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**Thermodynamics of Gas-Metal-Slag
Equilibria for Applications in
In Situ and Ex Situ Vitrification Melts**

**R. L. Miller
G. A. Reimann**

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ABSTRACT

An equilibrium thermodynamic model for melting mixed waste was evaluated using the STEPSOL computer code. STEPSOL uses free energy minimization techniques to predict equilibrium composition from input species and user selected species in the output. The model assumes equilibrium between gas, slag, and metallic phases. Input for the model was developed using compositional data from Pit 9 of the Subsurface Disposal Area at the Idaho National Engineering Laboratory. Thermodynamic data were primarily from compilations published by the U.S. Government. The results of model evaluation indicate that the amount of plutonium chloride or plutonium oxyhydroxide that would be evaporated into the vapor phase would be minor. Relatively more uranium chloride and uranium oxyhydroxide would be vaporized. However, a hazards analysis was not part of the present task. Minor amounts of plutonium and uranium would be reduced to the metallic state, but these amounts should alloy with the iron-chromium-nickel metallic phase. The vast majority of the plutonium and uranium are in the slag phase as oxides. Results of the calculations show that silica and silicates dominate the products and that the system is very reducing. The major gases are carbon monoxide and hydrogen, with lesser amounts of carbon dioxide and water. High vapor pressure metals are considered but were not analyzed using STEPSOL. STEPSOL does not make predictions of distribution of species between phases.

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ACRONYMS

ALRC	Albany (Oregon) Research Center
ANL	Argonne National Laboratory
CFR	Code of Federal Regulations
HVPM	high vapor pressure metal
IBM-PC	International Business Machines (Corp.) personal computer
INEL	Idaho National Engineering Laboratory
ISV	in situ vitrification
LLCM	low-level contaminated metal
ORNL	Oak Ridge National Laboratory
PC	personal computer
SDA	Solids Disposal Area
SI	Le Systeme International D' Unites (International System of Units)
TRU	transuranic
UMR	University of Missouri, Rolla
USGS	U.S. Geological Survey

Thermodynamics of Gas-Metal-Slag Equilibria for Applications in In Situ and Ex Situ Vitrification Melts

INTRODUCTION

Three main considerations are addressed in this report: (1) the disposition of uranium and plutonium in the slag-metal system during vitrification of soils and wastes in Pit 9 of the Idaho National Engineering Laboratory (INEL) Solids Disposal Area (SDA), (2) the disposition of uranium and plutonium in a slag-metal system treating the solid residues from an incinerator in a melter to reduce their volume, and (3) the production of plutonium and uranium oxyhydroxides and chlorides that might volatilize and become part of the gaseous emissions from a mixed-waste treatment system. The concepts discussed here are applicable to in situ vitrification (ISV) and to ex situ vitrification, e.g., the slags from an arc melter.

One school of thought is that the uranium and plutonium oxides in the wastes might be reduced by carbon or carbon compounds in the soil or in the waste to form uranium or plutonium metal. The problem is the high density of the metals compared to the melt (specific gravity of the metal referenced to the melt) and other materials that would form during waste melting. The high specific gravity of the metals is postulated to result in settling of the metallic particles, resulting in their accumulation in the lower regions of the melt. Too large of a localized mass of plutonium or enriched uranium is postulated to result in a critical mass, in the nuclear sense.

Equilibrium Thermodynamics in Slag-Metal Melts

In this report, the equilibrium thermodynamics of reactions between carbon and carbon monoxide, or other reducing agents, and the oxides of uranium and plutonium as oxidizing agents are estimated from available data. Other metal and metal oxide systems are also considered, since they are present in the soil and in the waste materials. In particular, zirconium, aluminum, iron, and their oxides are considered because of their presence in the waste materials. These metals and their oxides form a very effective reduction-oxidation "buffer" system in that the iron is reduced relatively easily by carbon, carbon monoxide, aluminum, and zirconium. Ellingham diagrams, described below, are used to identify the products that should be present. The method of making these equilibrium thermodynamic calculations is by using a computer program designed to estimate the Gibbs energy of formation of the various components and to estimate the relative amounts of each product in each phase, using a Gibbs energy minimization algorithm. This computer program is described below.

Uranium and plutonium oxyhydroxides and chlorides are given special consideration because of their high vapor pressures. High vapor pressure metals on the Environmental Protection Agency toxicity list (40 CFR 261.24), viz., arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver, are analyzed because of their toxicity. Zinc is another high vapor pressure metal included in the evaluation.

The equilibrium thermodynamics calculations considered here are not dynamic, i.e., they do not consider an advancing front of molten metal/slag/gas. The dynamic problem is somewhat more involved than could be considered in the present task. The dynamic problem would have to consider varying temperatures and the reaction of different materials as the hot zone approached. Further, the temperature of the melt would not be uniform due to heat losses through boundaries of the melt. The cooling portions of the melt would generate a suite of minerals in a glassy matrix. In mineralogical terms, this would be termed *facies*. The suite of minerals would change with temperature, reflecting the relative stabilities of the melt composition. Equilibrium thermodynamics could calculate these compositions, but they might not be seen due to slow diffusion in the solids.

Kinetics of In-Melt Reactions

One aspect of the kinetics problem must not go unstated: equilibrium thermodynamics do not predict kinetics. In the temperature range of interest in slag-metal interactions, a first approximation to the kinetics question can be made, viz., the reactions will be mass-transfer controlled. An ISV site resembles a single, very large batch reactor with large thermal and chemical gradients throughout the volume of the reactor. Because of these gradients and of low rates of diffusion of reactants and products, equilibrium will not be achieved. However, this does not restrain us from making calculations that would indicate the probable composition to occur if all materials in the melt were allowed to reach thermodynamic equilibrium. In addition, these calculations could be used to predict behavior in ex situ melters. A second aspect of the thermodynamics/kinetics problem is that, in general, the further removed from equilibrium the faster the rate of reaction.

Benchscale experiments at the INEL have shown that point-source contaminants are redistributed more-or-less uniformly in the melt, except for a thin shell of material adjacent to the outer surface of the crucible. These results suggest that at high temperatures the rates of reaction may not be controlled by diffusion processes. At low temperatures, where the viscosity of the glass is very high, the rates of reaction will likely be diffusion controlled. The cooled mass of the ISV materials resemble a glass, and glasses are actually very viscous liquids. Diffusion is slow and almost ceases at temperatures less than the glass transition temperature,¹ becoming similar to the rates of diffusion in metals and ceramics.

Gibbs energy minimization calculations show that the amount of elemental uranium or plutonium present in the alloy phase will be very small, i.e., these elements will be in the slag phase as oxides or chlorides.

EQUILIBRIUM THERMODYNAMICS

Ellingham Diagrams

Scoping calculations were made to estimate the probability of reduction of uranium and plutonium oxides by carbon monoxide and carbon or other reducing agents. These calculations are in the form of Ellingham diagrams, which are graphs of Gibbs energy of formation as a function of absolute temperature.² Compound stability increases (resists reaction) the more negative the Gibbs energy of formation. Figure 1 shows the Ellingham diagrams for carbon dioxide, carbon monoxide, methane, and water. This figure shows that water is the most stable of the compounds and that methane is the least stable at low temperatures. Above approximately 900 K, carbon monoxide becomes the most stable and methane or water the least stable; carbon dioxide has a nearly constant Gibbs energy of formation over the temperature range of interest. Carbon monoxide is more stable than carbon dioxide above approximately 900 K; thus, carbon will react with carbon dioxide to form carbon monoxide.³ Methane is of lesser importance at high temperatures.

Ellingham diagrams provide a qualitative indication of the relative stabilities of the compounds being considered. These diagrams do not provide an indication of the relative abundance of the compounds being considered. The amount of the various constituents present, at equilibrium, is provided by Gibbs energy minimization calculations. However, none of these techniques identify the compounds that need to be considered. The program user has to make the proper judgment on this point. For example, in the reactions between carbon, hydrogen, and oxygen, the formation of methane is not evident but needs to be considered. Methane is just the simplest of the hydrocarbon compounds; and the production of other, more complex hydrocarbons such as ethane, ethylene, acetylene, and benzene, may need to be considered in a detailed calculation.

Figure 2 shows the Ellingham diagrams for wuestite, FeO, magnetite, Fe_3O_4 , and hematite, Fe_2O_3 . This figure shows that hematite is the least stable of the compounds, except below approximately 400 K. Above approximately 900 K, wuestite is the most stable; below this temperature, magnetite is the most stable. This may be compared with the phase diagram for the iron-oxygen system, shown in Figure 3.² This phase diagram shows that there are regions of stability for all of the oxides, depending on temperature and oxygen content. Figure 3 shows that the iron-oxygen system is complex with respect to stable species; and above approximately 1,900 K, only liquids are present. These liquids are solutions of iron and/or iron oxides. In some cases, the liquids are not miscible, and more than one liquid phase may be present. The impact of this on the slags is that there may be a partitioning of nonferrous species between the separate liquid phases. There are few data available on the thermodynamic solution activities of species in the liquid phases. However, at equilibrium, the activities of any species are the same in two or more phases in contact.

Figure 4 is an overlay of Figure 1 onto Figure 2 and shows the relative stability of carbon monoxide, carbon dioxide, water, wuestite, magnetite, and hematite. Figure 4 shows that both

Figure 1. Ellingham diagrams for water, carbon monoxide, and carbon dioxide, methane, hydrogen chloride, and carbon tetrachloride, kJ/mole of oxygen, O₂, chlorine, Cl₂, or hydrogen, H₂.

Figure 2. Ellingham diagrams for iron oxides, kJ/mole of oxygen, O₂.

Figure 3. Temperature-composition diagram for the iron-oxygen system.

Figure 4. Ellingham diagrams for water, carbon monoxide, carbon dioxide and iron oxides, kJ/mole of oxygen, O_2 .

carbon dioxide and carbon monoxide are more stable than any of the iron oxides above approximately 1,000 K and that the oxides of iron will be reduced by carbon and carbon monoxide to elemental iron and carbon dioxide and carbon monoxide. This figure shows that reduction of iron oxides to elemental iron should be expected during ISV of soils and waste materials. As a first approximation, the iron oxides should be reduced early in the process and consume much of the reducing capacity of the ISV melt. The carbon necessary for the process would be found in the humus of the soils and in plastics, cellulose (in the form of paper, rags, and wood), and other organic materials in the wastes. As a further consideration, these easily reduced oxides form a buffering system in the melt, making it possible to consume the more easily oxidized constituents, such as metallic aluminum and zirconium in the reduction-oxidation process rather than the oxides of uranium and plutonium, discussed below.

