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THE COMPARISON OF ELEMENT PARTITIONING IN TWO TYPES OF THERMAL TREATMENT FACILITIES AND THE EFFECTS ON POTENTIAL RADIATION DOSE

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The U.S. Department of Energy (DOE) is performing a technical analysis to support the potential development of risk-based, numerical radiological control criteria (RCC) for mixed waste from DOE operations. As part of the technical analysis, potential future radiation doses are being calculated for workers at thermal treatment facilities and members of the public residing near such facilities.

This study compared two types of thermal treatment systems: a conventional combustion chamber with excess air, represented by a rotary kiln with afterburner, and an oxygen-deficient pyrolysis unit, represented by a plasma arc furnace.

The purpose of the first part of this study is to estimate the partitioning for significant radionuclides and elements in the two types of thermal treatment systems. Excess-air systems are generally found to produce heavy-metal chlorides, oxides, and sulfates; plasma-arc systems tend to produce more volatile free metals. This difference causes a change in source term dominance from halide volatility to free metal volatility. Chemical thermodynamic methodology is used to estimate partitioning in the two treatment systems.

The second part of the study examines how the potential radiation dose to workers handling residue materials is affected by partitioning of radionuclides at the different types of facilities.

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PURPOSE AND BACKGROUND

This paper is an extension of the technical analysis by the U.S. Department of Energy (DOE) supporting the development of risk-based, numerical radiological control criteria (RCC) for mixed waste from DOE operations. The initial dose assessment that developed RCC for treatment of very slightly radioactive contaminated waste in RCRA facilities is documented in a draft report (1). The assessment of doses for thermal treatment in the draft report is based on incineration of waste in an oxygen-rich rotary kiln.

This paper compares the potential worker doses based on the two types of thermal facility: the oxygen-rich rotary kiln, and the oxygen-deficient plasma arc furnace. Differences in the compositions of the residue streams are based on the chemistry of the primary combustion chambers. Each facility type is also assumed to have an oxygen-rich secondary combustion chamber. The emphasis is on waste materials retained by the facility rather than on airborne emissions, which are dependent upon the air pollution control treatment devices employed.

PARTITIONING METHODOLOGY

The chemical reactions in an incinerator can be very complex. The products and their fate, i.e., whether they volatilize or remain in the slag, depends on both kinetics and equilibria. At the temperatures of the incinerator, roughly 1000 to 2000 K, reactions are fast but diffusional problems still may exist; reaction rates can be a problem. On the other hand, equilibria can be calculated if free energy data as a function of temperature are available and thus the predominant species can be predicted for the ideal system. From the calculated concentrations and vapor pressures, the partitioning between the off-gas (fly ash) and the bottom ash (slag) may be estimated.

The chemical composition of the feed material and of the gas phase becomes very important. While most incinerators operate with an excess of air, the "starved air" or reducing concept has its advantages. The latter process includes simple pyrolysis as an initial step. The development of the plasma arc furnace has increased the interest in the reducing system.

Some of the feed composition issues as they relate to the oxidizing system were discussed in a Pacific Northwest Laboratory (PNL) report by Burger (2). It was predicted that many metals would volatilize as halides, some as oxides, and a few as free metals. As an example of feed composition effects, it was shown that the presence of sulfur (forming sulfate salts) could reduce the volatility of metal halides.

By contrast, in the reducing system the water gas reaction,

$$H_2O + C = H_2 + CO \qquad (1)$$

controls the atmosphere, modified by sulfur, halogens and other components. The result is that many metal compounds are reduced to the free metal. The generalized effect is that the volatilization of metals as halides and oxides in the conventional or oxidizing system is replaced by volatilization as free metals in the reducing system. The relative values of the vapor pressures of pertinent metals, their halides and oxides range over about nine orders of magnitude.

Elements were chosen for this study to represent different groups in the periodic table and thus different chemical behaviors. Other elements are added because they would normally be present in a waste feed, and most are directly involved in the incineration process; these include Cl, F, S, Fe, Ca, Si, Na, H and O. While the complete spectrum of possible elements in incinerator feed is far from being covered in this paper, it is felt that the chosen elements permit some comparison of the two types of processes.

Starting compositions were assumed using data from Burger (2), and the effect on the equilibrium compositions was computed as the atmosphere switched from reducing to oxidizing in a continuous fashion. Feed compositions assumed for the test cases are shown in Table I.

