

**Equilibrium Speciation of As, Cd, Cr, Hg, Ni, Pb, and Se
in Oxidative Thermal Conversion of Coal
- A Comparison of Thermodynamic Packages**

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Abstract

The equilibrium speciation of the trace elements As, Cd, Cr, Hg, Ni, Pb, and Se, in a model system, is predicted assuming ideal gas and pure condensed phases and taking into account the presence of a sorbent material for sulfur capture. The model system is based on a demonstration-scale pressurized fluidized-bed combustor, firing a Pittsburgh No. 8 bituminous coal, using dolomite as sorbent for sulfur capture, and equipped with a ceramic filter for particulate removal.

Results from four different thermodynamic packages (MINGTSYS, NASA-CET89, FACT, and SOLGASMIX) are compared over the temperature range [700 -2000 K], at pressures of 1 and 20 atmospheres. For the elements As, Hg, and Se almost identical equilibrium distributions were predicted by the four packages, while for the elements Cd, Cr, Ni, and Pb, differences in the output from the four packages were observed. These differences may be due to different solution techniques, convergence criteria, and/or thermodynamic input data utilized in the thermodynamic packages.

This paper contains an outline of the equilibrium distributions, the comparison, a discussion of the reasons for the different results obtained with the different thermodynamic packages, and a comparison between measured and predicted partitioning data.

Keywords

Coal, Combustion, Emission, Flue Gas Cleaning, Thermodynamic Calculations, PFBC, Trace Elements

1. Introduction

The elements contained in fossil and biomass fuels can be grouped into three concentration

levels: 1) the major elements, C, O, H, S, and N, building up the organic matrix of the fuel; 2) the ash forming elements, Al, Ca, Fe, K, Mg, Na, and Si, typically present in the concentration range from about 1000 ppmw to a few % (w/w) on a dry fuel basis; and 3) the trace elements (e.g., As, B, Cd, Cr, Hg, Ni, Pb, and Se) present typically in concentrations below 1000 ppmw [Swaine (1990)]. Several of the trace elements are vaporized during pyrolysis and combustion and recondensed on the surface of fly ash particles during subsequent cooling of the flue gas [see e.g., Davidson *et al.* (1974) and Swaine and Goodarzi (1995)]. Full-scale measurements have revealed significant amounts of some trace elements (e.g., B, Hg, and Se) in the flue gas leaving the stack [Meij *et al.* (1984), Clarke and Sloss (1992), and Sander (1993)]. Direct gaseous emission of these trace elements is undesired because of suspected toxicological effects on the environment and potential genetic or biological changes in living creatures [Swaine (1990), Clarke and Sloss (1992), Swaine and Goodarzi (1995), and Davidson and Clarke (1996)].

As a first approach, Global Equilibrium Analysis (GEA) has been used for several years in order to understand the various subprocesses in thermal fuel conversion systems. Frandsen *et al.* (1994) provided an introduction to the application of GEA on combustion systems, by utilizing the Gibbs energy minimization code MINGTSYS and reporting equilibrium distributions for 18 trace elements of concern with respect to coal utilization [Swaine (1990)]. Reducing and oxidizing conditions were considered, and the results were compared qualitatively to experimental results published in the literature [Frandsen *et al.* (1994) and Frandsen (1995)].

Numerous thermodynamic packages have been developed for the purpose of minimizing the Gibbs free energy of mass balance constrained combustion systems containing ash forming and trace element species [Vuthaluru *et al.* (1994)]. Differences in the output from those packages may be due to: 1) use of different thermochemical data, 2) different numerical solution techniques, or 3) different convergence criteria utilized. Thus, a GEA test was performed in order to compare the output from different available thermodynamic packages. This paper contains a summary and the major conclusions of this GEA test.

2. Description of the Modeling Approach

The total Gibbs energy, G^t , of a chemical system is given by:

$$\frac{G^t}{R \cdot T} = \sum_{i=1}^N n_i \cdot \left[\frac{G^{\circ}_{fi}}{R \cdot T} + \ln(a_i) \right]$$

where G symbolizes a Gibbs energy, superscript t denotes total, R is the universal gas constant, T is the absolute temperature, N is the total number of species, n_i is the number of moles of species i , superscript o denotes standard state, subscript fi denotes formation of species i , and a_i is the activity of species i . The function G^t is combined with the mass balance constraints of the system and minimized, using the method of undetermined Lagrangian multipliers [Eriksson (1975)].