Ellingham diagrams for uranium oxides are shown in Figure 5. Data for the Gibbs energy of formation for UO_3 are limited to approximately 2,000 K and for U_4O_9 to approximately 900 K. UO_2 is the most stable of the uranium oxides, and its data base extends to approximately 2,600 K. The uranium oxides are seen to have very negative Gibbs energies of formation, implying that they will be very difficult to reduce to the metallic state. Figure 6 is an overlay of Figure 1 onto Figure 5 and shows that UO_2 , the most stable of the uranium oxides, is not reduced by carbon below approximately 2,500 K. Further evaluation of this system using free energy minimization techniques is required to get a better estimate of the stability of UO_2 in this temperature regime. These evaluations are described in the results section.

Ellingham diagrams for the plutonium oxides are shown in Figure 7. The data base for these oxides is limited to 1,173 K for PuO , to 2,500 K for PuO_2 , and to 2,000 K for Pu_2O_3 . These

Figure 5. Ellingham diagrams for uranium oxides, oxyhydroxide and chlorides, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

Figure 6. Ellingham diagrams for water, carbon monoxide, carbon dioxide, and uranium compounds, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

Figure 7. Ellingham diagrams for plutonium oxides, oxyhydroxide and trichloride, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

oxides are seen to have very negative Gibbs energies of formation; PuO is the least stable of these oxides. Figure 8 is an overlay of Figure 1 onto Figure 7. The curve for CO is seen to cross that of PuO at approximately 2,100 K, indicating that carbon could reduce PuO above this temperature. Further evaluation of this system using Gibbs energy minimization techniques is required to get a better indication of the stability of PuO in this temperature regime. These evaluations are described in the results section.

Data for the Ellingham diagrams for plutonium trichloride, PuCl₃, were from U.S. Bureau of Mines Bulletin 674.⁴ This compound melts at 1,033 K; and beyond this temperature, we would be dealing with a liquid and probably a solution of various chlorides. These data were limited to 1,500 K and were extrapolated to 3,000 K. Data published by Rand⁵ for plutonium trichloride compare very favorably with those given in Bulletin 674. Figure 7 compares the data for the plutonium oxides and chlorides. Uranium trichloride, UCl₃, melts at 1,115 K while the tetrachloride, UCl₄, melts at 863 K. As with plutonium trichloride, or other chlorides, these would probably be present as solutions. The thermodynamic activities of these chlorides in the melt are unknown and assumed to be equal to their stoichiometric concentrations.

Ellingham diagrams for silicon dioxide, SiO₂, zirconium dioxide, ZrO₂, aluminum oxide, and calcium oxide are shown in Figure 9. Sources for these oxides are present in Pit 9 in the form of aluminum alloys, zircaloy, soil, sand, and concrete.⁶ This figure does not exhaust the number of important materials in the pit but represents significant constituents. Curves for aluminum and zirconium oxides are seen to cross at approximately 1,000 K, indicating that above this temperature aluminum oxide would be expected to react with zirconium, in zircaloy, for example, to form metallic aluminum and zirconium oxide. (Such a reaction is thought to have occurred in

Figure 8. Ellingham diagrams for water, carbon monoxide, carbon dioxide, and plutonium compounds, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

Figure 9. Ellingham diagrams for silicon dioxide, zirconium dioxide, aluminum oxide, and calcium oxide, kJ/mole of oxygen, O₂.

electrically heated zircaloy-4 clad pins, with alumina insulation, simulating fuel rods in thermal-hydraulic flow tests; the result was loss of the pins and their simulated fuel bundles.⁷ A simple thermodynamic analysis of the potential reaction⁸ followed by laboratory evaluation of the materials at the operating temperature showed that the zirconium-aluminum oxide reaction was the probable cause of the heater rod failure.⁹) Because of the stability of the oxide films on aluminum and zirconium in air, it is highly probable that these metals are present in Pit 9 in their metallic forms; and the possibility of reaction between these metals and other oxides in the pit should be considered.

Distribution of Uranium and Transuranics Between Iron and Slags in Melts

Figure 10 is an overlay of the Ellingham diagrams for the uranium oxides from Figure 6 onto the Ellingham diagrams for aluminum and zirconium oxides from Figure 9. Figure 10 shows that aluminum and zirconium oxides are more stable than UO_3 or U_4O_9 , indicating that if these oxides occur in the presence of metallic aluminum or zirconium they could be reduced to their metallic state. However, the amount of silica in Pit 9 is so large that any metallic aluminum or zirconium will most likely reduce the silica to silicon with concurrent formation of aluminum and zirconium oxides, i.e., the silica in Pit 9 will act as a powerful buffer for oxidation-reduction reactions in melts, and elemental silicon should be formed in preference to reduction of uranium oxides to metallic uranium. Figure 9 also shows that UO_2 is more stable than either of the oxides of aluminum or zirconium above approximately 1,000 K. However, below approximately 1,000 K, the oxides of aluminum and zirconium are more stable than any of the uranium oxides. This indicates that UO_2 could be reduced to metallic uranium by reaction with aluminum or zirconium above 1,000 K. However, this is near the glass transition temperature for the vitrified mass; and under these conditions, the rate of mass transfer is known to be very small. A more detailed analysis is required using Gibbs energy minimization techniques to estimate the relative amounts of the metals that could be formed in the proposed reactions.

Figure 11 is an overlay of the Ellingham diagrams for the plutonium oxides from Figure 7 onto the Ellingham diagrams for aluminum and zirconium oxides from Figure 9. Figure 11 shows that PuO and Pu_2O_3 are more stable than the oxides of aluminum or zirconium over the temperature range of the data. This indicates that these oxides would not be reduced by metallic aluminum or zirconium to form metallic plutonium and the oxides of aluminum or zirconium. Figure 11 shows that the oxides of aluminum and zirconium are more stable than PuO , indicating that metallic aluminum or zirconium could reduce this oxide to metallic plutonium. However, it is more probable that the PuO_2 would be reduced to PuO and Pu_2O_3 , which are more stable than zirconium or aluminum oxides. A further consideration is that zirconium and aluminum might be consumed by reducing other oxides such as iron oxides. This buffering action by the more easily reduced oxides is important in the overall analysis of the ISV system. Analysis of this system, with regard to uranium and plutonium, using Gibbs energy minimization techniques is the subject of the present study.

If metallic iron were formed (by carbon reduction, for example) during ISV, it could act as a solvent for trace levels of plutonium and uranium. The iron-uranium and iron-plutonium phase diagrams are shown in Figure 12 and Figure 13, respectively.¹⁰ These phase diagrams show that

Figure 10. Ellingham diagrams for aluminum oxide, zirconium oxide and uranium compounds, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

Figure 11. Ellingham diagrams for aluminum oxide, silicon dioxide, and plutonium compounds, kJ/mole of oxygen, O₂, or chlorine, Cl₂.

Figure 12. Temperature-composition diagram for the iron-uranium system.

Figure 13. Temperature-composition diagram for the iron-plutonium system.

intermetallic compounds such as Fe_2U and Fe_2Pu can form. If these intermetallic compounds form, they would be expected to be present as separate phases in iron alloys containing uranium and plutonium if the melt was cooled slowly into the solid phase. Slow cooling would be expected if a large mass of metal and slag were formed, as in ISV. It is conceivable that the higher specific gravity intermetallic compounds could settle to form regions of high fissile material concentration. Because it is thermodynamically favorable for large crystals to grow from smaller crystals, it might be possible for locally high concentrations of the intermetallic phases to form without significant settling in the molten mass. (In fact, this slag-metal separation is the basis smelting iron, copper, and other metals, from their ores and for the fire assay of gold and silver ores.)

Processing of spent nuclear fuel to separate useful isotopes from waste material is producing an increasing accumulation of low-level contaminated metals (LLCM) containing a variety of radioactive contaminants, including isotopes of plutonium and other transuranics (TRUs). This in turn, has led to a need for information regarding the distribution of radionuclides between slags and metals, similar to the need expressed for ISV systems. Recent experimental work dealing with this problem has been definitive in terms of the melting parameters as a function of composition. These results may be applicable here, even though none of the recent works have dealt with decontamination of LLCM on a production scale. A short review of the experimental protocols and results are given below.

In some slag-metal distribution studies, UO_2 has been used as a surrogate for PuO_2 ¹¹ because of very similar chemical behaviors in the environment produced by melt-refining. UO_2 is a major constituent in Pit 9; however, TRUs are present in very small amounts. Recent studies compared the effectiveness of various slag compositions, slag-refractory interactions, melt temperatures and times, and distribution of the isotopes as a result of refining processes. In all instances involving the melting of scrap, a major uncertainty is the scrap assay, as no method has yet been devised to sample heterogeneous scrap and obtain reliable and accurate values for the isotope content. This is analogous to the problem of sampling ores to obtain a reliable value for the precious metal content. For the sake of experimental accuracy, adding a known quantity of the contaminant to an uncontaminated heat of metal is the preferred approach.

Experimental metal decontamination programs at Argonne National Laboratory (ANL)^{12,13} and Oak Ridge National Laboratory (ORNL)^{14,15,16} investigated the removal of uranium, plutonium, and americium from ferrous and nonferrous melts using small (50 to 500 g) heats and benchscale equipment. These studies investigated, in some detail, the thermodynamics of the systems, slag compositions, slag-melt interactions, slag-refractory interactions, extraction ratios, etc., with emphases in these studies on reducing the volume of material requiring disposal, converting scrap into a readily assayable form, and reducing the mobility of the contaminants rather than attempting to decontaminate to the extent that the material was suitable for recycle. These studies were designed to lead to processes suitable for scaling up to treat the ever-increasing volumes of accumulated contaminated scrap and permit maximum utilization of shallow land burial with possible subsequent retrieval. If the total TRU content could be reduced to $< 10 \text{ nCi/g}$ (equivalent to about 0.1 ppm Pu) or less, the potential hazards would be reduced to the extent that retrievable shallow land burial would not be required and the metal castings could be disposed of in commercial landfills without concern for retrievability according to the regulations in effect at the time of burial. No figure is presently available for TRU concentrations considered to be "below regulatory concern," which would

enable sale of decontaminated ingots for recycling through commercial scrap channels. (The trivial unit of parts per million, "ppm," and parts per billion, "ppb," are equivalent to mg/kg and $\mu\text{g/kg}$, respectively. While the latter units are consistent with the International System of Units [Le Systeme International D' Unites (SI)], *ppm* and *ppb* are used here to be consistent with those reported in the cited literature.)

