



Project Summary

Chemical Speciation of Flue Gas Desulfurization (FGD) Sludge Constituents

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This project studies the problem of flue gas desulfurization (FGD) sludge disposal to land. Specifically, the chemical species of FGD sludge constituents are thermodynamically modeled using the equilibrium constant approach in an attempt to predict the constituent concentrations in fresh and aged FGD wastewater and sludge. This method involves solving the stoichiometric equations of various chemical species subject to constraints imposed by the equilibrium constants as well as mass balance and charge balance relations. Diagrams such as Eh-pH plots, ion-ratio plots, concentration pH figures, and species distribution figures are then used to display the stability field and speciation results.

The thermodynamic model used in this study was verified for suitability and accuracy by the analytical results of various FGD sludge samples taken from the Kansas City Power and Light (La Cygne plant). The model was also operated over a wide range of operational and chemical changes to theoretically determine their impacts on the concentration and speciation of various solid and soluble species. The impacts of (1) changes in pH and ionic strength; (2) addition of lime, silicates, hydrogen sulfide, and phosphates to the sludge; (3) variation of chloride, sulfate, and borate levels; (4) addition of magnesium to the sorbent; and (5) sulfite oxidation were all estimated using the model.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

A conventional environmental impact assessment of flue gas desulfurization (FGD) sludge disposal would include chemical analysis and identification of the total concentrations of constituents in the sludge and its leachate. However, public health effects of FGD waste disposal depend on which chemical forms or species of the constituents are released to surrounding waters and not necessarily on their total concentration.

Thermodynamic modeling is the only feasible means to obtain contaminant species information of FGD sludge. A thermodynamic model can also be used to predict migration trends of constituents when FGD wastes age; estimate final concentrations of constituents in FGD leachate (aged wastewater) without conducting expensive field monitoring; and predict effects of operational and chemical changes in FGD wastes.

Many available techniques can be used to construct and interpret a chemical thermodynamic model. In this study, the equilibrium constant approach is used.

Methodology of Species Analyses

Two principal graphical treatments, Eh-pH plots and the ion-ratio method, are used to describe the stability fields of constituents in FGD sludge. The Eh-pH plot is used for constituents with different redox species such as iron, manganese, mercury, arsenic, and selenium. The ion-ratio method is used for constituents with only one redox state or for reactions involving no electron transfer.

The speciation model is constructed by the equilibrium constant approach. The actual mathematical equilibrium model involves a series of simultaneous equations that describe the various interactions among components of the system. Seven general equations are involved (Table 1). To solve these equations simultaneously, the information on metal and ligand species, overall formation constants, solubility products (and/or Henry's constants), and activity coefficients must be compiled from the literature. A computer solution is necessary, as the expanded equations number in the hundreds. The resultant nonlinear equations are solved by Newton-Raphson iteration.

Because the chemical composition of FGD sludge can vary over an extremely wide range, this study focused on speciation at the lowest levels (ionic strength (I) = 0.05) and the highest levels (I = 0.8). All possible distributions of species are expected to be within this range.

Speciation of Solid and Soluble Chemical Species

Fresh FGD Sludge

Thermodynamic modeling of the fresh FGD wastewater system can be performed as if no solid was formed or dissolved because (1) the equilibrium conditions among soluble species can easily be reached and (2) the rates of nucleation and dissolution of the solid species are very low. A summary of the predominant soluble species shows that the major ions (i.e., calcium, magnesium, potassium, and sodium) and the manganese species exist as free ions in fresh FGD wastewaters (Table 2).

Other trace metals, however, can be complexed considerably in the same wastewaters. Chloride complexes may under certain conditions become the predominant species for cadmium, copper, lead, mercury, and zinc; borate

Table 1. General Models Used for Speciation Calculation

$$[M(i)_m L(j)_n] = \beta(i,j)_{nm} [M(i)_t]^m [L(j)_t]^n \cdot \frac{\gamma M^m(i) \gamma L^n(j)}{\gamma M(i)_m L(j)_n} \quad (1)$$

$$[M(i)_t] = \frac{{}^R M(i)_p L(j)_q \cdot {}^R M(i)_p L(j)_q \cdot {}^I M(i)_p L(j)_q}{M^p(i) \cdot L^q(j) \cdot [L(j)_t]^q} \quad (2)$$

$$[L(j)_t] = \frac{{}^R M(i)_u L(j)_v \cdot {}^R M(i)_u L(j)_v \cdot {}^I M(i)_u L(j)_v}{\gamma M^u(i) \cdot L^v(j) \cdot [M(i)_t]^u} \quad (3)$$