The procedure was first to test sets of about three or four metals with water, nitrogen, carbon, chlorine, and iodine. Oxygen was then added incrementally up to the point where the total oxygen was about three times the total carbon. Fluorine and sulfur were then included, then calcium, silicon and iron. In a third sequence, different mixtures of metals were assumed and potential interactions estimated. Finally, an attempt was made to approximate concentrations relevant to RCC considerations by reducing the concentration of significant radioactive elements (nuclides) by three to six orders of magnitude. The temperature chosen for comparisons was 1500 K. A few calculations were made at 1000 and 2000 K.

TABLE I. Assumed Feed Composition for Simulations

Constituent	Mols in Feed	Constituent	Mols in Feed
HCl	$2x10^{-2}$	Sb	$2x10^{-6}$
HI	$1x10^{-5}$	Zn	$1x10^{-6}$
HF	$1x10^{-2}$	Fe	$2x10^{-2}$
H_2O	1.0	Ca	$1x10^{-2}$
C	1.0	Co	$1x10^{-6}$
O_2	$1x10^{-4}$ to 2	Sr	$1x10^{-6}$
Si	$4x10^{-2}$	Cs	$2x10^{-6}$
N_2	$2x10^{-1}$	Zr	$1x10^{-6}$
Na	$4x10^{-2}$	U	$1x10^{-6}$
S	$2x10^{-2}$	Pu	$1x10^{-6}$

PARTITIONING CALCULATION RESULTS

Since the model used for most of the calculations (HSC Chemistry for Windows (3)), assumes ideal solutions and unit activity coefficients, concentration is not important per se. However, when two or more metals compete for the same anion, for example, large differences in concentration become very important. This is illustrated by cobalt in the present study. The only significantly volatile compounds are CoCl and $CoCl_2$. However, NaCl is much more stable than $CoCl_2$, so that if much sodium is present, the volatility of cobalt will drop by several orders of magnitude. Since the aim of this study is primarily to compare the oxidizing and reducing furnaces, an arbitrary overall composition was assumed that gives a significant cobalt volatility.

The effect of sulfur in the oxidizing atmosphere is to reduce metal chloride volatility since the sulfates are generally more stable. However, this stability tends to disappear at about 1100 to 1300 K, and the net effect at 1500 K is small. In the reducing system, it is the metal sulfide which competes; for metals such as Co and Zn, S is replaced by O as the concentration of the latter increases. Again, other metals may influence volatility by removing sulfur. Calcium is effective in doing this, forming CaS. However, one of the more stable compounds is sodium sulfite. It is likely that cesium sulfite would also form, which would reduce the concentration of the volatile species, Cs, CsI and CsCl. The necessary thermodynamic data for Cs_2SO_3 were not found.

Rather than a detailed discussion of the chemistry, a short summary of the results will be presented here. The assumed sulfur content of the feed (Table I) is probably somewhat higher than in some waste streams. Eliminating sulfur raises the volatile Co fraction by an order of magnitude. However, Co volatility is primarily dependent on the available chloride. Sulfur lowers the concentration of Zn(g) but has little effect in the oxidizing system, probably because Ca and Na (which both form exceptionally stable sulfates) are present in large excess.

Duplicate calculations were made with silica added to the feed to simulate the incineration of soils. The volatility of most of the metals dropped as silica was added because silicates were formed. The most stable silicates are the group one and two metals. Thus Sr volatility is reduced by 10^2 in the reducing system and by 10^4 in the oxidizing system. Cesium volatility is not reduced because Ca, Na, and Fe form more stable silicates and are in excess.

Table II shows the fraction of each element of interest in the off-gas from the first stage of the incinerator. The predicted effect of switching between the reducing and oxidizing atmosphere was observed in the simulated tests. The most dramatic differences are shown by Zn and Sb, both existing as the metal gas in the reducing system. Metals such as Zr, Pu, and U remain largely as oxides in both systems; thus the quantity in the gas phase is

similar and extremely low. Iron is intermediate and at the concentration used in the tests is an order of magnitude lower in the oxidizing system. The principal volatile species of Co is $CoCl_2$, but is several orders of magnitude lower in the reducing system.

TABLE II. Partitioning Values: Fraction of Element in Gas Phase for Oxidizing and Reducing Incineration Systems.

Element	Fraction in Gas Phase	
	Oxidizing	Reducing
Fe	$6x10^{-4}$	$2x10^{-3}$
Co	0.5	$7x10^{-5}$
Zn	0.6	0.98
Sr	5E-5	6E-5
Zr	$1x10^{-6}$	$1x10^{-6}$
Sb	0.9	0.2
I	0.8	0.98
Cs	0.99	0.99
U	$1x10^{-5}$	$1x10^{-4}$
Pu	$1x10^{-6}$	$1x10^{-6}$

DOSE CALCULATION METHODOLOGY

The scenario analysis is based on the RCC study performed for DOE (1), in which radionuclide concentrations which correspond to a limiting dose are estimated. The RCC study was based on RCRA facilities and workers, rather than DOE facilities and radiation workers. In the RCC study, screening concentrations were calculated from individual dose levels of 0.1 to 200 μSv.