The ANL program used a high-temperature furnace with a tungsten mesh resistance element that would enable the charge to be heated to 1,800°C in "any desired atmosphere" (presumably excluding those containing any oxygen; otherwise, the tungsten element would be destroyed). The furnace was evacuated and backfilled to an absolute pressure of 400 mm Hg with dry helium, and the crucible contents were heated to 1,500°C and held at that temperature for 1 h. The melts were allowed to solidify in their crucibles, and the resulting ingots and slags were analyzed by autoradiography and/or a fission track analysis technique. TRU contents as low as 0.002 ppm of ^{239}Pu equivalent could be detected by autoradiography, while the detection limit for Pu and Am using aqueous dissolution and radiochemical determination was 0.001 ppb. The fission track analysis technique also exhibited excellent sensitivity (to 0.04 ppb Pu). The radiography and fission track techniques would pinpoint localized concentrations, while the dissolution technique would provide information on the average concentration in the bulk sample.

Most of the melts in the ANL study were performed using 200 g of mild steel with about 20 g of slag, or a slag/metal ratio of 0.10. Alumina crucibles of 100 mL were used. Melts were contaminated with 400 ppm Pu (as PuO_2), although as much as 1.4% (14,000 ppm) Pu was added in one instance. The PuO_2 was added to a cavity machined into the bottom of the sample to be melted, which was then sealed with a metal plug or blended with the slag so that the slag would contaminate the melt. No differences in results were noted that could be traced to the method of adding the PuO_2 . A majority of the melts used a borosilicate slag,^a but CaSiO_3 and $\text{CaMgSi}_2\text{O}_6$ slags were used also. The results of this effort were similar to those achieved with the production-scale melting campaigns to reduce uranium and radium in contaminated scrap, in that the contaminants in the steel were reduced to very low levels and were concentrated in the slags. It was interesting to note that the Pu remaining in the ingots was concentrated at or near the ingot surface, possibly as adhering or entrained slag, or in nonmetallic inclusions in the ingot interior. Except for the Pu content, no analysis of the inclusions was given. However, it may be assumed that the composition of the inclusions was fairly close to that of the slag. In some instances, the Pu was concentrated in "clusters" within the ingot. The nature of these clusters was not clearly defined, but it was speculated that they resulted from precipitation of PuO_2 , which may have had a finite solubility in the molten steel. Where no inclusions or clusters were found, the Pu content of the metal was reported to be as low as 0.04 ppb. The dissolution and counting technique showed higher Pu contents than the autoradiography or fission track method on the metal matrix of the same samples, because the dissolution technique averaged in the inclusions, clusters, and any other casting defects in which Pu may have been concentrated.

In cases where more than 400 ppm Pu was added to the melt, the Pu content and distribution in the ingot were about the same, even when the Pu additions ranged between 660

a. A Dow Corning 7740 glass, 81.0% SiO_2 , 13.0% B_2O_3 , 4.0% Na_2O , 2.0% Al_2O_3 , and 0.5% K_2O , by weight.

and 13,700 ppm. These melts weighed only 11–13 g. The ANL reports did not specify how the Pu was added to these small melts, but it seems likely in these cases that the Pu was added to the slag and allowed to equilibrate with the molten steel rather than being sealed into the bottom of the cold metal charge as was done with the 200 g melts. In theory, the end result should have been the same; however, complications often occur in practice that are not accounted for by assumptions in the theory.

"Staged melting" was performed on one heat where portions of two previously melted ingots were remelted using a clean slag. The result of this experiment was an even greater reduction in Pu content. The initial content of the charge was reported as "about 0.1 ppm" Pu, while the ingot resulting from this melt averaged 0.002 ppm Pu. Based on what was reported previously, the cleanup must have resulted from a significant reduction of Pu-containing inclusions, since the dissolution and counting technique employed for analysis includes the Pu contained in these defects. It is possible that a similar result could have been obtained by a longer holding time in the crucible to allow time for the oxide particles suspended in the melt to coalesce and float into the slag. This is more easily done in the resistance furnace employed for this work, because the melt agitation developed by eddy currents during induction heating is absent and only convection currents are operative. The inclusions still trapped in the first melt had an additional hour to float to the surface in the second melt. The total melting time for both heats of the double melt was 2 h. Two other single melts held for this much time under a boro-silicate slag yielded similarly low Pu contents, leading to a conclusion that longer holding times may be nearly as effective as staged melting.

Copeland and coworkers at ORNL conducted experiments similar to those performed at ANL, but studied a wider range of metals and slags and relied more heavily on a thermodynamic approach to metal-slag interaction. The ORNL study used UO_2 and PuO_2 as contaminants, adding them to the flux and assuming that equilibration during melting would produce the same result as would adding it to the metal charge. Both mild steel and stainless steel (type unspecified) were melted, with induction being the primary melting method. Metal weights between 50 and 500 g were employed, with 100 g melts predominating. Flux was added so that it equaled 10 percent (5% in a few instances) of the metal weight, and UO_2 or PuO_2 was thoroughly mixed with the flux so that it would be equivalent to 500 ppm (≈ 440 ppm U or Pu) in the metal. Melting times were $\frac{1}{2}$ to 1 h, melts were allowed to solidify in the crucible, and ingots assaying between 0.01 to 0.1 mg/kg U and < 1 ppm Pu were obtained for both mild and stainless steel melts. The results for mild steel were not as low as those obtained by ANL, even though similar dissolution and counting analytical techniques were used. Halving the slag weight had no apparent effect on the refining capability, but double melting, i.e., melting-freezing-melting-freezing, reduced the Pu level in the metal phase to 0.1 ppm, which was a goal of their effort. The ORNL study concluded that halving the slag weight and double-refining was an effective approach and reduced the quantity of waste requiring disposal.

If uranium or plutonium were found in metallic iron, three obvious mechanisms could be postulated. One mechanism is to form solid solutions of uranium or plutonium. In the iron-rich phase, this could occur when the concentration of uranium or plutonium was very low. A second mechanism of incorporating uranium or plutonium in iron is as an intermetallic compound forming a separate phase; it is conceivable that the intermetallic compound could be present in solid solution at very low concentrations. The third mechanism of incorporating uranium or

plutonium in iron is as slag inclusions of the oxides. The presence of slag inclusions in metal melts is common, and care must be exercised to minimize their influence on the final metallic product. Slag inclusions in contact with the external slag would be dissolved into the slag phase. Considerations of the possibility of slag inclusions would be especially important in drawing conclusions from slag-metal distribution data such as that noted in References 10-12.

The distribution of uranium between a slag and iron has been studied in terms of the distribution coefficient.^{11,12} The distribution coefficient may be defined as the concentration of a solute in the slag phase divided by the concentration in the metal. This implies that the solute uranium is in true solution and not present as a slag inclusion. For example, the distribution of uranium between the oxide phase (slag) and iron metal is given by the partition coefficient, K_d , or distribution coefficient, D , where:

$$K_d = D = \text{uranium concentration in slag} / \text{uranium concentration in iron}$$

A more accurate relationship would involve the thermodynamic activity of the solute species in the metal and slag phases. At equilibrium, the activity of the solute species in the two phases will be equal, even though their analytical concentrations will not. This reflects the difference in chemical potential of the species in their respective environments.

Seitz et al.¹² reported distribution coefficient data for plutonium in mild steel, $D = 2 \times 10^6$; in stainless steel, $D = 8 \times 10^6$; and in nickel, $D = 5 \times 10^4$.

An important question in this regard is the solubility of uranium and plutonium in iron and in the slag. The amount of plutonium in the waste being considered is small enough that only the low plutonium region of the phase diagrams need to be considered. However, if enriched uranium in oxide form is a major constituent in the waste system, it must be considered more fully. In situations where a solid solution can be formed, the tendency for more dense metals to settle into a separate phase is minimized. Advantage may be taken of this to add slag-making materials that will dilute the fissile material. For example, depleted uranium, in the oxide form, could be added to the melt to dilute the fissile material to a concentration lower than that required for criticality. Similar diluents for plutonium may be available that will form solid solutions and thereby reduce the tendency to settle.

Experimental evidence substantiates the idea that uranium and plutonium oxides will preferentially remain in the slag or glass phase rather than be reduced to the metallic state and be dissolved into the molten iron.

COMPUTER CODES

There are several computer codes available for making equilibrium thermodynamic calculations. These codes were recently reviewed by Bale and Ericksson.¹⁷ Ericksson developed the SOLGASMIX algorithm for making these types of calculations. This code was subsequently modified by others and has become the basis for several codes. The Generic Mineral Technology Center for Pyrometallurgy (supported as a center of excellence by the U.S. Bureau of Mines) at the Department of Metallurgical Engineering, University of Missouri, Rolla (UMR) has been particularly active in this area and has recently issued Version 4.22 of STEPSOL. The program is capable of handling up to 14 input species, 84 output species, and 19 phases. This version was used in making the free energy minimization calculations reported here.

Besmann¹⁸ at ORNL also modified SOLGASMIX and issued a version named SOLGASMIX-PV. Besmann's modification uses the ideal gas law to permit calculating equilibria at a total gas volume with variable total pressure. Sheldon,¹⁹ also at ORNL, developed SOLGASMIX-PV for the IBM-PC. This program is capable of handling 10 elements, 99 substances, and 10 mixtures. The gas phase is considered to be a mixture. This version requires a math co-processor in the PC due to the large number of computations made during program execution. A FORTRAN compiler is also required to compile and link the programs.

In the chemical industry, a process was developed for production of sodium carbonate from sodium chloride and calcium carbonate. The process is relatively complicated, with intermediate products and recycled reagents. This is the Solvay process. Rudd and his students¹⁹ developed algorithms to model the Solvay process and explore additional process options. The Chemical Sciences Group at EG&G Idaho, Inc., made further developments²⁰ in these models for the High-Temperature Heat Pump program.

An analysis of the algorithms in STEPSOL will be made to provide the necessary documentation for the ISV program. This analysis will be reported separately.

