

# The effect of IGFC warm gas cleanup system conditions on the gas–solid partitioning and form of trace species in coal syngas and their interactions with SOFC anodes

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## Abstract

The U.S. Department of Energy is currently working on coupling coal gasification and high temperature fuel cell to produce electrical power in a highly efficient manner while being emissions free. Many investigations have already investigated the effects of major coal syngas species such as CO and H<sub>2</sub>S. However coal contains many trace species and the effect of these species on solid oxide fuel cell anode is not presently known. Warm gas cleanup systems are planned to be used with these advanced power generation systems for the removal of major constituents such as H<sub>2</sub>S and HCl but the operational parameters of such systems is not well defined at this point in time. This paper focuses on the effect of anticipated warm gas cleanup conditions has on trace specie partitioning between the vapor and condensed phase and the effects the trace vapor species have on the SOFC anode. Results show that Be, Cr, K, Na, V, and Z trace species will form condensed phases and should not effect SOFC anode performance since it is anticipated that the warm gas cleanup systems will have a high removal efficiency of particulate matter. Also the results show that Sb, As, Cd, Hg, Pb, P, and Se trace species form vapor phases and the Sb, As, and P vapor phase species show the ability to form secondary Ni phases in the SOFC anode.

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## 1. Introduction

Presently coal is the most economical fossil fuel in the United States (U.S.), and given the vast coal resources within the U.S., coal will be used for power generation for many years to come. With ever increasing scrutiny of coal fired power plant emissions, more efficient and cleaner power production processes are being sought. Gasification technology, along with new cleanup and sequestration technologies, allow for environmentally benign use of coal for power production. The U.S. Department of Energy is currently investing in the development of both fuel cell and coal gasification technologies for use in projects such as FutureGen [1], which will test the abilities of these technologies to generate clean power and clean fuels, such as hydrogen.

Coal gasification is a process in which coal is transformed into a gaseous fuel containing a mixture of CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, CH<sub>4</sub>, and N<sub>2</sub>. Coal is mixed with an oxidant (O<sub>2</sub>) and steam in a reactor operating between 500 and 1800 °C and 25 and 70 atm to produce the gaseous mixture known as syngas [2,3]. Oxygen blown gasification is typically used because less coal is needed to heat the reactants to the temperature required for gasification (600–1700 K) [4]. In addition, removing N<sub>2</sub>, which acts as a diluent, from the syngas stream also increases the options available for adding carbon sequestration technologies and thereby achieves a completely emissions-free plant. Three types of coal gasification systems have been used through industry (moving bed, fluidized bed, and entrained flow). Among the three types of gasification technologies, entrained flow gasification systems have been the choice of industry for current IGCC systems, such as Tampa Electric Company's Polk Power Station, and are anticipated to be used with future integrated gasification and fuel cell (IGFC) systems that incorporate solid oxide fuel cell (SOFC) technology [5]. Incorporation of SOFC technology

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into future power plant systems may help reduce plant costs due to the high efficiency of the electrochemical system which results in a smaller physical plant size for a given electric power output [5].

Recent studies have shown the feasibility of operating SOFC systems with coal syngas as fuel [6,7]. While these tests are encouraging, it is well known that coal contains many trace species which are volatilized in the reducing conditions of gasification. Cleanup technologies already exist, however, to remove certain of these species, such as  $H_2S$ , along with other material such as particulates. Current IGCC plants within the U.S. such as Wabash River, Polk Power, and DOW Chemical's Louisiana Gasification Technology Inc., use absorption systems such as chemical or physical washes for the removal of  $H_2S$  and water scrubbers for the removal of halide species [2]. Although these present systems are very effective in removing  $H_2S$ , halide, and particulate matter to very low levels (<1 ppm), they are not effective cleanup methods for achieving maximum system efficiency since these systems operate at ambient temperature thereby removing a significant portion of the syngas thermal energy. The U.S. DOE is currently working on the development of warm gas cleanup systems that will allow the removal of  $H_2S$ , HCN, HCl, particulate matter and alkali species from the coal syngas at temperatures of 250–500 °C [2,8]. Higher operational temperature systems have not been considered since alkaline species have been found to pass through the systems above 500 °C [2]. However, removal of the trace species at higher temperatures, if possible, will further increase the overall efficiency of the IGFC systems.