A GEA model, based on an actual operating combustion system, has been set up. The temperature, pressure, and total elemental composition are specified. The gas is assumed ideal, and all condensed phases are considered pure. Among the ash forming elements, only calcium, Ca, is taken into account as an As-, Cr-, and S-capturing sorbent, in the form of CaCO_3 . The trace elements As, Cd, Cr, Hg, Ni, Pb, and Se are considered one at a time. Four different thermodynamic packages, MINGTSYS, NASA-CET89, FACT, and SOLGASMIX, have been used to minimize the total Gibbs energy of a model system with a well-defined chemistry; i.e., a list

of chemical species to be considered, and elemental composition. MINGTSYS has been chosen since it provides a baseline study of trace element equilibrium chemistry in hot flue gases [Frandsen *et al.* (1994)], while the other packages are commercially available and commonly used worldwide. A detailed description of the combustion system, a list of the combustion products and trace element species, and an introduction to each of the thermodynamic packages utilized in this study will be given in a future paper.

3. Major Results of the GEA Test

In this section, the thermodynamic stable species of the trace elements As, Cd, Cr, Hg, Ni, Pb, and Se are outlined and compared internally. Concentrations used by the models are presented in Table 1.

For the elements As, Hg, and Se at standard pressure, 1 atm., all four codes predicted equilibrium distributions equal to those reported by Frandsen *et al.* (1994). At elevated pressure, 20 atm., the equilibrium distributions of As, Hg, and Se, predicted by the four codes, were also consistent. For the elements Cd, Cr, Ni, and Pb, observed differences in the equilibrium distributions predicted by the four codes are briefly outlined below.

3.1. Cadmium (Cd)

At standard pressure, 1 atm., the MINGTSYS code found Cd to exist as CdCl₂(cr) below and CdCl₂(g) above 750 K. Above 1200 K Cd(g) and CdO(g) are the stable species, Cd(g) accounting for more than 95 %(mol/mol) of the Cd present at all temperatures. CdO(g) is gradually decomposing as the temperature is raised above 1280 K, forming Cd(g) and O₂(g).

The NASA-CET89 code found CdCl₂(cr) to be stable below and Cd(g) to be the major stable form of Cd above 750 K. Small amounts [< 2 %(mol/mol)] of the Cd were present as CdO(g) in the temperature range 750 - 1000 K.

The FACT code found CdCl₂(cr) to be stable up to 750 K, above which temperature CdO(cr) is stable up to 1000 K, see Figure 1. Formation of Cd(g) and CdO(g) begins at 850 K, Cd(g) being the major species above 1000 K. CdO(g) gradually decomposes forming Cd(g) and O₂(g) above 1000 K.

The SOLGASMIX code found CdO(cr) to be the stable form of Cd at temperatures up to 1400 K. Formation of Cd(g) begins at 1200 K. Above 1600 K, Cd(g) is the major stable form of Cd present. In addition, minor amounts of CdO(g) and CdCl₂(g) were formed in the temperature ranges [1300 - 2000 K] and [700 - 1500 K], respectively.

At elevated pressure, 20 atm., all four codes found equilibrium distributions of Cd equal to the ones reported for 1 atm., but with an increase in temperature of about 100 K; i.e., the MINGTSYS and NASA-CET89 codes found CdCl₂(cr) to be stable below 850 K. The relative amount of CdO(g) formed in the system is increased when the pressure is increased from 1 to 20 atm. Thus, elevated pressure seems to favor formation of CdO(g) at high temperatures.

3.2. Chromium (Cr)

At standard pressure, 1 atm., MINGTSYS and NASA-CET89 found Cr₂O₃(cr) to exist at temperatures up to approx. 1200 K, where it is decomposing, forming CrO₂(OH)₂(g) (see Figure 2). The latter has a maximum occurrence around 1300 K. Above 1300 K, chromium showed a

very complex equilibrium chemistry, forming the gaseous components, $\text{CrO}(\text{OH})$, $\text{CrO}_2(\text{OH})$, $\text{CrO}(\text{OH})_2$, CrO_2 , and CrO_3 .

The FACT code showed a completely different distribution of Cr at 1 atm., primarily due to 1) a lack of thermodynamic data for the gaseous chromiumoxides and -hydroxyoxides provided by Ebbinghaus (1993) and 2) an implementation of the composed oxide, $\text{CaO.Cr}_2\text{O}_3(\text{cr})$, which was shown to be thermodynamically stable between 800 and 1800 K (see Figure 3).

The SOLGASMIX code found $\text{CaO.Cr}_2\text{O}_3(\text{cr})$ to be the major Cr-species stable in the temperature range [700 - 2000 K]. In addition, minor amounts of $\text{Cr}_2\text{O}_3(\text{cr})$, $\text{CrO}_2(\text{g})$, and $\text{CrO}_3(\text{g})$ were formed at temperatures above 1450 K. The thermochemical data for the gaseous chromiumoxides and -hydroxyoxides reported by Ebbinghaus (1993) have not been included in these calculations.

