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A Chemical Basis for the Partitioning of Radionuclides in Incinerator Operation

L. L. Burger

January 1995

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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ABSTRACT

Incineration as a method of treating radioactive or mixed waste is attractive because of volume reduction, but may result in high concentrations of some hazardous components. For safety reasons during operation, and because of the environmental impact of the plant, it is important to know how these materials partition between the furnace slay, the flay ash, and the stack emission. The chemistry of about 50 elements is discussed and through consideration of high temperature thermodynamic equilibria, an attempt is made to provide a basis for predicting how various radionuclides and heavy metals behave in a typical incinerator. The chemistry of the individual elements is first considered and a prediction of the most stable chemical species in the typical incinerator atmosphere is made. The treatment emphasizes volatility and the parameters considered are temperature, acidity, oxygen, sulfur, and halogen content, and the presence of several other key non-radioactive elements. A computer model is used to calculate equilibrium concentrations of many species in several systems at temperatures ranging from 500 to 1600°K. It is suggested that deliberate addition of various feed chemicals can have a major impact on the fate of many radionuclides and heavy metals. Several problems concerning limitations and application of the data are considered.

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INTRODUCTION

For waste containing small amounts of radioactivity, rad waste (RW), or mixed waste (MW) containing both radioactive and hazardous wastes (HW), incineration is a logical management candidate because of inherent safety, waste volume reduction, and low costs. However, the large decrease in waste volume achieved by incineration also results in a higher concentration of most of the radionuclides and nonradioactive heavy metals in the ash products. These concentrations impact subsequent treatment and disposal. The various constituents (chemical elements) are not equal in concentration in the various incinerator feed materials, nor are they equal in their contribution to health risks on subsequent handling, or accidental release. Thus, for management of the wastes it is important to know how the nuclides may partition among the primary combustion residues, which may be either an ash or a fused slag; the fine particulates or fly ash that is carried in the burner off-gas and trapped by several different techniques; and/or a final airborne fraction that escapes to the atmosphere.

The objective of this report is to provide an estimate of how different elements of concern may behave in the chemical environment of the incinerator. The study examines the properties of the elements of concern, and employs thermodynamic calculations, to help predict the fate of these RW and MW constituents. Some comparisons are made with reported element behavior.

Many types and configurations of incinerators have been designed and tested (SAI Corp 1991, Travis and Cook 1989, Steverson 1991). The most common employ ordinary air combustion, usually in a two-stage burner. The primary stage operates at about 800 to 1000°C (1073 to 1273 K) and may or may not be oxygen deficient. The second stage is oxidizing, which employs a higher temperature, often 1200 to 1400°C. For a typical device, the off-gas, which contains volatile species as well as particulates, flows to a water quencher and a venturi scrubber or perhaps a cyclone separator. The filter stages that follow may be very simple, such as having the waste stream flow through a bag

filter, or very sophisticated, such as using a series of treatment steps, combining filters, aqueous scrubbers, and electrostatic devices. HEPA filters are occasionally included. Several combinations of these air pollution control devices (APCD) are discussed by Chao (1988).

Of 23 HW incinerators surveyed by Sedman and Esparza (1991), three included HEPA filters as part of the system, seven had no off-gas treatment, and the remaining had various assortments of liquid scrubbers and filters. A decade earlier, a survey found that more than half of the HW incinerators had no air pollution control systems (Opelt 1986).

Rad waste (RW) has been incinerated at nuclear sites for over 40 years. Perkins (1976) gave considerable detail about 50 RW incinerators in use by that date, worldwide. The requirements, along with facility descriptions of incinerators for both low-level and intermediate-level wastes, were described in a recent DOE publication (DOE 1979). Medical incinerators for RW are usually smaller and normally handle only a few short-lived radioisotopes, but they do provide additional data. An example is The University of North Carolina Environmental Control Products incinerator, which was tested with radioactive microspheres (Emery and Watson 1990).

Kyle and Bellinger (1988) compiled a literature review of radioactive partitioning in incinerators of low-level waste with emphasis on institutional waste sources. Of the 17 references, 11 contained partitioning data.

The feeds for RW and MW incinerators may be quite different from each other, and more different yet from wastes burned in an industrial or municipal incinerator. Thus, we may expect the chemical reactions and the products to vary considerably.

Finally, coal-fired power stations and cement kilns provide different dimensions with respect to operating temperatures, feeds, and products. Cement kilns (Mantus 1992), for example, employ a long residence time, a high temperature, and in addition, operate with an alkaline environment, instead

of the acid environment characteristic of HW or RW incinerators which normally burn chlorinated and other acid-forming materials

The elements, including the radionuclides, that are of interest in this study are listed in Table 1. Some are a radiation hazard, some a chemical hazard; others are included because their chemistry is significant in incinerator operation. A typical incinerator is shown in Figure 1 in simplified form.

Radionuclides and other elements of concern can be carried from the combustion zone as particulate matter. The formation of volatile species is a second mechanism. Condensation as the gases cool may produce either new particulates or aerosols. More frequently, however, they adsorb on existing fly-ash particles. The fly-ash may cover a range of particle sizes from less than one μm to several mm.

Until recently the emphasis with regard to HW has been on the destruction and removal of toxic organic materials. However, Waterland et al. (1991) point out that with otherwise properly operated incinerators, the trace metal emissions may pose the largest risk to human health and the environment. Also, the control of solids, i.e., particulate emissions, has been historically one of the most difficult problems (Steverson 1991). Although many nonmetals are included in Table 1, the metals receive the major emphasis of the present paper.

Several investigators have examined the chemistry of the elements of concern as the waste products move through the incinerator system. Greenberg, Zoller, and Gordon (1978) pointed out the possible significance of HCl in incinerator gases and the appreciable volatility of metal halides. Trichon and Feldman (1988) again noted the importance of the metal oxide/metal halide equilibria and noted that different regions of the combustion chamber could show different behavior. Fernandez et al. (1992) recently considered the role

TABLE 1. Elements for Partitioning Evaluation Indicated in **Bold Type**,
with Position on the Periodic Table of the Elements Shown

IA	IIA	----- Transition Elements -----										IIIA	IVA	VA	VIA	VIIA	VIIIA
H (T)																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	IIIB	IVB	VB	VIB	VII B	--- VIII B ---	IB	IIB			Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

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FIGURE 1. Simplified Schematic Diagram of an Incinerator

of halogen reactions in more detail and calculated free energies for several metals for the reaction metal plus O_2 plus HCl. The possible role of other anionic species seems to have received little attention in incinerator studies.

DISCUSSION

For some of the elements in Table 1 we may expect the elemental form to be stable and volatile; for some it is the halides, and for others, the oxides or hydroxides. Although several metals may be in elemental vapor form during the high-temperature destruction process, removal in the off-gas system more likely becomes a problem of trapping metal-containing solids or gases such as oxides or halides. In turn, this introduces the questions of the chemical stability of the several compounds as well as their vapor pressures and water solubilities. Thus, it becomes important to examine the nature of the chemical species that may form in the incinerator as well as the equilibria that may exist among them. Reference data are primarily from the National Bureau of Standards (Wagman 1982, Barin 1989, and Outokumpu Research 1994). Additional data come from Glassner (1958), Ephraïm (1967), Bailar (1973), Dean (1993), and Weast (1976).

GENERAL CONSIDERATIONS

Combustion of typical wastes in an excess of air will result in a gas mixture approximating the composition of Table 2.

TABLE 2. Reference Composition of Combustion Off-gas

Gas	Mole Percent
H ₂ O	15-25
O ₂	6-12
CO ₂	6-10
CO	trace
HCl, HF	0.1-5
NO _x	~1
SO _x	~2
PO _x	~1
N ₂	Remainder

The system as defined by Table 2 is oxidizing, and is acidic. However, the slag or residue after the volatile gases have been driven off could become alkaline, depending on the ratios of the bulk constituent elements. Thus, many metals could remain in the ash as silicates, borates, arsenates, etc. Elements that might be in the metallic state include Au, Hg, and Ag, at least in the absence of halogens. Under special conditions, other elements can be reduced to the metallic state.

Because vapor pressures will be especially important, Tables 3, 4, and 5 give data for several important metals, plus their halides and oxides arranged in descending order of their volatility, in the temperature range of interest. Several oxyhalides, such as CrO_2Cl_2 , are also very volatile.

The very large range of vapor pressures is best seen in Figure 2 which presents the 1000 K data.

However, the most volatile compound of an element is often not the most stable. For example, the compounds SnCl_2 and InCl_3 are very volatile but in the $\text{O}_2 - \text{H}_2\text{O}$ atmosphere the former would be converted to SnO_2 , while the latter would form In_2O_3 , or InF_3 ; these are all nonvolatile. Thus, the free energies of formation of the various compounds are important, but more significant are the free energies as a function of temperature of the actual reactions that may occur. Table 6 compares some ΔG formation data for various salts and oxides at 1000 K. Several very volatile halides, such as ZrCl_4 and TiCl_4 , like those of Sn and In are unstable in the presence of oxygen and water and are not included in the table.

TABLE 3. Calculated Equilibrium Vapor Pressures of Some Stable Metal Halides Pressures in atm

Gaseous Form	P, 1000 K	P, 1500 K
HgCl ₂	9.7E+01	(3.66E+02) ^(a)
SbCl ₃	7.96E+01	1.38E+02
BiCl ₃	2.79E+01	1.96E+02
SnCl ₂	2.19	3.67E+01
FeCl ₃	2.05	2.38E+01
ZnCl ₂	9.31E-01	7.93E+01
PbCl ₂	5.31E-02	8.72
CoCl ₂	8.13E-03	3.55
NiCl ₂	3.41E-03	2.96E+01
CdCl ₂	(3.05E-03)	(8.7)
FeCl ₂	3.03E-02	5.12
MnCl ₂	1.74E-03	9.69E-01
CsF	1.66E-03	7.9E-01
CsI	1.48E-03	5.5E-01
Hg ₂ Cl ₂	1.04E-03	2.24
CsCl	7.02E-04	3.94E-01
Cs ₂ Cl ₂	3.57E-04	1.10E-01
NaCl	6.02E-05	1.11E-01
AgCl	3.55E-05	6.24E-02
Na ₂ Cl ₂	2.2E-05	2.9E-02
CuCl	1.39E-05	3.61E-02
NaF	1.3E-07	2.9E-03
CaCl ₂	2.19E-08	1.58E-03
SrCl ₂	2.03E-09	5.86E-04

(a) Estimated quantities in parentheses.