Although the effect of major coal contaminant species such as sulfur and chlorine on fuel cell performance has been recognized, the effect of trace species has thus far not been considered. Coal contains trace amounts of nearly all of the naturally occurring elements. The elements and their respective concentrations typically depend on the rank and geographic origin of the coal, and some of the elements are potentially toxic to the environment and human health [3]. Eleven trace elements contained in coal are considered hazardous air pollutants (HAPs) by the 1990 Clean Air Act Amendments (CAAA). The elements of greatest concern are As, B, Cd, Pb, Hg, Mo, Se, Cr, V, and Zn. During coal gasification, these elements are volatilized in the reducing atmosphere and are subsequently partitioned between ash and gaseous stream fractions. The volatility of any trace species may be used to estimate its partitioning behavior between the gas and solid phases. Hence, the trace elements contained in coal are classified into three groups based upon their volatility: *Class I* elements are the least volatile and will remain in the ash, *Class II* elements are more volatile and partition between the condensed and gaseous phases, and *Class III* elements are highly volatile and show little to no tendency to condense from the vapor phase [2]. Many of the elements which are of concern with respect to environment and human health are *Class II* or *Class III* elements. Due to the difficulty in accurately measuring the concentration of trace species and the relative newness of IGCC technology, little information is known about the fate of these species after the gasification reactor. Previous IGCC performance reports have shown high levels of removal for B, Be,

Cd, Co, Cr, Mn, Mo, Ni, Pb, V, Zn and low levels of recovery for As, Cd, Pb, Hg, Se [2,9–11]. However, these reported IGCC systems used cleanup processes such as water scrubbing for the removal of particulate matter and chemical or physical washes for the removal of sulfur compounds which significantly reduces the thermal efficiency of the process, and may not be relevant to future warm gas cleanup systems.

Thermodynamic simulations may be used to predict the partitioning behavior of trace elements in coal syngas between the gas and solid phases. Although thermodynamic calculations do not give the amount of time required to reach the equilibrium concentrations, they provide a very important first level analysis of chemical systems. Many thermodynamic studies have focused on determining the partitioning behavior of trace elements in coal combustion and gasification systems [12–18]. From the previously published studies, one investigation considered the effects of coal syngas, with and without  $H_2S$  and HCl, warm gas cleanup temperatures (200–500 °C) and pressures of 1–40 atm on trace elements contained in coal syngas [11]. The authors concluded that Se, Hg, and B are mainly present in vapor form and Sb, As, Cd, Pb, Zn, Ni, Cr, and V were distributed between the gas and condensed phases. However this study only investigated the effect of system temperature, pressure, and syngas species ( $H_2S$  and HCl) on individual trace elements, and did not examine their interactions with each other or with the SOFC anode. In order to better design future SOFC modules to be coupled with coal gasification technology, the form of trace coal syngas species when reacted with anode materials must be determined. Such information will enable designers to consider mitigation strategies to avoid material degradation that reduces cell performance. This paper presents thermodynamic investigations that take into account the effect of warm gas cleanup temperature (200–500 °C), SOFC operational pressure (1–15 atm), and the interactions of the trace element species in order to determine which species may travel through the gasification cleanup systems and possibly effect the operation of SOFCs.

## 2. Theory

Thermodynamic equilibrium calculations provide a quantitative method for determining the stable chemical forms of a system of elements/compounds. The present work used such an analysis, but the analysis is separated into two parts. The first analysis, referred to as the cleanup stage analysis (CSA), determined the likely trace species that can form and be transported from the cleanup system to the SOFC anode. Here, thermodynamic equilibrium calculations are used to determine the effect of system operation (temperature and pressure) on the partitioning between the gas and condensed phases and compositional form of the trace coal syngas species. The assumption is that only the gas phase species will transport to the anode, and only these species will need to be considered for reaction with the anode. The second analysis, anode reaction analysis (ARA), determined which of the vapor species from the CSA will likely react with the nickel-based anode materials thereby causing degraded fuel cell performance. Both the CSA and ARA analyzed the ideal

Table 1  
Coal syngas composition

Component	Composition (vol%)
H <sub>2</sub>	29.3
CO	28.7
CO <sub>2</sub>	11.8
N <sub>2</sub>	3.0
H <sub>2</sub> O	27.2

and real thermodynamic states of any given specie using the thermodynamic software package, FactSage (v. 5.4) [19].