$$\sum_{j=1}^h \sum_{p=1}^a \sum_{q=1}^b {}^R M(i)_p L(j)_q = 1 \quad (4)$$

$$\sum_{i=1}^g \sum_{u=1}^c \sum_{v=1}^d {}^R M(i)_u L(j)_v = 1 \quad (5)$$

$$[M(i)_t] = [M(i)_t] + \sum_{m=1}^k \sum_{n=1}^l \sum_{j=1}^h m [M(i)_m L(j)_n] + \sum_{j=1}^h \sum_{p=1}^a \sum_{q=1}^b p [M(i)_p L(j)_q] + \sum_{j=1}^h \sum_{u=1}^c \sum_{v=1}^d n [M(i)_u L(j)_v] \quad (6)$$

$$[L(j)_t] = [L(j)_t] + \sum_{m=1}^k \sum_{n=1}^l \sum_{j=1}^g n [M(i)_m L(j)_n] + \sum_{i=1}^g \sum_{p=1}^a \sum_{q=1}^b [M(i)_p L(j)_q] + \sum_{i=1}^g \sum_{u=1}^c \sum_{v=1}^d [M(i)_u L(j)_v] \quad (7)$$

where:

$[M(i)_m L(j)_n]$ = concentration of complex $M(i)_m L(j)_n$ (in moles/liter)

$[M(i)_t]$ = free metal ion concentration of i th metal (in moles/liter)

$[L(j)_t]$ = free concentration of j th ligand (in moles/liter)

$[M(i)_t]$ = total concentration of i th metal in the system (in moles/liter)

${}^R M(i)_p L(j)_q$

and

${}^R M(i)_u L(j)_v$ = mole fraction of solid or gas species for metal or ligand solids

i = metal species

Table 1. (continued)

j	= ligand species
g	= total number of metals
h	= total number of ligands
k	= maximum number of metals $M(i)$ coordinating ligands $L(j)$
l	= maximum number of ligands $L(j)$ coordinating metal $M(i)$
$a, b, c,$ and d	= positive integer showing maximum number of metals or ligands in the solids or gases
$\beta(i,j)_{nm}$	= overall formation constant of complex $M(i)_m L(j)_n$
γ_x	= thermodynamic activity coefficient of soluble species x
f_x	= thermodynamic activity coefficient of solid (or gas) species x (in this study, assume $f_x \approx 1$)
K	= solubility products or Henry's constants

complexes may become the predominant species for copper and lead; sulfite complexes may become the predominant species for cadmium and iron; and hydroxide complexes may become the predominant species for mercury, zinc, and the trivalent metals such as chromium and iron. In fresh FGD wastewater, arsenic and selenium exist primarily as arsenate and selenite species. The predominance of a given species can be affected significantly by the pH level of the wastewater. The ionic strength (or more specifically, the soluble levels of the related ligands) also plays an important role in the speciation of most constituents:

Aged FGD Sludge

The speciation of constituents in the solid and soluble phases of aged FGD sludge was computed assuming that the equilibrium condition among all the soluble and solid species had been reached. Because of the long contact period, equilibrium conditions between solid and liquid phases probably can be reached in aged FGD wastes. The calculated results are summarized in Table 3.

Results show that sulfur dioxide removed from the flue gas reacts to form $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}(\text{s})$ and $\text{CaSO}_3 \cdot 1/2\text{H}_2\text{O}(\text{s})$ in the FGD sludge. In the aged sludge, carbonate solids may become the predominant species for cadmium, calcium (when pH is greater than 7), copper, lead (at pH greater than about 9), manganese (at pH greater than about 7.5), and zinc

(at high ionic strength and pH around 8). Hydroxide solids are the predominant species for chromium, iron, cadmium (at pH greater than 9), magnesium (at pH greater than 9), manganese (at pH greater than about 9), and zinc (at low ionic strength and pH greater than about 9) in the aged sludge. Arsenic, mercury, and selenium exist primarily as elemental metals in the aged sludge. Aluminum forms predominantly phosphate solids at low pH and oxide solids at high pH. In aged sludge, the molybdate and silicate solids are usually the predominant species for lead and zinc, respectively.

The predominant soluble species of constituents in aged FGD leachates are similar to those found in fresh FGD wastewater. However, the concentrations of these soluble species are generally decreased through aging because of the nature of solids found. The predominant soluble species and their concentrations for each individual constituent at two different ionic strengths are shown in Table 3. In most cases, the predominant species alone will account for a major portion of the concentration. Therefore, knowing the predominant solid and soluble species, the total soluble concentration of a constituent in FGD leachate can be easily calculated without the aid of the computer.

Model Verification

The thermodynamic model was verified by checking the model results

against both analytical data and certain theoretical considerations.

The model, in relation to analytical data, was evaluated by comparing the known soluble concentrations of constituents in aged FGD wastes to those predicted by the model. The calculated results for aluminum, arsenic, boron, cadmium, cobalt, copper, iron, manganese, mercury, potassium, selenium, sodium, and zinc either approach or are very close to the concentration levels experienced in the field (Table 4). For other elements (specifically calcium, chromium, fluoride, lead, and magnesium), the model was not as effective. The low levels of calcium predicted are due primarily to the interaction of calcite with CaCO_3 and CaSO_3 complexes in the model. The high levels of chromium and lead calculated are due to the inclusion of hydroxide and carbonate complexes in the model. For fluoride and magnesium, the discrepancy may be caused by certain unsuitable solids included in the model. The discrepancies also may be due to (1) errors in the stability constants and activity coefficients; (2) effects of other mechanisms such as adsorption by hydroxide solids or clay minerals; and (3) effects of kinetic constraints.

