THERMODYNAMIC MODELING OF THE CHEMICAL COMPOSITION OF CALCINE
AT
THE IDAHO NUCLEAR TECHNOLOGY AND ENGINEERING CENTER

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ABSTRACT

To send calcine produced at Idaho National Engineering and Environmental Laboratory to the Yucca Mountain Project for disposal, characterization information will be required. To sample calcine from its existing storage location would require extensive personnel exposure. Sufficient analyses of the chemical composition of the calcine would be extremely difficult and very expensive. In support of characterization development, the chemical composition of calcine from Bin 3 of Calcine Solid Storage Facility II was thermodynamic modeled. This calcine was produced in the Waste Calcination Facility during its second processing campaign, operating with indirect heating at 400°C and 0.744 bar (0.734 atm) during processing of aluminum high-level liquid waste (first cycle extraction raffinate from reprocessing aluminum-clad fuels) from tanks WM-180 and -182 from December 27, 1966 through August 26, 1967.

The current modeling effort documents the input compositional data (liquid feed and calciner off-gas) for Batches 300 - 620 and a methodology for estimating the calcine chemical composition. The results, along with assumptions and limitations of the thermodynamic calculations, will serve as a basis for benchmarking subsequent calculations. This will be done by comparing the predictions against extensive analytical results that are currently being obtained on representative samples of the modeled calcine.   A commercial free-energy minimization program and database, HSC 5.1, was used to perform the thermodynamic calculations. Currently available experimental data and process information on the calcine were used to make judgments about specific phases and compounds to include and eliminate in the thermodynamic calculations. Some off-gas species were eliminated based on kinetics restrictions evidenced by experimental data and other estimates, and some calcine components and off-gas compounds were eliminated as improbable species (unreliable thermodynamic data).

The current Yucca Mountain Project level of concern is 0.1 wt % of individual cations in the waste package. Chemical composition of the individual calcine components was calculated down to 0.02 mol % and 0.09 wt % of metal components of the calcine. The results reproduce closely existing experimental information on calcine chemical and phase composition. This paper discusses specific conditions accepted for the final calculations.

The major calcine components, exceeding 0.15 mol % and 0.65 wt %, are: amorphous Al_2O_3 (85.30 mol %, 81.20 wt %); amorphous $NaNO_3$ (8.23 mol %, 6.53 wt %); dolomite – $CaMg_{0.9235}(CO_3)_{1.9235}$ (1.66 mol %, 2.75 wt %); amorphous HgO (0.99 mol %, 2.00 wt %); $CaSO_4$ (0.64 mol %, 0.82 wt %); amorphous KNO_3 (0.63 mol %, 0.59 wt %); amorphous $Al_4B_2O_9$ (0.54 mol %, 1.37 wt %); and amorphous $Al_{18}B_4O_{33}$ (0.16 mol %, 1.57 wt %). Na is present 99.8 % as $NaNO_3$, 99.9 % of K is present as KNO_3, and 53 % NO_x is $NO_2(g)$, showing that the kinetics limiting effects have been empirically accounted for in the modeling. Approximately 87 % of the mercury is in calcine.

BACKGROUND AND INTRODUCTION

An option under consideration for disposing of the high-level waste calcine currently stored in stainless steel bin sets at the Idaho Nuclear Technology and Engineering Center is to retrieve it from the bins and process it to place it into canisters that will be shipped to the proposed Yucca Mountain geologic repository for burial. Before receiving the calcine, the Yucca Mountain Project will require documenting of its chemical composition. To sample calcine from its existing storage location would require extensive personnel exposure. In addition, sufficient analyses of the

chemical composition of the calcine would be extremely difficult and very expensive. The use of thermodynamic modeling of calcine is desirable for three reasons. First, producing a thermodynamic model, instead of physical sampling will reduce the risk of radiation exposure and contamination to workers and the environment. Second, modeling results will be compared with the new experimental analytical information from a few samples to benchmark the modeling methodology. If adequate, modeling can be extended to calcines that have not been experimentally characterized. Third, even with actual sample results, it is not possible to determine the complete chemical composition of the calcine, primarily only the elemental distribution. While elemental and radiochemical analysis can be completed, the actual chemical forms are difficult to establish. Therefore, thermodynamic calculations provide the most complete assessment of the chemical forms that may be present.

This paper documents the extensive thermodynamic modeling conducted to characterize the aluminum calcine in Bin 3 of Calcine Solid Storage Facility II. This calcine was produced during fluidized-bed calcination of the aluminum high-level liquid waste resulting from the reprocessing of spent nuclear fuels with aluminum cladding and matrix material that was dissolved. The thermodynamic software selected to perform the modeling calculations is HSC Chemistry® for Windows, version 5.1.[1] HSC 5.1 contains a database with entries of standard enthalpy of formation, entropy, and heat capacity temperature function for more than 17,000 substances with data from 884 sources that include many major compilations. [Product Disclaimer: References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government, any agency thereof, or any company affiliated with the Idaho National Engineering and Environmental Laboratory.]

CALCINE SAMPLE MODELED

This study models the calcine from Bin 3 of Calcine Solid Storage Facility II based on average composition from the liquid feed sample analyses during the filling of the bin. Elemental composition is currently known from data obtained at the time of calcination. Primarily, the feed data was obtained from a report that contains extensive compilations of the feed compositions for specific segments of calcine in the bins.[2] The calcine in Bin 3 was generated from Batches 300 through 620 during Run H-2 in the Waste Calcining Facility from December 27, 1966 through August 26, 1967. This waste was aluminum type waste from tanks WM-180 and WM-182. The weighted average composition of the waste was calculated by summing the number of g-mols of each constituent in the feed batches and dividing by the total volume in liters. The Waste Calcining Facility operated at 400°C using heated liquid sodium and potassium (NaK) alloy that was circulated through a tube bundle in the fluidized bed.

APPROACHES AND LIMITATIONS OF THERMODYNAMIC MODELING

Chemical thermodynamics uses enthalpy, entropy, and heat capacity data for compounds and elements to evaluate chemical equilibria in a system. For each identified potential reaction,

$$aA + bB + \cdots = cC + dD + \cdots$$
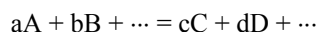
the thermodynamic equilibrium constant, K, for the reaction is

$$K = \frac{a_A^a a_B^b \cdots}{a_C^c a_D^d \cdots}$$

(Eq. 1)

where a_I^i represents the activity of species I with stoichiometric coefficient i in the reaction, all at equilibrium. The thermodynamic equilibrium constant is related to the standard free energy of the reaction, ΔG^0, by

$$\Delta G^0 = -RT \ln K$$

(Eq. 2)

R is the gas constant (1.9872 cal deg^{-1} mol^{-1} or 8.3145 joules deg^{-1} mol^{-1}) and T is absolute temperature in kelvins.