At elevated pressure, 20 atm., MINGTSYS and NASA-CET89 found $\text{CrO}_2(\text{OH})_2(\text{g})$ to be the major stable form of Cr in the temperature range [900 - 1800 K]. Below 900 K, $\text{Cr}_2\text{O}_3(\text{cr})$ was stable, and below 1500 K, $\text{CrO}_2(\text{OH})_2(\text{g})$ was decomposing, forming primarily the gaseous Cr-species $\text{CrO}(\text{OH})$, $\text{CrO}_2(\text{OH})$, $\text{CrO}(\text{OH})_2$, and $\text{CrO}(\text{OH})_3$.

The FACT code found almost the same equilibrium distribution of Cr as reported for 1 atm., but with an increase in temperature of about 150 K. $\text{CaO.Cr}_2\text{O}_3(\text{cr})$ was found to be stable in the temperature range [900 - 1900 K].

In case $\text{CaO.Cr}_2\text{O}_3(\text{cr})$ was *not taken into account*, the SOLGASMIX code found $\text{Cr}_2\text{O}_3(\text{cr})$ to be the major stable form of Cr in the temperature range [700 - 2000 K]. In addition, minor amounts of $\text{CrO}_2(\text{g})$ and $\text{CrO}_3(\text{g})$ were formed above 1600 K. If taken into account, $\text{CaO.Cr}_2\text{O}_3(\text{cr})$ was the major Cr-species formed in the temperature range [700 - 2000 K].

3.3. Nickel (Ni)

At standard pressure, 1 atm., the MINGTSYS and FACT codes found Ni to form $\text{NiO}(\text{cr})$, being stable up to approximately 1500 K, where $\text{NiO}(\text{g})$, $\text{Ni}(\text{g})$, and $\text{NiCl}(\text{g})$ were formed, see Figure 4. Formation of $\text{NiCl}_2(\text{g})$ begins at 1000 K. $\text{NiO}(\text{g})$, $\text{NiCl}(\text{g})$, and $\text{NiCl}_2(\text{g})$ were stable up to 1800 K, where the last trace amount of $\text{NiO}(\text{cr})$ disappeared. Above 1825 K, existing equilibrium relations among $\text{NiO}(\text{g})$, $\text{NiCl}(\text{g})$, $\text{NiCl}_2(\text{g})$, and $\text{Ni}(\text{g})$ were shifted towards $\text{Ni}(\text{g})$ as the temperature was increased. Calculations performed with the FACT code indicated that implementation of $\text{Ni}(\text{OH})_2(\text{g})$, which was not included in the common list of species taken into account in this study, could affect the stability of $\text{NiO}(\text{cr})$. The NASA-CET89 code also predicted $\text{NiO}(\text{cr})$ to be stable at temperatures up to 1500 K, where formation of $\text{NiO}(\text{g})$, $\text{Ni}(\text{g})$, and $\text{NiCl}(\text{g})$ has started, but this code predicted a much higher concentration of $\text{Ni}(\text{g})$ and correspondingly lower concentrations of $\text{NiO}(\text{g})$, $\text{NiCl}(\text{g})$, and $\text{NiCl}_2(\text{g})$ above 1750 K, than the MINGTSYS and FACT codes.

The SOLGASMIX code found $\text{NiO}(\text{cr})$ to be the major stable form of Ni. Various gaseous Ni-species (Ni , NiO , NiCl , and NiCl_2) were formed at temperatures above 1600 K. As with the FACT code, the output from the SOLGASMIX code indicated that $\text{Ni}(\text{OH})_2(\text{g})$ may affect the stability of $\text{NiO}(\text{cr})$.

At elevated pressure, 20 atm., all four codes found the crystalline nickel oxide, $\text{NiO}(\text{cr})$, to be stable at temperatures below 1850 K, and the SOLGASMIX code, even up to 2000 K. Above 1100 K, varying amounts of $\text{NiO}(\text{g})$, $\text{Ni}(\text{g})$, $\text{NiCl}(\text{g})$, and $\text{NiCl}_2(\text{g})$ were formed. The NASA-

CET89 code again predicted a much higher concentration of Ni(g) and correspondingly lower concentrations of NiO(g), NiCl(g), and NiCl₂(g) above 1750 K than the other codes.