**TABLE 4. Boiling Points and Vapor Pressures of Metals
Pressure in atm**

Metal Vapor	Boiling Point, K		P, 1000 K	P, 1500 K
Se	598	Se ₂	1.30	(82)
		Se	1.52E-06	9.94E-03
		Se ₂	1.30	8.15E+01
Hg	630			
As ₄	888 sub			
Cs	948		1.69	(50.8)
		Cs ₂	7.18E-02	1.01E-02
K	1038		6.92E-01	15.5
		K ₂	3.55E-02	2.11
Cd	1039		6.41E-01	34.3
Na	1170		1.80E-01	8.64
		Na ₂	2.59E-02	2.42
Zn	1179		1.20E-01	12.0
Te	1273		2.00E-05	3.0E-02
		Te ₂	4.93E-02	2.57
Sr	1685		7.40E-04	2.46E-01
Ra	(1700)			
Ca	1755		2.55E-04	1.63E-01
Sb ^(a)	1891		8.08E-04	6.8E-02
Bi	1934		2.61E-05	3.65E-02
Pb	2019		1.62E-05	2.49E-02
Ba	2167		5.01E-05	2.67E-02
In	2343		9.59E-08	1.20E-03
Mn	2368		2.32E-08	1.09E-03
Ag	2433		6.60E-09	3.64E-04
Ga	2475		6.15E-09	2.51E-04
Sn	2900		8.57E-11	1.17E-05
Al	2790		5.07E-11	1.32E-05
Cu	2843		1.56E-11	9.23E-06
Fe	3132		1.46E-14	1.50E-07
Ni	3200		2.24E-18	5.13E-08

(a) Primarily Sb₄ at 1000 K, Sb₂ at 1500 K

TABLE 5. Boiling Points and Vapor Pressures of Oxides and Hydroxides

Compound	Boiling Point, K	P(atm), 1000 K
RuO_4	373	
P_4O_6	446	
P_4O_{10}	532 sub ^(a)	
Tc_2O_7	584	
SeO_2	602 sub	
TcO_2	(1000) sub	
As_2O_3 (As_4O_6)	738	
Sb_4O_6		1.84-02
CsOH	1263	4.14-02
$\text{Cs}_2(\text{OH})_2$		9.86-03
KOH		1.16-03
$\text{K}_2(\text{OH})_2$		1.51-04
TeO_2		1.48-04
NaOH	1828	3.72-05
Cs_2O		1.7-05
$\text{Na}_2(\text{OH})_2$		1.31-06
PbO		2.6-07
CrO_3		8.2-08

(a) Sub indicates compound sublimes

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FIGURE 2. Vapor Pressures of Metals, Metal Oxides, and Hydroxides, and Metal Halides at 1000 K

TABLE 6. Free Energies of Formation of Important Metal Salts and Oxides

Element	$-\Delta G_f$, kJ at 1000 K				
	2Cl	O	2F	SO ₄	2/3PO ₄
H	202	193	557	441	536
Na	638	281	1048	984	903
	476(g)				
K	683	224	934	2033	1027
Cs	690	212	904	1018	
	570(g)	172(g)	797(g)		
	625(dimer g)	824(dimer g)			
Be	378(g)	510	874	815	
Ca	642	531	1057	1045	1108
Sr	672	494	1047	1066	
Mn	354	312	713	695	
	-	(169)(a)			
Mn(IV)	220	207	568	570	
Fe(II)	187(g)		568(g)		
Fe(III)	197(dimer g)		527(g)		
Co	156(g)	187	547	490	
Ni	153(dimer g)		527(g)		
Cu(I)	178	164	528	525	
Cu(II)	138(g)		398(g)		
Zn	156	149	502	494	
	115(g)		373(g)		
	223	96	435	409	
	161(trimer g)				
	(78)	66	388	396	
	272	248	596	592	700
Y	511	538	979		
Zr(IV)	378	454	326		
Ag	161	dec	295	391	
Cd	242	157	530	544	
Hg	108(g)	dec	245(g)	(270)	
Al	338(g)	454	833	755	896
-	349(dimer g)				
Ga	245(g)	254	614		
-	229(dimer g)				
Sn(II)	219(g)	185	507	544	
-	167(g)		501(g)		
Sn(IV)	-	186			
Pb(II)	248	119	532	545	
As(III)	146(g)	142(g)	489(g)		
Sb(III)	178(g)	145	509(g)		
Np(III)	454		852		
(IV)	347	426			

(a) Estimated quantities in parentheses.

A few metals, such as ruthenium, have very volatile oxides (in this case RuO_4), some of which are more stable than the halides, depending on the concentrations of water, oxygen, and halogens. Others have volatile hydroxides. For example, if the $\text{H}_2\text{O}/\text{CO}_2$ ratio is high, Cs_2CO_3 , normally stable, will convert to the hydroxide, which is volatile (Table 5).

The oxides of most of the nonmetals of interest to this study might be expected to volatilize since the acidic conditions would tend to make the anionic forms unstable. Although arsenic is usually considered a nonmetal, it and phosphorus are included in Table 5.

The significance of thermodynamic stability and chemical equilibria is illustrated using several examples. An equally important question is kinetics, the rates at which both chemical and physical reactions occur. This is seen as a much more difficult question, especially since the time intervals in the incinerator system may be very short (a few seconds in most parts of the system), and the temperature gradients are extreme.

THE ACIDIC GASES

The amounts of the acidic gases, which include P_2O_5 , may vary greatly. The halogens can exist as the element or as acids, e.g., X_2 or HX . The stability of HX decreases with an increase in the atomic number of X . For example, the reaction below:

The free energies at 500, 1000, and 1500 K are respectively -24.7, +8.9, and +43.0 kJ. The corresponding equilibrium constants are $3.8\text{E}+02$, 3.4, and $3.2\text{E}-02$. For the concentrations of Table 2, about 0.01 mol fraction total Cl, we calculate about 27% as Cl_2 at 500 K, 0.2% at 1000 K, but only 0.01% at 1500K. Reaction (1) for HBr gives corresponding ΔG values of -105.2, -71.2, and -36.6 kJ. Also, the $\text{HX} - \text{X}_2$ equilibrium ratios are concentration dependent, with the ratio X_2/HX increasing with concentration.

The total Br concentration in the incinerator is expected to be much lower than that of Cl. At 0.01 mol% total Br, the element is mostly Br₂ at 500 K; about 50% at 1000 K, and mostly HBr at 1500 K. Because of the high stability of HF, no F₂ will be present. For the same reason, many metal fluorides, including those of Group I and of many of the transition metals, although normally very stable compounds, will convert to chlorides and HF in the presence of excess HCl.

Iodine may be of special interest because of its biological significance. In contrast to the other halogens, only a trace of HI would exist at ordinary concentrations. I₂ may be the dominant species along with ICl. However, at concentrations below about 1E-04 mol%, and under the conditions of Table 2, equilibrium favors HI above about 1000 K.

Nitrates and nitrites will decompose completely at the burner temperatures to NO, NO₂, and N₂ (Stern 1972, Ephraïm 1953). Some N₂O is also expected from reduction by organic compounds. Sulfur is important because it is one of the acid gas formers. Also, because of the stability of many of the sulfate salts, it can play an important role in metal partitioning. Of similar importance is phosphorus, since, like the sulfates, many metal phosphates are very stable and are nonvolatile. Carbon can exist as thermally stable Group I carbonates if other acid gases are absent. Otherwise, ¹⁴C should escape the combustion chamber as CO₂ with a trace as CO. If the system becomes sufficiently basic, other salts such as titanates and zirconates may form as nonvolatile ash components.

Volatile oxides or metal salts of volatile acidic oxides, which may be unstable at high temperatures, can, of course, re-form as the vapors cool.

As seen from Table 3, many of the metal halides are moderately volatile. As an example of important equilibria we may write for a metal M:

where x may be a fractional as well as a whole number. HF or HBr could be substituted for HCl in the equations. The equilibrium constant for a reaction is

$$K = \exp(-\Delta G_f/RT) \quad (5)$$

where ΔG_f is the free energy of reaction at the temperature T . If MCl_x is a gas, then for reaction (3), for example, its partial pressure, at low concentrations of HCl, would be

$$P_{\text{MCl}_2} = K(\text{HCl})^{2x}/(\text{H}_2\text{O})^x, \quad (6)$$

or for reaction (4)

$$P_{\text{MCl}_2} = K(\text{HCl})^{2x}(\text{O}_2)^{x/2}/(\text{H}_2\text{O})^x. \quad (7)$$

If MCl_x exists as a solid or liquid at the temperature in question, e.g., with high concentrations of HCl, then its partial pressure is limited by the free energy change for the equilibrium $\text{MCl(s,l)} = \text{MCl(g)}$ and

$$P_{\text{MCl}_2} = \exp(-\Delta G_v/RT) \quad (8)$$

where ΔG_v is the free energy of vaporization of the halide. A similar expression would be written for the metal vapor pressure where the metal exists in its free state. ΔG data or vapor pressure tables are available for many metals and compounds, or can be estimated from boiling points plus ΔH_{vap} data. Representative data are presented in Table 4.

Many of the metals, such as iron, have several oxidation states. The free energy data indicate that at temperatures up to about 2000 K the most

stable oxide of Fe is Fe_2O_3 . The most stable iron chloride is usually FeCl_3 , which exists in the gas phase as both FeCl_3 and Fe_2Cl_6 .

In other cases, oxidation or reduction of the metal may occur. An example is copper. Since the most stable oxide is CuO , and the most stable chloride (which also happens to be volatile) is CuCl , the significant reactions are expected to be

and

and similar expressions for the formation of Cu_3Cl_3 , which is the more stable gaseous species. For (9), $\Delta G = -31 \text{ kJ}$ at 500 K and -41 kJ at 1000 K. For copper, the most stable gaseous species is the trimer of CuCl and its partial pressure would be

$$P_{\text{Cu}_3\text{Cl}_3} = (\text{HCl})^3 K_{12} / (\text{H}_2\text{O})^{3/2} (\text{O}_2)^{3/4} \quad (11)$$

from the reaction

An opposite case is tin. Although SnCl_2 is exceptionally volatile, the stability of SnO_2 (nonvolatile) is great enough that extensive volatilization should be prevented by the reaction

or, more accurately, by

For reaction (14), $\Delta G = -163$ kJ at 1000 K and -93 kJ at 1500 K.

Using free-energy data, and equations similar to (2 through 14), values of the equilibrium constant, K , and the partial pressures of volatile compounds that are estimated to be significant have been calculated for many compounds of the elements in Table 1 at 500, 1000, and 1500 K.