The free energy is, in turn, related to tabulated standard thermodynamic functions:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$
(Eq. 3)

where the standard enthalpy (H^0) and entropy (S^0) changes for the reaction are functions of temperature via the change in heat capacity for the reaction.

For a simple reaction, the equations can be readily solved by hand to yield the individual activities of the species in the reaction that result in the value of the equilibrium constant, given the starting compositions. For more complex systems, especially those that involve numerous species that can undergo a multitude of reactions, the problem is solved by means of the relation

$$\Delta G = \Delta G^0 + RT \ln Q$$
(Eq. 4)

where Q is the product ratio of the species activities raised to their stoichiometric coefficients [similar to equation (1)] before equilibrium is established and ΔG is the free energy of reaction at that point. At equilibrium, $\Delta G = 0$ and equation (2) results. Computer algorithms are set up to adjust the composition to minimize ΔG for the system.

Generally, the true minimum is determined, although, on rare occasion in complex systems, a false minimum may be settled on. The validity of the results are tested by calculating an equilibrium constant for a simple reaction from the resulting composition and comparing the value with that calculated directly from the tabulated thermodynamic data (a back calculation). This is rarely necessary, but one must always be alert to consistency and checks in results. Another approach that may provide indication of a true minimum is to input starting compositions in two ways, e.g., as all elements or as compounds and determine that both have the same results. The HSC 5.1 methods and its database used for the Bin 3 modeling has been formally verified and validated using these methods. [3]

Another, generally, more limiting aspect is accuracy of the thermodynamic data in the database accessed by the free-energy minimization program. The HSC database is imported largely from standard compilations and some original literature data. The developer, Outokumpu, does not critically assess the data that it uses and some errors have been known to be present because of errors in the primary compilation used, for example, a sign error for the enthalpy of formation. Outokumpu apparently inputs the data by hand; the authors have found a number of input errors in the past, both in sign errors and incorrect chemical formulas. Errors pertinent to the calcine modeling have been provided to Outokumpu and corrections incorporated into the 5.1 database.   Any subsequent errors or required changes were implemented in the Own Database or by eliminating a specific species, as discussed in the results.

New compound data for several pertinent species have been compiled in the HSC 5.1 database, which improves the modeling results vis-à-vis calcine data. In some cases, however, duplicate species have been retained with older data from the HSC 4.1 database that can perturb results and must be deleted. These are all discussed in the "Summary of Results" section. In general, when two equivalent species were present in the database, but had different sources and values of data, and both were significant in the output results, the calculation was rerun with the species of less reliable data deleted. Of course, when they did not appear as significant output species, there was no concern. Thus, it was not necessary to screen all compounds for duplicates, only when two equivalent species both appeared as significant.

The following approach was taken to validate data for the calcine modeling to support quality assurance when results or data were suspicious. The calcine modeling results indicate that only about a dozen major species, are the most important. For key species when there was a question of the tabulated data the data were checked by going, first to the referenced data compilations and, then, from their references, to the original literature. In a specific application, if a compound that is suspected to be important is not predicted, its data should be similarly checked.

When doing free-energy minimization or equilibrium calculations with any program (or by hand) to find the equilibrium position of a system, if the database does not contain data for a potentially significant species, the output can be in error. For example, when modeling was done to predict precipitation in the Idaho Nuclear Technology and Engineering Center high-level waste tanks, the precipitation of $PbMoO_4$ was incorrectly predicted. The error is that the database did not include the molybdenyl ion, MoO_2^{2+}. In an acidic system, the molybdate ion, MoO_4^{2-}, does not

exist. Molybdenum is amphoteric and it is converted to MoO_2^{2+} in the acidic medium. Consequently, Pb^{2+} and Mo^{6+} remain in solution. When data for MoO_2^{2+} was obtained from the literature and incorporated into the HSC database, the correct result was obtained. The lesson is that often one needs to know enough about the chemistry of the species involved in order to ensure that necessary species are included.

When doing solid-state reaction/equilibrium calculations, HSC by default puts all condensed species into a single phase or a series of phases of similar compounds (oxides, sulfates, etc.) and treats each phase as an ideal (Raoult's law) solution, calculating "concentrations" (activities) in the solid solution. If separate (pure) phases are expected, one must put the individual species into separate phases in the input table. This will give a different, and correct, result. The solid solution effects for a few major species will be relatively small, but minor species they can be very large. The considerations of phases are discussed in the "HSC Modeling" section of this paper.

For those species that are in a solid solution, as mentioned above, HSC treats them as though the solution is an ideal solution. While HSC provides the option of user input activity coefficients, these are not generally available. Thus, uncertainties exist when unknown quantitative activity coefficients may come into play. This can cause the calculated concentrations to differ from actual concentrations that result from activity coefficient effects. For example, this could affect $NaNO_3$ concentrations in an amorphous solution phase.

If a stoichiometric excess of a reacting gas phase is present, the results will be largely independent of how much one starts with. If it is deficient relative to the amount consumed by the condensed species that one starts with, there will be a dependency. Therefore, attention is given in this study to estimating the gas phase quantity relative to the liquid feed or calcine quantity.

Of course, the output composition calculated by thermodynamics is no better than the accuracy of input data. Generally, measurements with Inductively Coupled Plasma spectroscopy (ICP) used for the tank waste analyses are accurate to within 5 %. Additional discussion on analytical uncertainties is provided in the "Input Compositional Data" section. Specifically, the uncertainties result in charge imbalance. Allowing the nitrate to float to achieve charge balance, since it is not involved in the calcine composition or the acidity of the solution accommodates this. When quantities of solid inorganic compounds are inputted as a starting composition, allowing oxygen to float for charge balance achieves the same result.