3.4. Lead (Pb)

At standard pressure, 1 atm., MINGTSYS and NASA-CET89 found PbCl₄(g) to be the major stable form of Pb below 1100 K (see Figure 5). Above 1300 K, PbO(g) was the major stable Pb-species, but it was gradually decomposed with increasing temperatures above 1500 K, forming Pb(g). Peaks of PbCl₂(g) and PbCl(g) were in the temperature ranges [1000 - 1500 K] and [1100 - 2000 K], respectively. PbCl₂(g) has a maximum occurrence of approx. 48 %(mol/mol) at 1200 K, while PbCl(g) has a maximum occurrence of approx. 8 %(mol/mol) at 1250 K.

The FACT and SOLGASMIX codes showed an equilibrium distribution of Pb similar to that reported above, but the relative amounts of PbCl(g) and PbCl₂(g) formed were smaller than predicted by the MINGTSYS and NASA-CET89 codes.

The output from the SOLGASMIX code indicated formation of significant amounts of PbO(cr) in the intermediate temperature range [1050 - 1800 K]. No condensed phases of Pb were found below 1000 K.

At elevated pressure, 20 atm., all four codes predict equilibrium distributions of Pb equal to those reported at 1 atm., but at about 150 K higher temperature. And again, the relative amounts of PbCl(g) and PbCl₂(g) predicted by MINGTSYS and NASA-CET89 were higher than those predicted by FACT and SOLGASMIX. Also, the SOLGASMIX code predicted formation of significant amounts of PbO(cr) in the intermediate temperature range [1100 - 2000 K], but no condensed phases were formed below 1100 K.

4. Comparison with Experimental Data

As part of this work, the calculated equilibrium distributions presented above have been compared to trace element partitioning measured in the demonstration-scale 70 MW_e full load Tidd pressurized bubbling fluidized-bed combustor located in Brilliant, Ohio. This plant is operated by Ohio Power Company, a subsidiary of American Electric Power.

Crushed Pittsburgh No. 8, bituminous coal is combined with water from a nearby river to produce a coal paste of approximately 25 % (w/w) moisture. The paste is fed to the combustor along with crushed dolomite. The material is fluidized by high velocity combustion air in the water-cooled boiler. Mean temperature in the combustor was controlled at approximately 1100 K [Radian (1994)]. After releasing heat to the in-bed, water-cooled tubes, the particulate-laden combustion gases are led into seven parallel, two-stage cyclones. The cyclones remove approximately 93 %(w/w) of the entrained solids (primarily sulfated lime, unreacted lime, ash, and unburned carbon). After the cyclones, the combustion gases flow through a gas turbine, to an electrostatic precipitator before the gases are released to the atmosphere. Bed ash, comprising about 45 % (w/w) of the total ash produced, is removed from the bottom of the combustor periodically through a lock hopper system [Radian (1994)].

A research feature of the Tidd plant is a demonstration scale hot gas cleanup system. Treated gas from one of the seven cyclone systems is diverted to a ceramic barrier advanced particle filter (APF) and backup cyclone, and directed back to the outlet header of the secondary cyclone. The APF uses Schumacher silicon carbide candles in a cluster/plenum arrangement developed by

Westinghouse Corporation to filter the gas [Radian (1994)]. In Table 2, the total trace element concentration in $\mu\text{g}/\text{Nm}^3$ including gas and particulate material at the APF inlet (1000 K and 9.2 atm.) and outlet is shown.

Notice in Table 2, that the total concentration of the trace elements As, Cd, Cr, Ni, and Pb is reduced significantly in the APF. For the elements Hg and Se, a moderate reduction in the total concentration is observed. These results correspond well with the trace element partitioning outlined in section 3, since (as also indicated in Table 2) the trace elements As, Cd, Cr, and Ni are expected to be in a condensed form at 1000 K and 9.2 atm. Anyhow, the output from the four codes indicate that gaseous forms of Cd and Cr could be stable at 1000 K. The predicted behavior of lead is in discrepancy with observations. All four codes predict Pb to be in the gas phase in the form of $\text{PbCl}_4(\text{g})$ at 1000 K. However, the high reduction of Pb across the APF suggests a condensed Pb species. The condensation of $\text{PbO}(\text{g})$ on solid SiO_2 is the likely removal mechanism [Owens and Biswas (1996)]. For Hg and Se, all four codes predict thermodynamic stable gaseous forms at 1000 K. Thus, the moderate reduction in the total concentration across the APF is not very surprising.

5. Summary and Discussion

The equilibrium speciation of As, Cd, Cr, Hg, Ni, Pb, and Se has been predicted at 1 and 20 atm. in the temperature range [700 - 2000 K], by use of the thermodynamic packages MINGTSYS, NASA-CET89, FACT, and SOLGASMIX.

