

(Use average isotopic weight for uranium instead of 235, or weight conc (g/L) of uranium instead of "235 U", if available)

$$Calcine_Wt_{tot} = 141.5 \cdot gm \text{ (per liter of solution)}$$

5. Estimated bulk density of calcined solids product and fines from plant or pilot plant data:

$$\rho_{b_p} = 1.75 \cdot \frac{gm}{cm^3} \quad (\text{average for pilot plant Run SBW4-46})$$

6. Conservatively estimate density of product and fines mixture based on expected product to fines ratio. Use 95% of product bulk density in most cases. Use 90% of product bulk density if P/F ratio is less than 2.

$$\rho_{b_m} := .90 \cdot \rho_{b_p} \quad (P/F \text{ ratio for the run was } 1.45, \text{ so use } 90\% \text{ of product bulk density for product and fines mixture})$$

$$\rho_{b_m} = 1.575 \cdot \frac{gm}{cm^3}$$

7. Volume reduction factor = ratio of volume of liquid feed to volume of calcine solid produced:

$$\text{VRF} := \frac{\rho_{b_m} \cdot 1000 \cdot \text{cm}^3 \cdot \text{liter}^{-1}}{\text{Calcine_Wt}_{\text{tot}} \cdot \text{liter}^{-1}} \quad \text{VRF} = 11.129 \frac{\text{liter_feed}}{\text{liter_calcine}}$$

8. The VRF is usually corrected for feed additives (such as Calcium nitrate and aluminum nitrate) to give the ratio of volume of tank farm waste to volume of calcine solid produced. This allows a direct calculation of bin volumes from tank farm depletion.

(Calculation basis was 1 liter) $V_{\text{totalfeed}} := 1 \cdot \text{liter}$

The feed concentrations for SBW4-46 in TJM-03-93 were based on blending 2.26 vol ANN to 1 Vol 180, and assumed volumes of liquid $\text{Ca}(\text{NO}_3)_2$ and boric acid were negligible:

$$V_{\text{feed_additives}} := \frac{2.26 + 0 + 0}{(1.0 + 2.26 + 0 + 0)} \cdot \text{liter} \quad \text{per liter of total feed}$$

$$V_{\text{feed_additives}} = 0.693 \cdot \text{liter} \quad \text{per liter of total feed}$$

The volume of tank farm waste in the blend is then:

$$V_{\text{tankfarm_waste}} := V_{\text{totalfeed}} - V_{\text{feed_additives}}$$

$$V_{\text{tankfarm_waste}} = 0.307 \cdot \text{liter}$$

$$\text{VRF}_{\text{TF}} := \text{VRF} \cdot \left(\frac{V_{\text{totalfeed}} - V_{\text{feed_additives}}}{V_{\text{totalfeed}}} \right)$$

$$\text{VRF}_{\text{TF}} = 3.414 \frac{\text{volumes_tank_farm_waste}}{\text{volume_calcine}}$$

9. Calculate heat generation rate of calcine from VRF and liquid heat generation rate:

$$Q_{\text{liq}} := 0.322 \cdot \frac{\text{watt}}{\text{m}^3} \quad \text{for WM-180 tank farm waste (see Appendix E), so use } \text{VRF}_{\text{TF}} \text{ rather than VRF.}$$

$$Q_{\text{calcine}} := Q_{\text{liq}} \cdot \text{VRF}_{\text{TF}}$$

$$Q_{\text{calcine}} = 1.099 \cdot \frac{\text{watt}}{\text{m}^3}$$

Appendix D
Comparision of Updated Calculation Method
with Previous Methods

Appendix D
Comparison the Updated of Sodium Plus Potassium Content and
Weight of Calcined Solids with Previous Methods

Wanted: Compare updated calculation methods with the previous methods and develop equations for converting old method numbers to new numbers.

- Method:** 1. a. The previous methods did not apply if species volatilized, so the simplified oxygen calculation can be used for comparison.
 b. Calculate mole % Na+K by updated method and the method in letter Nby-08-90.
 c. Derive an equation relating the two mole percents.
 2. Calcule and compare weight of calcine solids by the updated method and the method in ENICO-1100.