Finally, an important limitation of thermodynamic calculations is that they provide an estimate of the equilibrium position of a system. Kinetics effects can prevent the establishment of true equilibrium. These are much more difficult to determine and evaluate. As an aid to overcome such possible limitations and activity coefficient effects, the thermodynamic results are compared to known experimental information regarding the calcine composition relative to the input composition to the calciner and calcination off-gas composition. This is discussed in the sections "Experimental Data on Calcine Conditions and Calcine Composition" and "Summary of Results". The residence time of gases in contact with the calcine bed is about 4 seconds. During this time, the vapors are flashed off and the solid phase equilibrium of the components laid down on the bed particles during that process is likely generally established.

INPUT COMPOSITIONAL DATA

The net mass outputs from the calciner are the calcine/fines and the off-gas. The off- gas consists of the fluidizing air, the sparge ring air, the atomizing air for the feed nozzles, and the dissociation gaseous and vaporized products created during the calcination process. These are derived from the inputs of gross feed solution composition and feed rate, the fluidizing/sparge ring air input rate, and the nozzle-air-to-feed ratio. The quantitative descriptions and relationships are described below to provide results in a form suitable for input to the HSC modeling program. Excel spreadsheets were used for inputting the raw data information described below and automatically calculating the input values for HSC modeling.

WM-180 and WM-182 Average Feed

The gross input to the calciner is the result of adding the WM-180 and WM-182 feed, adding boric acid to prevent the formation of crystalline aluminum oxide, and including the nitric acid scrub solution used to remove entrained

calcine fines from the off-gas. The net output to the bins does not include the recycled dissolved entrained solids, since they are accounted for in the WM-180 and WM-182 feed.

The weighted average feed composition from tanks WM-180 and WM-182 during the processing of batches 300-620 was used. Elemental compositions of fission, transuranic, and activation products were obtained from ORIGEN II calculations.   The volume of WM-180 and WM-182 feed processed in Batches 300-620 was 1,456,009 liters (384,638 gallons) during 5,151 operating hours.

Recycle Scrub Solution

When the feed is calcined, a fraction of the resulting solids particles are in the form of fines that become entrained into the off-gas system where they are dissolved in the acidic scrub solution, which is periodically recycled into the gross feed. Since this recycle addition is part of the bed composition at the time of equilibration, it is added to the raw feed to obtain the average input composition for HSC. The composition of the fines is assumed to be the same as in the bulk calcine. The fraction of calcine that is entrained past the cyclone to the scrub solution is estimated from limited data for the processing campaigns that have been summarized from the campaign reports.[4] In the first campaign with indirect heating at 400°C with aluminum waste, 16.7 % carryover occurred. During Campaign 5 in the Waste Calcining Facility with in-bed combustion at 500°C while calcining zirconium, aluminum and stainless steel wastes, but mostly zirconium, 8.3 % carryover occurred. No direct measurements were reported during other campaigns. For the current modeling of aluminum waste with indirect heating at 400°C, 15 % entrainment of calcine fines of similar composition to the bed is assumed as a reasonable estimate. Thus, all ions in the combined tank and H_3BO_3 feed, except for H^+ and NO_3^- that are accounted for in the 3 M recycled HNO_3 (see below), are multiplied by 1.15 to calculate the gross feed composition.

While including recycled dissolved solids does not substantially affect the relative composition of the salts in solution for the gross feed, it puts the solids-to-gas compositions in the correct mole ratios for the purpose of calculating the equilibrium composition.

Since the fines dissolved by the scrub solution have already been accounted for in the net feed and boric acid, they are not added to them for calculating the net transfer to the bins. That is, the net solids to the bins is what enters in the raw tank feed plus boric acid added and the recycled dissolved solids are not counted again for this purpose. Since the HNO_3 and H_2O are recycled and added to the off-gas from the raw tank feed in and above the calcine bed, it results in a net contribution to the gas species to those evaporated from the raw waste tank feed that need to be included in the equilibrium calculations, along with the recycled dissolved fines, for the calcine and off-gas composition.

The dolomite startup bed $[CaMg_{0.9235}(CO_3)_{1.9235}]$ requires special consideration for the overall mass balance in the input compositions. Thermodynamic modeling shows that it will not dissociate at 400 or 500°C and that it will not react with the calciner gases NO_2 and O_2 to convert to nitrate or oxide. Thus, carbonate need not be included for HSC input and output species. During startup operations, approximately 50 % of the dolomite bed is carried over to the scrub solution; the balance goes directly to the bin. Thus 50 % of the dolomite constituents, rather than 15 %, is treated as carried to the scrub solution and recycled as dissolved calcium and magnesium nitrates.   The evolved $CO_2(g)$ is beyond the calciner and, thus, not included in the gas phase at the calciner bed. In practice, 57.5 % of the dolomite is modeled as dissolved in the scrub solution so that when the calculated calcine product species quantities are divided by 1.15 to obtain the net quantities to the bin, it results in 50% of the dolomite in the form of calcine species being added. This is an approximation, along with the overall treatment of the recycled scrub solution. That is, the treatment does not completely account for the periodic nature of the recycles or the fact that quantities increase gradually throughout a run. But, the effects are small and the simplifications are adequate. This is because the corrections from incorporating the dissolved solids in the scrub solution are quite small to begin with so that simplifying approximations are acceptable.

The average scrub acid concentration for Batches 300-620 was 3 M HNO_3. The density of a nitric acid solution at 25°C is calculated from the equation derived from tabulated data:[5]

Density $(25°C) = -2.1404 \times 10^{-5}[HNO_3]^3 - 1.2190 \times 10^{-4}[HNO_3]^2 + 0.03367[HNO_3] + 0.9971$, g/mL   (Eq. 5)

where [HNO$_3$] is the molar concentration. For 3 M HNO$_3$, the density is 1.0965 g/mL.

The addition to the density of the nitric acid solution from the presence of the 15 % of calcine dissolved in the scrub solution is estimated as 0.15[(density tank solution plus H$_3$BO$_3$) – 0.9971].

The volume of scrub solution recycled during Batches 300-620 was 369,758 liters (97,680 gallons).

Boric Acid Solution Addition

During calcination of batches 300-620, 23,356 liters (6,170 gallons) of 0.748 M H$_3$BO$_3$ solution was added to the feed. The quantity of H$_3$BO$_3$ added from this source was 17,470 g-moles (2,382 lbs).