For the elements As, Hg, and Se, almost identical equilibrium distributions were predicted by the four packages, while for the elements Cd, Cr, Ni, and Pb, differences in the output from the four packages were observed in this study. The greatest differences were due to the presence or absence of specific chemical species, such as $\text{Ni}(\text{OH})_2(\text{g})$ and the chromium oxyhydroxides, in the respective databases of the four packages. Differences due to the thermodynamic data for individual chemical species were also significant. For example, the amount of $\text{Ni}(\text{g})$ at 2000 K predicted by the NASA-CET89 code suggests that other thermodynamic data have been used than in the remaining packages.

When GEA is used on a thermal fuel conversion system one has to be aware of the following [Frandsen *et al.* (1994), Linak and Wendt (1994)]:

- 1) All relevant chemical species occurring in the thermal fuel conversion system must be taken into account, otherwise the output from the GEA will be misleading.
- 2) Consistent thermodynamic data must be used.
- 3) Appropriate mixing models (pure phases, ideal or non-ideal mixing) should be applied in the condensed phases.
- 4) In thermal fuel conversion systems, mixing phenomena and/or boiler design characteristics may introduce local conditions (e.g., temperature and/or composition gradients) ignored in the GEA.

Item 1) above has been illustrated through the comparison of thermodynamic packages performed in this study. All possible chemical species in an actual thermal fuel conversion system must be included when performing a GEA, otherwise the results and conclusions will be misleading. A complete proof of this will require a systematic combination of the different Gibbs energy minimization codes and thermochemical databases utilized in the four thermodynamic

packages compared. Thus, a certain standardization of the available thermochemical data for trace element species may eliminate some of the differences outlined in section 3 of this paper. This will also help to provide a relative accountability of the four packages.

In addition, this study has revealed the necessity of a systematic scanning for possible compounds of trace element fixation by ash species; e.g., $\text{CaO}\cdot\text{Cr}_2\text{O}_3$ or $(\text{PbO})_n\cdot\text{SiO}_2$. This may also help to clarify the equilibrium chemistry of trace elements in flue gases from thermal fuel conversion systems.

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<u>Reactor feedstock mass flows (kg/hr):</u>		
Coal : Sorbent : Moisture = 15.2 : 8.7 : 5.2		
<u>%(w/w)[db]:</u>	<u>Coal:</u>	<u>Sorbent:</u>
Carbon	83.3	12.0
Oxygen	9.0	48.0
Hydrogen	5.0	
Sulfur	1.2	
Nitrogen	1.5	
Calcium		40.0
<u>ppmw:</u>		
Chlorine	1200.0	320.0
Arsenic	45.0	1.9
Cadmium	0.11	0.14
Chromium	16.0	2.8
Mercury	0.15	0.0012
Nickel	13.0	12.0
Lead	6.3	6.9
Selenium	1.8	0.79

Table 1: Reactor feedstock mass flows and compositions used in this study.

Element:	APF Inlet:	APF Outlet:	Stable Species (1000 K, 9.2 atm.):
As	1100	3.9	Ca ₃ (AsO ₄) ₂ (cr)
Cd	6.8	ND(0.005)	CdO(cr), CdO(g), Cd(g), CdCl ₂ (g)
Cr	520	60	CrO ₂ (OH) ₂ (g), CaO.Cr ₂ O ₃ (cr)
Hg	16	15	Hg(g), HgO(g), HgCl ₂ (g)
Ni	220	51	NiO(cr)
Pb	240	0.029	PbCl ₄ (g)
Se	67	49	SeO ₂ (g)

Table 2: Total concentration at 1000 K and 9.2 atm - including gas-phase and particulate material - in µg/Nm³ before and after the advanced particulate filter (APF) of the Tidd plant. Thermodynamic stable phases predicted by the four thermodynamic packages are indicated.

ND: Not detected at the concentration in parentheses.

Source (measured data): Radian (1994).