Because the precise specification of the warm gas cleanup system is not yet available, for the CSA, chemical equilibrium was calculated by minimizing the total Gibb's free energy of the system over a range of system temperatures and pressures anticipated for warm gas cleanup (200–500 °C, 1–15 atm). Although warm gas cleanup systems are already being developed for the removal of both sulfur and halide species, the ability of such systems to remove trace species from coal syngas has not been readily investigated. Due to this lack of information a thermodynamic study of the system will provide the best evaluation of the warm gas cleanup system at this time by only considering the formation of condensed or vapor species as a means to estimate removal efficiency. The bulk composition of the syngas used in the calculations was based on oxygen blown entrained flow gasification as shown in Table 1 [4].

The trace element loadings in the coal syngas were based on data collected from past measurements made at various entrained flow gasification systems [17,20–22]. The trace species that were taken into account in the CSA equilibrium calculations were AsH<sub>3</sub>, HCl, PH<sub>3</sub>, Sb, Cd, Be, Cr, Hg, K, Se, Na, V, Pb, and Zn. The trace element concentrations used in the calculations and each specie's volatility classification are shown in Table 2.

The trace species that were found in vapor form from the Gibb's free energy minimization calculations in concentrations greater than 0.01% of the inputted values were then used in the ARA to determine interactions with the Ni-YSZ cermet of

Table 2  
Trace specie concentrations

Component	Concentration (ppmv)	Volatility class
AsH <sub>3</sub>	0.6	II
HCl	1	III
PH <sub>3</sub>	1.91	II
Sb	0.07	II
Cd	0.011	II
Be	0.025	II
Cr	6	II
Hg	0.025	II
K	512	I
Se	0.15	II
Na	320	I
V	0.025	II
Pb	0.26	II
Zn	9	II

a SOFC. Interactions between the trace vapor species and the three main components of the SOFC anode (Ni, ZrO<sub>2</sub>, and Y<sub>2</sub>O<sub>3</sub>) were examined. The calculations were completed over the SOFC operational temperature range of 700–900 °C. With this procedure, possible chemical interactions with the anode cermet were investigated.

### 3. Results

#### 3.1. Gas-condensed partitioning and specie forms—CSA study

The partitioning between the gas and condensed phases and equilibrium form of the species listed in Table 2 was investigated over the proposed warm gas cleanup system temperatures and pressures (250–500 °C, 1–15 atm). The results from these equilibrium calculations are discussed in the following subsections.

##### 3.1.1. Antimony (Class II)

Antimony showed no tendency to condense over the operational temperatures and pressures of the gas cleanup system. The prevailing form of antimony over the gas cleanup system operational parameters was SbO<sub>2</sub>H<sub>2</sub>(g). The other minority form, As<sub>3</sub>Sb(g), was found at the operational temperatures of 500 °C with Sb molar balances of 14.3, 3.8, 2.2, and 1.6% at pressures of 1, 5, 10, and 15 atm, respectively.