The density of a boric acid solution at 25°C is estimated from the density equations derived from literature data at 23°C, corrected to 25°C:[6]

Density (25°C) = 1.0001+0.0165[H$_3$BO$_3$], g/mL   (Eq. 6)

where [H$_3$BO$_3$] is the molar concentration. For 0.748 M H$_3$BO$_3$, the density is 1.0124 g/mL.

Gross Feed

Combining the WM-180 and WM-182 feed, recycle solution, and H$_3$BO$_3$ solution results in the gross feed composition shown in Table I. The total gross feed volume processed is 1,849,122 liters (488,488 gallons). The weighted average 25°C density of the combined solutions is 1.2453 g/mL.
As noted in the discussion about the composition of the recycled scrub solution, the dissolved solids that were entrained from the bed and scrubbed out were added to the dissolved solids of the raw tank feed and the H$_3$BO$_3$ to obtain the gross feed dissolved solids. Then, that same fraction of the calculated product composition was subtracted from the product calcine. This was to prevent double-counting of calcine entrained in the off-gas with what was sent to the bins. The effect of the recycled fines on the gross equilibrium composition (percent distribution of compounds) was, generally, small.

Charge Balance for Input to HSC; H$_2$O Content and Metal Percent Compositions

When complete chemical analyses are done in a complex system, the analytical precision errors result in slight misbalance of charges between the cations and anions. This is corrected in modeling by allowing the nitrate to float to achieve charge balance. An Excel spreadsheet was set up to automatically do this. The adjusted nitrate for charge balance is indicated in parentheses in Table I.

The H$_2$O content of the liquid waste must be calculated for input to HSC for two reasons. The first is related to aqueous solution equilibrium calculations (which are not really of concern here, other than to provide HSC with a starting aqueous solution composition), which is further discussed in the "Summary of Results" section. HSC does solution calculations in terms of molalities. Thus, it requires inputs of the solution species quantities relative to 1000 g solvent (55.508 mols H$_2$O). The conversions may be done by one of two ways. One would be to use the conversion formula

$$m_i = \frac{1000 M_i}{1000 d - \sum_i M_i (MW)_i}$$ (Eq. 7)

where m$_i$ is molality of solute species i, M$_i$ is its molarity, (MW)$_i$ is its molecular weight (g/g-mol), and d is the solution density in g/mL. The individually calculated molalities would be summed for the HSC input quantities along with 55.508 for H$_2$O. The second approach, used here, is to convert each solute molar concentration to g/L by multiplying the molarity by the molecular weight, summing the results, and subtracting from 1000 times the density

Table I Gross feed composition for batches 300-620 with charge balanced with nitrate ion and calculated H_2O

Species	Concentration, Molar
H^+	1.137
Al^{3+}	1.410
B^{3+}	0.01389
Fe^{3+}	1.961E-4
K^+	0.004951
Na^+	0.06493
Hg^{2+}	0.008992
Zr^{4+}	4.294E-5
NO_3^-	6.578 (5.525 for charge balance)
PO_4^{3-}	0.004596
SO_4^{2-}	0.005225
Ca^{2+}	0.01304
Mg^{2+}	0.01204
Cs^+	1.285E-4
Rb^+	4.720E-5
Sr^{2+}	9.248E-5
Y^{3+}	5.837E-5
Nb^{5+}	1.84E-9
Mo^{6+}	3.026E-4
Tc^{7+}	7.366E-5
Ru^{3+}	1.395E-4
Rh^{3+}	3.708E-5
Pd^{2+}	2.309E-5
Sn^{4+}	2.46E-6
Te^{4+}	2.417E-5
$U^{5.33+}$	1.986E-5
Ba^{2+}	1.331E-4
La^{3+}	7.863E-5
Ce^{3+}	1.504E-4
Pr^{3+}	7.171E-5
Nd^{3+}	2.521E-4
Pm^{3+}	1.98E-10
Sm^{3+}	4.867E-5
Eu^{3+}	3.31E-6
Gd^{3+}	1.09E-6
Tb^{3+}	1.67E-8
Dy^{3+}	3.56E-9
H_2O	47.75
Density, 25°C, g/mL	1.2453
Volume, L	1,849,122

to obtain the mass of H_2O in grams, which is converted to g-mols by dividing by its molecular weight. This results in no change in the solute quantity for input, but, rather a decrease in H_2O from 55.508. In this way, if the H_2O does not significantly change due to reactions in the solution, the solution output composition is still in units of molarity (in cases when the water is not evaporated). This is calculated automatically with an Excel spreadsheet.

The second reason for calculating the H_2O content of the liquid waste is to obtain the quantity of $H_2O(g)$ that will ultimately be added to the calciner off-gas content, either from the liquid entry or by entering directly as the gas, as when inputting an assumed calcine composition or elemental composition to HSC. With these considerations, the final gross feed aqueous composition for input to HSC and subsequently derived compositions is as given in Table I. The nitrate concentration decreased 16.0 % to achieve charge balance.

When the input composition is expressed in terms of solid calcine species (oxides, sulfates, etc.) or as elements, where nitrates have been largely or completely dissociated, charge balance may be obtained by allowing oxygen to float. Or, the charge-balanced composition may be derived from the nitrates by dissociating them.

The characterization requirements for the calcine include all metals (cations) exceeding 0.1 wt % of total metals (cations) present in the compounds. Thus, the composition in Table I was converted to g/L for each metal cation. The values were divided by the sum of g/L for all metal ions to obtain the wt % of each. Results show that only the metal cations Al, Hg, Na, Ca, Mg, K, and B must be retained. They add to 99.496 wt % and 99.876 mol % of all metal ions. They include all individual metal ions greater than 0.084 wt% and 0.020 mol%. The associated cations NO_3^-, PO_4^{3-}, and SO_4^{2-} are retained with them, with the nitrate adjusted for overall charge balance of the retained species.

Fluidizing, Sparge, and Nozzle Air-to Feed Ratio Atomizing Air

The sparge ring flowrate averaged 15 scfm and the fluidizing air averaged 180 scfm. The typical combined flowrate is about 195 scfm. The definition of standard temperature is not provided in the recorded values. While the plant was designed by Fluor-Daniels on the basis of 60°F as the standard temperature, flow instruments are calibrated at Idaho Nuclear Technology and Engineering Center with flows expressed in terms of 70°F as the standard temperature. Standard pressure is accepted as 1 atm at sea level. We interpret the scfm values as being expressed at 1 atm and 70°F (294.26K). The nozzle air-to-feed ratio (NAR) is 550 std L air/L feed. Again, standard conditions are considered to be 1 atm at sea level and 70°F.