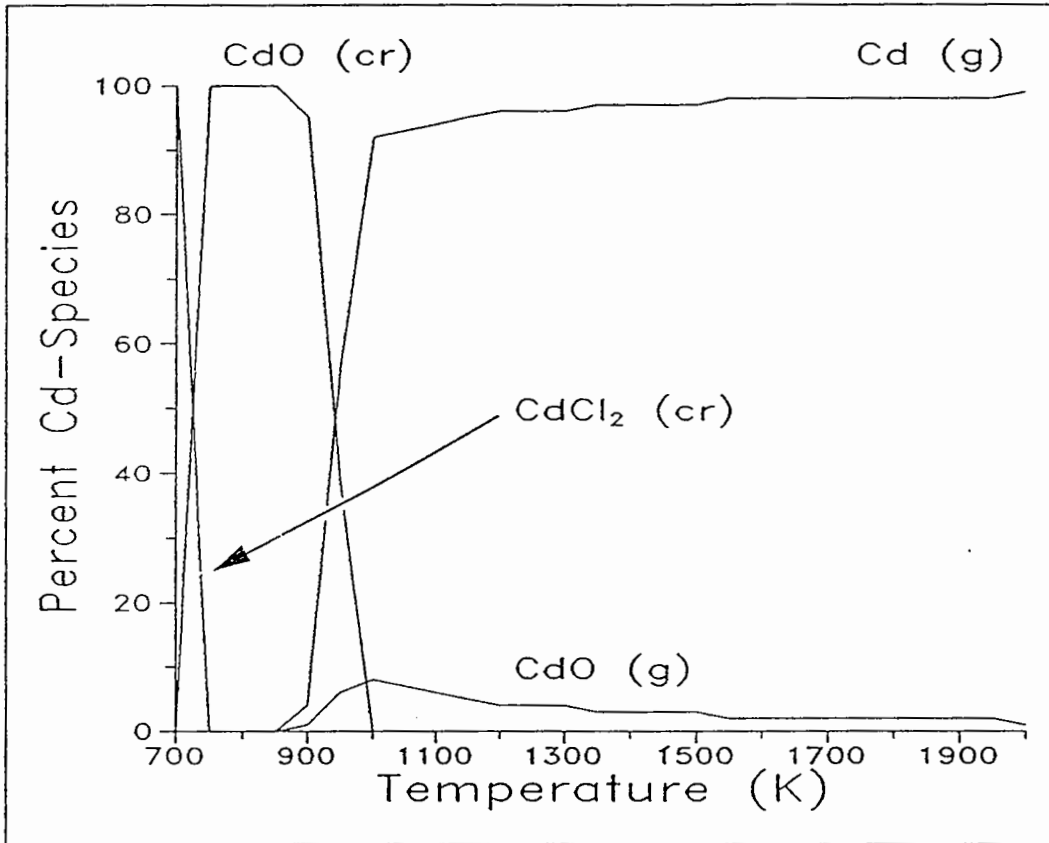


Figure 1: Equilibrium distribution of Cd at 1 atm. as found by the FACT code.

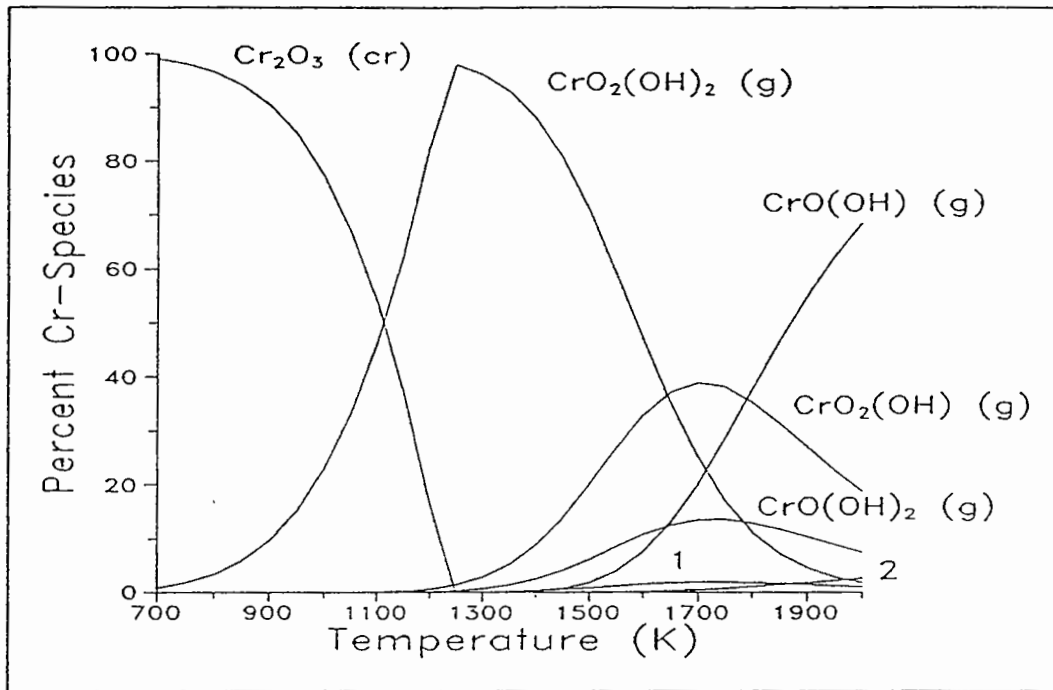


Figure 2: Equilibrium distribution of Cr at 1 atm. as found by the MINGTSYS and NASA-CET89 codes. 1: CrO_3 (g) and 2: CrO_2 (g).