Figures 3 through 5 show the calculated free energies of the reactions forming chlorides for metals of concern. In each case, the starting compound is taken as the most stable compound in the air-CO₂-water vapor system at the temperature in question. Most often this is an oxide. As noted above, for the alkali metals the most stable is the carbonate, and for Au, Ag, and Hg it is the free metal. The reference point used for free-energy data of a compound involved in a reaction is that of the element in its standard state. The superscript zero (e.g., ΔG^0 indicating the referenced standard state) has been omitted in this paper. For liquids and solids, the requirement of the pure respective phases, liquid or solid, will not generally be met since solutions of widely varying concentrations may be more common. No attempt was made to estimate activity coefficients of the components. For the plotted data, the pure condensed phases are assumed. The inflection points will normally be transition points, e.g., melting, or vaporization.

The extremes in chloride stability are seen in Figure 3, while Figures 4 and 5 show differences among the transition and similar metals.

Since the total metals may be in excess of the halogens it is important to compare the free energies for reactions such as (3) and (4) for the various elements. As an example, with limited HCl, FeCl₃ (the above example), or its dimer may not form at all. This is because it is chemically much less stable than the chlorides of many of the other metals (see Figure 3).

In many cases, other salts may be more stable than the chlorides, thus preventing volatilization. The sulfates of most metals, for example, are more stable than the chlorides and are nonvolatile. However, in turn, most of them decompose at temperatures well below 1500 K. Thus, sulfates from sulfur in

S9409030.5

FIGURE 3. Calculated Free Energies of Reaction, as a Function of Temperature (500 K to 1500 K), for Metal Oxides Forming Chlorides: Cr, Cn, Fe, Ni, and Hg.

S9409030.7

FIGURE 4. Calculated Free Energies of Reaction, as a Function of Temperature (500 K to 1750 K), for Metal Oxides Forming Chlorides: Na, Cs, Be, Ca, Sr, Ge, Sn, Sb, Bi, Th, and Pu

S9409030.6

FIGURE 5. Calculated Free Energies of Reaction, as a Function of Temperature (500 K to 1500 K), for Metal Oxides Forming Chlorides: Co, Cu, Zn, Cd, and Pb

the incinerator feed could significantly reduce volatility of many metals at temperatures up to slightly greater than 1000 K, provided that the kinetics are such that appreciable SO_2 is converted to SO_3 . Sulfur would normally be burned to SO_2 . Although SO_3 is thermodynamically more stable at the lower temperatures of interest, it is not easily formed in the absence of catalysts. Its stability decreases with increase in temperature and by 1500 K it has mostly converted back to SO_2 (Ephraïm 1973). Nitric oxide, which will be present, both as a result of nitrate/nitrite decomposition and from the high temperature N-O reaction, is a potential homogeneous catalyst for oxidation of SO_2 .

The relative stability of several sulfates is shown in Figure 6. Data are for the reaction $\text{MO} + \text{SO}_3(\text{g})$. Extrapolation to temperatures below about 800 K requires correction for the reaction $\text{SO}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{H}_2\text{SO}_4(\text{g})$. At the higher temperatures the reactive species is SO_2 . The correction for SO_2 at 1200 K is about +13 kJ/mol and at 1400 K about +30 kJ.

Fluorine also forms very stable metal compounds and those of the higher oxidation states of all the elements are generally volatile. In a very few cases the fluoride may be the principal volatile species, although the metals that form volatile fluorides normally form oxides that are equally or more stable.

In the absence of more stable anionic species, and if sufficient HCl, for example, is present, the metals that form stable volatile chlorides will theoretically exist as metal chlorides. If there is a deficiency, then the available Cl will partition among the metals according to thermodynamic equilibria. It becomes obvious that determination of chemical species and their equilibrium concentrations in a mixture of metals and Cl, F, O, S, P, and C as major components is not a trivial task, even at a single temperature.

Chlorinated solvents and polyvinyl chloride, PVC, are ready sources of HCl. Teflon and similar polymers are sources of F. Various other organic materials may be sources of S and P.

S9409030.8

FIGURE 6. Calculated Free Energies of Reaction, as a Function of Temperature (800 K to 1200 K), for Metal Oxides Forming Sulfates from SO₃: Mg, Mn, Fe, Co, Ni, Cu, Zn, Zr, Ag, Cd, Sn, Hg, Pb, and Pu

Formation of volatile species is one issue. Formation of intractible solids may be another. Similar chemistry will affect the composition of, and hence the physical properties of, the ash or slag. For example, borates form low melting glasses with many metals. Silicates may comprise a major fraction of the solid products. The proportions of major elements such as Na, Ca, Al, Si, Fe, S, and B may determine the melting points and other physical properties of the burner ash and thus the nature of the slag.

The other Group VI elements in Table 1 also show nonmetallic properties, and the oxides are very volatile. Tellurium shows some metallic properties, but TeO_2 still has a calculated vapor pressure of 0.1 torr at 1000 K and 8 torr at 1200 K. SeO_2 is quite soluble in water as is SO_3 ; SO_2 is slightly soluble; and TeO_2 is insoluble (Ephraïm 1953).

The most stable form of phosphorus is P_4O_{10} , sublimation point 259°C (532 K), although some P_4O_6 , bp 173°C (446 K), may exist. However, P_4O_{10} has a high affinity for H_2O , and it may exist in the form of an H_3PO_4 mist below about 800 K. Alternatively, it may be retained in the ash as solid metal phosphates. Calcium phosphate is one of the more stable metal phosphates. Strontium phosphate is expected to be similar. Data to prepare plots for phosphates similar to those in Figures 3 through 6 are not available. A few cases will be considered later.

Arsenic has both acidic and metallic properties. The stability of the 5-valent oxides of Group V elements decreases with atomic number and also as the temperature rises. It is likely that the 3-valent As_2O_3 is the most stable As compound in our system and can readily volatilize, largely as As_4O_6 . It is slightly soluble in H_2O . Antimony continues the trend. The gas Sb_4O_6 is stable to very high temperatures (Ephraïm 1953). Its calculated vapor pressure is 3.6 torr at 900 K and 14 torr at 1000 K.

The halides of As and Sb are very volatile. Although they are hydrolyzed by H_2O , both the trifluorides and the trichlorides could readily volatilize if the respective acid concentrations are great enough. For HCl at

a concentration of 0.01 atm (~8 torr), and when $H_2O = 0.25$ atm (190 torr) (Table 2), the calculated partial pressure of $SbCl_3$ at 1000 K is $4E-04$ atm (0.3 torr). If the HF concentration exceeds the HCl concentration by an order of magnitude, the gas phase would become SbF_3 . At low halogen concentrations the predominant gaseous species should be Sb_4O_6 .

Bismuth shows little acidic character but is discussed here since it is in Group V. It forms stable oxides and halides; the latter are volatile. Bismuth appears to be the only one of this family whose chloride, $BiCl_3$, is sufficiently more stable than the oxide such that it can preferentially exist in the H_2O environment. Its partial pressure at 1000 K is calculated to be, for $H_2O = 0.25$ atm,

$$P_{BiCl_3} = 1 E+04(HCl)^3 \text{ atm.} \quad (15)$$

The cubic dependence of HCl indicates that its concentration must be about 0.01 atm or greater to give an appreciable gaseous $BiCl_3$ concentration. The oxychloride, $BiOCl$, can also form.

Boron, aluminum, and silicon may have a different role. The halides are very volatile but should not form due to the great stability of the oxides. Their importance could be that they can combine with many metal oxides, forming borates, aluminates, and silicates, respectively. With abundant sodium or calcium, for example, they can influence the nature of the burner ash or slag, especially the melting point. As mentioned above, Ti and Zr can behave similarly.

Tritium and ^{14}C were discussed earlier. Since CO_2 is in great excess over the other acidic gases, it is possible that a portion may remain with the ash, depending on the temperature and the total quantities of Groups IA and IIA elements, and, of course, on the concentrations of other acid gases.

GROUPS IA AND IIA ELEMENTS

The alkali and alkaline earth metals need special mention for two reasons. Their salts, especially the halides, the sulfates, and many of the phosphates, are stable to very high temperatures. The vapor pressures of Group IIA compounds are generally low, but those of the halides of Group IA are appreciable as the data of Table 3 show.

The metals of Groups IA and IIA are expected to be present in large amounts in incinerator feed materials. Thus, they can act as potential sinks for compounds that would otherwise promote low-temperature volatility. But, they could also scavenge compounds that prevent volatility, e.g., sulfates.

Calcium forms the most stable fluoride of the metals likely to be present in waste in appreciable concentrations. For chloride the most stable is Na. It is notable that the corresponding salts of Sr are often more stable than the Ca salts (examples are the carbonate, sulfate and chloride salts), and those of Cs are more stable than the Na salts.

Sodium and Cs, elements of concern here (Table 1), are expected to be stable as the solid sulfates if the H_2SO_4 , ($\text{SO}_3 + \text{H}_2\text{O}$), concentration is high. Otherwise, appreciable vaporization as the chloride could occur at moderately high temperatures. At still higher temperatures, above about 1200 or 1300 K, the sulfates may be too unstable to offer any protection. Strontium and Ra are expected to remain as solids, primarily as sulfates or phosphates, or, in the absence of the latter, as chlorides or fluorides. The fluoride of Sr is more stable than the chloride. This is not true for Ba and, thus, presumably not for Ra. Strontium forms one of the most stable sulfates.

Beryllium is potentially different in that the chloride is very volatile (bp = 804 K), but the oxide is sufficiently stable that the partial pressure of BeCl_2 becomes extremely low. The sulfate should preferentially form in place of chloride but will decompose before 1000 K is reached. The fluoride appears to be the most stable Be salt and it is slightly volatile. However, its calculated equilibrium partial pressure with HF = 0.01 atm (1 mol%) is

only about $3\text{E-}04$ torr at 1500 K. Thus, Group II elements are predicted to preferentially stay in the ash. The same should be true for Group I elements if the halogen concentration is low.

TRANSITION ELEMENTS AND GROUP IIB

The transition elements include many of the elements in Table 1. Characteristically they show multiple oxidation states and the volatility of their compounds increases with oxidation number. The fluorides are of special interest for the first members of the series; as the d shell fills, the chlorides become relatively more stable. Equilibria of the type expressed in Equations (2) through (14) should be important.

In general, the oxides will be the stable species. This is especially true for the first elements of the three rows. Thus, although Zr, V, and Nb form volatile halides, they readily hydrolyze to stable oxides and are nonvolatile. In the case of Zr, the fluoride ZrF_4 , with $P = 0.019$ atm at 1000 K, could volatilize only if the HF concentration were exceptionally high, i.e., $\text{HF} \gg \text{H}_2\text{O}$. Technetium and ruthenium have very volatile oxides (Table 5). The oxide RuO_4 is a gas above a few hundred degrees K (bp 373 K). It may be formed from RuO_2 and O_2 or NO_2 . It has a tendency to collect on solid surfaces or particles. There is some evidence that other volatile Ru compounds exist perhaps involving nitroso groups (Christian 1990). The lower-oxide RuO_2 is volatile at temperatures above about 1000 K.