We need to express these flows in terms of g-moles N_2 and O_2 per L gross feed processed, which puts them on the same basis (molar) as the liquid feed for input to HSC. The conversion factor from standard L-atm to g-mols is made using the perfect gas law,

$PV = RT = 0.08206$ L-atm/(mol-K)$\times$294.26 K = 24.147 L-atm/mol

The other needed inputs are gross feed volume and the number of hours during which it was fed. The latter is 5151 hours for the processing of Batches 300 - 620.
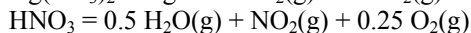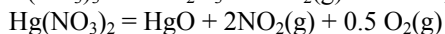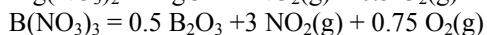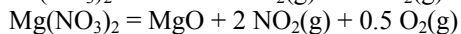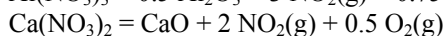
The g-mols air/L gross feed is, thus, calculated as

$$\frac{195 \text{ ft}^3\text{atm min}^{-1} \text{ x } 28.317 \text{ L ft}^{-3}\text{x}60 \text{ min hr}^{-1}\text{x } 5151 \text{ hr}}{24.147 \text{ L-atm mol}^{-1} \text{ x } 1{,}849{,}122 \text{ L feed}} + \frac{550 \text{ L-atm(L feed)}^{-1}}{24.147 \text{ L-atm mol}^{-1}} = 61.00 \text{ mols air (L feed)}^{-1}$$

Air is comprised of 78.04 % N_2 and 20.94 % O_2[5]. Thus, the nitrogen and oxygen contents of these gases are 47.60 and 12.78 g-mols N_2 and O_2, respectively, per L feed. These are calculated in the spreadsheet automatically from the input raw flow rates, feed volume, and operating hours.

Gases from Dissociation of Feed to Initially Assumed Calcine for Input to HSC

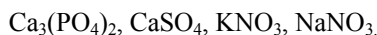The gases from the calcination of the gross feed are added as follows. When the aqueous composition is inputted to HSC, only the solution composition is inputted, along with the above operating gases. When the inputs are in the form of initially assumed calcine solids, the H_2O is evaporated and added and the NO_2 and O_2 gases from the decomposition of nitrates are added. The following starting 'calcined' species are used, for which the stoichiometric off-gases are calculated according to the given reactions. The metal nitrates listed are all those with cations exceeding 0.1 wt % of total metal cations in the feed (excluding H^+). Non-nitrates, e.g., phosphates and sulfates, are retained in the calcine without dissociation:

$Al(NO_3)_3 = 0.5\ Al_2O_3 + 3\ NO_2(g) + 0.75\ O_2(g)$
$Ca(NO_3)_2 = CaO + 2\ NO_2(g) + 0.5\ O_2(g)$
$Mg(NO_3)_2 = MgO + 2\ NO_2(g) + 0.5\ O_2(g)$
$B(NO_3)_3 = 0.5\ B_2O_3 + 3\ NO_2(g) + 0.75\ O_2(g)$
$Hg(NO_3)_2 = HgO + 2NO_2(g) + 0.5\ O_2(g)$
$HNO_3 = 0.5\ H_2O(g) + NO_2(g) + 0.25\ O_2(g)$
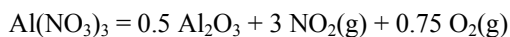
Other calcined species assumed as a starting composition are:

$Ca_3(PO_4)_2$, $CaSO_4$, KNO_3, $NaNO_3$.

For the gross feed composition given in Table I, these reactions result in the quantitative additions for the HSC input shown in Table II.
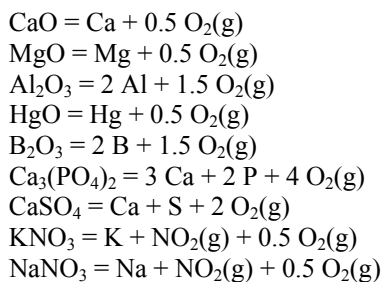
Table II Condensed species and gases produced during conversion of nitrates to oxides

Initial Composition		Assumed Calcination Products			
Salt	Mols/L	Oxide or Salt	Mols/L	$NO_2(g)$, Mols/L	$O_2(g)$, Mols/L
$Al(NO_3)_3$	1.4099	Al_2O_3	0.7050	4.2298	1.0574
$Ca(NO_3)_2$	0.000919	CaO	0.000919	0.001839	0.000460
$Mg(NO_3)_2$	0.01204	MgO	0.01204	0.02408	0.006021
$Hg(NO_3)_2$	0.008992	HgO	0.008992	0.017984	0.004496
$B(NO_3)_3$	0.013894	B_2O_3	0.006947	0.04168	0.01042
HNO_3	1.1372	$H_2O(g)$	0.5686	1.1372	0.2843
$Ca_3(PO_4)_2$	0.002298	$Ca_3(PO_4)_2$	0.002298		
$CaSO_4$	0.005225	$CaSO_4$	0.005225		
KNO_3	0.004951	KNO_3	0.004951		
$NaNO_3$	0.06493	$NaNO_3$	0.06493		
H_2O^*	47.7458	$H_2O(g)$	47.7458		
TOTAL				**5.453**	**1.3631**

*Total H_2O gross feed solvent. Total H_2O for input to HSC, including that from HNO_3 dissociation, above, is 48.3144 mols/L.

Gases from Hypothetical Conversion of Calcine to Elements for Input to HSC

To further dissociate the above assumed calcine solids to elements, the following stoichiometric reactions occur, from which one calculates the elemental inputs, including additional gaseous products to add to the gas phase in the HSC input.

$CaO = Ca + 0.5\ O_2(g)$
$MgO = Mg + 0.5\ O_2(g)$
$Al_2O_3 = 2\ Al + 1.5\ O_2(g)$
$HgO = Hg + 0.5\ O_2(g)$
$B_2O_3 = 2\ B + 1.5\ O_2(g)$
$Ca_3(PO_4)_2 = 3\ Ca + 2\ P + 4\ O_2(g)$
$CaSO_4 = Ca + S + 2\ O_2(g)$
$KNO_3 = K + NO_2(g) + 0.5\ O_2(g)$
$NaNO_3 = Na + NO_2(g) + 0.5\ O_2(g)$

Combining the gases from the various processes, the total gas inputs for HSC calculations for the input cases of assumed calcine initial composition and elemental composition are given in Table III.