Given:

Test Case Solution Content for 1 liter of Solution-Case Nby1 (Values from letter Nby-08-90, case 1):

Solution is a 5:1 blend of Typical Fluorinel and Na waste.

$$\begin{aligned}
 F &:= \frac{5 \cdot 2.27 + 0.049}{6} \cdot \text{mole} & Al &:= \frac{5 \cdot 0.36 + .45}{6} \cdot \text{mole} & Ca &:= 0.7 \cdot F & Cr &:= .0 \cdot \text{mole} \\
 SO_4 &:= \frac{5 \cdot 0.079 + .048}{6} \cdot \text{mole} & Zr &:= \frac{5 \cdot 0.29 + 0}{6} \cdot \text{mole} & B &:= \frac{5 \cdot 0.17 + 0.024}{6} \cdot \text{mole} & Pb &:= 0 \cdot \text{mole} \\
 Cl &:= \frac{5 \cdot 0.0016 + 0.031}{6} \cdot \text{mole} & Na &:= \frac{5 \cdot 0.028 + 1.46}{6} \cdot \text{mole} & Fe &:= \frac{5 \cdot 0.0072 + 0.023}{6} \cdot \text{mole} & U &:= 0 \cdot \text{mole} \\
 PO_4 &:= .0 \cdot \text{mole} & K &:= \frac{5 \cdot 0.0028 + .21}{6} \cdot \text{mole} & Cd &:= \frac{5 \cdot 0.11 + 0}{6} \cdot \text{mole} \\
 NO_3 &:= \left(\frac{5 \cdot 2.37 + 4.47}{6} \right) \cdot \text{mole} + 2 \cdot Ca & \text{Acid } Na &:= \frac{5 \cdot 2.04 + 1.69}{6} \cdot \text{mole} & UDS &:= \frac{5 \cdot 2 + 1}{6} \cdot \text{gm}
 \end{aligned}$$

Calculated concentrations for 5:1 blend:

$$\begin{aligned}
 F &= 1.9 \cdot \text{mole} & Al &= 0.375 \cdot \text{mole} & Ca &= 1.33 \cdot \text{mole} & Cr &= 0 \cdot \text{mole} \\
 SO_4 &= 0.074 \cdot \text{mole} & Zr &= 0.242 \cdot \text{mole} & B &= 0.146 \cdot \text{mole} & Pb &= 0 \cdot \text{mole} \\
 Cl &= 0.006 \cdot \text{mole} & Na &= 0.267 \cdot \text{mole} & Fe &= 0.01 & U &= 0 \cdot \text{mole} \\
 PO_4 &= 0 \cdot \text{mole} & K &= 0.037 \cdot \text{mole} & Cd &= 0.092 \cdot \text{mole} & UDS &= 1.833 \cdot \text{gm}
 \end{aligned}$$

(Nitrate and acid concentrations in feed are not used in the calculation, but are given here for completeness)

$$\begin{aligned}
 NO_3 &= 5.38 \cdot \text{mole} & Na + K &= 0.304 \cdot \text{mole} & \text{Acid } Na &= 1.982 \cdot \text{mole}
 \end{aligned}$$

1. Calculate Na+K mole percent using updated method and Newby's method.

A. Updated Method:

Check to make sure there is enough Ca, Na, K, and Al to form compounds with all PO₄, F, SO₄, and Cl:

$$\left[\left[2 \cdot \text{Ca} + (1 - X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) \right] \geq (3 \cdot \text{PO}_4 + \text{F} + 2 \cdot \text{SO}_4 + \text{Cl}) \right] = 1 \quad (=0 \text{ for false, } 1 \text{ for true})$$

(This is somewhat conservative since it doesn't account for possible CdSO₄)

Average Mole fraction of Na and K as nitrates based on analysis of calcine:

$$X_{\text{NO}_3} = 0.66 \frac{\text{mole} \cdot \text{NO}_3}{\text{mole} \cdot (\text{Na} + \text{K})}$$