Technetium forms a series of oxides, the most stable of which are probably TcO_3 and Tc_2O_7 . The latter is very volatile, bp 584 K, and may be the predominant form in the incinerator.

Chromium is important because the VI state is toxic. The oxide Cr_2O_3 should normally be the stable species. However, in the presence of alkali metal salts, such as nitrate or carbonate, it may be converted to Na_2CrO_4 (Ephraïm 1953). The reaction

is very favorable in the incinerator atmosphere. The compound CrO_2Cl_2 is very volatile, b.p. 390 K, but is only stable at high HCl concentrations, $(\text{HCl}) \gg (\text{H}_2\text{O})$. No other volatile Cr(VI) compounds are expected. It is notable that many Cr(VI) compounds are soluble in water, important in off-gas scrubbing. The most stable oxide of Mn is Mn_2O_3 although the stability of MnO increases at the higher temperatures. The dichloride is intermediate in stability in the transition metals, but the boiling point of MnCl_2 is 1463 K and little volatility would be expected. The higher chlorides are more volatile but should be unstable in the incinerator atmosphere.

Towards the Cu end of the series, the chlorides, along with those of Group IIB, become more stable relative to the oxides and fluorides. As illustrated in Section 4.1, many could volatilize as the chlorides if the HCl concentration is high, the H_2O concentration low, and competing anions are absent. The metals Fe and Cu were discussed earlier.

An interesting example is Zn since the chloride is very volatile, bp = 999 K. For the metal oxide-chloride equilibrium with 0.25 atm H_2O , we find at 1000 K

$$P_{\text{ZnCl}_2} = 2.6\text{E}+03(\text{HCl})^2 \text{ atm.} \quad (17)$$

At $\text{HCl} = 0.01$ atm, $P = 198$ torr, and at $\text{HCl} = 0.001$, $P = 2.0$ torr. Thus, we might expect ZnCl_2 to readily vaporize. Again, however, the sulfate is more stable, and the presence of sulfur may reduce volatility. On the other hand, 1000 K is approximately the temperature at which ZnSO_4 begins to decompose, and thus it is questionable whether the available SO_3 can prevent volatilization if the temperature is much greater than 1000 K.

The same complex behavior would be expected for Cd, Hg, and Pb. However, differences might be predicted: The vapor pressures of the pure dichlorides are in the order $\text{Hg} > \text{Zn} > \text{Pb} > \text{Cd}$ (Table 3). The thermodynamic

stability of the sulfates with respect to the oxides is in the order $\text{Pb} > \text{Cd} > \text{Zn} > \text{Hg}$ (Figure 5). Thus, the resulting volatility under the conditions of Table 3, depending on the sulfate concentration and the temperature, could conceivably be $\text{Hg} > \text{Cd} > \text{Zn}, > \text{Pb}$. In the absence of complexing anions such as sulfate and halides, compounds of these elements, e.g., carbonates, could decompose to the free metals above about 1300 K. The relative volatility might then become $\text{Hg} \gg \text{Cd} \gg \text{Pb} \gg \text{Zn}$.

Lead, of course, does not belong in Group IIB but is often compared in behavior to the other three metals. Its vapor pressure is low compared with that of Cd. The metal vapor pressures were compared in Table 5. The extreme range of vapor pressures of several metals of interest is shown in Table 7.

TABLE 7. Approximate Temperatures Giving Vapor Pressures Equal to that of Hg at 298 K, $2.4\text{E}-06$ atm

Hg	298 K	Mn	1150
Cd	490	Ag	1220
Na	520	Ga	1240
Zn	570	Al	1380
Sr	740	Cu	1430
Sb	770	Au	1550
Bi	870	Pu	1650
Pb	910	Ni	1710

GROUPS IIIA AND IVA ELEMENTS

Aluminum has been discussed earlier. Its chloride is very volatile, $\text{bp} = 454$ K, but the oxide is so stable that the concentrations of Al halides should be negligible.

Gallium, Ge, In, Sn, and Pb fall into this group. It is notable that the fluoride of In is more stable than the oxide. However, it is not volatile.

Lead is often a metal of concern in incineration. Of the oxides, PbO is the most stable over most of the temperature range considered. Yet, chloride volatility could result from the relatively low stability of the oxide. But lead forms one of the more stable sulfates and the compound may exist at temperatures well above 1000 K and prevent the chloride from forming. Lead was considered in examples in Section 2.2.

Tin was discussed as an example in Section 2.2, Equations (11) and (12). The boiling point of SnCl_2 is only 885 K. However, the oxide, SnO_2 , is so much more stable that in our system of $\text{O}_2 = 0.1$ and $\text{H}_2\text{O} = 0.2$ atm, the partial pressure of SnCl_2 is not significant at low HCl concentrations, about $1\text{E-}06$ atm at 1500 K if HCl is 1 %.

LANTHANIDE AND ACTINIDE ELEMENTS

The lanthanides and actinides are characterized by very stable oxides and fluorides. The higher oxidation state chlorides and fluorides of the actinides are very volatile. Inspection of ΔG_f data suggests that CeF_3 could form as the solid but would not be volatile. No volatile lanthanide species are likely.

The actinides present a more involved case in that they exhibit more oxidation states and the stability of each state varies throughout the series. Although the chlorides and fluorides are very stable and the higher ones are very volatile, it appears from the gas composition of Table 2 that the oxides will be the important species. The predominant compounds are expected to be ThO_2 , UO_3 and U_3O_8 , NpO_2 , PuO_2 , and Am_2O_3 and AmO_2 .

COMPLEX EQUILIBRIA MODEL CALCULATIONS

Several programs are available for calculating thermodynamic equilibria of mixtures. "HSC Chemistry for Windows"^(a) was used here for a large

(a) "HSC Chemistry for Windows" Version 2.01, Outokumpu Research, Finland. Distributed by ARS Software, Landover, MD.

number of calculations, many involving 50 to 100 chemical species in the condensed and gaseous states. Many uncertainties exist, in large part due to a lack of knowledge of the composition of the condensed state, i.e., how many phases exist and which compounds are in a given phase. Also, no information on thermodynamic activities is available. However, it appears worthwhile to use the calculations to predict relative concentrations of species in several mixtures. A few of the results are reported here.

As an example, using the initial gas compositions, similar to those of Table 2, the equilibrium composition as a function of temperature at 1 atm pressure was calculated for 27 compounds, conceivably significant in the equilibrium mixture at 1000 K to 1500 K. The starting composition, mols added, is listed as Test 1 in Table 8 (Figures 7 through 13 show calculations for each test noted in Table 8). Compounds calculated to have concentrations above $1\text{E-}08$ mol % are shown in Figures 7a and 7b. The gases N_2 , CO_2 , and H_2O were essentially unchanged and are not shown. Note that above 1000 K the most stable compounds of Cl, N, S, and P are the gases HCl , NO , SO_2 , and P_4O_{10} , respectively, as suggested in Section 2.2.

Table 8 lists the feed compositions used for several other calculations. The model uses the most stable species that will exist, based on the element input, using its data base of about 7000 compounds. We reduce this list to normally 40 to 100 compounds based on compatibility with a "wet" oxidizing system for the temperature range to be studied. Figure 8 shows the behavior of Na and Ni when added to the $\text{HCl-H}_2\text{O-O}_2$ atmosphere. The composition of the initial mixture is listed as Test 2. For Figure 8b, the HCl concentration was increased by a factor of 5 over that in Figure 8a. The increases in partial pressures of NaCl and NiCl_2 are roughly as expected from Equation (7). Figures 8c and 8d show the result of reducing the sodium carbonate from 0.1 to 0.01 mols, leaving the system highly acidic. Under these conditions, nearly all the Cl is in the vapor phase, mostly as HCl and NaCl(g) . At 0.1 mol Na_2CO_3 , most of the Cl appears as condensed NaCl . The condensed phase components for the high-acid case are shown in Figure 8d. Nickel sulphate

TABLE 8. Feed Compositions used for HSC Tests

moles added, P = 1.0 atm

Compound	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7
H ₂ O	0.20	0.20	0.10	0.10	0.15	0.15	0.15
O ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10
CO ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10
N ₂	0.60	0.60	0.60	0.40	0.40	0.40	0.60
NO ₂	0.01	0.01	0.02	0	0.02	0.02	0.02
P ₂ O ₅	0.003	0	0	0	0	0	0
SO ₂	0.02	0.01	0	0.01	0.02	0.02	0.01
HCl	0.01	0.01 0.05 ^(a)	0.02	0.0	0.02	^(d)	^(e)
HF	0	0	0	0	0.02	0.02	0.01
NaOH	0	0	0.02	0	0.01	0.01	0
Na ₂ CO ₃	0	0.10 ^(a) 0.01	0	0	0	0	0.005
Na ₂ SO ₄	0	0.01	0	0	0	0	0
CsOH	0	0	0	0.02	0.01	0.01	0
Cs ₂ CO ₃	0	0	0	0.01	0	0	0.005
CaO	0	0	0.03	0.01	0.005	0.005	0.005
CaCl ₂	0	0	0.05	^(c)	0	0	0
SrO	0	0	0	0	0	0	0.005
MnO	0	0	0	0	0.005	0.005	0
FeO	0	0	0	0	0.005	0.005	0
CoO	0	0	0	0	0.005	0.005	0.005
NiO	0	0.01	0.01	0.01	0	0	0
CuO	0	0	0.01	0.01	0.005	0.005	0
CuSO ₄	0	0	^(b)	0	0	0	0
ZnO	0	0	0.01	0.01	0.005	0.005	0.005
ZrO ₂	0	0	0	0	0	0	0.005
SnO	0	0	0	0	0	0.005	0
PbO	0	0	0.01	0.01	0	0.005	0
SbO ₂	0	0	0	0	0	0	0.005
Figure	7	8	9	10	11	12	13

(a) Three different combinations were used in Test 2. See text.

(b) CuSO₄ initial = 1.0E-04, and added as 20 increments of 0.004 moles each.

(c) CaCl₂ initial = 1.0E-03, and added in 15 increments of 0.003 moles each.

(d) HCl initial = 2.0E-04, added in 20 increments of 0.002 moles each.

(e) HCl initial = 1.0E-03, added in 20 increments of 0.0025 each.