Table III Total gas input concentrations for assumed calcine input composition and elemental input composition, Mols/L gross feed

Gas Species	Source				
	Air & Evaporation of H_2O	Dissociation of Nitrates to Calcine	Total for Calcine Input to HSC	Dissociation of Calcine to Elements	Total for Elements Input to HSC
N_2	47.60		47.60		47.60
O_2	12.78	1.363	14.143	1.1334	15.274
NO_2		5.453	5.453	0.06988	5.522
H_2O	47.746	0.5686	48.314		48.314

EXPERIMENTAL DATA ON CALCINATION CONDITIONS AND CALCINE COMPOSITION

Past experimental results on aluminum calcine composition, compared to high-level waste feed composition, can provide a guide to help evaluate the results of HSC thermodynamic modeling in terms of species to include or exclude and phases to consider. Three issues are pertinent. One is determination of accuracy of thermodynamic data of some species that are calculated to form. The second is a characterization of kinetic limitations that would prevent primary reactions from occurring. As is discussed in the "Summary of Results" section, some questionable boron-containing vapor species results in complete vaporization of the boron, a result inconsistent with experimental data on the calcine, and are eliminated. Also, if $N_2(g)$ is permitted to form, all nitrates and nitrogen oxide gases are decomposed to N_2 at equilibrium. The third is an evaluation of pertinent phases to consider. These issues are addressed in detail here using experimental information and parametric modeling results.

The aluminum high-level waste in the WM-180 and WM-182 tanks originated from processing aluminum-clad fuels with aluminum matrix (meat) that contained UAl_x fuel particles in the G-Cell at the Idaho Nuclear Technology and Engineering Center by dissolving them in mercuric nitrate-catalyzed nitric acid. Staples et al. determined the elemental compositions of alumina calcine samples retrieved from Bin 3 of the Calcine Solid Storage Facility II. [7] Three samples were taken from the bin, one each from the top, middle, and bottom. The results for the alumina calcine are summarized in Table IV. The aluminum analyses in the Staples sample is about 25 % low compared with that in calcine obtained directly from the calciner and historical processing data. [8]

Table IV Composition of retrieved alumina calcine from Bin 3 of the Calcine Solid Storage Facility II

Species	Top	Middle	Bottom	Average
	Weight Percent			
B	<0.2	<0.2	<0.2	<0.2
Ca	0.92	1.10	3.54	1.85
F	0.21	0.14	3.54	
Zr	<0.5	<0.5	<0.5	<0.5
Al	35.53	35.93	39.75	37.1
Hg	1.6	1.8	1.9	1.7_7
K	0.5	0.5	0.4	0.4_7
Na	3.1	2.0	1.7	2.1_7
NO_3^-	6.87	5.14	5.70	5.90
Mole Ratio				
NO_3^-/Na	0.82	0.95	1.24	1.01 ± 0.22 std dev
$NO_3^-/(Na +K)$	0.75	0.83	1.09	0.89 ± 0.18 std dev

Note from Table IV that the $NO_3^-/(Na + K)$ mole ratio of Bin 3 is about 0.89 (encompassing unity within one standard deviation), indicating that the majority of these alkali nitrates remain in the calcine, un-decomposed. Therefore, the modeling phases should be such that some nitrate is retained in the calcine in the form of alkali nitrates, as was also determined for zirconium calcine.

The estimated NO_2 mole percent (actually, NO_x, the sum of NO_2 and NO) in the calciner off-gas during the processing of Batches 300 -620 calculated from the data in Table IV (5.43 mols NO_2/L) and the other off-gas composition (47.60 mols N_2/L, 14.14 mols O_2/L, and 50.13 mols H_2O/L) is 5.43 %. This is consistent with concentrations measured in the off-gas, taking into consideration dilutions by numerous purges and vessel sparges to the equipment vent, and with the design basis[9] of the Waste Calcining Facility, which considered that the nitrates $Al(NO_3)_3$, HNO_3, and $Hg(NO_3)_2$ converted entirely to NO_2; only $NaNO_3$ was considered to be partially retained as the nitrate, along with some oxide. Therefore, kinetic limitations prevent the NO_2 and residual nitrates from dissociating to N_2 that would be predicted thermodynamically by HSC. To prevent the calculation of this, $N_2(g)$ is deleted from the product species in the HSC database. When this is done, $N_2O(g)$ is formed, containing about 70 % of the gaseous nitrogen. Again, this is contrary to experience, and $N_2O(g)$ is also deleted from allowed species.

X-ray diffraction of the retrieved alumina calcine samples showed the presence of predominately amorphous alumina with a small amount of α-alumina in only one sample, indicating that it is appropriate to consider Al_2O_3 in an oxide solid solution phase. [7]

Early calcination development studies of alumina calcine determined that aluminum nitrate decomposes to both amorphous and crystalline alumina in varying amounts, with as much as 90 % amorphous alumina being produced under certain conditions. Formation of amorphous alumina was favored by the presence of oxides of nitrogen and water vapor in the gaseous atmosphere.[10,11] It is formed, also, only if a small amount of sodium ion is present in the alumina product.[12] Boron addition was used to prevent formation of crystalline alumina.[11,12,13]We will consider here that that alumina in the alumina calcine will exist as an amorphous phase with $NaNO_3$ and KNO_3.

The behavior of mercury during calcination of simulated aluminum waste feed in a two-foot square pilot plant calciner was characterized by Wheeler.[14] The average volatility from the bed at 400°C was about 35%, with a range from 20 to 40 %. The fraction of volatilized mercury removed in the scrub system was a linear function of acidity of the scrub solution:

% volatilized Hg removed = 8.14×[HNO_3] + 20.6   (Eq. 8)

With a 3 M HNO_3 scrub solution; about 45 % of the volatilized mercury was scrubbed from the off-gas.

During the first operating campaign of the Waste Calcining Facility feeding aluminum waste at 400°C with indirect heating, 5 % of the mercury volatilized.[15] This was under conditions of very low chloride in the waste, as is modeled here for Bin 3. The average scrub solution nitric acid concentration was 4.12 M and it removed 80 % of the volatilized mercury (compared to the prediction from the above relationship of 54 %).