According to scientific considerations, in general, the model results behave in accordance with basic chemical and thermodynamic principles, including the effects of changing pH, Eh, and ligand levels.

Effects of FGD System and Sludge Variables on Chemical Speciation

To select a sludge treatment or disposal procedure, observing the possible beneficial or adverse effects of operational or chemical changes in a FGD system on sludge speciation is useful. The chemical changes studied here include those of pH, ionic strength, chloride concentration, borate concentration, sulfate concentration, and sulfite oxidation (Table 5). The operational changes were limited to the addition of lime, silicates, hydrogen sulfide, phosphates, and magnesium (Table 6).

A change in pH can influence the direction of the alteration processes (dissolution, precipitation, adsorption, or complexation) in any chemical system. In general, a pH increase in the FGD sludge system tends to dissolve more

Table 2. Predominant Species of Soluble Constituents in Fresh FGD Wastewater

Constituent	Ionic Strength	Predominant Species ^a		
		pH = 5	pH = 7	pH = 9
Al	0.05	$AlF_2^+(34), Al(OH)^{2+}(20),$ $AlF_2^+(17)$	$Al(OH)_4^-(100)$	$Al(OH)_4^-(100)$
	0.8	$AlF_2^+(55)$	$AlF_2^+(38), AlF_3(31)$	$Al(OH)_4^-(100)$
As	0.05	$H_2AsO_4^-(98)$	$HAsO_4^{2-}(68)$	$HAsO_4^{2-}(100)$
	0.8	$H_2AsO_4^-(95)$	$HAsO_4^{2-}(78)$	$HAsO_4^{2-}(97)$
Cd	0.05	$Cd^{2+}(50), CdCO_3(aq)(40)$	$Cd^{2+}(49), CdCl^+(40)$	$CdCO_3(35), Cd^{2+}(21),$ $CdCl(OH)^{2+}(20)$
	0.8	$CdCl^+(66)$	$Cd(SO_3)_2^{2-}(59)$	$Cd(SO_3)_2^{2-}(65)$
Ca	0.05	$Ca^{2+}(83)$	$Ca^{2+}(89)$	$Ca^{2+}(81)$
	0.8	$Ca^{2+}(71)$	$Ca^{2+}(71)$	$Ca^{2+}(71)$
Cr	0.05	$Cr(OH)^{2+}(79)$	$Cr(OH)_2^+(85)$	$Cr(OH)_4^-(100)$
	0.8	$Cr(OH)^{2+}(65)$	$Cr(OH)_2^+(81)$	$Cr(OH)_4^-(100)$
Co	0.05	$Co^{2+}(69)$	$Co^{2+}(68)$	$CoCO_3(aq)(44), Co^{2+}(26)$
	0.8	$Co^{2+}(40), CoSO_4(aq)(26)$	$Co^{2+}(40), CoSO_4(aq)(26)$	$CoCO_3(aq)(28), Co^{2+}(25),$ $CoCl^+(20)$
Cu	0.05	$Cu^{2+}(54)$	$Cu(B(OH)_4)_2(aq)(51)$	$Cu(B(OH)_4)_2(aq)(97),$ $Cu(B(OH)_4)_2(aq)$
	0.8	$CuB(OH)_4^+(35), CuCl^+(26)$	$Cu(B(OH)_4)_2(aq)(83)$	$Cu(B(OH)_4)_2(aq)(100)$
F	0.05	$F^-(25), SnF^+(52)$	$F^-(91)$	$F^-(93)$
	0.8	$CaF^+(40), F^-(38)$	$F^-(40), MgF^+(44)$	$MgF^+(47), F^-(45)$
Fe	0.05	$Fe(OH)^{2+}(83)$	$Fe(OH)_2^+(100)$	$Fe(OH)_4^-(93)$
	0.8	$FeSO_3^+(97)$	$Fe(OH)_2^+(84)$	$Fe(OH)_2^+(93)$
Pb	0.05	$Pb^{2+}(55)$	$Pb(B(OH)_4)_2(aq)(45),$ $Pb^{2+}(19)$	$Pb(B(OH)_4)_2(aq)(95),$ $Pb(B(OH)_4)_2(aq)$
	0.8	$PbCl^+(33),$ $PbSO_4(22), Pb^{2+}(21)$	$Pb(B(OH)_4)_2(aq)(87)$	$Pb(B(OH)_4)_2(aq)(100)$
Mg	0.05	$Mg^{2+}(79)$	$Mg^{2+}(79)$	$Mg^{2+}(78)$
	0.8	$Mg^{2+}(66)$	$Mg^{2+}(66)$	$Mg^{2+}(65)$
Mn	0.05	$Mn^{2+}(79)$	$Mn^{2+}(78)$	$Mn^{2+}(76)$
	0.8	$Mn^{2+}(55)$	$Mn^{2+}(55)$	$Mn^{2+}(54)$
Hg	0.05	$HgCl_2(aq)(87)$	$HgCl_2(aq)(62)$	$Hg(OH)_2(aq)(65)$
	0.8	$HgCl_3^-(47), HgCl_4^{2-}(26)$ $HgCl_2(aq)(27)$	$HgCl_3^-(46),$	$HgClOH(aq)(52)$
K	0.05	$K^+(97)$	$K^+(97)$	$K^+(98)$
	0.8	$K^+(89)$	$K^+(89)$	$K^+(89)$
Se	0.05	$HSeO_3^-(97)$	$SeO_3^{2-}(74)$	$SeO_3^{2-}(99)$
	0.8	$HSeO_3^-(97)$	$SeO_3^{2-}(74)$	$SeO_3^{2-}(99)$
Na	0.05	$Na^+(95)$	$Na^+(95)$	$Na^+(97)$
	0.8	$Na^+(95)$	$Na^+(95)$	$Na^+(95)$
Zn	0.05	$Zn^{2+}(74)$	$Zn^{2+}(74)$	$Zn(OH)_2(aq)(68)$
	0.8	$Zn^{2+}(47), ZnCl^+(34)$	$Zn^{2+}(43), ZnCl^+(33)$	$Zn(OH)_2(aq)(42),$ $ZnClOH(aq)(26)$