For the RCC study, scenarios for workers potentially exposed to incinerator residues were devised to describe waste-handling activities at a rotary kiln incinerator, based on routine work activities that involve interaction with residue materials. The scenarios were based on reports of DOE studies, including supporting information gathered for the RCC study (4,5,6). Fly-ash handling scenarios involve handling sludge from a wet scrubber or particulate waste from a baghouse. The slag-handling scenario may include incinerator maintenance or clean-out and refractory replacement as well as routine handling of solid residue.

Dose calculations in the current study are based on radiation exposure scenarios involving workers at a hazardous waste incinerator. Collective dose to workers and dose to off-site populations are beyond the scope of this paper. Pathways were assumed to include inhalation, incidental ingestion of particulate material containing radioactive contaminants, and external exposure to gamma radiation from residue materials.

In assessing the potential dose to the maximally exposed worker for incinerator residue-handling scenarios, both internal and external exposure pathways must be considered. External exposure, although not a routine concern at RCRA facilities, is an important factor to consider with feed material containing radioactive materials. Factors that affect doses are summarized in Table III.

TABLE III. Factors that Affect Doses to Workers Exposed to Radioactive Materials

Pathway	Exposure Parameters
External	Exposure time, radionuclide concentration, shielding, distance, geometry
Inhalation	Exposure time, radionuclide concentration, airborne particulate loading, protective clothing (mask)
Ingestion	Protective clothing requirements, transfer of contaminants from hands to mouth (secondary ingestion)

Dose comparisons for the reducing system are more qualitative, based on similar scenarios, but different distribution and concentrations of the radioactive constituents in residue materials. Exposure parameters used in the residue-handling scenarios are given in Table IV; exposure parameters chosen for the scenarios representing the oxidizing system were the same as for the RCC analysis.

TABLE IV. Exposure Parameters Used in Dose Calculations

Parameter Description	Scenario	
	Fly Ash Handling	Slag-Handling
Inhalation		
Exposure time, h	2000 (1000)[a]	2000
Dust loading, g/m3[b]	8×10^{-6}	9×10^{-6}
Ingestion		
Ingestion rate, g/h	0.01	0.01
Exposure time, h	500	500 (100)
External		
Exposure time, h	2000[c]	2000

(a) Value in parentheses () indicates modification made for reducing system.
(b) Dust loading is a weighted average of all occupational exposures
(c) The dose factor for external exposure is calculated as a weighted average of the shielding and the geometry encountered.

For the reducing system, similar parameters were used, but assumptions regarding inhalation and ingestion of particulate material were modified. To illustrate potential differences between facility types, inhalation exposure time for particulate matter was reduced to account for less material in the off-gas of the reducing system; incidental ingestion exposure to the bottom product was reduced to account for the more monolithic (less dusty) form of the product.

Dose to an individual worker was estimated for exposure to either bottom ash or fine particulate matter, in order to assess potential differences from radionuclide partitioning. Scenarios represent interaction of waste (residue) workers with the highest potential for exposure to contaminants. It is likely that workers could be exposed to both media during routine operations.

To perform a comparison on an equivalent basis, exposure scenarios are assumed to be similar for both types of treatment facilities. Differences in facility type which may affect exposure parameters are noted below:

- facility size (oxidizing system, base case 30,000 t/yr, or about 4 t/hr of operation vs. about 1 t/hr for a large plasma arc unit)
- quantity of residue materials
- proportion of fine particulate matter
- characteristics of residue material (particle size; dust concentration)
- automation of residue handling
- time involved in contact maintenance of the system.

Radionuclides chosen for this study represent not only a wide range of chemical properties, but also a wide range of properties from a health physics standpoint, as illustrated in Table V. The nuclides chosen for this study represent alpha-emitters, high and low gamma energies, and pure beta-emitters. As a result, different exposure pathways dominate the dose from different radionuclides.