No data on mercury volatility is included in the Waste Calcining Second Processing Campaign Report which is when Bin 3 was filled. Based on an average of the two studies reported above, a prediction in the vicinity of 22 ± 13 % mercury volatilized is expected.

Cesium volatilization is not observed at 400°C. It is very slightly volatile at 500°C.[16]

HSC MODELING

Initial HSC calculations using aqueous composition inputs did not converge correctly because of quirks in its calculation of H_2O vapor pressure at the high temperature and, consequently, showed presence of H_2O in the calcine. This difficulty was overcome by entering compositional data in the form of assumed starting calcine or elemental components, with the solution H_2O evaporated and entered in the gas phase. That is, H_2O was not an allowed component of the oxide solid solution phase, only as pure H_2O.

HSC modeling was done by varying the input species; elements vs. assumed calcine compounds, and associated gases, to confirm that the same convergence point occurred in both cases. It did. Some specific product species whose stability was questionable were evaluated to assess their effects, in particular $HBO(g)/BOH(g)$, which were deleted as potential product species. They caused boron to evaporate, which contradicts observation. The species $H_3BO_2(Bg)$ and its data, new in HSC 5.1, is a duplicate of the HSC 5.1 $H_3BO_2(g)$ and should be deleted. The reduced boron species H_3BO_2 was predicted to form. However, this is not reasonable in the oxidizing environment. The data source for H_3BO_2 is Karapet and is listed as Class 3, the lowest reliability, by HSC. Its enthalpy and entropy are similar to the values for H_3BO_3. Experience has shown that data from Karapet are often suspect. This species, H_3BO_2, is not considered a plausible species and was eliminated from the calculation of calcine composition.

Some significant species in the modeling results had two sources of data for equivalent compounds in the HSC 5.1 database. Including both would lead to over prediction of the total contribution in the products. A systematic evaluation led to deletion of $H_3BO_3(g)$, H_3BO_3, $*3Ca_3(PO_4)_2*CaF_2$, $*3Ca_3(PO_4)_2*Ca(OH)_2$, and HgO as duplicates, respectively, of $B(OH)_3(g)$, $B(OH)_3$, $Ca_5(PO_4)_3F$, $Ca_5(PO_4)_3OH$, and $HgO(R)$, which have superior, more recent data. Also, $Ca(OH)_2*Ca_3(PO_4)_2$ data is Karapet 70, Class 3 reliability and is suspect; it was deleted. The fluoride species are not pertinent to the current Bin 3 composition, but may be in other systems.

Other significant or potentially significant species with slightly different new data in HSC 5.1 pertinent to the Bin 3 (or Bin 7 zirconium calcine) composition are: AlF_3, Al_2O_3, $Al_2O_3(D)$, $Al_2O_3(G)$, $Al_2O_3(K)$, $HF(g)$, $HNO_3(g)$, $NO(g)$, $NO_2(g)$, Na_3AlF_6, $Na_5Al_3F_{14}$, and $NaNO_3$. With the exception of Na_3AlF_6, the newer, HSC 5.1, data were used with minor effects on results. The Na_3AlF_6 was not a species in Bin 3, but the HSC 4.1 data are retained permanently because it results in compositions for Bin 7, when used in combination with HSC 5.1 data for all other species, in a somewhat better match to experimental observations. In this regard, the Bin 7 composition and modeling results provide an empirical basis for the selection.

With regard to aluminum oxide species, the forms $Al_2O_3(D)$ (delta phase) and $Al_2O_3(K)$ (kappa phase) will form only when the temperature exceeds 978 K. As the temperature is decreased, they transform irreversibly to the alpha form of corundum, $Al_2O_3(C)$. They are metastable species that can be formed at the lower temperatures only by quenching from the high temperature.[17] The thermodynamic data for them, when extrapolated to 400°C, would indicate a small equilibrium quantity of a few percent relative to the alpha form. They are deleted from the output species list. The crystalline gamma phase, $Al_2O_3(G)$, is retained as a species, since it has been observed in calcine,[18,11] although not after the addition of boric acid to the waste to cause the formation of amorphous alumina by suppressing the formation of crystalline $NaNO_3$.[12,11] By placing all Al_2O_3 species in the oxide-nitrate phase, it becomes amorphous and all the Al_2O_3 species are summed to obtain the total amorphous quantity.

The remaining issue for Al_2O_3 is that duplicate entries exist in the HSC database, as Al_2O_3 and as $Al_2O_3(C)$, for the crystalline alpha phase.   In HSC 4.1, the $Al_2O_3(C)$ data are from the more recent Barin 89 compilation, whereas the Al_2O_3 data are from the older Barin 77 compilation. Therefore, when doing calculations with HSC 4.1, the $Al_2O_3(C)$ data are retained and Al_2O_3 is deleted.   In HSC 5.1, Al_2O_3 data are from the recent JANAF 98 compilation, whereas the $Al_2O_3(C)$ data are the same as in HSC 4.1, from Barin 89.   Thus, when doing calculations with HSC 5.1, the Al_2O_3 data is retained and $Al_2O_3(C)$ is deleted. The only significant difference in all these cases is in heat capacity terms. For both databases, $Al_2O_3(G)$ is retained.

Significant changes were made in the HSC 5.1 database for HgO species.   In 1996, Frederickson and Hager[19] published results of a very thorough characterization of the system that vastly improved the data for mercuric oxide red and yellow allotropes. Their data showed them to be more stable, i.e., less volatile as $HgO(g)$, than previously. HSC 5.1, in addition to incorporating Frederickson's data for $HgO(R)$ and $HgO(Y)$, retained different data for the species listed as HgO, which is a duplication of the red allotrope. That was deleted for the calcine modeling studies. The basis for the preference of Frederickson's data is that it correctly predicts the observed volatility of HgO during calcination of the Bin 3 feeds. This is discussed in more detail in the "Summary of Results" section.
Frederickson's data for $HgSO_4$, Hg_2SO_4, $HgSO_4*H_2O$, and $Hg_2SO_4*H_2O$ are also incorporated into the HSC 5.1 database, although, they turn out to be insignificant products in the calcine.