Note: Values in the parentheses indicate the percent of the total concentration.

^aIf one species accounts for less than 50 percent of the total concentration, then more than one species will appear.

elemental constituents such as $As^0(s)$, $Hg^0(l)$, and $Se^0(s)$ and to transform some of the carbonate, phosphate, or other solids into hydroxide solids, thus affecting the concentration of soluble constituents. A pH change may also affect the ligand concentrations and, thereby, change the concentration of soluble constituents.

The overall effects of pH on total constituent concentration depend on

the solubility constants of the new solids formed, the new ligand concentrations, and the formation constants of the complexes. For example, a high pH level can increase total soluble mercury and selenium and yet decrease most of the other bivalent trace metals. For trivalent metals such as chromium and iron, the minimum soluble constituent concentrations occur in the neutral pH region.

Although a change in ionic strength in the FGD sludge can affect the stability

constants, its effects on the soluble levels of constituents or on the stability fields of various solids are usually negligible if their related ligand levels are unchanged. The soluble chloride concentration of FGD waste is a very important factor in determining the total soluble level of cadmium, copper, lead, mercury, and zinc. Variations in borate concentration have an impact primarily on total soluble copper and lead concentrations. The soluble sulfate concentration may affect the total soluble calcium,

*s = solid
l = liquid

Table 3. Predominant Species of Constituents in Aged FGD Sludge

Constituent	Ionic Strength	Predominant Solid Species ^a			Predominant Soluble Species ^a		
		pH = 5	pH = 7	pH = 9	pH = 5	pH = 7	pH = 9
Al	0.05	$Al(H_2PO_4)(OH)_2(s)$	$Al(H_2PO_4)(OH)_2(s)$	$Al_2O_3 \cdot 3H_2O(s)$	$AlF_2^+(6.04)$	$Al(OH)_3(aq)(6.26)$	$Al(OH)_3(aq)(5.95)$
	0.8	$Al(H_2PO_4)(OH)_2(s)$	$Al(H_2PO_4)(OH)_2(s)$	$Al_2O_3 \cdot 3H_2O(s)$	$AlF_2^+(5.05)$	$Al(OH)_3(aq)(6.89)$	$Al(OH)_3(aq)(5.36)$
As	0.05	$As^0(s)$	$As^0(s)$	$As^0(s)$	$H_2AsO_4^-(8.03)$	$HAsO_4^{2-}(11.23)$	$HAsO_4^{2-}(8.82)$
	0.8	$As^0(s)$	$As^0(s)$	$As^0(s)$	$H_2AsO_4^-(7.51)$	$HAsO_4^{2-}(10.87)$	$HAsO_4^{2-}(10.91)$
Cd	0.05	$CdCO_3(s)$	$CdCO_3(s)$	$Cd(OH)_2(s)$	$Cd^{2+}(5.23)$	$Cd^{2+}(6.03)$	$Cd(SO_4)_2^-(7.72)$
	0.8	$CdCO_3(s)$	$CdCO_3(s)$	$Cd(OH)_2(s)$, $CdCO_3(s)$	$CdCl^+(5.12)$	$CdCl^+(5.13)$	$CdClOH(aq)(6.07)$