Feed Composition (mols)			
H_2O	0.2	NO_2	0.01
O_2	0.1	P_2O_5	0.003
CO_2	0.1	SO_2	0.02
N_2	0.6	HCl	0.01

FIGURE 7a,b. Calculated Equilibrium Concentrations, as a Function of Temperature, (500 K to 1500 K), in Incinerator Off-Gas for an Initial Mixture of H_2O , O_2 , CO_2 , N_2 , NO_2 , SO_2 , P_2O_5 , and HCl (Test 1)

Feed Composition (mols)			
H ₂ O	0.2	NO ₂	0.01
O ₂	0.1	Na ₂ CO ₃	0.10
CO ₂	0.1	Na ₂ SO ₄	0.01
N ₂	0.6	NiO	0.01
SO ₂	0.01	HCl	0.01, 0.05 ^(a)

FIGURE 8a,b. Calculated Equilibrium Concentrations, as a Function of Temperature (500 K to 1500 K), in Incinerator Off-gas with Ni and Na Added to Initial Mixture and (a) 0.01 mol HCl and (b) 0.05 mol HCl in Initial Feed (Test 2)

Feed Composition (mols)

H_2O	0.2	SO_2	0.01
O_2	0.1	HCl	0.05
CO_2	0.1	Na_2CO_3	0.01
N_2	0.6	Na_2SO_4	0.01
NO_2	0.01	NiO	0.01

FIGURE 8c,d. Calculated Equilibrium Concentrations, as a Function of Temperature (500 K to 1500 K), in Incinerator Off-Gas with Ni and Na Added to Initial Mixture and with Increased HCl (0.05 mol) and Reduced Na_2CO_3 (from 0.1 to 0.01 mol)

Feed Composition (mols)			
H_2O	0.1	CaCl_2	0.05
O_2	0.1	CaO	0.03
CO_2	0.1	NiO	0.01
N_2	0.6	CuO	0.01
NO_2	0.02	ZnO	0.01
HCl	0.02	PbO	0.01
NaOH	0.02	CuSO_4	0.0001-0.08

FIGURE 9a,b. Calculated Equilibrium Concentrations, as a Function of Added CuSO_4 (Test 3) in Incinerator Off-Gas: Gaseous Chlorides of Na, Ca, Ni, Cu, Zn, and Pb at Temperatures (a) 1000 K and (b) 1500 K

Feed Composition (mols)			
H ₂ O	0.1	CaCl ₂	0.05
O ₂	0.1	CaO	0.03
CO ₂	0.1	NiO	0.01
N ₂	0.6	CuO	0.01
NO ₂	0.02	ZnO	0.01
HCl	0.02	PbO	0.01
NaOH	0.02	CuSO ₄	0.0001-0.08

FIGURE 9c,d. Calculated Equilibrium Concentrations, as a Function of Added CuSO₄, of Condensed Phase Products in an Incinerator: Sulfates of Na, Ca, Ni, Cu, Zn, and Pb at Temperatures (c) 1000 K and (d) 1500 K

Feed Composition (mols)			
H_2O	0.10	CaO	0.01
O_2	0.10	NiO	0.01
CO_2	0.10	CuO	0.01
N_2	0.40	ZnO	0.01
SO_2	0.01	PbO	0.01
CsOH	0.02	CaCl_2	0.001-0.045

FIGURE 10a,b. Calculated Equilibrium Concentrations, as a Function of Added CaCl_2 (Test 4), in Incinerator Off-Gas: Gaseous Chlorides of Cs, Ca, Ni, Cu, Zn, and Pb at Temperatures (a) 1100 K and (b) 1500 K

Feed Composition (mols)			
H ₂ O	0.10	CaO	0.01
O ₂	0.10	NiO	0.01
CO ₂	0.10	CuO	0.01
N ₂	0.40	ZnO	0.01
SO ₂	0.01	PbO	0.01
CsOH	0.02	CaCl ₂	0.001-0.045

FIGURE 10c,d. Calculated Equilibrium Concentrations, as a Function of Added CaCl₂, of Condensed Phase Products in an Incinerator: Oxides of Ca, Ni, Cu, Zn, and Pb at Temperatures at (c) 1100 K and (d) 1500 K

Feed Composition (mols)			
H ₂ O	0.10	CaO	0.01
O ₂	0.10	NiO	0.01
CO ₂	0.10	CuO	0.01
N ₂	0.40	ZnO	0.01
SO ₂	0.01	PbO	0.01
CsOH	0.02	CaCl ₂	0.001-0.045

FIGURE 10e,f. Calculated Equilibrium Concentrations, as a Function of Added CaCl₂, of Condensed Phase Products in an Incinerator: Sulfates of Cs, Ca, Ni, Cu, Zn, and Pb at Temperatures (e) 1000 K and (f) 1500 K

Feed Composition (mols)			
H ₂ O	0.15	NaOH	0.01
O ₂	0.10	CsOH	0.01
CO ₂	0.10	CaO	0.005
N ₂	0.40	MnO	0.005
NO ₂	0.02	FeO	0.005
SO ₂	0.02	CoO	0.005
HCl	0.02	CuO	0.005
HF	0.02	ZnO	0.005

FIGURE 11a,b. Calculated Equilibrium Concentrations, as a Function of Temperature (700 K to 1700 K), in Incinerator Off-Gas of (a) S, N, and C Oxides and Acid Gases and (b) Chlorides and Fluorides of Cs, Na, and Cu (Test 5)

Feed Composition (mols)			
H ₂ O	0.15	NaOH	0.01
O ₂	0.10	CsOH	0.01
CO ₂	0.10	CaO	0.005
N ₂	0.40	MnO	0.005
NO ₂	0.02	FeO	0.005
SO ₂	0.02	CoO	0.005
HCl	0.02	CuO	0.005
HF	0.02	ZnO	0.005

FIGURE 11c,d. Calculated Equilibrium Concentrations, as a Function of Temperature (700 K to 1700 K), in Incinerator Off-Gas (Test 5) of (c) Chlorides, Fluorides, and Hydroxides of Na, Cs, Ca, Mn, Fe, Co, and Zn and (d) Condensed Phase Chlorides of Na, Cs, Ca, Mn, Fe, Co, Cu, and Zn

Feed Composition (mols)			
H ₂ O	0.15	NaOH	0.01
O ₂	0.10	C ₅ OH	0.01
CO ₂	0.10	CaO	0.005
N ₂	0.40	MnO	0.005
NO ₂	0.02	FeO	0.005
SO ₂	0.02	CoO	0.005
HCl	0.02	CuO	0.005
F	0.02	ZnO	0.005

FIGURE 11e,f. Calculated Equilibrium Concentrations, as a Function of Temperature (700 K to 1700 K) in an Incinerator (Test 5) of (e) Condensed Phase Fluorides of Na, Cs, Ca, Mn, Fe, Co, Cu, and Zn and (f) Condensed Phase Sulfates of Na, Cs, Ca, Mn, Co, and Zn

Feed Composition (mols)			
H ₂ O	0.15	NaOH	0.01
O ₂	0.10	CsOH	0.01
CO ₂	0.10	CaO	0.005
N ₂	0.40	MnO	0.005
NO ₂	0.02	FeO	0.005
SO ₂	0.02	CoO	0.005
HCl	0.02	CuO	0.005
HF	0.02	ZnO	0.005

FIGURE 11g,h. Calculated Equilibrium Concentrations, as a Function of Temperature (700 K to 1700 K) in Incinerator Off-Gas (Test 5) of (g) Condensed Phase Oxides of Ca, Mn, Fe, Co, Cu, and Zn and (h) Condensed Phase Carbonates of Na, Cs, Ca, Mn, Co, and Zn

Feed Composition (mols)			
H ₂ O	0.15	CaO	0.005
O ₂	0.10	MnO	0.005
CO ₂	0.10	FeO	0.005
N ₂	0.40	CoO	0.005
NO ₂	0.02	CuO	0.005
SO ₂	0.02	ZnO	0.005
HF	0.02	SnO	0.005
NaOH	0.01	PbO	0.005
CsOH	0.01	HCl	0.0002-0.04

FIGURE 12a,b. Calculated Equilibrium Concentrations, as a Function of HCl Feed, in Incinerator Off-Gas at Temperature 1500 K (Test 6), Showing the HCl Effect on Volatility of (a) Chlorides of Na, Cs, Ca, Mn, Co, Cu, Zn, and Pb and (b) Fluorides, Chlorides, and Hydroxides of Na, Cs, Fe, and Sn

Feed Composition (mols)			
H ₂ O	0.15	Cs ₂ CO ₃	0.005
O ₂	0.10	CaO	0.005
CO ₂	0.10	SrO	0.005
N ₂	0.60	CoO	0.005
NO ₂	0.02	ZnO	0.005
SO ₂	0.01	ZrO ₂	0.005
HF	0.01	SbO ₂	0.005
Na ₂ CO ₃	0.005	HCl	0.001-0.05

FIGURE 13a,b. Calculated Equilibrium Concentrations, as a Function of HCl Feed, in Incinerator Off-Gas (Test 7), Showing the HCl Effect on Volatility of Na, Cs, Co, Zn, and Sb at Temperatures (a) 1000 K and (b) 1500 K

Feed Composition (mols)			
H ₂ O	0.15	Cs ₂ CO ₃	0.005
O ₂	0.10	CaO	0.005
CO ₂	0.10	SrO	0.005
N ₂	0.60	CoO	0.005
NO ₂	0.02	ZnO	0.005
SO ₂	0.01	ZrO ₂	0.005
HF	0.01	SbO ₂	0.005
Na ₂ CO ₃	0.005	HCl	0.001-0.05

FIGURE 13c,d. Calculated Equilibrium Concentrations, as a Function of HCl Feed, in Condensed Phase Products in an Incinerator (Test 7), Showing the Effect of HCl Concentration on Metal Oxides and Salts at 1000 K for (c) Cs, Ca, Sr, Co, Zn, Zr, and Sb; and (d) Na, Ca, Sr, Zn

Feed Composition (mols)			
H ₂ O	0.15	Cs ₂ CO ₃	0.005
O ₂	0.10	CaO	0.005
CO ₂	0.10	SrO	0.005
N ₂	0.60	CoO	0.005
NO ₂	0.02	ZnO	0.005
SO ₂	0.01	ZrO ₂	0.005
HF	0.01	SbO ₂	0.005
Na ₂ CO ₃	0.005	HCl	0.001-0.05

FIGURE 13e,f. Calculated Equilibrium Concentrations, as a Function of HCl Feed, in Condensed Phase Products in an Incinerator (Test 7), Showing the Effect of HCl Concentration on Metal Vaporization at 1000 K for (e) Na, Ca, Sr, Co, Zn, and Sb; and (f) Na, Cs, Ca, Co, Zr, and Sb

begins to decompose as the temperature reaches about 1000 K and NiO becomes the dominant species.