The pyrometallurgy center at UMR has also developed a code for simulating reaction kinetics between metal, slag, and gas phases. The program assumes equilibrium at the interface and calculates the rate of mass transfer of species to or from the interface. This program, RSMAC, was not used as part of the present ISV evaluation. It may be useful in making reaction kinetics studies in the ISV system, if the present task is extended into that area.

THERMODYNAMIC DATA BASES

There are a number of large data bases available for making equilibrium thermodynamics calculations. Those considered in this study are discussed below.

JANNAF

The JANNAF (Joint Army, Navy, Air Force) data base²¹ is large and contains a significant amount of useful information. Much of the data in STEPSOL was abstracted from the JANNAF data base.

BARIN and KNACKE

The Barin and Knacke²² data base covers more soil-like materials than the JANNAF tables and is largely based on the earlier work of Kubaschewski, Alcock, and Evans.²³

U.S. BUREAU OF MINES

There was a long-term effort at the U.S. Bureau of Mines Research Center at Albany, Oregon (ALRC), to develop thermodynamic data bases for making metallurgical calculations. Earlier ALRC data compilations have been widely used. Compilations of data for oxides²⁴ and halides⁴ have been published and are available for reference. Selected compounds from these tables could be entered into the programs to supplement the Barin and Kanake or JANNAF data bases.

U.S. GEOLOGICAL SURVEY

Thermodynamic data for making calculations of the geochemical conditions in rock formations have been collected by the U.S. Geological Survey (USGS).²⁵ These data are not as extensive as the JANNAF, Bureau of Mines, or the Barin and Kanake data bases. Limited data from these sources have been included in the STEPSOL computer program.

TEXAS A&M UNIVERSITY

This data base is largely devoted to hydrocarbon and similar petroleum materials.²⁶ There may be some halocarbon data in these tables that could be used for making calculations involving reactions of chlorocarbons that have been dumped in the INEL waste area.

A detailed evaluation of the data in the above thermodynamic data bases is beyond the scope of the present task.

BASELINE COMPOSITION

The nominal composition of the wastes being considered were extracted from Appendix A of "Modeling Requirements for ISV."⁶ Data in the tables of composition for Pit 9 are given in m³, in kg, or both. The conversion factor between kg and metric tons is 1,000. The metric ton is termed a *tonne* (t). This term is commonly used in engineering, but it is deprecated by SI.²⁷ The conversion between specific gravity, with respect to water, or density in g/mL to t/m³ is suggested by

$$1 \text{ t} = 10^6 \text{ g}$$

and

$$1 \text{ m}^3 = 10^6 \text{ mL.}$$

Comparing these two equations yields

$$1 \text{ t/m}^3 = 1 \text{ g/mL.}$$

Thus, merely changing the names of the units suffices to make the conversion.

The STEPSOL computer code is limited to 14 species that can be specified for the input. This limitation requires that many simplifying assumptions be made regarding similarity of species and possible interactions that could give rise to chemicals at low temperatures. For example, rather than specifying both ferric chloride and hydrochloric acid as inputs, the decision was made to consider hydrolysis products such as hydrochloric acid and iron oxide.

Inorganic Chemicals in Pit 9

Of the numerous inorganic chemicals identified in Pit 9, only those having large concentrations or particular reactivity are considered in the slag-metal study. Amounts discussed below are listed in Table 1.

There are about 2.3 t of aluminum compounds in Pit 9. For calculational purposes, this is assumed to be present as aluminum oxide, Al₂O₃. This was a common insulating material in electrically heated pins simulating nuclear fuel pins in the Semiscale tests, for example. This is in addition to hydrous aluminum oxides noted below.

There are about 24.5 t of barium compounds in Pit 9. Barium sulfate or barite, BaSO₄, is commonly used for high density concretes, such as those used for radiation shielding. For purposes of this analysis, the barium compounds are assumed to be 24.5 t (0.103 t mol) of barite. In the model, this is considered to be equivalent to 5.8 t (0.103 t mol) of calcium oxide.

There are 0.3 t (0.0156 t mol) of beryllium in Pit 9. Beryllium metal is a strong reducing agent and could react with oxides of uranium and plutonium to yield metallic uranium and

Table 1. Inorganic components of Pit 9 for modeling purposes.

Species	Tonnes	Species	Tonnes
Al ₂ O ₃	2,830.27	KNO ₃	28.25 (02)
BaSO ₄	24.5	K ₂ O	618.43
Be	0.3	Li	6.2
C	85.2	MgO	56.8
CO ₂	35.0	Mn	1.4
CaO	2,489.6	Na	12.74
Cr	57.3	Na ₂ O	327.4
Cr ₂ O ₃	1.7	NaNO ₃	64.74 (02)
Fe	543.8	Ni	29.4
Fe ₃ O ₄	998.4	PbO	7.0
Fe ₂ O ₃	37.46	SO ₃	0.72
FeCl ₃	2.7	Si	0.8
H ₂	0.06	SiO ₂	17,206.7
H ₂ O	132.04	Zr	17.4
Hg	17.7	Other	262.9

plutonium. There is more than enough beryllium present to reduce all of the plutonium oxides to metallic plutonium. For modeling purposes, the beryllium is assumed to be BeO and in the model is considered to be equivalent to 0.87 t (0.0156 t mol) of calcium oxide.

There are 58.8 t of calcium silicate, 3CaO.SiO₂, in Pit 9. This is a composition similar to some constituents in soil and cement and is lumped with those materials for this analysis. The calcium silicate is equivalent to 43.3 t of CaO and 15.5 t of SiO₂.

There are 1.7 t of chromium compounds in Pit 9. Chromates were widely used at the INEL for corrosion control in recirculating water systems. The chromates in Pit 9 could be reduced to metallic chromium by appropriate reducing agents. For analysis purposes, the chromium is assumed to be present at 1.7 t (0.011 t mol) of chromium oxide, Cr₂O₃. This is equivalent to 1.14 t of chromium, or, for the model, 1.96 t of nickel.

Pit 9 contains 2.7 t of iron compounds. Since carbon steel and hydrous iron oxides are listed separately, the iron compounds are considered chlorides. Iron(III) chloride is commonly used in

water treatment as a coagulating agent; it is also used to etch printed circuit boards. In the presence of reducing agents, it is reduced to iron(II); in the presence of air, iron(II) is oxidized to iron(III). Thus, modeling the iron compounds as iron(III) chloride is a reasonable compromise. The iron is considered to be 2.7 t of iron(III) chloride, FeCl_3 . For the model, this is equivalent to 1.329 t of hematite and 1.82 t of hydrogen chloride (this hydrogen chloride is made equivalent to carbon tetrachloride and water in the model); 0.449 t of water is consumed.

Pit 9 contains 7 t of lead compounds. In the absence of further information, this lead is presumed to be present as 7 t (0.03 t mol) of lead oxide, PbO , also termed *litharge*. This compound is stable at process temperatures and is modeled as 1.76 t (0.03 t mol) of calcium oxide.

There are 6.2 t of lithium compounds in Pit 9. Lithium is a reactive metal, similar to sodium in its chemical properties. Experiments using liquid metals, including liquid lithium, have been conducted at the INEL. However, for analysis purposes, the lithium is presumed to be present as 2.208 t mol of lithium oxide, Li_2O . This is modeled as being equivalent to 12.87 t (0.208 t mol) of sodium oxide.

Pit 9 contains 87.5 t of asbestos. Even though thermodynamic data for asbestos are available, its stoichiometry is $2\text{MgO} \cdot \text{SiO}_2$, similar to soil and cement constituents, and will be modeled as magnesium and silicon oxides. The asbestos in Pit 9 is equivalent to 56.5 t of MgO and 30.9 t of SiO_2 . For the model, the magnesium oxide is considered to be equivalent to 78.5 t (1.40 t mol) of calcium oxide.

There are 17.7 t of mercury in Pit 9. Mercuric nitrate has been used to promote dissolution of aluminum fuel plates. This material should have been contained in the high-level waste materials from fuel reprocessing and should not be in Pit 9. Metallic mercury has also been used at the INEL. For thermodynamic evaluations, all of the mercury is assumed to be present as the metal. Mercury oxides are quite unstable and decompose to liberate oxygen and elemental mercury at 900 to 1,000 K; thus, they may serve as an oxygen source and as oxidizing agents. Further, the boiling point of mercury is about 630 K (357°C), indicating that the mercury should leave the hot zone of the molten mass of waste, probably during the heatup stage. Mercury is not included in the thermodynamic model.

Pit 9 contains 80.2 t (0.793 t mol) of potassium nitrate and 172 t (2.024 t mol) of sodium nitrate. Both of these compounds are strong oxidizing agents and are commonly used as the oxidant in black gun powder. Upon strong heating, they decompose irreversibly into oxygen and nitrite salt, thus:

With heavy metal nitrates, e.g., copper nitrate, a reaction such as:

could be expected. If the hot nitrates come into contact with organic wastes, such as ion exchange resins, paper, rags, or wood, there is a strong possibility that very rapid oxidation could

occur resulting in a deflagration or explosion. Thermodynamic data are available for both nitrates and nitric oxide but not for the nitrite salts. The data show that the nitrates have large negative Gibbs energies of formation, and the nitric and nitrous oxides have large positive Gibbs energies of formation. This indicates that modeling the nitrates in a Gibbs energy minimization study will not reflect the above equations. The first approximation is to model the nitrates as equivalent amounts of sodium oxide and oxygen. This yields 27.60 t of oxygen from the potassium nitrate and 64.75 t of oxygen from the sodium nitrate, a total of 92.35 t of oxygen that could be released during the melting process. The sodium and potassium nitrates are considered to be equivalent to 109.8 t (2.8165 t mol) of sodium oxide.

There are 17.4 t of zirconium chemicals in Pit 9. Zirconium metal is the major constituent in zircaloy, and zirconium oxide is a widely used insulating material. There may be other zirconium compounds in the wastes, but the assumption here is that all of the zirconium is present as zirconium oxide, ZrO_2 . In the melt, it would be expected to form zirconium silicate; and for this reason, it is modeled as 7.43 t 0.133 (t mol) of calcium oxide.