Ca	0.05	$CaSO_3 \cdot 1/2H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$CaSO_3 \cdot 1/2H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$CaCO_3(s)$, $CaSO_3 \cdot 1/2H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$Ca^{2+}(0.21)$	$Ca^{2+}(0.53)$	$Ca^{2+}(2.19)$
	0.8	$CaSO_3 \cdot H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$CaSO_3 \cdot H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$CaCO_3(s)$, $CaSO_3 \cdot 1/2H_2O(s)$, $CaSO_4 \cdot 2H_2O(s)$	$Ca^{2+}(0.25)$	$Ca^{2+}(0.32)$	$Ca^{2+}(2.0)$
Cr	0.05	$Cr(OH)_3(s)$	$Cr(OH)_3(s)$	$Cr(OH)_3(s)$	$Cr(OH)_2^+(4.13)$	$Cr(OH)_2^+(4.76)$	$Cr(OH)_4^-(4.03)$
	0.8	$Cr(OH)_3(s)$	$Cr(OH)_3(s)$	$Cr(OH)_3(s)$	$Cr(OH)_2^+(5.0)$	$Cr(OH)_2^+(4.72)$	$Cr(OH)_4^-(3.99)$
Cu	0.05	$Cu_2CO_3(OH)_2(s)$	$Cu_2CO_3(OH)_2(s)$	$Cu_2CO_3(OH)_2(s)$	$CuB(OH)_4^+(15.38)$	$CuB(OH)_4(aq)$ (16.78)	$CuB(OH)_4(aq)$
	0.8	$Cu_2CO_3(OH)_2(s)$	$Cu_2CO_3(OH)_2(s)$	$Cu_2CO_3(OH)_2(s)$	$CuB(OH)_4^+(14.99)$ (16.09)	$CuB(OH)_4(aq)$ (16.4)	$CuB(OH)_4(aq)$
Fe	0.05	$Fe(OH)_3(s)$	$Fe(OH)_3(s)$	$Fe(OH)_3(s)$	$Fe(OH)_2^+(7.16)$	$Fe(OH)_2^+(9.16)$	$Fe(OH)_4^-(10.07)$
	0.8	$Fe(OH)_3(s)$	$Fe(OH)_3(s)$	$Fe(OH)_3(s)$	$FeSO_3^+(6.98)$	$Fe(OH)_2^+(9.12)$	$Fe(OH)_4^-(8.96)$
Pb	0.05	$PbMoO_4(s)$	$PbMoO_4(s)$	$PbMoO_4(s)$	$Pb^{2+}(5.80)$	$PbB(OH)_4^+(5.82)$	$PbB(OH)_4^-(7.14)$
	0.8	$PbMoO_4(s)$	$PbMoO_4(s)$	$PbMoO_4(s)$, $PbCO_3(s)$	$PbCl^+(5.67)$	$PbB(OH)_4^+(5.44)$	$PbB(OH)_4^-(5.55)$
Mg	0.05	— ^b	— ^b	$Mg(OH)_2(s)$	$Mg^{2+}(3.91)$	$Mg^{2+}(3.92)$	$Mg^{2+}(4.16)$
	0.8	— ^b	— ^b	$Mg(OH)_2(s)$	$Mg^{2+}(0.95)$	$Mg^{2+}(0.95)$	$Mg^{2+}(1.13)$
Mn	0.05	— ^b	— ^b	$MnCO_3(s)$	$Mn^{2+}(3.49)$	$Mn^{2+}(3.49)$	$MnSO_4(aq)(4.10)$
	0.8	— ^b	— ^b	$Mn(OH)_2(s)$, $MnCO_3(s)$	$Mn^{2+}(3.56)$	$Mn^{2+}(3.56)$	$Mn^{2+}(4.33)$
Hg	0.05	$Hg^0(1)$	$Hg^0(1)$	$Hg^0(1)$	$HgCl_2(aq)(22.1)$	$HgCl_2(aq)(20.4)$	$Hg(OH)_2(aq)(17.9)$
	0.8	$Hg^0(1)$	$Hg^0(1)$	$Hg^0(1)$	$HgCl_3^-(19.9)$	$HgCl_3^-(18.2)$	$HgClOH(aq)(17.0)$
K	0.05	— ^b	— ^b	— ^b	$K^+(1.89)$	$K^+(1.89)$	$K^+(1.93)$
	0.8	— ^b	— ^b	— ^b	$K^+(1.87)$	$K^+(1.87)$	$K^+(1.91)$
Se	0.05	$Se^0(s)$	$Se^0(s)$	$Se^0(s)$	$HSeO_3^-(28.6)$	$SeO_3^{2-}(18.2)$	$SeO_3^{2-}(6.19)$
	0.8	$Se^0(s)$	$Se^0(s)$	$Se^0(s)$	$HSeO_3^-(28.6)$	$SeO_3^{2-}(18.2)$	$SeO_3^{2-}(6.19)$
Na	0.05	— ^b	— ^b	— ^b	$Na^+(1.36)$	$Na^+(1.36)$	$Na^+(1.37)$
	0.8	— ^b	— ^b	— ^b	$Na^+(0.83)$	$Na^+(0.83)$	$Na^+(0.85)$
Zn	0.05	— ^b	$ZnSiO_3(s)$	$Zn(OH)_2(s)$	$Zn^{2+}(3.63)$	$Zn^{2+}(3.65)$	$ZnSO_4(aq)(5.67)$
	0.8	$ZnSiO_3(s)$	$ZnSiO_3(s)$	$ZnSiO_3(s)$, $Zn(OH)_2(s)$	$Zn^{2+}(3.84)$	$Zn^{2+}(4.06)$	$Zn(OH)_2(aq)(5.9)$

Note. Values in parentheses indicate the -log molar concentration.