Another simulation is to observe the effects of adding one component incrementally while holding the temperature constant. Using the compositions of Test 3, CuSO_4 was added in 20 increments of 0.004 mols each. Copper sulfate is relatively unstable and the effect should be that of adding SO_3 to the mixture (H_2SO_4 at low temperatures and SO_2 at high temperatures). Calculations were made at 1000 K and 1500 K with 0.02 mols HCl present. This mixture includes the metals Ni, Zn, and Pb, along with the Na and Cu. The gaseous data at 1000 K and 1500 K are shown in Figures 9a and 9b, respectively.

Several features can be noted. The increasing acidity as the sulfate is added increases the partial pressures of those metal chlorides that have low or moderate metal sulfate stability, e.g., Zn. Lead sulfate is more stable, and both it and sodium show a lowered partial pressure, but most significantly only after sufficient sulfate has been added to completely remove the calcium. The principal driving force for volatilization in this high chloride mixture appears to be the volatility of the metal chlorides. PbCl_2 and ZnCl_2 are both very volatile; Pb, having the more stable sulfate, drops below Zn at the highest SO_4 levels. At 1500 K all the sulfates except CaSO_4 are sufficiently unstable that there is little effect from the sulfate addition. The calculated volatility of NaCl is higher than expected.

Raising the temperature from 1000 K to 1500 K changes the volatility order, NaCl replacing PbCl_2 and CuCl replacing ZnCl_2 . The computed partial pressures of the different chlorides are not always in the same order as the vapor pressures of the pure compounds, the stability of the chlorides, nor, inversely, as the stability of the sulfates. This illustrates the need to consider the free energy (stability) of each specie; in the present system these are primarily the chlorides, sulfates, oxides, and carbonates of each of the metals, and occasionally the fluorides.

The relative sulfate concentrations in the condensed phase are shown in Figures 9c and 9d. Note the Ca "titration endpoint" at 0.05 mols SO_4 .

In contrast to sulfate, the stepwise addition of CaCl_2 should have a positive effect on the volatility of most metals. The stability of CaCl_2 is intermediate, as can be seen from Figure 3. However, the stability of CaSO_4 is great enough that if sulfur is present, CaCl_2 should become a good chlorinating agent. For example, for the reaction

the free energy (condensed phases) is -82 kJ at 1000 K, even though CaCl_2 is more stable than ZnCl_2 . Corresponding data at 1000 K for Ni, Co, Cu(II), and 2Cs are -64, -64, -71, and -75 kJ.

Figures 10a and 10b show the computed partial pressures of the chlorides of five metals as CaCl_2 is added stepwise to the mixture shown as Test 4. Data are shown for two Pb compounds as well as for the dimer of CsCl. (Dimer concentrations have been calculated in all cases in this study but are generally not shown in the figures.)

Computations for Test 4 were made at 1100 and 1500 K. Table 9 shows the percent of each of the metals at 1100 K in the gas phase and in the predominant condensed form, initially, after two additions of CaCl_2 , and at the end of the additions.

It is seen that the largest change occurs with a small increment of CaCl_2 . At the second increment, the partial pressures of Pb, Zn, and Ni chlorides have increased by a factor of several hundred, for Cs and Cu about 1.5 and 15, respectively. The change from 1100 to 1500 K increased the partial pressures for Pb, Cs, Zn, Cu, and Ni by factors of 0.9, 3, 5, 320, and 100 at the second increment, and 1.2, 3, 40, 1000, and 1300 at the end of the addition. The smaller change in Pb volatility, both with respect to CaCl_2 addition and with temperature change, probably reflects the higher stability

TABLE 9. Amounts of Metal Compounds Present During CaCl_2 Additions, Test 4

	Percent at 1100 K			
Mols CaCl_2 Added:	0.001	0.004	0.007	0.040
Mols Total Ca	<u>0.011</u>	<u>0.014</u>	<u>0.017</u>	<u>0.050</u>
<u>Compound</u>				
CsCl(g)	6.7	8.0	8.0	4.0
CsCl	49	73	86	95
Cs_2SO_4	41.1	14	1.1	0
$\text{Cs}_2\text{Cl}_2(\text{g})$	3.3	5.0	4.9	1
$\text{CaCl}_2(\text{g})$	3.3-07	3.0-06	1.9-05	3.0-04
CaCl_2	1.6-02	1.0-01	1.2	46.2
CaSO_4	53.1	61.5	58.2	21.0
CaO	46.5	38.4	40.5	32.8
$\text{NiCl}_2(\text{g})$	8-07	6-06	6-05	1.3-03
NiCl_2	2.8-07	2.1-06	2.8-5	1.2-03
NiSO_4	1.6-05	2.5-04	2.0-05	9.0-06
NiO	100	100	100	100
CuCl(g)	6.0-04	1.4-03	4.3-03	8.7-03
CuCl	1.5	4.4	15.4	64.4
$\text{Cu}_3\text{Cl}_3(\text{g})$	1.5-07	2.0-06	5.4-05	4.5-04
CuCl_2	5.1-07	3.7-06	4.3-05	8.3-04
CuSO_4	2.0-07	2.7-07	2.2-07	3.9-08
CuO	93.4	90.1	80.7	34.1
Cu_2O	5.2	4.9	4.0	1.7
$\text{ZnCl}_2(\text{g})$	3.8-04	2.3-03	2.6-02	0.56
ZnCl_2	2.7-06	2.0-05	2.7-04	1.2-02
ZnSO_4	1.1-06	1.5-06	1.4-06	5.8-07
ZnO	100	100	99.9	99.4
$\text{PbCl}_2(\text{g})$	0.13	0.76	7.1	53
PbCl(g)	1.8-03	4.3-03	1.3-02	2.0-02
PbCl_2	1.5-02	0.11	1.3	19
PbSO_4	1.4-02	1.9-02	1.6-02	2.0-03
PbO	99.7	99.0	91.6	28
PbO_2	0.15	0.15	0.14	4.3-02

of PbSO_4 as compared with the sulfates of Cu, Ni, and Zn. Figures 10c, 10d, 10e, and 10f show major components of the condensed phases.

There are two effects to be noted; in addition to providing chloride, the calcium in CaCl_2 is also effectively complexing the sulfate.

Examination of the material balances indicates several interesting points: 1) essentially all of the chloride as metal halides in the vapor is in the form of CsCl , Cs_2Cl_2 , and PbCl_2 gas; 2) less than 1E-04% of the NiO has reacted and only 0.03% of the ZnO at the second addition point ($\text{CaCl}_2 = 0.007$ mols).

The description of the condensed phases is difficult since the mutual solubilities are largely unknown. At 1500 K, available phase diagrams (Levin et al. 1964) indicate that there is likely just one phase (liquid) for most of the tests considered here. At 1000 K the description is more difficult. The absolute values of the gas pressures are a function of the condensed phase activities, in turn a function of the phase designations. However, various computation tests indicated that computed gas concentrations relative to each other were not too sensitive to the condensed-phase designations. Tests that produced singularities, concentrations dropping precipitously to E-36, were assumed to have incorrectly specified phases. Typical components of limited solubility may be CaO and ZrO_2 . Activity coefficients of unity were used throughout this work.

The model assumes Raoult's law. Thus, since activity coefficients of unity were used for the condensed phase, it is not surprising that

$$X_{\text{MX}_2}(\text{g}) = X_{\text{MX}_2}(\text{l}) * P_{\text{MX}_2}^0, \quad (19)$$

where X is the mol fraction in the condensed phase and $P_{\text{MX}_2}^0$ is the vapor pressure for the pure compounds, as in Table 3. Mol per cent in each phase is calculated by the HSC program.

Test 5 is a temperature study of eight metals, each at the same concentration, under typical incinerator conditions, e.g., as in Table 2. A total of 74 compounds were included in the calculation. Pertinent data as a function of temperature from 700 to 1700 K are plotted in Figures 11a through 11g.

NO_x is initially destroyed, but a small amount is present at 1600 K. About 2/3 of the HF and 2/3 of the HCl are used initially, but by 1600 K the metal fluorides have largely disappeared and 90% of the HF gas remains. About 85% of the chloride is as metal chlorides at 1600 K. The SO_2 - SO_3 is consumed at the lower temperatures, but in turn the sulfates formed have largely decomposed by 1600 K, and most of the sulfur is present as SO_2 .

The volatility order of the metal halides changes with temperature due to the changing stability of the several condensed-phase compounds. The computed compositions are shown in Figures 11c through 11g. It is interesting that very high temperatures, greater than 1500 K, appear to actually reduce the metal chlorides in the vapor, except for Group I elements. Again, the relative volatilities are not in the same order as vapor pressures of pure compounds or the free energies of formation of the individual chlorides, sulfates, oxides, etc. The relation is complex and changes with temperature.

The significance of HCl has been noted throughout these studies, and the likely introduction of variable amounts of chlorides introduced in incinerator feeds emphasizes its importance. Test 6 studies the effect of changing the HCl concentration for 10 metals significant in incinerator partitioning. The HCl was varied from $2.0\text{E-}04$ to $3.8\text{E-}02$ mols. The gas composition for metals showing amounts greater than $1\text{E-}08$ mols are plotted in Figures 12a and 12b. The temperature is 1500 K. These data illustrate typical volatility trends and, along with data from Test 7, are used in a later section to help predict partitioning.

Test 7 is a slightly modified version of Test 6 with Sb, Zr, and Sr added. The HCl was increased stepwise as before. Figures 13a and 13b show

the gas composition at 1000 and 1500 K, while Figures 13c through 13f indicate major components in the condensed phase.

At 1000 K, the volatility of SbCl_3 falls between that of CoCl_2 and CoCl_3 . At 1500 K, Sb_4O_6 is the major gaseous species and represents about 10% of the total Sb.^(a) The gaseous antimony chlorides increase in concentration by many orders of magnitude as the HCl is increased from 0.01 to 0.05 mols.

Neither Zr nor Sr show marked volatility in this mixture, although 0.3% of the Sr is present as $\text{SrCl}_2(\text{g})$ when 1500 K is reached.

These calculations based on the conditions of Table 9 support earlier conclusions that acidity is of prime importance and that sulfate, calcium, and sodium, for example, could play important roles in controlling volatility of the halides of other metals. Unfortunately, the database does not presently contain sufficient information to permit similar calculations to be performed for phosphates. Available data show that $\text{Ca}_2\text{P}_2\text{O}_7$ and CaHPO_4 are the most stable Ca compounds. For Na it is NaPO_3 followed by $\text{Na}_4\text{P}_2\text{O}_7$. But the sulfates of both metals seem to be somewhat more stable than the phosphates. For example, Barin (1989) gives data for zinc phosphate, and for the reaction

the free-energy change is -135 kJ at 1000 K and about -67 kJ at 1500 K.