Other Miscellaneous Chemicals in Pit 9

There are 60.84 m³ of hydrated oxides in Pit 9. These are identified as hydrated oxides of aluminum, iron, silicon, magnesium, plutonium, and americium. In the absence of a more accurate analysis, two assumptions were made. First, these oxides could be represented on average as about half aluminum oxides and half iron oxides. Second, the radioisotopes are accounted for in the category "Radionuclides in Pit 9." Aluminum hydroxide, $\text{Al}(\text{OH})_3$, was selected as the average hydrous aluminum oxide in Pit 9. Iron(III) hydroxide, $\text{Fe}(\text{OH})_3$, was selected as the average hydrous iron oxide present. Thermodynamic data are available for both compounds.

As another assumption, the bulk density of these hydrous oxides was taken to be similar to soil, about 100 lb/ft³, or 1.6 t/m³. The mass of this waste is 97.5 t of mixed hydrous oxides and yields 48.75 t of aluminum hydroxide and 48.75 t of iron(III) hydroxide. Both of these compounds are unstable as temperature rises. For example, analytical methods for gravimetric determination of these metals rely on their instability.²⁸ Hydrous iron oxide decomposes in the range of 1,100 to 1,300 K to form Fe_2O_3 (see Figure 3 for a phase diagram showing the relative stability of iron-oxygen compounds as a function of temperature). Hydrous aluminum oxide decomposes to gamma-aluminum oxide at approximately 600 K. Because of these instabilities, these hydrous oxides are modeled as their respective oxides and water. The 48.75 t of iron(III) hydroxide becomes 36.4 t of Fe_2O_3 and 12.3 t of water. The 48.75 t of hydrous aluminum oxide becomes 31.9 t of Al_2O_3 and 16.8 t of water.

Pit 9 contains 13.13 m³ of sodium and sodium compounds. Numerous tests involving sodium-cooled reactors and sodium-potassium (NaK) cooled reactors have been performed at the INEL; much of the NaK was hydrolyzed with water to form hydroxides, for example. Since there is little information regarding the subject material, it is modeled as sodium hydroxide. Sodium hydroxide has a density of 2.13 t/m³. This yields 27.97 t (0.35 t mol) of sodium hydroxide, which is equivalent to 21.68 t (0.36 t mol) of sodium oxide and 6.29 t (0.35 t mol) of water.

There are 12.68 m³ of miscellaneous solutions, identified as 10% solutions of sodium and potassium nitrates. In the absence of other data, the assumption is made that these are mixed; and each t of solution contains sodium and potassium nitrates in equal amounts, i.e., a 5% solution of each compound. The density of these 5% solutions is 1.03 t/m³. This yields 13.06 t of solution, containing 0.65 t of each nitrate and 11.67 t of water. As noted above for the potassium and sodium nitrates, these nitrates can be expected to decompose on heating to yield oxygen and nonreactive nitrite salts. The potassium nitrate would yield 0.44 t (0.0052 t mol) of potassium nitrite, equivalent to 0.22 t (0.0052 t mol) of sodium hydroxide and 0.22 t of oxygen. The sodium nitrate would yield 0.41 t (0.0059 t mol) of sodium nitrite, equivalent to 0.24 t (0.0059 t mol) of sodium hydroxide and 0.24 t of oxygen for a total of 0.46 t of oxygen from these solutions.

Pit 9 contains 4.75 m³ of acids, identified only as HCl, HF, etc. For purposes of this analysis, the "acid" is considered to be hydrochloric acid. Concentrated hydrochloric acid has a specific gravity of 1.19 (1.19 t/m³) and a concentration of approximately 12.1 N (.4412 kg/L or 0.4412 t/m³) resulting in 2.10 t (0.0133 t mol) of hydrogen chloride [in the model, this hydrochloric acid is made equivalent to 2.05 t (.00666 t mol) of carbon tetrachloride and 0.48 t (0.0266 t mol) of water].

There are 3.25 m³ of caustic compounds (listed as NaOH, etc.) in Pit 9. For this analysis, these materials are considered solid NaOH. Sodium hydroxide has distinctly different slag-making properties compared to sodium carbonate, for example.^{29,30} Sodium hydroxide has a density of 2.13 t/m³, yielding 6.9 t (0.086 t mol) of NaOH, equivalent to 5.35 t (0.086 t mol) of sodium hydroxide and 0.24 t of water.

Pit 9 contains 187.7 t of paper, rags, and wood. These are cellulose materials, being polymers of glucose. These are more appropriately modeled with the other organic materials, such as oils, alcohols, and chlorinated solvents, noted below.

There are 72.8 t of concrete and asphalt in Pit 9. Without other identification, these are modeled as half concrete and half asphalt from sources such as facility decontamination and decommissioning. Concrete used at the INEL is typically 15.8% cement, 7.9% water, 47.4% rock, and 29.0% sand and has a density of 2.2 to 2.3 t/m³. This amounts to 5.7 t of Portland cement (in addition to that identified below), 2.9 t of water, 17.2 t of rock, and 10.5 t of sand. Concrete formulated by vendors in Idaho Falls consists of quartz and other high silica materials for the aggregate, while concrete formulated at the Central Facilities Area will frequently contain large amounts of basalt and calcareous materials in the aggregate. This aggregate is assumed to be 27.7 t of silica, SiO₂ for modeling purposes. The 5.7 t of Portland cement has a nominal stoichiometry and (amount) of K₂O 0.51% (0.03 t), Na₂O 0.21% (0.01 t), Al₂O₃ 5.6% (0.32 t), CaO 64.2% (3.66 t), MgO 3.7% (0.21 t), Fe₂O₃ 2.4% (0.14 t), SiO₂ 20.7% (1.18 t), TiO₂ 0.23% (0.01 t), SO₃ 1.6% (0.09 t) and undefined other 0.85% (0.05 t). The 0.03 t (0.00032 t mol) of potassium oxide is modeled as 0.00032 t mol (0.02 t) of sodium oxide. The 0.21 t (0.0052 t mol) of magnesium oxide is modeled as 0.052 t mol (0.29 t) of calcium oxide. The contributions of titanium oxide and sulfur trioxide are not considered in the model.

The asphalt is typically 5 to 6% asphalt oil and aggregate. Asphalt oil is typically 30 to 40% petroleum distillate, with the remainder being high carbon solids. This yields 0.73 t of petroleum distillates having about 0.62 t of carbon and 0.11 t of hydrogen. The high carbon solids were

estimated to be 95% carbon and 5% hydrogen, yielding an additional 1.0 t of carbon and 0.06 t of hydrogen. The quantity of hydrogen is small enough to neglect in the model. The aggregate is similar to the concrete aggregate, but it is washed to remove fines. This is modeled as silica, yielding 34.6 t of silica, SiO_2 .

There are 7.2 t of glass in Pit 9. Without additional information, this is modeled as window glass rather than borosilicate laboratory glassware. Window glass varies considerably in composition, principally in silica, alumina, and soda concentrations. For the present purposes, a nominal stoichiometry and (amount) of 72% SiO_2 (5.2 t), 1.3% Al_2O_3 (0.1 t), 8.2% CaO (0.6 t), 3.5% MgO (0.25 t), 14.3% Na_2O (1.0 t), 0.3% K_2O (0.021 t), and 0.3% SO_3 (0.02 t), was used to model the glass. The 0.25 t (0.0063 t mol) of magnesium oxide is equivalent to 0.35 t (0.0063 t mol) of calcium oxide. The 0.021 t (0.00023 t mol) of potassium oxide is equivalent to 0.014 t (0.00023 t mol) of sodium oxide. The sulfur trioxide is not considered in the model.

Pit 9 contains 16.4 t of graphite. This is modeled as carbon in the present analysis.

Most of the wastes in Pit 9 are contained in 55-gal steel drums. The iron in these drums could be considered as a reducing agent. However, above approximately 900 K, the oxides of carbon are more stable than those of iron; and carbon and carbon monoxide are better reducing agents than metallic iron. The iron will melt, but it will not be a significant reactant in the ISV melt. However, it may be a significant solvent for some molten constituents. There are 326.5 t of carbon steel in Pit 9. This is assumed to be similar to AISI-type 1020 carbon steel, e.g., ASTM A 285, having a nominal composition and (amount) of iron 99.2% (323.9 t), carbon 0.2% (0.7 t), manganese 0.45% (1.4 t, equivalent to 1.5 t of nickel), and silicon 0.25% (0.8 t).

Pit 9 contains 309.7 t of stainless steel. This is assumed to be similar to AISI-type 304 stainless steel, e.g., ASTM A 240, having a nominal composition and (amount) of iron 72% (219.9 t), chromium 18.5% (57.3 t), nickel 9.5% (29.4 t), and carbon 0.08% (0.3 t). For the analytical model, the 57.3 t (1.102 t mol) of chromium is equivalent to 64.7 t (1.102 t mol) of metallic nickel.

Soil and Portland Cement

The soil and Portland cement are listed under "Oxide Compositions of Materials in Pit 9."

During the last glaciation, large amounts of rock were ground into powder by the abrasion of rocks trapped in the moving glacier. Locally, these powders were carried from glacier outflow by water action then deposited onto the Snake River plain by a combination of water and wind action. These sediments are referred to as loess.²⁹ The loess has also been mobilized by water and wind action so that the deposits now have both windblown and waterborne characteristics. There is evidence of soil sediments between various lava formations at the INEL.³⁰

Weathering of the loess has resulted in changes in the composition of these sediments such that the uppermost layers may have very different compositions from lower layers. In particular, the loess constituents that weather to form calcium carbonate, calcite, and CaCO_3 have greatly diminished since they were laid in place. This leaching action and subsequent disequilibrium has resulted in deposition of calcite in the underlying basalt formations, giving the basalt a coating of

white calcite. These formations are seen, for example, in some road cuts between Idaho Falls and the INEL Site. The soils of interest for the calculations reported here were taken from Pit 9 of the SDA. There are 24,531 t of soil in Pit 9. This has a nominal stoichiometry and (amount) of K_2O 2.52% (618.2 t), Na_2O 1.33% (326.3 t), Al_2O_3 11.40% (2,796.5 t), $CaO \& MgO$ 9.97% (2,445.7 t), Fe_2O_3 4.07% (998.4 t), SiO_2 69.64% (17,083.4 t), and undefined other 1.07% (262.5 t). The 618.2 t (6.56 t mol) of potassium oxide is equivalent to 406.9 t (6.56 t mol) of sodium oxide. These amounts are used in the model.