^aIf one species accounts for less than 50 percent of the total concentration, then more than one species will appear for each condition

^b—indicates that there is no stable solid or that the stable solid is in complex forms (e.g., complex silicates)

magnesium, cadmium, and zinc concentrations. In general, if the total soluble levels of the above-mentioned ligands (e.g., chloride, borate, and sulfate) are known, the total soluble metal concentrations in the aged FGD leachates can be approximated without extensive computation.

For operational changes, sulfite oxidation may reduce the concentration of sulfite complexes and increase the concentration of sulfate complexes but have very little impact on the total soluble concentration of most metals. The most significant effect of sulfite oxidation is the transformation of $CaSO_3 \cdot 1/2H_2O(s)$ to $CaSO_4 \cdot 2H_2O(s)$ or $CaCO_3(s)$, depending on pH levels. This transformation may affect the soluble levels of arsenic, mercury, and selenium if the redox potential is controlled by sulfate/sulfite species.

Adding lime to FGD sludge is used in pozzolanic fixation processes to improve the engineering properties of dewatered sludge. The model shows, however that adding lime may adversely affect constituent solubility. Adding lime may reduce the total soluble levels of certain constituents such as arsenic and manganese; however, the total soluble levels of most other trace toxic metals such as cadmium, chromium, copper, lead, mercury, selenium, and zinc, increase in aged FGD sludge following lime addition. This may actually increase the potential for environmental damage should the concentration increase outweigh the dilution factor decrease that results from permeability reduction.

Adding silicates may reduce the total soluble aluminum and zinc concentrations, but other elements studied are virtually unaffected.

Phosphate addition will only reduce two soluble major ions (calcium and magnesium) while increasing the soluble cadmium level. Phosphate itself is also a water pollutant, so adding phosphates is not recommended for the treatment of FGD wastewater.

The addition of hydrogen sulfide may reduce the soluble concentrations of trace metals substantially (Table 6). This operational change, however, may not be desirable for an FGD system because (1) hydrogen sulfide itself is a pollutant, and (2) the diffusion of oxygen into the sludge, followed by the oxidation process, will eventually return the soluble metals to their original concentration.

Magnesium improves the efficiency of wet FGD systems; therefore, use of high magnesium reagents could become commonplace. The model shows that, in general, adding magnesium will not

Table 4. *Validity of the Thermodynamic Model for the Prediction of FGD Sludge Speciation^a*

<i>Constituent</i>	<i>Validity of Model^b</i>	<i>Reason for Discrepancy</i>
<i>Al</i>	<i>Excellent</i>	
<i>As</i>	<i>Good</i>	
<i>B</i>	<i>Excellent</i>	
<i>Cd</i>	<i>Excellent</i>	
<i>Ca</i>	<i>Not applicable</i>	<i>Form strong CaCO₃(s) when pH >7</i>
<i>Cr</i>	<i>Not applicable</i>	<i>Form strong Cr-OH complexes</i>
<i>Co</i>	<i>Good</i>	
<i>Cu</i>	<i>Excellent</i>	
<i>F</i>	<i>Not applicable</i>	<i>Solubility-controlling solid unknown</i>
<i>Fe</i>	<i>Good</i>	
<i>Pb</i>	<i>Not applicable</i>	<i>Form strong Pb-CO₃ and Pb-OH complexes</i>
<i>Mg</i>	<i>Not applicable</i>	<i>Solubility-controlling solid unknown</i>
<i>Mn</i>	<i>Excellent</i>	
<i>Hg</i>	<i>Excellent</i>	
<i>K</i>	<i>Good</i>	
<i>Se</i>	<i>Good</i>	
<i>Na</i>	<i>Good</i>	
<i>Zn</i>	<i>Excellent</i>	

^a*Based on comparison of modeling results with Kansas City Power and Light FGD sludge analysis.*

^b*Excellent means that the migration trends of the constituent follow those predicted by the model and that measured levels in the aged leachate are within 30 percent of those estimated by the model; Good means that both estimated and calculated levels of constituents show the same migration trends when FGD waste ages.*

significantly affect the total soluble levels of most constituents.