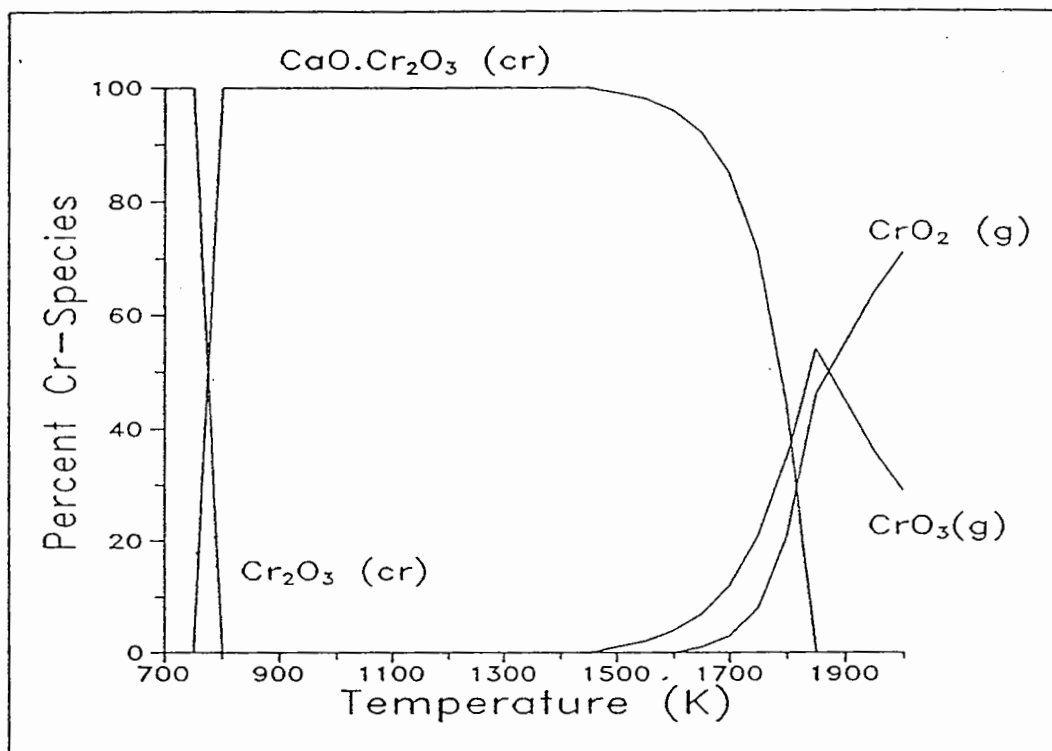


Figure 3: Equilibrium distribution of Cr at 1 atm. as found by the FACT code.