TABLE V. Characteristic Emissions from Radionuclides Considered

Emissions from Radioactive Decay	Example	Other Examples
Alpha-emitters	^{238}U, ^{239}Pu	U, Th isotopes
No photon, high radiotoxicity	^{90}Sr	^{241}Pu
No photon, low to moderate radiotoxicity	^{93}Zr	^{63}Ni, ^{79}Se, ^{99}Tc, ^{147}Pm
Photon < 0.3 MeV	^{129}I	^{55}Fe, ^{125}Te, ^{125}I, ^{144}Ce, ^{151}Sm
Photon > 0.3 - 1 MeV	^{125}Sb	^{7}Be, ^{54}Mn, ^{57}Co, ^{94}Nb, ^{131}I, ^{137}Cs
Photon > 1 MeV	^{60}Co	^{65}Zn, ^{106}Ru, ^{110}Ag, ^{133}I, ^{134}Cs, ^{152}Eu, ^{154}Eu

DOSE CALCULATIONS RESULTS

Doses to incinerator workers exposed to residue materials were calculated from exposure parameters and element partitioning discussed above. Potential worker doses for both systems, based on feed of 1 Bq/g (27 pCi/g) of each radionuclide, are listed in Table VI. The magnitudes of the potential annual dose on doses range from essentially none (for interactions with elements which are all in the other residue category) to 200 to 300 μSv per Bq/g.

TABLE VI. Summary of Doses Calculated for a Worker Exposed to Residue from 1 Bq/g in Waste for Oxidizing and Reducing Systems

	Dose to Worker Handling Residue, μSv per Bq/g			
	Oxidizing		Reducing	
Nuclide	Fly ash	Slag	Fly ash	Slag/metal
^{60}Co	200	100	0.1	300
^{65}Zn	50	30	300	2
^{90}Sr	$5x10^{-5}$	0.4	$2x10^{-8}$	$1x10^{-3}$
^{93}Zr	$1x10^{-8}$	$5x10^{-3}$	$5x10^{-8}$	$1x10^{-3}$
^{125}Sb	40	4	40	40
^{129}I	4	$4x10^{-3}$	20	$1x10^{-3}$
^{137}Cs	60	0.5	200	1
^{238}U	$3x10^{-5}$	2	$8x10^{-4}$	0.3
^{239}Pu	$4x10^{-5}$	20	$1x10^{-4}$	4

Pathways of significance are dependent on both the radionuclide and the form of the residue material. Inhalation dose, the primary exposure route for alpha-emitters, was estimated to be fairly low, based on theoretical partitioning into the bottom product. It should be noted that the partitioning was based on chemistry alone, without correction for non-ideal behavior, such as particulate carry-over into the gas stream.

Although the chemical form of radionuclides (e.g. oxide vs. chloride) may affect the solubility class (thus, the dose factors), for this study, the solubility class has not been important. Most of the elements discussed in this paper exist as chlorides in the volatile phase for both the oxidizing and reducing systems. For all metals considered in this paper, the solubility

class of the oxide and chloride is the same, with the exception of Pu. The dose factor used for Pu is for class W (chloride) rather than class Y, which represents the oxide. If there is fluoride in the incinerator feed, the volatile form of U will be UF_4, (class W), with an inhalation dose factor about 5% of that of the oxide or chloride.

The elements Zn and Sb exist as the metal gas in the reducing system; in the oxidizing system, Zn exists as chloride ($ZnCl_2$) in the vapor, while Sb exists primarily as oxide (Sb_2O_6). The volatilities depend on the concentrations of HCl and O_2. For these elements as well as for other gamma-emitters, the concentration of chloride in the feed makes a potential difference in the external dose from of the fly-ash residue.

Incidental ingestion is the most important exposure pathway for both ^{90}Sr and ^{93}Zr, which are beta-emitters. It was noted in the discussion of partitioning that the presence of Si reduces the amount of Sr in the gas phase (by 2 to 4 orders of magnitude), thus reducing the availability of the radionuclide for ingestion.

Most of the radionuclides illustrated are gamma-emitters, for which external radiation is the most important exposure pathway. External exposure is an important factor to consider for incinerator feed containing radioactive materials, which is not considered for incinerators designed to handle purely hazardous (nonradioactive) waste. The external exposure scenarios include close contact with waste materials (filter press or bag filter contact-handling), which may be performed differently at a facility designed to handle radioactive materials. However, with the low concentrations, contact-handling is appropriate.

CONCLUSION

Potential dose to workers in an RCRA-type incinerator can be influenced by many factors.

The feed material may influence the fraction of material which volatilizes and becomes a potential source of airborne material and possibly of emissions. In addition to ideal partitioning, carry-over of particulate material from the primary to secondary combustion chamber could influence the mix of elements in the fly ash fraction.

The overall design of the facility, and degree of automation is a significant factor in actual worker exposure hours.

Although the type of system, with either oxidizing or reducing atmosphere will influence the waste stream into which some elements are distributed, the overall dose to workers would be less dependent upon partitioning than on routine work practices.

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