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Table 5. Effects of Chemical Changes on the Speciation of Constituents in FGD Sludge

Constituent	pH	Ionic Strength	Chloride Concentration	Borate Concentration	Sulfate Concentration	Sulfite Oxidation
Al	Solid: High pH levels favor the formation of $Al_2O_3 \cdot 3H_2O(s)$; low pH levels favor the formation of $Al(H_2PO_4)(OH)_2(s)$ Soluble: When pH is higher than about 6, the predominant species will change from AlF_2^+ to $Al^{3+} \cdot OH^-$ complexes	Negligible (when related ligand concentrations are unchanged)	Negligible	Negligible	Negligible	Negligible Negligible
As	High pH levels tend to dissolve $As^+(s)$ and form arsenate species	Negligible	Negligible	Negligible	Negligible	Negligible, if the redox potential is not controlled by sulfate/sulfite species
Cd	Solid: When pH is higher than 10.5, $CdCO_3(s)$ may gradually transform to $Cd(OH)_2(s)$ Soluble: High pH level can lower the total Cd level	The relative distribution of Cd^{2+} and $Cd-Cl$ complexes can be altered by ionic strength changes	Can greatly affect the total soluble Cd levels when chloride is higher than certain levels	Negligible	$Cd-SO_4$ complex may become predominant when Cl^- , SO_3^{2-} , or OH^- complexes are not significant	Will reduce $Cd(SO_3)_2^{2-}$ and increase $CdSO_4(aq)$ levels. However, effects on total soluble Cd and Cd solids are negligible
Ca	Solid: $CaCO_3(s)$ may greatly increase in the sludge when $pH > 7$ Soluble: When $pH > 7$ the total Ca and Ca^{2+} are reduced significantly	Negligible	Negligible	Negligible	When $pH > 5$, and the sulfate level is higher than about 5,000 ppm, the $CaSO_4(aq)$ species may become predominant	Will convert the sulfite solid into sulfate or carbonate solids. Will have very little effect, however, on soluble Ca
Cr	Solid: $Cr(OH)_3(s)$ is significant when pH ranges from 6 to 9 Soluble: When pH is higher than about 4, the predominant species will change from Cr^{3+} to $Cr-OH$ complexes	Negligible	Negligible	Negligible	Negligible	Negligible
Cu	Solid: Negligible Soluble: When $pH > 4.8$, the predominant species will change from Cu^{2+} to $Cu-B(OH)_4$ complexes	Negligible	When $pH < 4.7$, $Cu-Cl$ complexes may become predominant when the chloride level is higher than 2,000 ppm	When the borate level increases from 5 ppm to 200 ppm, the soluble lead level can be increased about 2,000	Negligible	Negligible
Fe	Solid: Negligible Soluble: High pH levels ($pH > 8.5$) tend to increase $Fe-OH^-$ complexes but reduce the total Fe levels	Negligible	Negligible	Negligible	Negligible	Will transform $FeSO_3^+$ to $Fe(SO)_2^-$, but the solid phase will remain unchanged
Pb	Solid: When $pH < 9$, $PbMoO_4(s)$ is predominant, otherwise, $PbCO_3(s)$ is predominant Soluble: At high pH levels, $Pb-CO_3$ may increase the total Pb levels	Negligible	When $pH > 7$, $Pb-Cl$ complexes may become predominant when the chloride level is higher than 1,500 ppm	When the borate level increases from 5 ppm to 200 ppm, the soluble lead level can be increased about 10,000 times	Negligible	Negligible

Table 5. (continued)

Mg	Solid: High pH levels (pH >9) favor the formation of $Mg(OH)_2(s)$ Soluble: When pH is increased, the $MgSO_4(aq)$ species may become significant	Negligible	Negligible	Negligible	When the soluble sulfate level is raised to as high as 3,000 to 5,000 ppm, the level of $MgSO_4(aq)$ may exceed the Mg^{2+} level	Negligible
Mn	No significant effect on predominant soluble species. However, the total soluble level will be decreased at high pH levels because of the formation of more solid	Negligible	May affect the levels of Mn-Cl complexes, but will not change the total soluble levels significantly	Negligible	Negligible	Negligible
Hg	Low pH levels favor the formation of $Hg^{2+}(l)$ in the sludge. High pH levels tend to increase the soluble levels of $HgCl_2$, $HgCl_3^-$, $Hg(OH)_2(aq)$, and $HgClOH(aq)$	Negligible	When the chloride level varies from 50 to 6,000 ppm, the total soluble Hg can be increased for more than four orders of magnitude	Negligible	Negligible	If the redox potential is controlled by sulfate/sulfite species, sulfite oxidation can increase the soluble Hg level
K	Slightly reduces the K^+ levels when pH is increased	Negligible	Negligible	Negligible	Can affect the $K_2SO_4(aq)$ level. Will not, however, affect the total soluble level of K	Will increase the $K_2SO_4(aq)$ level and reduce the K^+ level, but will not have a significant effect on total soluble K
Se	High pH levels tend to dissolve $Se^{2+}(s)$ and form selenate species	Negligible	Negligible	Negligible	Negligible	If the redox potential is controlled by sulfate/sulfite species, sulfite oxidation can increase the soluble Se level
Na	Will slightly reduce the Na^+ levels when pH increases	Negligible	Negligible	Negligible	Can affect the $Na_2SO_4(aq)$ level. Will not, however, affect the total soluble level of Na	Will increase the $Na_2SO_4(aq)$ level and reduce the Na^+ level, but will not have a significant effect on total soluble Na
Zn	Solid: High pH levels favor the formation of $Zn(OH)_2(s)$. When pH decreases, $ZnSiO_3(s)$ will replace $Zn(OH)_2(s)$ Soluble: Will reduce total levels when pH increases	Negligible	When pH <9, the total soluble Zn exists predominantly as $ZnCl^+$ if the chloride level is higher than 3,000 ppm	Negligible	$ZnSO_4(aq)$ may become predominant at a pH around 9 when Cl^- and OH^- complexes are not significant	Negligible