Total Moles of oxygen for updated method:

$$\begin{aligned} \text{O}_{\text{tot}} := & \frac{3}{2} \cdot \text{Al} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{Na} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{K} + \text{Ca} - \text{SO}_4 - \frac{1}{2} \cdot \text{Cl} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F} + \text{Cd} \dots \\ & + 2 \cdot \text{Zr} + \frac{3}{2} \cdot \text{B} + \frac{3}{2} \cdot \text{Fe} + \frac{3}{2} \cdot \text{Cr} + \text{Pb} + 3 \cdot \text{U} \end{aligned}$$

$\text{O}_{\text{tot}} = 1.725 \cdot \text{mole}$

Total Moles is sum of oxygen + nitrates + feed components- volatiles:

$$\begin{aligned} \text{Mol}_{\text{tot}} := & \text{O}_{\text{tot}} + \text{Al} + (1 + X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) + \text{Ca} \dots \\ & + \text{PO}_4 + \text{F} + \text{SO}_4 + \text{Cl} + \text{Zr} + \text{B} + \text{Fe} + \text{Cd} + \text{Cr} + \text{Pb} + \text{U} \end{aligned}$$

$\text{Mol}_{\text{tot}} = 6.404 \cdot \text{mole}$

$$\text{Mol}\% \text{NaK} := \frac{(\text{Na} + \text{K})}{\text{Mol}_{\text{tot}}} \cdot 100\%$$

$\text{Mol}\% \text{NaK} = 4.747\%$

B. Calculate mole percent using Newby's method:

B.J.Newby Method for Na+K mole % (letter Nby-08-90), which assumes no nitrates and neglects species less than about 0.05 molar:

$$\begin{aligned} \text{O}_{\text{nby}} := & \frac{1}{2} \cdot (\text{Na} + \text{K}) + \frac{3}{2} \cdot \text{Al} + \text{Ca} - \frac{1}{2} \cdot \text{F} - \text{SO}_4 + 2 \cdot \text{Zr} + \text{Cd} + \frac{3}{2} \cdot \text{B} & \text{O}_{\text{nby}} = 1.814 \\ \text{Mol}_{\text{nby}} := & \text{O}_{\text{nby}} + \text{Al} + \text{Na} + \text{K} + \text{Ca} + \text{F} + \text{SO}_4 + \text{Zr} + \text{B} + \text{Cd} & \text{Mol}_{\text{nby}} = 6.276 \\ \text{Mol}\% \text{NaK}_{\text{nby}} := & \frac{(\text{Na} + \text{K})}{\text{Mol}_{\text{nby}}} \cdot 100\% & \text{Mol}\% \text{NaK}_{\text{nby}} = 4.844\% \end{aligned}$$

The relative difference between methods is:

$$\frac{\text{Mol}\% \text{NaK}_{\text{nby}} - \text{Mol}\% \text{NaK}}{\text{Mol}\% \text{NaK}} \cdot 100\% = 2.042\%$$

The updated method gives a smaller mole percent than Newby's method for the same feed solution. This is because Newby's method has fewer total moles due to 1) no nitrates were assumed in the calcine, and 2) only major feed components were used and others were neglected.

C. Relate mole percent value of updated method to that of Newby's method:

Since the mole percent sodium plus potassium values calculated using Newby's method are available for most previous flowsheets, it is desirable to have a quick way to convert between them and the updated method without having to use the entire feed composition. The following is the derivation of an equation which gives an approximate value of mole percent for the updated method which requires knowing only the Newby mole percent.