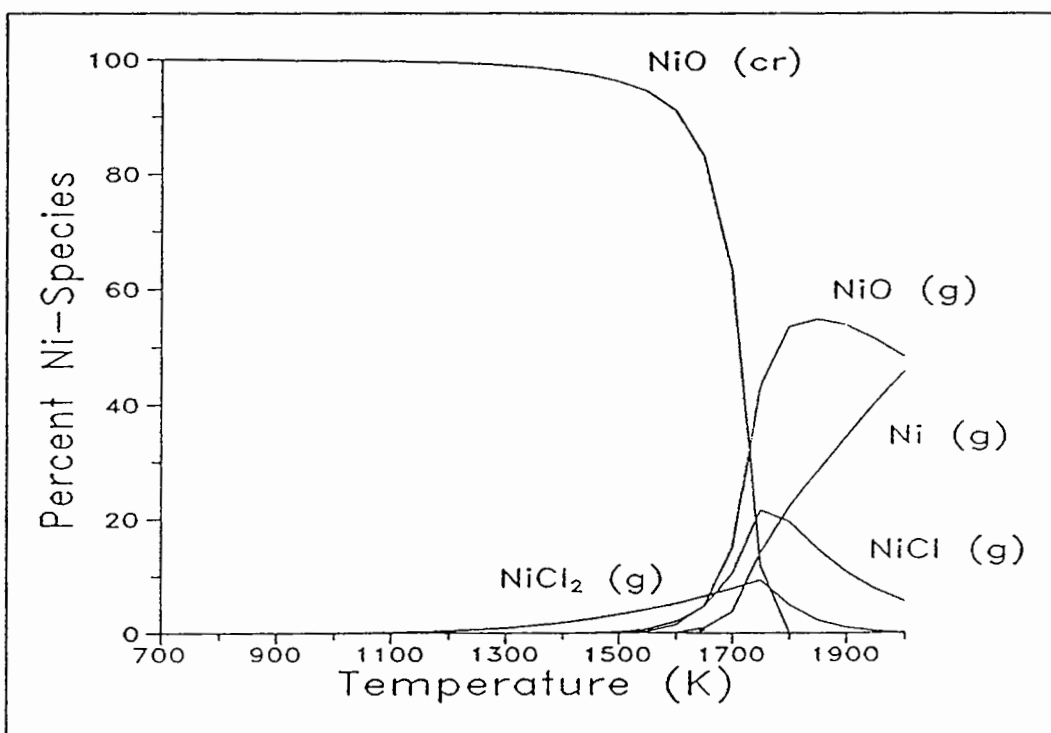


Figure 4: Equilibrium distribution of Ni at 1 atm. as found by the MINGTSYS and FACT codes.

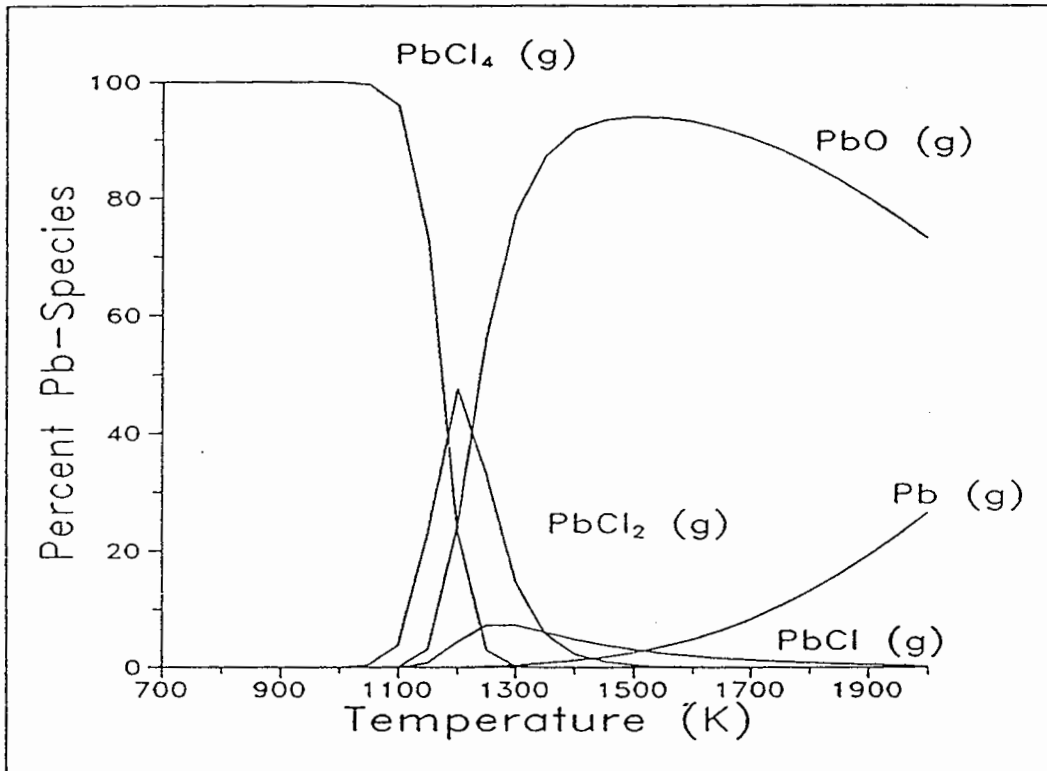


Figure 5: Equilibrium distribution of Pb at 1 atm. as found by the MINGTSYS and NASA-CET89 codes.

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16. ABSTRACT The paper predicts the equilibrium speciation of the trace elements As, Cd, Cr, Hg, Ni, Pb, and Se in a model system, assuming ideal gas and pure condensed phases and taking into account the presence of a sorbent material for sulfur capture. The model system is based on a demonstration-scale pressurized fluidized-bed combustor, firing a Pittsburgh No. 8 bituminous coal, using dolomite as sorbent for sulfur capture and a ceramic filter for particulate removal. Results from four different thermodynamic packages (MINGTSYS, NASA-CET89, FACT, and SOLGASMIX) are compared over the temperature range 700-2000 K, at pressures of 1 and 20 atm. For As, Hg, and Se, almost identical equilibrium distributions were predicted by the four packages; while for Cd, Cr, Ni, and Pb, differences in the output from the four packages were observed. These differences may be due to different solution techniques, convergence criteria, and/or thermodynamic input data utilized in the thermodynamic packages. The paper outlines the equilibrium distributions, the comparison, a discussion of the reasons for the different results obtained with the different thermodynamic packages, and a comparison between measured and predicted partitioning data.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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