In addition to the elements considered in these calculations, several other elements could play a role in retention of metals in the furnace slag. These include Si, Ti, Zr, and Al as mentioned in Section 2.1. The present discussion with its emphasis on chloride volatility treats only a portion of a very complex chemical system.

(a) Barin references work edited by Glushkov, which gives free energy values making $\text{SbO}(\text{g})$ the major high-temperature species. The original work has not been found.

PARTITIONING OF THE ELEMENTS

Based on the above considerations, Table 10 lists the Table 1 elements and the compounds most likely to exist at 1000 to 1300 K. The conditions are the gas composition of Table 2, with the assumption that equilibrium is reached.

An estimate of partitioning behavior can be made based on the data presented and the assumptions described. From the foregoing discussion, it is clear that this behavior depends strongly on the relative concentrations of HCl, HF, SO₃, H₂O, P₂O₅, O₂, and a few likely abundant metals such as Ca and Na. Without knowledge of these concentration ratios, such an estimate is little more than a guess. The estimates in Table 11 assume $H_2O > CO_2 \approx O_2$, $HF \approx HCl = 1.0-2.0\%$, $SO_x > PO_x$, and consider the water solubilities of the stable compounds. The basic incinerator of Figure 1 is assumed, with the temperature about 1400-1500 K and component efficiencies typical of operations reported in the literature. As noted earlier, the fraction going to the stack can always be reduced by adding additional clean-up options. Because of this uncertain factor, the table includes only the burner ash and the fly ash. In a few cases, e.g., tritium and iodine, losses to the stack may be very large unless special trapping devices are employed. The table also includes a range of values reported in the literature.

For a smaller group of elements, an attempt was made to make a closer estimate of partitioning on the basis of the equilibrium calculations described above and solubilities, assuming a water scrub of the off-gas. The eight elements so estimated, listed in Table 13, represent different regions of the periodic table, and have quite different properties from each other.

Strontium is similar to calcium except that the sulfate is much more stable. The stability of the chloride is somewhat greater, but its vapor pressure is lower than for calcium. Thus, a large change in Sr release is not expected with increased HCl. Zirconium is different in that the sulfate is

TABLE 10. Most Likely Compounds in the Oxidizing Incinerator

Element	Probable Form	Comments
T	HTO	Some TX (X = halogen)
Na	Na ₂ SO ₄ , NaCl	Na ₂ CO ₃ if system alkaline
Cs	CsCl, Cs ₂ SO ₄ , CsI	Cs ₂ CO ₃ if system alkaline
Be	BeSO ₄ , BeF ₂ , BeO	
Ca	CaF ₂ , CaSO ₄ , Ca ₂ P ₂ O ₇ , CaO	CaCO ₃ stable to ~1200 K if acids absent.
Sr	SrSO ₄ , SrF ₂ , Sr ₂ P ₂ O ₇	SrZrO ₃ if S absent
Ra	RaO ₃ , RaSO ₄	
V	V ₂ O ₅	metal vanadates, e.g., NaVO ₃ . VOCl ₃ possible at high HCl conc
Cr	Cr ₂ O ₃ , Na ₂ CrO ₄	CrO ₂ Cl ₂ very volatile but requires (HCl)>>(H ₂ O)
Mn	Mn ₂ O ₃ , MnO, MnSO ₄	MnCl ₂ bp=1450 K. MnF ₂ has equal stability. MnSiO ₃ possible
Fe	Fe ₂ O ₃ , Fe ₃ O ₄ , Fe ₂ (SO ₄) ₃	FeCl ₃ bp=603 K. FeCl ₂ (g) more stable at T > 1200 ³ K. Silicates also possible.
Co	CoO, CoSO ₄	CoCl ₂ bp=1342 K, phosphate also
Ni	NiO, NiSO ₄	NiCl ₂ bp=1303 K, phosphate also
Cu	Cu ₂ O, CuSO ₄	CuCl bp=(1485) K, (vapor Cu ₃ Cl ₃), CuCl ₂ unstable
Zn	ZnO, ZnSO ₄	ZnCl ₂ bp=1000 K
Y	YF ₃ , Y ₂ O ₃	YF ₃ most stable compound
Zr	ZrO ₂ , ZrF ₂	
Nb	Nb ₂ O ₅	NbOCl possibly stable, sublimes at 550K
Tc	Tc ₂ O ₇ , TcO ₃	
Ru	RuO ₂ , RuO ₄	RuO ₄ readily formed, bp=333 K, RuO ₂ volatile at about 1000 K
Ag	AgCl, Ag ₂ SO ₄ , Ag	
Cd	CdO, CdSO ₄	CdCl ₂ bp=1236 K
Au	Au	AuCl ₃ if high conc HCl
Hg	Hg ₂ Cl ₂ , HgCl ₂	Some HgSO ₄ , Some Hg at high temp
Ga	Ga ₂ O ₃	Halides not stable towards H ₂ O
In	In ₂ O ₃	Possibly InF ₃
C	CO ₂ , Na ₂ CO ₃	Hydrocarbon traces
Ge	GeO ₂ , GeCl ₄	GeCl ₄ bp=356 K, stable at low temperature, hydrolyze at high temperature. GeO slightly vol.
Sn	SnO ₂	SnCl ₄ bp=388 K, SnCl ₂ bp=925 Requires high HCl conc.
Pb	PbO ₂ , PbO	PbCl ₂ bp=1223 K
P	P ₄ O ₁₀ , H ₃ PO ₄	Also as metal phosphates
As	As ₂ O ₃ , As ₂ O ₅	As ₂ O ₅ not stable at high temp. As ₂ O ₃ bp=732 K. May also exist as arsenates.
Sb	Sb ₄ O ₆ , SbCl ₃ , SbO(g)(?)	Some SbCl ₃ if HCl = 0.01 atm
Bi	Bi ₂ O ₃ , BiOCl, BiCl ₃	Both BiCl ₃ and BiOCl volatile and moderately stable
S	SO ₂ , SO ₃ , H ₂ SO ₄	Also as metal sulfates, especially Na ₂ SO ₄
Se	SeO ₂	Sublimes 602 K
Te	TeO ₂	P = 0.1 torr at 1000 K, 50 torr at 1300 K
I	I ₂ , ICl, CH ₃ I, CsI	Some HI
Ce	Ce ₂ O ₃	
Pm	Pm ₂ O ₃	
Eu	Eu ₂ O ₃	
Th	ThO ₂	
U	UO ₃ , U ₃ O ₈	
Np	NpO ₂	
Pu	PuO ₂	
Am	Am ₂ O ₃	

TABLE 11. Estimated Partition Values

<u>Element</u>	<u>Ash</u>		<u>Fly Ash</u>	
	<u>Lit</u>	<u>Est</u>	<u>Lit</u>	<u>Est</u>
H (T)	0	0	0	10
Na	60-90	90	30-50	10
Cs	60-90	85	30-50	15
Be	90-99	90	2-10	10
Sr	45-95	95	2-20	5
Ra	80-95	90	-	10
V	90-99	90	10	10
Cr	80-100	65	70	34
Mn	50-99	65	25-45	34
Fe	60-98	55	3-20	44
Co	70-98	60	12-20	39
Ni	40-100	60	10-20	9
Cu	50-99	55	20-60	45
Zn	30-70	50	20-60	49
Y	60-95	95	40-60	5
Zr	60-95	95	40-60	5
Nb	65-75	95	-	5
Tc	10-95	40	-	50
Ru	70-90	40	5-25	59
Ag	30-99	80	15-45	20
Cd	30-90	40	20-40	58
Au	70-80	80	-	19
Hg	1-25	5	30-90	90
Ga	-	90	-	10
In	-	98	-	2
C	0.2-1	0-10	-	2
Ge	-	50	-	50
Sn	30-95	98	-	2
Pb	30-97	40	40-80	60
P	95	85	-	13
As	70-99	50	5-25	50
Sb	10-80	55	20-80	44
Bi	10-75	30	15-60	70
S	72	30	-	65
Se	1-20	10	-	80
Br	-	10	-	90
Te	50	50	-	49
I	< 1	2	-	68
Cl	~1	10	-	89
Ce	75-95	95	30-60	5
Pm	90-95	95	-	5
Sm	45-95	95	30-60	5
Eu	50-95	95	30-60	5
Th	40-90	98	20-50	2
U	65-100	98	1-35	2
Np	-	98	-	2
Pu	85-95	98	-	2
Am	-	98	-	2

TABLE 12. Estimated Partition of Selected Nuclides Temperature 1500 K

	<u>Slag, %</u>		<u>Fly Ash, %</u>		<u>Stack, %</u>	
HCl:	0.005	0.05	0.005	0.05	0.005	0.05
Cs	70	4	29	94	< 1	2
Sr	96	95	4	5	E-04	E-04
Zr	97	96	3	4	E-04	E-04
Co	>99	97	E-03	2	E-04	0.4
Zn	>99	60	E-03	36	E-04	4
Sb	>99	97	E-02	2	E-03	0.2
I	2	3	70	75	28	22
U	98	96	2	4	<< 1	<< 1

not very stable, but the oxide is so stable with respect to the chloride that little $ZrCl_4(g)$ should form. The conversion curve lies close to that of Ge in Figure 3. Formation of $ZrF_4(g)$ is only slightly more favorable, and in the presence of a small amount of water it appears impossible to vaporize Zr as the halide. Uranium should behave the same way.

Iodine is completely different. There may be little change with HCl concentration; an increased Cl level could increase the ICl concentration, which may be easier to remove with a water scrub than is I_2 . The remaining elements in Table 12, Cs, Co, Zn, and Sb, by contrast, are greatly affected by HCl concentration, as seen in Figures 13a and 13b.

Table 12 lists the resulting estimated partitions for two HCl levels. The temperature is 1500 K. The estimated changes in element percentages as the HCl is increased are based on the calculated changing compositions, primarily the metal chloride concentration. The uncertainties are large. Since it is assumed that HEPA filters are not present, particulate losses depend on the efficiency of the other components of the off-gas cleaning system, and the absolute numbers have limited significance.