There are 45.3 t of Portland cement (not defined as concrete) in Pit 9. In addition to the cement used to formulate concrete, Portland cement was used to fill some drums of waste. The cement has a nominal stoichiometry and (amount) of K_2O 0.51% (0.2 t), Na_2O 0.21% (0.1 t), Al_2O_3 5.6% (2.5 t), CaO 64.2% (29.1 t), MgO 3.7% (1.7 t), Fe_2O_3 2.4% (1.1 t), SiO_2 20.7% (9.4 t), TiO_2 0.23% (0.1 t), SO_3 1.6% (0.7 t), and undefined other 0.85% (0.4 t). The 0.2 t (0.0031 t mol) of potassium oxide is equivalent to 0.19 t (0.0031 t mol) of sodium oxide. The 1.7 t (0.042 t mol) of magnesium oxide is equivalent to 2.36 t (0.042 t mol) of calcium oxide. The sulfur trioxide and titania are insignificant in the present analysis. The other amounts are used in the model.

The inorganic components, paper, rags, and wood in Pit 9 are summarized in Table 1. These data were used for modeling the equilibrium concentrations of materials in the ISV melt.

Organic Materials in Pit 9

The paper, rags, and wood in Pit 9, listed under Other Miscellaneous Chemicals, are modeled here as carbon, carbon dioxide, and water. There are a number of other organic materials in the wastes, primarily oils, solvents, and alcohol, which are modeled in this section. The overall composition of the organic materials in Pit 9 is given in Table 2. This includes the paper, rags, and wood. These data were used to estimate the equilibrium concentration of materials in the ISV melt.

Table 2. Components equivalent to organic chemicals in Pit 9 for modeling purposes.

Species	Tonnes
C	14.877
CH ₄	19.129
CCl ₄	30.984
H ₂ O	5.640

The 187.7 t of paper, rags, and wood in Pit 9 are cellulose materials, and cellulose is a polymer of glucose. The polymer has a nominal composition of $[C_6H_9O_6]_n$ and is about 40.7% C, 54.2% O, and 5.1% H. Cellulose decomposes at temperatures below those of the molten mass from the ISV process. According to the following stoichiometry:

the decomposition products are carbon dioxide gas, 35.0 t; water (steam), 85.9 t; solid carbon, 66.8 t. These values are used in the model.

There are several chlorinated hydrocarbon solvents in Pit 9. For this evaluation, these were modeled as carbon, methane, and carbon tetrachloride. There are 13.92 m³ of carbon tetrachloride in the pit, yielding 22.2 t of carbon tetrachloride. There are 2.85 m³ of trichloroethylene in the pit, yielding an equivalent of 5.50 t of carbon tetrachloride, 0.19 t of methane, and 0.57 t of carbon. There are 4.28 t of trichloroethanes in the pit, yielding an equivalent of 3.30 t of carbon tetrachloride, 0.34 t of methane (equivalent to 0.51 t of carbon and 0.765 t of water), and 0.17 t of carbon.

The alcohols in Pit 9 were probably methanol, ethanol, and 2-propanol; for the model it was assumed to be ethanol, C₂H₆O. The ethanol was assumed to decompose into carbon, methane, and water. There were 4.87 m³ of ethanol in the pit, yielding 1.31 t of methane (equivalent to 2.0 t of carbon and 2.95 t of water), 0.98 t of carbon, and 0.98 t of water.

There are gasoline and oil in Pit 9. These were modeled as saturated hydrocarbons having 12 carbon atoms in the chain. These have a nominal composition of 85% carbon and 15% hydrogen. They were assumed to decompose into carbon and methane during melting. There are 22.24 m³ of Texaco Regal oils, equivalent to 7.44 t of carbon and 12.4 t of methane. There are 9.00 m³ of used oil and 0.19 m³ of gasoline. These were modeled as 9.19 m³ of oil, yielding 2.87 t of carbon and 4.31 t of methane.

Radionuclides in Pit 9

There are a number of radionuclides in Pit 9. However, only uranium and plutonium have high enough concentrations to be of concern in the present analysis. The uranium amounts to 11.76 t, including unirradiated fuel. The uranium is modeled as UO₂. The plutonium amounts to 0.016 t of PuO₂. There are 3.59 t of other radioactive wastes in Pit 9, but these are probably fission products and cannot be modeled without more data.

The radioisotopes in Pit 9 are summarized in Table 3. These data were used to estimate the equilibrium concentration of materials in the ISV melt.

For purposes of the present model, the "other" radionuclides are considered to be fission products such as ⁹⁰Sr and ¹³⁷Cs. These are considered to be strontium compounds, which are chemically similar to calcium compounds. The 3.59 t of "other" radioisotopes is equivalent to 0.040 t mol of strontium oxide or equivalent to 0.040 t mol of calcium oxide or 2.233 t of CaO.

Table 3. Radioisotopes in Pit 9 for modeling purposes.

Species	Tonnes
PuO ₂	0.016
UO ₂	11.76
Other	3.59

One aspect of the composition not addressed above is the relative accuracy of the data. For the uranium and plutonium oxides, the data are probably accurate to approximately 1%. However, such accuracy should not be assumed throughout the entire Pit 9 data base. For example, the soil (24,531 t) is probably not known to the nearest 1%, or 245 t; in fact, there is 1.07% of "undefined other" in the soil for 262.5 t. Thus, the total of all of the assumptions regarding composition of the Pit 9 materials, e.g., hydrous oxides, are far less than the "undefined other" in the soil. In the radioisotopes, there are 3.59 t of "unidentified" radioisotopes, probably fission products such as cobalt. Modeling these as iron oxide, Fe₂O₃, is probably a reasonable modeling assumption. Further, the round-off error from three figures behind the decimal point to one or two is also within the probable error of the overall material balance in the pit.

The species and quantities noted in Table 4 were used as input for the STEPSOL computer code to estimate the equilibrium composition of the melt and its gas phase.

Table 4. Input data for STEPSOL model of Pit 9.

Species	Formula	Tonnes
Carbon	C	89.84
Oxygen	O ₂	178.71
Water	H ₂ O	49.42
Carbon dioxide	CO ₂	18.4
Carbon tetrachloride	CCl ₄	15.84
Iron oxide, hematite	Fe ₂ O ₃	1,168.9
Iron	Fe	543.8
Nickel + chromium and manganese + chromium oxide	Ni	90.26
Calcium oxide + magnesium oxide + beryllia + barite + zirconia + fission products	CaO	2,618.41
Sodium oxide + potassium oxide + lithium oxide + sodium and potassium nitrates	Na ₂ O	909.84
Aluminum oxide	Al ₂ O ₃	2,806.9
Silicon dioxide	SiO ₂	17,173.8
Uranium oxide	UO ₂	11.76
Plutonium oxide	PuO ₂	0.016

MODEL

The model developed should be applicable to in situ and ex situ vitrification, to incineration, and to a melter. The melter in question would be at the outlet of an incinerator and would melt the solids and thereby reduce the volume.

Temperature

Temperatures ranged from 800 to 2,400 K (527°C/980.6°F to 2,127°C/3,861.6°F). This covers the range of interest for hazardous waste incineration. The calculations were made in 100 K increments. These are equilibrium calculations, and there is no differentiation between the solid and gas phases.

Pressure

Pressure input to STEPSOL is in atmospheres rather than the SI unit of pascals. The pressure was set at one atmosphere, 1.013×10^5 pascals.

Composition of Input Waste

Table 4 provides the input composition for the model. STEPSOL is limited to 14 constituents in the input. The model assumes that no fuel or air is admitted to the system, i.e., the melting is done by joule heating or is heated by an external energy source that does not add to the melt composition.

There are insufficient options in the input of STEPSOL to include the toxic and high vapor pressure metals (HVPMS). However, all of the HVPMS except barium should be reducible by the carbon or aluminum in Pit 9. On this basis, a separate analysis of the HVPMS was made. In this separate analysis, the vapor pressures of the metals were estimated as a function of temperature. The algorithm used is the logarithm of the reported vapor pressure plotted versus the reciprocal of the absolute temperature, yielding straight lines, shown in Figure 14 and Figure 15. Some metals, such as mercury, would be completely vaporized at low temperatures. In other cases, the partial pressure of each of the metals was estimated, and a summation of the partial pressure of the HVPMS was made. This was then compared with the gas phase composition at a pressure of one atmosphere. An estimate of the compositions of the HVPMS and the gas phase was then made at a total pressure of one atmosphere.

Composition of Output Streams

Table 5 is a list of the constituents in the output gas stream. The model assumes that all gases remain in the system and are in thermodynamic equilibrium with the slag and metal phases. For purposes of the model, it was assumed that any plutonium or uranium oxyhydroxides would be in the gas phase. This may be an unwarranted assumption. The HVPMS are listed in this table.

Figure 14. Vapor pressure of zinc and selected higher vapor pressure metals as a function of temperature.

Figure 15. Vapor pressure of zinc and selected lower vapor pressure metals as a function of temperature.

Table 5. Constituents of the output gas phase.

Species	Formula
Elements	
Hydrogen	H ₂
Chlorine	Cl ₂
Oxygen	O ₂
Oxides	
Water	H ₂ O
Carbon monoxide	CO
Carbon dioxide	CO ₂
Chlorides	
Aluminum chloride	AlCl ₃ (g)
Carbon tetrachloride	CCl ₄
Hydrogen chloride	HCl
Iron (II) chloride	FeCl ₂ (g)
Iron (III) chloride	FeCl ₃ (g)
Other	
Methane	CH ₄
Plutonium oxyhydroxide	PuO ₂ (OH) ₂
Uranium oxyhydroxide	UO ₂ (OH) ₂
Toxic and high vapor pressure metals	
Antimony	Sb
Arsenic	As
Barium	Ba
Bismuth	Bi
Cadmium	Cd
Chromium	Cr
Potassium	K
Lead	Pb
Magnesium	Mg
Mercury	Hg
Selenium	Se
Tellurium	Te
Silver	Ag
Sodium	Na
Zinc	Zn

Table 6 lists the constituents of the slag phase. Some of the constituents melt before the highest temperature of the system model is reached. Upon melting, these constituents lose their identity. In some cases, the available thermodynamic data are limited. Further, the liquid phase may provide a solvent for dissolving other constituents of the slag or metal phases. No account is taken of these melting phases. Plutonium and uranium compounds are listed in Table 7.