Table 6. Effects of Adding Chemical Compounds on the Speciation of FGD Sludge Constituents

Constituent	Addition of Lime	Addition of Silicates	Addition of Hydrogen Sulfide	Addition of Phosphates	Addition of Magnesium
Al	Effect on total soluble Al is negligible	The soluble Al level can be greatly reduced when silicate addition is higher than 280 ppm as Si	Negligible	Effect on total soluble Al is negligible	Will not affect the total soluble Al
As	Lime addition can cause more $Ba_3(AsSO_4)_2(s)$ to form, so reduce the total soluble As slightly	Negligible	Negligible	Negligible	Will not affect the total soluble As
Cd	When the lime dosage is higher than 1,500 ppm, soluble Cd can be increased from 0.01 ppb to 1.45 ppb	Negligible	Cd can be reduced to trace levels when sulfide addition is higher than 0.2 ppm	When phosphate addition is higher than 310 ppm (as P), the soluble Cd can be increased about 2 times	Will not affect the total soluble Cd
Ca	When the dosage of lime is from 100 to 10,000 ppm, the total soluble Ca will increase from 200 ppm to 400 ppm	Negligible	Negligible	If phosphate addition is higher than 310 ppm (as P), soluble Ca can be reduced slightly	Magnesium addition may decrease the $Ca-SO_4$ and $Ca-F$ complexes but will not change the total soluble Ca
Cr	Lime addition tends to increase the total soluble Cr because of hydroxide complexes formation	Negligible	Negligible	Negligible	May affect the total soluble Cr through the CrF^{2+} reduction
Cu	Lime addition tends to increase soluble Cu but will not raise the soluble Cu above the detectable level	Negligible	Cu can be reduced to trace levels by adding as little as 0.001 ppm of sulfide	Negligible	Will not affect the total soluble Cu
Fe	When the lime dosage is higher than 1,500 ppm, the soluble Fe level will be increased from 0.012 ppb to 22 ppb	Negligible	Negligible	Negligible	Will not affect the total soluble Fe
Pb	Lime addition tends to increase the total soluble Pb because of carbonate complex formation	Negligible	Pb can be reduced to trace levels by adding as little as 0.001 ppm of sulfide	Negligible	Will not affect the total soluble Pb
Mg	Lime addition will only affect the total soluble Mg slightly but will significantly transform $Mg-CO_3$ complexes	Negligible	Negligible	Soluble Mg will be reduced about 2.5 times as the phosphate level is increased from 0.3 to 3,100 ppm (as P)	Will cause the increase of soluble Mg
Mn	Lime addition tends to reduce the soluble Mn to the 20-36 ppb range	Negligible	Negligible	Negligible	Will not affect the total soluble Mn
Hg	Lime addition tends to increase the total soluble Hg slightly because of an increase in pH	Negligible	Hg can be reduced to trace levels by adding as little as 0.001 ppm of sulfide	Negligible	Will not affect the total soluble Hg
K	Negligible	Negligible	Negligible	Negligible	Magnesium addition may decrease the $K_2SO_4(aq)$ level but will not affect the total soluble K
Se	Lime addition will increase the total soluble Se because of an increase in pH	Negligible	Negligible	Negligible	Will not affect the total soluble Se
Na	Negligible	Negligible	Negligible	Negligible	Magnesium addition may decrease the $Na_2SO_4(aq)$ level but will not affect the total soluble Na
Zn	Lime addition may increase the total soluble Zn to ppm levels	The soluble Zn level is reduced when silicate addition exceeds 280 ppm as Si	Zn will be reduced to trace levels when sulfide addition is higher than 0.5 ppm	Negligible	Will not affect the total soluble Zn

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***Donald E. Sanning** is the EPA Project Officer (see below).*

The complete report, entitled "Chemical Speciation of Flue Gas Desulfurization (FGD) Sludge Constituents," (Order No. PB 81-187 205; Cost: \$24.50, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

Springfield, VA 22161

Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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