Total Moles of oxygen for updated method:

$$O_{\text{tot}} := \frac{3}{2} \cdot \text{Al} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{Na} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{K} + \text{Ca} - \text{SO}_4 - \frac{1}{2} \cdot \text{Cl} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F} + \text{Cd} \dots$$

$$+ 2 \cdot \text{Zr} + \frac{3}{2} \cdot \text{B} + \frac{3}{2} \cdot \text{Fe} + \frac{3}{2} \cdot \text{Cr} + \text{Pb} + 3 \cdot \text{U}$$

Total Moles is sum of oxygen + nitrates + feed components:

$$\text{Mol}_{\text{tot}} := O_{\text{tot}} + \text{Al} + (1 + X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) + \text{Ca} \dots$$

$$+ \text{PO}_4 + \text{F} + \text{SO}_4 + \text{Cl} + \text{Zr} + \text{B} + \text{Fe} + \text{Cd} + \text{Cr} + \text{Pb} + \text{U}$$

by substitution for total moles of oxygen, yields

$$\text{Mol}_{\text{tot}} := \frac{3}{2} \cdot \text{Al} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{Na} + \frac{1}{2} \cdot (1 - X_{\text{NO}_3}) \cdot \text{K} + \text{Ca} - \text{SO}_4 - \frac{1}{2} \cdot \text{Cl} - \frac{3}{2} \cdot \text{PO}_4 - \frac{1}{2} \cdot \text{F} + \text{Cd} \dots$$

$$+ 2 \cdot \text{Zr} + \frac{3}{2} \cdot \text{B} + \frac{3}{2} \cdot \text{Fe} + \frac{3}{2} \cdot \text{Cr} + \text{Pb} + 3 \cdot \text{U} + [\text{Al} + (1 + X_{\text{NO}_3}) \cdot (\text{Na} + \text{K}) + \text{Ca}] \dots$$

$$+ \text{PO}_4 + \text{F} + \text{SO}_4 + \text{Cl} + \text{Zr} + \text{B} + \text{Fe} + \text{Cd} + \text{Cr} + \text{Pb} + \text{U}$$

simplifies to

$$\text{Mol}_{\text{tot}} := 3 \cdot \text{Zr} + \frac{5}{2} \cdot \text{B} + \frac{5}{2} \cdot \text{Fe} + 2 \cdot \text{Cd} + \frac{3}{2} \cdot \text{K} + \frac{1}{2} \cdot \text{K} \cdot X_{\text{NO}_3} + \frac{3}{2} \cdot \text{Na} + \frac{1}{2} \cdot X_{\text{NO}_3} \cdot \text{Na} \dots$$

$$+ \frac{1}{2} \cdot \text{F} + 4 \cdot \text{U} + \frac{5}{2} \cdot \text{Cr} + 2 \cdot \text{Pb} + 2 \cdot \text{Ca} + \frac{1}{2} \cdot \text{Cl} - \frac{1}{2} \cdot \text{PO}_4 + \frac{5}{2} \cdot \text{Al}$$

C. Relate mole percent value of updated method to that of Newby's method (cont.):

B.J.Newby Method for Na+K mole % (letter Nby-08-90), which assumes no nitrates, and neglects species less than about 0.05 molar:

$$O_{nby} := \frac{1}{2} \cdot (Na + K) + \frac{3}{2} \cdot Al + Ca - \frac{1}{2} \cdot F - SO_4 + 2 \cdot Zr + Cd + \frac{3}{2} \cdot B$$

$$Mol_{nby} := O_{nby} + Al + Na + K + Ca + F + SO_4 + Zr + B + Cd$$

Substituting for moles of oxygen:

$$Mol_{nby} := \left[\frac{1}{2} \cdot (Na + K) + \frac{3}{2} \cdot Al + Ca - \frac{1}{2} \cdot F - SO_4 + 2 \cdot Zr + Cd + \frac{3}{2} \cdot B \right] \dots \\ + Al + Na + K + Ca + F + SO_4 + Zr + B + Cd$$

simplifies to

$$Mol_{nby} := \frac{3}{2} \cdot Na + \frac{3}{2} \cdot K + \frac{5}{2} \cdot Al + 2 \cdot Ca + \frac{1}{2} \cdot F + 3 \cdot Zr + 2 \cdot Cd + \frac{5}{2} \cdot B$$