Additional details regarding thermodynamic data for specific species, including species not pertinent to Bin 3 but to Bin 7 and future compositions, are given in the verification and validation report.[3]

SUMMARY OF RESULTS

This modeling study evaluated phase designations and other conditions, such as gas species to include or delete, for modeling. The specific conclusions reached are that oxides and nitrates are retained in a single phase, H_2O is present only as a gas or allowed, in addition to the gas, as its own single, pure liquid phase, i.e., not present in the oxide-nitrate phase that it would normally default to. Sulfates, phosphates, and fluorides all have their own phases, except the fluoride phase does not contain the alkaline fluorides CaF_2, MgF_2, and SrF_2, which are placed together in a separate alkaline fluoride phase. (Fluorides are not present in the current system but are in zirconium calcine). Nitrides, phosphides, and elements are deleted as species that do not form – to enable HSC to run. Sulfides are eliminated, also, except that CaS is retained both in the amorphous phase and as a pure phase, since Brewer's X-Ray Physical Electron Spectroscopy data on zirconium calcine indicates its possible presence.

Additionally, $N_2(g)$ and $N_2O(g)$ were deleted to simulate kinetic constraints on their formation. The total pressure is retained (0.744 bar) and $Ar(g)$ is substituted for $N_2(g)$. The total pressure was set at 0.744 bar. This is a small increase (0.003 bar) of the pressure above the vapor space pressure above the bed of 0.741 bar (0.732 atm)[9] (based on a Δp of −0.107 bar in the calciner vapor space relative to ambient pressure and the average atmospheric pressure at the INEEL[20] of 0.8486 bar (0.8375 atm) to partially account for a slightly greater pressure within the bed. Modeling calculations are done at two temperatures (400°C and 500°C) to obtain HSC results that can be displayed, because a quirk in the software requires two points to display results. Results for the operating temperature 400°C are used.

The HSC algorithm will sometimes not run and converge when the number of possible products and phases is very large. Therefore, it was necessary when building the output file to systematically delete species that are known to be or are intuitively negligible to enable the program to run.

In the aluminum calcine, alkali metals remain virtually completely as un-dissociated nitrates. Approximately 87 % of the mercury remains in the calcine. About 97 % of the boron is formed as binary oxide compounds with aluminum. About equal molar amounts of NO_2 and NO gases were formed in the calciner.

The final results of predicted calcine composition are shown in Table V.   They correspond closely to the experimental data on the calcine for NO_3^-/Na and NO_3^-/(Na + K) ratios, percent mercury volatilized, and the NO_2/NO mole ratio above the calcine bed. The 2.00 wt% HgO in calcine corresponds to 1.86 wt% Hg, compared with Staples' analytical results of $1.7_7 \pm 0.1_5$ wt% Hg (the subscripted numbers indicate figures beyond significant figures in averages, but they are retained to minimize precision errors in subsequent comparisons).

Table V Calculated final calcine[*a] and off-gas compositions. Calcine tabulated through 0.01% individual species Contributions

Species	Phase[**b]	Mols/L Gross Feed	Mol % in Calcine	Wt % in Calcine
Al_2O_3	Amorphous	5.843E-01	85.30	81.20
$NaNO_3$	Amorphous	5.635E-02	8.23	6.53
$CaMg_{0.9235}(CO_3)_{1.9235}$	Dolomite	1.134E-02	1.66	2.75
$MgO*Al_2O_3$	Amorphous	9.704E-03	1.42	1.88
HgO	Amorphous	6.788E-03	0.991	2.00
$CaSO_4$	Sulfate	4.390E-03	0.64	0.82
KNO_3	Amorphous	4.300E-03	0.63	0.59
$Al_4B_2O_9$	Amorphous	3.682E-03	0.54	1.37
$Al_{18}B_4O_{33}$	Amorphous	1.091E-03	0.16	1.57
$Ca_5(PO_4)_3(OH)$	Phosphate	9.383E-04	0.14	0.64
$MgAl_2O_4$	Amorphous	5.205E-04	0.076	0.101
$Ca_3(PO_4)_2$	Phosphate	5.905E-04	0.086	0.250
HBO_2	Amorphous	1.911E-04	0.028	0.011
$CaO*6Al_2O_3$	Amorphous	1.906E-04	0.028	0.173
$MgSO_4$	Sulfate	1.382E-04	0.020	0.023
$CaO*2Al_2O_3$	Amorphous	1.043E-04	0.015	0.037
MgO	Amorphous	1.036E-04	0.015	0.006
$Ca(NO_3)_2$	Amorphous	1.010E-04	0.015	0.023
Total Calcine		0.6848	99.98[†♣c]	99.97[♣]
		Mols/L Gross Feed	Average Partial Pressure, atm	
H_2O	Gas	4.829E+01	3.036E-01	
N_2	Gas	4.760E+01	2.993E-01	
O_2	Gas	1.544E+01	9.708E-02	
NO_2	Gas	2.841E+00	1.786E-02	
NO	Gas	2.569E+00	1.615E-02	
HNO_2	Gas	2.268E-02	2.55E-04	
HNO_3	Gas	2.365E-03	1.49E-05	
Hg	Gas	1.082E-03	6.80E-06	
Total Gases		116.78	0.734[♣c]	

[*a]Amorphous is considered to be an oxide-nitrate phase that includes all oxides and nitrates

[**b]No distinction is made among the different allotropic forms of Al_2O_3 [Al_2O_3, $Al_2O_3(G)$, Al_2O3*H_2O, $Al_2O3*H_2O(B)$]; $CaSO_4$ [$CaSO_4$; $CaSO_4(A)$; $CaSO_4(B)$, $CaSO_4*0.5H_2O$, $CaSO_4*0.5H_2O(A)$, $CaSO_4*0.5H_2O(B)$; $MgSO_4$ [$MgSO_4(A)$, $MgSO_4(B)$; MgO [MgO, $MgO(M)$]; HgO [$HgO(R)$, $HgO(Y)$]; and $Ca_3(PO_4)_2$ [$Ca_3(PO_4)_2$, $Ca_3(PO_4)_2(A)$, $Ca_3(PO_4)_2(B)$].

[♣c]Sums from spreadsheet, as percentage of total calcine composition or sum of gas partial pressures. Above sums are slightly different due to roundings. Additional gas species not reported are negligible, each less than $9x10^{-5}$ % of this sum. This list of gases includes any significant amount of a calcined species that may have vaporized. Total gases present in calciner operating gases and produced from dissociation of the feed, exclusive of N_2, comprise 99.0 % of the total species, including calcine, in the process.

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