Many questions remain. Predominant among them are kinetics, which determine whether favorable chemical reactions can actually take place, whether volatile species are in equilibrium with a condensed phase, and what

role diffusion plays in solids and liquids. It can be imagined that chemistry in micro dimensions in a combustion chamber where neither equilibrium nor steady state may exist can be significantly different from an ideal uniform system. Temperatures at the surface of a burning particle may exceed the bulk temperature. Metals returning to the solid state from the gas tend to form extremely small particles or "fumes" and become more difficult to trap. It is also expected that gaseous products (metals or metal salts) may condense or adsorb on particulates in the rapidly moving gas stream and reach a lower-temperature regime before equilibrium can be reached. Temperature may be the most important variable in the kinetics; as it is in equilibria.

As an example of the temperature effect on volatility, a change of 100°C at about 1200 K will change the vapor pressure of CsCl by a factor of about 10, and of Pb by over 20. Thus, several metals, metal halides, and hydroxides can change from having negligible vapor pressures to becoming quite volatile over the range of temperatures that have been used in incinerator operation.

At about 800 to 1100 K, sulfate ion could have an effect of reducing the volatility of some metals such as halides by several factors of ten. But, at 1300 K much of the protection may be gone. Temperature is also important in defining the nature of the slag, e.g., clinker formation, and as noted above is also the most important parameter in reaction rates. The temperature factor is graphically illustrated in the modeling calculations.

OTHER INCINERATOR MODIFICATIONS

THE CONTROLLED AIR INCINERATOR

The controlled air or limited oxygen incinerator has at least three major differences, a temperature lower by perhaps 200 to 300°C, a lower oxidation potential in the burner, and a lower gas velocity. The effect of the first is obvious. The effect of the second is more subtle. Possible changes would be lower oxidation states of some of the metals and an increase in the stability of the chlorides relative to the oxides. The effect of the third is one of the arguments for the controlled air operation, i.e., reduction of the flow of particulate matter from the combustion zone due to the reduced gas velocity, and the overall decreased load on the air pollution control equipment.

The chemistry of the limited oxidation incinerator is not discussed in this paper. Some of the thermodynamic discussion above would need revision for a reducing system. However, the controlled air burner is normally followed by a second-stage oxidizing system.

THE CEMENT KILN

The use of cement kilns for even low-level RW will probably not be accepted, but the kilns can tolerate many hazardous wastes. Some of the characteristics - the higher temperature and the alkaline environment - were mentioned in the introduction. The chemistry of the cement kiln may be better understood since it is governed by a only few major feed components. Thus the fate of minor nuclides in the feed materials should be more consistent than for a RW incinerator. The behavior of several metals and other additives was surveyed by Mantus (1992). It is suggested that the behavior of low-concentration metals in the cement kiln is worthy of further detailed study.

EFFICIENCY OF AQUEOUS SCRUBS

Improving the efficiency of aqueous scrubs is a problem with all gas cleaning systems. Removing a very soluble gas like HCl is relatively easy; iodine provides a more difficult task (Brown et al. 1983; Bunger and Scheele 1991). Particulate matter may be even more difficult to remove, depending on the particle size. Fortunately, most metal chlorides and bromides are at least moderately soluble in water. This is less true for the fluorides. However, a well-designed, combined mechanical-aqueous scrub system seems to offer the best hope of keeping most undesirable effluents from the exhaust stack.

DELIBERATE ADDITIONS TO THE FEED

It appears that a knowledge of the chemical composition of the incinerator feed is desirable to manage the off-gas behavior effectively. It should be possible to greatly influence metal partitioning by controlling the feed composition. Elements such as P, S, Al, Si, Ca, Na, and the halogens can change the volatility of other metals as well as the physical nature of the solids removed. Specific compounds could be introduced; for example, NaNO_3 or Na_2CO_3 would raise the alkalinity of the condensed phase, and the sodium also preferentially ties up the chlorine, thus reducing volatility of many metals. Adding sulfates would reduce low-temperature volatility since the sulfates of most of the metals of concern are more stable than the chlorides up to about 1000 K. By contrast, CaCl_2 becomes a chlorinating agent and could be employed if desired to deliberately increase volatility of several metals. Calcium, added as lime, would also raise the melting point of the ash or slag.

Other elements may form complexes that help retain metals in the slag. These include the conventional glass-formers normally present in the feed, such as silicates from glass waste as well as from paper, borates from glass and decontaminating agents, and phosphorous from organic solvents. Titanium will be introduced from paper waste.

CONCLUSION

The chemical properties of 50 nuclides have been considered and thermodynamic equilibria calculated at elevated temperatures to predict the chemical species present in an oxidizing incinerator. Combined with the physical properties of these species, the data help predict their likely retention in the ash or slag from the burner, their escape from the burner to be trapped in the off-gas treatment system as fly ash, or their possible release to the atmosphere. Particular emphasis was given to the formation and volatility of metal halides and the influence of other elements on this volatility. In addition to consideration of individual element properties, several calculations were made on multicomponent systems using a computer model. These were used to predict relative concentrations of different chemical species for different feed compositions, and as a function of temperature. These findings support predictions made with calculations for individual elements and show promise for more detailed computation.

Using the data developed, an estimate is then made as to how partitioning of these nuclides might be affected for a general case, and for selected elements, as a function of HCl concentration.

It must be emphasized that incineration is a complex phenomenon; chemical equilibrium is not necessarily achieved, and kinetics not only of chemical reaction but also involving adsorption and diffusion will be important. Thus, the numerical data derived from the calculations presented here should be viewed as guides, not as absolute quantities. In spite of these uncertainties, it is suggested that deliberate control of the types and amounts of various compounds entering the incinerator can greatly influence partitioning and thus affect potential releases and the management of incinerator wastes.

REFERENCES

- Bailar, J. C., Jr. et al. 1973. Comprehensive Inorganic Chemistry. Pergamon Press, New York.
- Barin, O. 1989. Thermochemical Data of Pure Substances. VCH, Weinheim, Germany.
- Brown, A. R., J. D. Christian, and T. R. Thomas. 1983. Airborne Radionuclide Waste Management Reference Document. ENICO-1133, Exxon Nuclear Idaho Company, Inc., Idaho Falls, Idaho.
- Bunger, L. L., and R. d. Scheele. 1991. HWVP Iodine Trap Evaluation. PNL-7851, Pacific Northwest Laboratory, Richland, Washington.
- Chao, C. C. 1988. "Assessment of Alternative Flue Gas Treatment for Hazardous Waste Incineration." In Proceedings, The International Conference on Incineration of Hazardous, Radioactive and Mixed Wastes, San Francisco, California.
- Christian, J. D. 1990. Behavior and Control of Ruthenium During Operation of the New Waste Calcining Facility at the Idaho Chemical Processing Plant. WINCO-11640, Westinghouse Idaho Nuclear Co. Inc., Idaho Falls, Idaho.
- Dean, J. A. 1992. Lange's Handbook of Chemistry. McGraw-Hill, Inc., New York.
- Emery, R. J., and J. E. Watson. 1990. "Retention and Subsequent Release of Radioactivity from the Incineration of Wastes Containing Microspheres." Health Phys. 59:911-914.
- Ephraïm, F. 1953. Inorganic Chemistry. Nordeman Publishing Co., New York.
- Fernandez, M. A., et al. 1992. "Behavior of Heavy Metals in the Combustion Gases of Urban Waste Incinerators." Environ. Sci. Technol. 26(5):1040-1047.
- Glassner, A. 1958. The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500 K. ANL-5750, U.S. Argonne National Laboratory, University of Chicago. Chicago, Illinois.
- Greenberg, R. R., W. H. Zoller, and G. E. Gordon. 1978. "Composition and Size Distributions of Particles Released in Refuse Incineration." Environ. Sci. Technol. 12:566-573.

Kyle, S., and E. Bellinger. 1988. Radioactivity Partitioning in Incinerators for Miscellaneous Low-Level Wastes. DOE/RW/88069, University of Manchester, Manchester, United Kingdom.

Levin, E. M., C. A. Roberts, and H. F. McMurdie. 1964. Phase Diagrams for Ceramists. American Ceramics Society, Columbus, Ohio.

Mantus, E. K. 1992. All Fired Up--Burning Hazardous Wastes in Cement Kilns. Environmental Toxicology International, Inc., Seattle, Washington.

Oppelt, E. T. 1986. "Hazardous Waste Destruction." Environ. Sci. Technol. 20(4):312-318.

Outokumpu Research. 1994. HSC Chemistry for Windows. Outokumpu Research, Finland.

Perkins, B. L. 1976. Incineration Facilities for Treatment of Radioactive Wastes: A Review. LA-6252, Los Alamos Scientific Laboratory, Los Alamos, New Mexico.

Science Applications International Corporation (SAI Corp). 1991. An Assessment of Thermal Destruction Technologies for Application to Department of Energy Mixed Wastes, Vol 1, Technology Assessment, Vol 2, Technology Data Sheets. DOE/HWP-106-Vol 2, Idaho Falls, Idaho.

Sedman, R. M., and J. R. Esparza. 1991. "Evaluation of the Public Health Risks Associated with Semivolatile Metal and Dioxin Emissions from Hazardous Waste Incinerators." Environ. Health Perspect. 94:181-187.

Stern, K. H. 1972. "High Temperature Properties and Decomposition of Inorganic Salts. Part 3, Nitrates and Nitrites of sodium and Potassium." J. Phys. Chem. Ref. Data 1(3):747.

Steverson, E. M. 1991. "Provoking a Firestorm: Waste Incineration." Environ. Sci. Technol. 25(11):1808-1814.

Travis, C. C., and S. C. Cook. 1989. Hazardous Waste Incineration and Human Health. CRC Press, Boca Raton, Florida.

Trichon, M., and J. Feldman. 1988. "Metallic Halide Emissions from Fixed and Hazardous Waste: Meeting Regulatory Requirements with New Technology." In Proceedings, International Conference on Incineration of Hazardous Radioactive and Mixed Wastes, San Francisco, California.

U.S. Department of Energy (DOE). 1979. Technology for Commercial Radioactive Waste Management. DOE/ET-0028, Volume 2, Section 4, Washington, D.C.

U.S. Environmental Protection Agency (EPA). 1991. Radiation and Mixed Waste Incineration. Background Information Document Vol 1. EPA 520/1-91-1:Technology.

Wagman, D. D., et al. 1982. The NBS Tables of Chemical Thermodynamic Properties, American Chemical Society and American Institute of Physics. J. Phys. Chem. Ref. Data 11(Suppl. 2).

Waterland, L. R., et al. 1991. "Trace Metal Fate in a Rotary Kiln Incinerator with an Ionizing Wet Scrubber." Waste Management 11:103-109.

Weast, R. C. (ed.). 1978. Handbook of Chemistry and Physics. The Chemical Rubber Co., Cleveland, Ohio.

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