The difference in total moles for the new method versus Newby's method is:

$$Mol_{dif} := Mol_{tot} - Mol_{nby}$$

Substituting for the equations for total moles:

$$Mol_{dif} := \left[3 \cdot Zr + \frac{5}{2} \cdot B + \frac{5}{2} \cdot Fe + 2 \cdot Cd + \frac{3}{2} \cdot K + \frac{1}{2} \cdot K \cdot X_{NO_3} + \frac{3}{2} \cdot Na + \frac{1}{2} \cdot X_{NO_3} \cdot Na \dots \right] \dots \\ + \frac{1}{2} \cdot F + 4 \cdot U + \frac{5}{2} \cdot Cr + 2 \cdot Pb + 2 \cdot Ca + \frac{1}{2} \cdot Cl - \frac{1}{2} \cdot PO_4 + \frac{5}{2} \cdot Al \\ + -1 \cdot \left(\frac{3}{2} \cdot Na + \frac{3}{2} \cdot K + \frac{5}{2} \cdot Al + 2 \cdot Ca + \frac{1}{2} \cdot F + 3 \cdot Zr + 2 \cdot Cd + \frac{5}{2} \cdot B \right)$$

simplifies to

$$Mol_{dif} := \frac{5}{2} \cdot Fe + \frac{1}{2} \cdot X_{NO_3} \cdot (Na + K) + 4 \cdot U + \frac{5}{2} \cdot Cr + 2 \cdot Pb + \frac{1}{2} \cdot Cl - \frac{1}{2} \cdot PO_4$$

Updated mole percent is:

$$\text{Mol\% NaK} := \frac{(\text{Na} + \text{K})}{\text{Mol}_{\text{tot}}} \cdot 100\%$$

Substituting for total moles in terms of Newby's moles and the difference:

$$\text{Mol\% NaK} := \frac{(\text{Na} + \text{K})}{\text{Mol}_{\text{nby}} + \text{Mol}_{\text{dif}}} \cdot 100\%$$

Substituting for terms for Newby's moles and the difference:

$$\text{Mol\% NaK} := \frac{(\text{Na} + \text{K})}{\left[\frac{(\text{Na} + \text{K})}{\text{Mol\% NaK}_{\text{nby}}} \cdot 100 \right] + \left[\frac{5}{2} \cdot \text{Fe} + \frac{1}{2} \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) + 4 \cdot \text{U} + \frac{5}{2} \cdot \text{Cr} + 2 \cdot \text{Pb} + \frac{1}{2} \cdot \text{Cl} - \frac{1}{2} \cdot \text{PO}_4 \right]} \cdot 100\%$$

rearranges to

$$\text{Mol\% NaK} := \frac{\text{Mol\% NaK}_{\text{nby}}}{100 + \frac{\text{Mol\% NaK}_{\text{nby}}}{(\text{Na} + \text{K})} \cdot \left[\frac{1}{2} \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) + \frac{5}{2} \cdot \text{Fe} + 4 \cdot \text{U} + \frac{5}{2} \cdot \text{Cr} + 2 \cdot \text{Pb} + \frac{1}{2} \cdot \text{Cl} - \frac{1}{2} \cdot \text{PO}_4 \right]} \cdot 100\%$$

If Fe, U, Cr, Pb, Cl and PO4 are small (they are usually less than 0.02 molar), then the mole% can be approximated from Newby's mole % by:

$$\text{Mol\% NaK}_{\text{approx}} := \frac{\text{Mol\% NaK}_{\text{nby}}}{100\% + \frac{\text{Mol\% NaK}_{\text{nby}}}{(\text{Na} + \text{K})} \cdot \left[\frac{1}{2} \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) \right]} \cdot 100\%$$

Which simplifies to:

$$\text{Mol\% NaK}_{\text{approx}} := \frac{\text{Mol\% NaK}_{\text{nby}}}{100\% + \text{Mol\% NaK}_{\text{nby}} \cdot \left(\frac{1}{2} \cdot X_{\text{NO}_3} \right)} \cdot 100\%$$