Table 8 lists the constituents of the metal phase and their melting temperatures. All of these metals melt before the highest temperature of the system model is reached. Molten metals may be solvents for some of the slag or gas phase constituents. However, when freezing occurs, the gases would be exsolved; and most of the slag constituents would be in the slag phase. In this respect, the metal and slag phases act in the same manner as a solvent extraction system. Table 5 also lists the HVPMS considered in the present analysis.

Table 6. Slag phase species that would be generated from the materials in Pit 9. Plutonium and uranium compounds are not included even though they may be in the slag phase.

Species	Formula
Chlorides	
Aluminum chloride	AlCl_3
Calcium chloride	CaCl_2
Iron (II) chloride	FeCl_2
Iron (III) chloride	FeCl_3
Sodium chloride	NaCl
Oxides	
Alumina	Al_2O_3
Silica	SiO_2
Wuestite	FeO
Magnetite	Fe_3O_4
Hematite	Fe_2O_3
Nickel oxide	NiO
Silicates	
Calcium olivine	Ca_2SiO_4
Anorthite	$\text{CaAl}_2\text{Si}_2\text{O}_8$
Grossular	$\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{12}$
Wustite	Fe_2SiO_4
Sodium silicate	Na_2SiO_5
High albite	$\text{NaAlSi}_3\text{O}_8$
Jadeite	$\text{NaAlSi}_2\text{O}_6$

Table 7. Uranium and plutonium species that would be generated from the materials in Pit 9. Some species will be in the gas phase, some in the slag phase, and others in the metal phase.

Species	Formula
Plutonium	Pu
Plutonium dioxide	PuO ₂
Plutonium monoxide	PuO
Plutonium oxyhydroxide	PuO ₂ (OH) ₂
Plutonium trichloride	PuCl ₃
Uranium	U
Uranium dioxide	UO ₂
Uranium trioxide	UO ₃
Uranium trichloride	UCl ₃
Uranium tetrachloride	UCl ₄
Uranium oxyhydroxide	UO ₂ (OH) ₂
Sodium uranate	Na ₂ UO ₄
Sodium uranium oxide	Na ₃ UO ₄

Table 8. Metallic phase species that would be generated from the materials in Pit 9.

Species	Melting point	Kelvin
Aluminum	Al	933
Carbon	C	4,100
Iron	Fe	1,809
Nickel	Ni	1,726
Plutonium	Pu	910
Silicon	Si	1,685
Uranium	U	1,405

RESULTS AND DISCUSSION

As noted earlier, thermodynamic relationships between the elements and their compounds may be presented graphically. These graphs are termed Ellingham diagrams and are curves of Gibbs energy of formation as a function of absolute temperature. When mixtures of reacting elements and compounds are encountered, it becomes necessary to estimate the thermodynamic relationships between the various components. For example, in the carbon-hydrogen-oxygen system, it is necessary to consider methane, in addition to the elements and their oxides.

The difference between two curves on an Ellingham diagram is a measure of the thermodynamic tendency towards reaction. Simply finding the difference in the Gibbs energy between two compounds is only part of the solution to the equilibrium thermodynamics problem, e.g., it does not estimate the relative abundance of the reactants and products in an equilibrium mixture after reaction. This is estimated by Gibbs energy minimization calculations. The major problem of the present study is to make these calculations using the materials in Pit 9.

STEPSOL was used in estimating the relative stability of the Pit 9 materials to find the minimum Gibbs energy that satisfied the stoichiometry of the system. However, this program is limited to 14 species that can be specified for the input of a problem. For this reason, a number of simplifying assumptions were made concerning the composition of the materials in Pit 9. Table 4 lists the species and the amounts used in the present analysis.

Table 9 provides the amounts of gas, slag, and metal phases from the Pit 9 materials as a function of temperature. The data show that the mass of the gas phase increases by a factor of more than 10 between 800 and 2,400 K. This would be expected because the stability of slag phase compounds decreases while the stability of carbon monoxide increases with temperature. The Gibbs energy of formation for carbon dioxide shows little change with temperature.

Table 10 gives the amounts of uranium and plutonium and their oxyhydroxides and chlorides that would be generated from the materials in Pit 9. Of particular concern are the uranium and plutonium oxyhydroxides, because these were thought to have very high vapor pressures at high temperatures and pressures. Under the conditions of incineration, melting, or ISV of Pit 9, the pressure would be about one atmosphere. The amount of plutonium oxyhydroxide that would be in equilibrium with the slag would be 3.4 μg at 2,000 K. The uranium oxyhydroxide could be as much as 19 mg at 2,000 K and 50 g at 2,400 K. Metal chlorides tend to have high vapor pressures, which increase with temperature. The largest amount of plutonium chloride, PuCl_3 , that would be formed is less than 1.3 mg at 2,000 K. The largest combined amounts of uranium trichloride and uranium tetrachloride that would be formed are less than 1 μg at 2,000 K, respectively. These compounds may have high vapor pressures and could, therefore, be found in the gas phase. However, vapor pressure data as a function of temperature are not available for making predictions of the amount of each of the compounds that might be found in the vapor phase. Further, the thermodynamic activity of the compounds in the slag phase is unknown. These data are required for estimation of the pressure of the compounds in the vapor phase that would be in equilibrium with the same compounds in the slag phase using Henry's law. A risk analysis with respect to allowable plutonium and uranium releases is beyond the scope of the present task.

Table 9. Calculated masses of gas, slag, and metal phases that would be generated from materials in Pit 9. Masses are given in metric tons (tonnes) and temperatures are in Kelvin.

Phase	800	1,000	1,200	1,400	1,600	1,800	2,000	2,200	2,400
Gas	281	354	299	294	296	296	298	300	301
Slag	25300	25300	25400	25400	25400	25400	25400	25400	25400
Metal	86.7	58.9	21.7	0.0	0.0	0.0	0.0	0.0	0.0

Table 10. Calculated masses of uranium and plutonium species that would be generated from materials in Pit 9. Masses are given in metric tons (tonnes) and temperatures are in Kelvin.

Species	800	1,000	1,200	1,400	1,600	1,800	2,000	2,200	2,400
Pu	1.9E-37	1.5E-29	2.4E-24	0.0	0.0	0.0	0.0	0.0	0.0
PuO ₂	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02	1.6E-02
PuO	3.3E-16	1.4E-12	1.4E-10	3.5E-09	3.5E-08	4.4E-04	8.9E-07	2.9E-06	7.7E-06
PuO ₂ (OH) ₂	8.6E-29	5.7E-24	3.6E-20	2.2E-17	3.2E-15	1.5E-13	3.4E-12	4.3E-11	3.5E-10
PCl ₃	2.3E-21	1.1E-17	9.5E-16	1.9E-14	1.5E-13	5.9E-13	1.3E-12	1.7E-12	1.6E-12
U	2.7E-37	4.1E-29	1.1E-24	0.0	0.0	0.0	0.0	0.0	0.0
UO ₂	11.76	11.76	11.76	11.76	11.76	11.76	11.76	11.76	11.76
UO ₃	7.7E-08	6.1E-07	6.2E-06	3.5E-05	1.5E-04	4.4E-06	1.1E-03	2.2E-03	4.0E-03
UCl ₃	4.2E-27	1.0E-21	1.2E-18	1.6E-16	5.3E-15	6.1E-14	3.8E-13	8.4E-15	1.5E-12
UCl ₄	9.8E-33	1.0E-26	4.1E-23	1.2E-20	8.1E-19	1.4E-17	9.2E-19	2.8E-18	5.0E-16
UO ₂ (OH) ₂	5.4E-18	8.3E-15	4.1E-12	3.9E-10	1.4E-08	2.7E-07	1.9E-08	1.1E-05	5.0E-05
Na ₂ UO ₄	5.9E-10	1.2E-12	6.8E-09	2.7E-08	8.1E-08	1.8E-07	3.3E-07	5.4E-07	7.8E-07
Na ₃ UO ₄	5.7E-15	6.8E-14	9.0E-13	5.9E-12	2.3E-11	5.8E-11	1.1E-10	1.8E-10	2.5E-10

Table 11 shows the calculated masses of gas phase species that would be generated from the materials in Pit 9. Plutonium and uranium compounds are not included. The system is very reducing as seen by the amounts of hydrogen and oxygen in the gas phase. The methane concentration decreases with increasing temperature while the carbon monoxide concentration increases with temperature. These trends are a reflection of their Gibbs energy of formation as a function of temperature.

As noted previously, the chlorinated hydrocarbons in Pit 9 were modeled as carbon tetrachloride. The calculated amount of carbon tetrachloride would be less than 1 μg at any temperature. The carbon tetrachloride decomposes to form hydrogen chloride. Hydrogen chloride is the second most abundant material in the gas phase at temperatures reaching 2,400 K. This indicates that chlorinated hydrocarbons should not be a problem if they can be retained in the hot zone long enough to react with other materials. (Upon cooling, a portion of the hydrogen chloride would combine with the water to form highly corrosive hydrochloric acid.)

Table 12 gives the calculated masses of metallic phase species that would be generated from the materials in Pit 9. Nickel, chromium, manganese, and molybdenum are combined as nickel. Iron is the most abundant component of the metals in the system and amounts to 600 to 1,200 t. Nickel is the next most abundant metal, being about 90 t. Carbon was included with the metals because of its tendency to form alloys with transition metals. The amount of carbon varies from approximately 0.11 t at 2,400 K to 94.7 t at 1,000 K. This exceeds that which could be dissolved into the metals, and a separate carbon phase would be expected to form upon cooling. Note that the amounts of metallic plutonium and uranium are small.

Table 13 gives the calculated masses of chloride, oxide, and silicate species in the slag phase that would be generated from the materials in Pit 9. Plutonium and uranium compounds are not included. Sodium chloride is the most abundant of the chlorides, and its mass decreases from 24.1 t at 800 K to 7.7 t at 2,400 K. The mass of iron(II) chloride is seen to increase from less than 1 g at 800 K to 2 kg at 2,400 K. The amount of calcium chloride increases from 32 g to 40 kg between 800 K and 1,000 K then decreases to 7.7 t at 2,400 K. Iron(III) chloride and aluminum chloride are present in trace amounts. Calcium, iron(II), and sodium chloride have high vapor pressures and would be expected to be present in the gas phase. However, their thermodynamic solution activities in the slag are unknown, and their vapor pressures cannot be estimated without these data. Aluminum chloride forms a dimer, Al_2Cl_6 , in the vapor phase. However, the amount of aluminum chloride formed from Pit 9 materials is less than a gram at any temperature. Similarly, iron(III) chloride forms a dimer, Fe_2Cl_6 , in the gas phase. However, only about 0.8 g would be formed from Pit 9 materials.