For the test case the calculated values are:

$$\text{Mol\% NaK}_{\text{nby}} = 4.844\%$$

$$\text{Mol\% NaK} = 4.747\%$$

$$\text{Mol\% NaK}_{\text{approx}} = 4.768\%$$

Relative error of the approximate solution for the test case is:

$$\text{Error}_{\text{approx}} := \frac{\text{Mol\% NaK}_{\text{approx}} - \text{Mol\% NaK}}{\text{Mol\% NaK}} \cdot 100\%$$

$$\text{Error}_{\text{approx}} = 0.437\%$$

2. Compare updated equation for weight of calcine with to previous method.

Updated equation for weight of calcine, assuming that nothing volatilizes is:

$$\text{Calcine_Wt}_{\text{tot}} := \left[\begin{array}{l} 15.9994 \cdot O_{\text{tot}} + 26.98154 \cdot \text{Al} + 62.005 \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K}) \dots \\ + 22.98977 \cdot \text{Na} + 39.0983 \cdot \text{K} + 40.08 \cdot \text{Ca} \dots \\ + 94.971 \cdot \text{PO}_4 + 18.9984 \cdot \text{F} \dots \\ + 96.062 \cdot \text{SO}_4 + 35.453 \cdot \text{Cl} \dots \\ + 91.22 \cdot \text{Zr} + 10.81 \cdot \text{B} + 55.847 \cdot \text{Fe} + 112.41 \cdot \text{Cd} + 51.996 \cdot \text{Cr} \dots \\ + 207.19 \cdot \text{Pb} + 235 \cdot \text{U} \end{array} \right] \cdot \frac{\text{gm}}{\text{mole}} + \text{UDS}$$

$$\text{Calcine_Wt}_{\text{tot}} = 190.8 \cdot \text{gm} \text{ (of calcine formed per liter of solution)}$$

Check calculated weight percent of NO3 in calcine to see how it compares:

$$X_{\text{NO}_3} = 0.66$$

$$\text{Wt}_{\text{NO}_3} := 62.005 \cdot \frac{\text{gm}}{\text{mole}} \cdot X_{\text{NO}_3} \cdot (\text{Na} + \text{K})$$

$$\text{Wt}_{\text{NO}_3} = 12.441 \cdot \text{gm} \text{ (of NO}_3 \text{ formed per liter of solution)}$$

$$\text{Wt}\% \text{ NO}_3 := \frac{\text{Wt}_{\text{NO}_3}}{\text{Calcine_Wt}_{\text{tot}}}$$

$$\text{Wt}\% \text{ NO}_3 = 6.5 \cdot \%$$

Calcine weight using method in the report ENICO-1100 (Ninth Campaign, WCF):

Additional concentrations needed are negligible for the Newby test case:

$$\text{Ni} \approx 0.0 \cdot \text{mole} \quad \text{Mo} \approx 0.0 \cdot \text{mole} \quad \text{Mn} \approx 0.0 \cdot \text{mole} \quad \text{Gd} \approx 0.0 \cdot \text{mole} \quad \text{Sn} \approx 0.0 \cdot \text{mole} \quad \text{Nb} \approx 0.0 \cdot \text{mole}$$

$$\text{Calcine_Wt_old} := \left[\begin{array}{l} 85.00 \cdot \text{Na} + 101.11 \cdot \text{K} + 50.98 \cdot \text{Al} + 123.22 \cdot \text{Zr} + 34.81 \cdot \text{B} + 79.85 \cdot \text{Fe} \dots \\ + 76.00 \cdot \text{Cr} + 74.71 \cdot \text{Ni} + 143.94 \cdot \text{Mo} + 86.94 \cdot \text{Mn} + 181.25 \cdot \text{Gd} \dots \\ + 150.69 \cdot \text{Sn} - 16.01 \cdot \text{F} - 5.02 \cdot \text{PO}_4 + 110.09 \cdot \text{Ca} + 132.91 \cdot \text{Nb} \dots \\ + \text{if}(\text{Cd} > \text{SO}_4, (80.06 \cdot \text{SO}_4 + 128.40 \cdot \text{Cd}), (182.41 \cdot \text{Cd} + 26.05 \cdot \text{SO}_4)) \end{array} \right] \cdot \frac{\text{gm}}{\text{mole}} + \text{UDS}$$

$$\text{Calcine_Wt_old} = 216.7 \cdot \text{gm} \quad (\text{of calcine formed per liter of solution})$$