Of the oxides, silica (SiO_2), wuestite (FeO), and alumina (Al_2O_3) are the most abundant in the slag. Silica accounts for approximately 13,000 t of the slag phase; alumina is about 2.5 t. Wuestite, FeO , is present in moderate amounts, but accounts for less than 1 t; the other iron oxides, magnetite, Fe_3O_4 , and hematite, Fe_2O_3 , have very low concentrations in the slag. This reflects the reducing nature of the system.

Calcium olivine, Ca_2SiO_4 , fayalite, Fe_2SiO_4 , and sodium silicate, $\text{Na}_2\text{Si}_2\text{O}_5$, are the most abundant of the simple silicates, amounting to about 3,200 t of the slag at 2,400 K. The amounts

Table 11. Calculated masses of gas phase species that would be generated from materials in Pit 9. Plutonium and uranium compounds are not included. Masses are given in metric tons (tonnes) and temperatures are in Kelvin.

Species	800	1,000	1,200	1,400	1,600	1,800	2,000	2,200	2,400
Elements									
H ₂	2.1	4.3	4.1	3.8	3.4	3.2	3.0	2.9	2.8
Cl ₂	2.3E-22	5.0E-17	2.5E-13	1.0E-10	9.5E-09	2.7E-07	3.1E-06	1.8E-05	6.7E-05
O ₂	3.4E-24	1.4E-18	3.2E-14	5.6E-11	1.9E-08	1.7E-07	6.4E-05	1.2E-03	1.4E-02
Oxides									
H ₂ O	40.2	24.9	26.6	28.8	31.8	33.7	34.8	35.5	36.0
CO	16.0	112	146	160	165	169	172	174	175
CO ₂	221	164	123	100	92.7	87.0	82.7	79.5	77.2
Chlorides									
HCl	2.0E-04	8.0E-03	0.084	0.043	1.4	3.3	5.7	8.1	9.8
FeCl ₂ (g)	5.9E-13	1.2E-08	4.3E-06	2.4E-04	4.3E-03	0.033	0.13	0.32	0.56
FeCl ₃ (g)	3.5E-21	1.0E-15	3.0E-12	7.3E-10	4.0E-08	6.9E-07	4.6E-06	1.6E-05	3.3E-05
AlCl ₃ (g)	7.9E-28	3.0E-20	1.1E-15	1.0E-09	3.1E-10	1.4E-08	2.1E-07	1.4E-06	5.3E-06
CCl ₄	1.3E-47	1.0E-38	3.0E-33	1.6E-12	1.3E-26	1.4E-24	3.9E-23	3.9E-22	1.9E-21
Other									
CH ₄	19	0.13	1.3E-03	3.7E-05	1.9E-06	1.8E-07	2.2E-05	5.7E-09	1.5E-09

Table 12. Calculated masses of metallic phase species that would be generated from materials in Pit 9. Plutonium and uranium compounds are not included. Masses are given in metric tons (tonnes) and temperatures are in Kelvin.

Species	800	1,000	1,200	1,400	1,600	1,800	2,000	2,200	2,400
Fe	0.55	1.5	0.63	0.0	0.0	0.0	0.0	0.0	0.0
Ni	58.7	54.2	21.0	0.0	0.0	0.0	0.0	0.0	0.0
C	27.5	3.2	0.073	0.0	0.0	0.0	0.0	0.0	0.0
Si	5.3E-23	5.0E-17	4.4E-14	0.0	0.0	0.0	0.0	0.0	0.0
Al	6.9E-28	5.0E-21	2.2E-17	0.0	0.0	0.0	0.0	0.0	0.0
U	2.6E-37	4.1E-29	1.1E-24	0.0	0.0	0.0	0.0	0.0	0.0
Pu	1.9E-37	1.5E-29	2.4E-25	0.0	0.0	0.0	0.0	0.0	0.0

Table 13. Calculated masses of slag phase species that would be generated from materials in Pit 9. Plutonium and uranium compounds are not included. Masses are given in metric tons (tonnes) and temperatures are in Kelvin.

Species	800	1,000	1,200	1,400	1,600	1,800	2,000	2,200	2,400
Chlorides									
CaCl ₂	3.2E-05	0.0012	0.0079	0.023	0.046	0.065	0.068	0.050	0.040
FeCl ₂	1.5E-07	8.9E-06	8.3E-05	3.6E-04	0.001	0.0018	0.0024	0.0024	0.0020
NaCl	24.1	24.1	24.9	23.4	21.7	18.7	14.7	10.8	7.7
FeCl ₃	4.8E-19	9.5E-15	4.9E-12	3.7E-10	8.2E-09	6.9E-08	2.6E-07	5.5E-07	8.1E-07
AlCl ₃	5.8E-27	2.1E-20	1.9E-16	9.9E-14	9.1E-12	2.4E-10	2.2E-09	1.0E-08	2.8E-08
Oxides									
SiO ₂	9151	9239	9318	9375	9420	9459	9495	9533	9574
FeO	1038	1306	1459	1544	1594	1627	1649	1665	1676
Al ₂ O ₃	1.9	14.9	38.1	65.1	96.6	133	175	221	270
NiO	40.2	45.8	88.1	115	115	115	115	115	115
Fe ₃ O ₄	9.1	1.4	0.98	0.87	0.92	1.0	1.1	1.2	1.4
Fe ₂ O ₃	3.4	0.9	0.59	0.58	0.65	0.71	0.78	0.85	0.92
Silicates									
CaAl ₂ Si ₂ O ₈	352	1902	3108	3385	3376	3291	3176	3045	2906
Ca ₃ Al ₂ Si ₂ O ₁₂	5444	2805	745	181	54.9	20.6	9.2	4.5	2.5
Na ₂ Si ₂ O ₅	56.2	26.5	25.4	27.4	29.1	30.3	31.0	31.5	31.8
Fe ₂ SiO ₄	994	627	412	293	221	175	143	120	103
Ca ₂ SiO ₄	788	1823	2630	2869	2945	2990	3032	3075	3119
NaAlSi ₃ O ₈	7319	7437	7458	7465	7476	7490	7509	7528	7543
NaAlSi ₂ O ₆	352	58.1	45.0	37.0	31.6	27.9	25.2	21.2	21.6

increase with increasing temperature. Anorthite, $\text{CaAl}_2\text{Si}_2\text{O}_8$, is the most abundant of the silicates and accounts for 3,385 t at 1,400 K. The amounts of anorthite decrease at lower and at higher temperatures. Grossular, $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, is the next most abundant of the silicates and accounts for 5,444 t at 800 K. The amount of grossular decreases with increasing temperature. Other complex silicates, such as jadeite, $\text{NaAl}(\text{SiO}_3)_2$, and albite, $\text{NaAlSi}_3\text{O}_8$, have very low concentrations at low temperatures, but could be as much as 3.4 t at 2,400 K.

CONCLUSIONS

STEPSOL is limited to 14 input species, which limits the accuracy of the resulting estimates of phase composition.

There are about 16 kg of plutonium oxide in Pit 9. The amount of this plutonium present in the gas phase may be represented by the mass of plutonium oxyhydroxide, $\text{PuO}_2(\text{OH})_2$. This varies from less than 10^{-28} g at 800 K to less than 10^{-9} g at 2,400 K. There are 11.76 t of uranium oxide in Pit 9. The amount of this uranium that could be in the gas phase may be represented by the calculated mass of uranium oxyhydroxide, $\text{UO}_2(\text{OH})_2$. This varies from less than 10^{-17} g at 800 K to 50 g at 2,400 K. A risk analysis for these compounds was beyond the scope of this task and was not made.

The calculations show that the system is reducing but becomes less so with increasing temperature. Reference to Figure 3 shows that the iron-oxygen system is complex with respect to stable species. Above approximately 1,900 K, only liquids are present. These liquids are solutions of iron and/or iron oxides. In some cases, the liquids are not miscible; and more than one liquid phase may be present. The impact of this on the metals and slags is that partitioning of species between the separate liquid phases will occur. The partition coefficient provides some measure of the thermodynamics. Plutonium, for example, favors the slag phase of iron or stainless steel over the metallic phase by a factor of approximately 10^6 . From this, it may be concluded that any plutonium produced would tend to be rejected from the metallic phase into the slag phase. The amounts of metallic plutonium that would be produced from the 16 kg of plutonium oxide in Pit 9 varies from less than 10^{-31} t at 700 K to less than 10^{-10} t at 2,000 K. There are 11.76 t of uranium oxide in Pit 9. At 700 K, less than 10^{-30} t will be in the metallic phase; and at 2,000 K, less than 10^{-9} t would be in the metallic phase. Except for similar amounts of uranium and plutonium compounds in the gas phase, the remainder would be in the slag phase.

The slag phase is largely silica and silicates, accounting for approximately 21,000 t of the materials in Pit 9. Lesser amounts of iron oxides are produced, and wuestite, FeO , is the most predominant iron oxide. Magnetite, Fe_3O_4 , and hematite, Fe_2O_3 , are present in small amounts. The very small concentrations of higher oxidation-state iron oxides indicate that the slag is reducing. Simple silicates of sodium, calcium, and iron account for approximately 1,800 t of the slag. Complex silicates such as jadeite and albite represent 7,400 to 7,600 t.

One feature of the reducing state of the slag and resulting high concentrations of wuestite, FeO , is the higher leachability of this oxide compared with other iron oxides. This, coupled with the sodium chloride and sodium silicate in the slag could make these slags more susceptible to leaching, compared, for example, to iron-enriched basalt.

Metal chlorides account for small amounts of the slag. Calcium, sodium, and iron(II) and iron(III) chlorides have relatively high vapor pressures. These compounds could be present in the gas phase or the slag phase, depending on temperature and thermodynamic activity.

Thermodynamic solution-activity data are not available for most of the products that could contribute to the pressure of the gases in the system. For this reason, accurate concentration calculations cannot be made.

The high vapor pressure metals could not be analyzed using STEPSOL. However, as a first approximation, all of the mercury should be in the gas phase. Similarly, any arsenic, selenium, or tellurium should be vaporized during incineration or melting.

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