Determine weight percent of NO₃ in calcine for old method to see how it compares:

In the old method, 10% of the sodium plus potassium forms nitrates and 50% of the excess calcium forms Ca(NO₃)₂. For the test case, there is enough cadmium that all cadmium forms cadmium sulfate and no calcium sulfate forms. Fluoride left after formation of Na₃AlF₆ and K₃AlF₆. Excess calcium is that left after formation of Ca₃(PO₄)₂, CaF₂, and CaCl₂:

$$\text{Ca}_{\text{xs_old}} := \text{Ca} - \frac{3}{2} \cdot 0.5 \cdot \text{PO}_4 - \frac{1}{2} \cdot \left[\text{F} - \frac{6}{3} \cdot (1 - 0.1) \cdot (\text{Na} + \text{K}) \right] - \frac{1}{2} \cdot \text{Cl} \quad \text{Ca}_{\text{xs_old}} = 0.65 \cdot \text{mole}$$

$$\text{NO}_3_{\text{old}} := 0.1 \cdot (\text{Na} + \text{K}) + 0.5 \cdot (2) \cdot \text{Ca}_{\text{xs_old}} \quad \text{NO}_3_{\text{old}} = 0.681 \cdot \text{mole}$$

$$\text{Wt}_{\text{NO}_3_{\text{old}}} := 62.005 \cdot \frac{\text{gm}}{\text{mole}} \cdot \text{NO}_3_{\text{old}} \quad \text{Wt}_{\text{NO}_3_{\text{old}}} = 42.208 \cdot \text{gm} \quad (\text{of NO}_3 \text{ formed per liter of solution})$$

$$\text{Wt\% NO}_3_{\text{old}} := \frac{\text{Wt}_{\text{NO}_3_{\text{old}}}}{\text{Calcine_Wt_old}} \quad \text{Wt\% NO}_3_{\text{old}} = 19.5\%$$

For the test case, the old method overestimates the amount of nitrates by about:

$$\text{Wt}_{\text{NO}_3_{\text{old}}} - \text{Wt}_{\text{NO}_3} = 29.8 \cdot \text{gm}$$

And the total weight of calcined solids differs from the updated method by:

$$\text{Calcine_Wt_old} - \text{Calcine_Wt_tot} = 25.9 \cdot \text{gm} \quad (\text{of calcine formed per liter of solution})$$

$$\text{or: } \frac{\text{Calcine_Wt_old} - \text{Calcine_Wt_tot}}{\text{Calcine_Wt_tot}} \cdot 100\% = 13.6\%$$

Appendix E
Calculation of Liquid Waste Decay Heat

APPENDIX E

Calculation of Liquid and Calcine Waste Decay Heat

The heat generation rates for calcine are calculated using the same method prepared by R. E. Schindler for Appendix F of Reference 1 except that decay energy values have been updated, and more radionuclides are included.

The decay heat generation of the liquid waste can be calculated by summing the decay heat contributions of each of the radionuclides whose concentrations are determined by sample analysis. The calculation procedure is outlined below and an example shown in Table E-1. The energy values in the table were obtained from D. R. Wenzel (Reference 15) who extracted them from ORIGIN2 version 2.1. Only prominent radionuclides in current tank farm waste are included in the table, and other radionuclides which contribute less than about 0.2% to the total decay energy were not included. Half-lives are given in addition to decay energy so that measured concentrations of the individual nuclides can be adjusted for decay from the time of analysis to the proposed time of calcination. The products of the concentrations of the concentrations and decay heats are summed to get the total decay heat of the liquid, which is converted to watts per cubic meter. Multiplication by the volume reduction factor gives the decay heat generation rate for the calcined solids.

Some of the less prominent nuclides will sometimes be omitted from an analytical report because their concentrations are below detection limits. The error introduced by these omissions is slight because the major radionuclides (Sr-90, Cs-134, Cs-137 and Ce-144) account for over 98% of the heat generation rate as shown at the bottom of the table.

The summing procedure is valid for current ICPP wastes which have aged several years (at least 2.5 yrs) out of reactor. With fresher waste, either additional nuclides should be included, or the ORIGIN2 code should be used for calculation of heat generation. Also, only short-lived daughters are included in the decay energy values, so if analytical data is more than a couple of years old (>2 to 3), rather than using decayed values, I would recommend either 1) using the undecayed concentrations to give a conservatively high heat generation rate, or 2) using the ORIGIN2 code to determine heat generation from decay.

Table E-1							
Recoverable Decay Energy for Calcined Liquid Waste							
Radio-Nuclide	Half-Life	Q Value		Waste Analyses for WM-180*		WM-188/183/189:ANN High Sodium Blend**	
	(s)	(Mev/dis)	(Watts/Ci)	(mCi/L)	(W/m ³)	(mCi/L)	(W/m ³)
Co-60	1.663e+08	2.601	1.542e-02	0	0	0.5559	0.008571
Sr-Y-90	9.190e+08	1.1308	6.704e-03	25	0.167588	184.6615	1.237879
Ru-Rh-106	3.181e+07	1.6280	9.651e-03	0	0	0	0
Sb-125	8.741e+07	0.5274	3.126e-03	0	0	0	0
Cs-134	6.508e+07	1.717	1.018e-02	0.12	0.001221	3.4905	0.035528
Cs-Ba-137	9.467e+08	0.849	5.033e-03	30	0.150989	200.6717	1.009974
Ce-Pr-144	2.456e+07	1.3519	8.014e-03	0	0	4.1703	0.033422
Eu-154	2.714e+08	1.509	8.946e-03	0.00078	0.000007	1.706	0.015261
Eu-155	1.565e+08	0.1227	7.274e-04	0	0	1.2965	0.000943
Pu-238	2.769e+09	5.591	3.314e-02	0	0	0.2205	0.007308
Pu-239	7.594e+11	5.199	3.082e-02	0	0	0	0
Am-241	1.364e+10	5.604	3.322e-02	0.063	0.002093	0.0379	0.001259
			Sum=		0.3219		2.350
			Sum of Sr+Cs+Ce=		0.3198		2.317
			Sr+Cs+Ce % of Total=		99.35%		98.58%

*Reference 21

**References 19 and 20

Activity decay equation :

$$A = A_0 e^{\left(-\frac{\ln 2}{t_{1/2}} t\right)} \quad (E1)$$

where: A = Activity at time t, disintegrations/s-mL or mCi/L

A₀ = Activity at analysis, disintegrations/s-mL or mCi/L

t = Time elapsed since analysis, seconds

t_{1/2} = half life of radionuclide, seconds (or of parent radionuclide where daughter energies are included)

This is also sometimes represented as:

$$A = A_0 e^{(-\lambda t)} \quad (E2)$$

where: λ = decay constant (sec⁻¹)

Decay heat of liquid:

$$Q_{liq}(W/m^3) = \sum ((E_{decay} \text{ W/Ci}) (10^{-3} \text{ Ci/mCi}) (A \text{ mCi/L}) (10^3 \text{ L/m}^3)) \quad (E3)$$

or

$$Q_{liq}(W/m^3) = \sum ((E_{decay} \text{ Mev/dis}) (A \text{ dis/s-mL})) (10^6 \text{ mL/m}^3) (1.602 \cdot 10^{-13} \text{ W-s/Mev}) \quad (E4)$$

Decay heat of calcined solids:

$$Q_{calcine} = Q_{liq} VRF_{liq} \quad (E5)$$

where: VRF_{liq} = Volume Reduction Factor, ratio of volume of feed blend or tank farm waste to volume of calcine produced