##### 3.1.2. Arsenic (Class II)

Both cleanup temperature and pressure showed an effect on the partitioning of arsenic between the gas and condensed phases as well as the equilibrium composition formed. At 200 °C, arsenic partitioned between solid and gaseous phases, with As(s) composing of 80.8, 96.15, 98.1, and 98.7% of available As(s) on a molar basis at 1, 5, 10, and 15 atm, respectively. The vapor form of arsenic found in equilibrium with the As(s) at the operational temperature of 200 °C and pressures of 1, 5, 10, and 15 atm was As<sub>4</sub>(g). Arsenic was not found to partition between the condensed and gaseous phases at higher temperatures. The prevailing vapor form of arsenic at the higher operational temperatures was As<sub>4</sub>(g). However two minority arsenic species, AsH<sub>3</sub>(g) and As<sub>3</sub>Pb(g), were found to form at various gas cleanup system temperatures and pressures. AsH<sub>3</sub>(g) was found to form at gas cleanup system temperatures of 300–500 °C and all pressures with a minimum of 0.03 molar percent of available As at 300 °C and 1 atm, and a maximum of 2.5% at 500 °C and 15 atm. As<sub>3</sub>Sb(g) was found to form at operational temperatures of 400 °C at 1 and 5 atm with As molar balance concentrations of 0.06 and 0.02%, respectively. The maximum concentrations of As<sub>3</sub>Sb(g) were found at 500 °C with molar balance concentrations of 4.4, 1.3, 0.08, and 0.06% at pressures of 1, 5, 10, and 15 atm, respectively.

##### 3.1.3. Beryllium (Class II)

The cleanup system temperature and pressure did not effect the partitioning between the gas and solid phases or equilibrium composition of beryllium. The condensed phase form BeO(s)

was found to exist over all temperatures and pressures with all of the trace beryllium in the syngas condensing into the solid phase. Since beryllium shows such a high tendency to condense out of the syngas vapor phase the trace specie is not considered to be a potential problem for SOFC anode operation since a high removal efficiency is anticipated.

### 3.1.4. Cadmium (Class II)

The gas cleanup up system pressure was shown to have an effect on the partitioning of cadmium in the syngas stream. At temperatures of 200 °C and all investigated pressures cadmium was found in the condensed phase in two equilibrium forms CdS(s) and CdSe(s). At 300 °C cadmium partitioned between the vapor phase (Cd(g)) and condensed phase (CdSe(s)) at varying levels based upon the operational pressures. The percentage of the condensed phase compound CdSe(s) increased from 26.7% of the Cd at 1 atm to 92.7% at 15 atm. At temperatures of 400 and 500 °C and all pressures Cd(g) was the only equilibrium form of cadmium found in the system.

### 3.1.5. Chromium (Class II)

The cleanup system temperature and pressure were not found to have an effect on the partitioning of trace chromium species between gas and solid phase, however the system pressure was found to have a slight effect on the equilibrium composition formed. Chromium was found to form condensed solid phase species at all system temperatures and pressures. At the lower operational temperatures, 200 and 300 °C, and 15 atm the equilibrium form of chromium was found to be (Na<sub>2</sub>O)(CrO<sub>3</sub>)(s) and the equilibrium form at higher temperatures and all pressures was Cr<sub>2</sub>O<sub>3</sub>(s). Since the trace chromium species in coal syngas show a high degree of removal (since filtering may be used to remove condense phase species) chromium is not expected to pose problems associated with SOFC anode operation.

### 3.1.6. Lead (Class II)

The gas cleanup system temperature and pressure was found to have an impact on the partitioning between the gas and solid phases and equilibrium composition of lead. At gas cleanup temperatures of 200 and 300 °C, lead was found to form two condensed phases Pb(s) and PbSe(s). The partitioning between the two compounds was effected by the temperature and pressure. The percentage of lead in the form of Pb(s) at 200 and 300 °C was found to be 42.9 and 42.7%, respectively, at 1 atm, and 43.4 and 46.3%, respectively, at 15 atm. At 400 °C Pb(l) and PbSe(s) were found to form at equilibrium with 43.5 and 42.6% Pb(l) at 1 and 15 atm, respectively. At 500 °C Pb vapor species were also formed. At 500 °C, four lead species (Pb(l), PbSe(s), PbSe(g), and Pb(g)) were formed. Table 3 presents the equilibrium partitioning percentages of Pb between the four phases at 500 °C.

### 3.1.7. Mercury (Class III)

The operational temperature and pressure of the gas cleanup system was not found to influence the partitioning behavior or equilibrium form of mercury. Hg(g) was found to form over

Table 3  
Equilibrium forms of Pb at 500 °C

Pressure (atm)	Pb(l) (%)	PbSe(s) (%)	Pb(g) (%)	PbSe(g) (%)
1	75.3	0.0	7.0	17.7
5	62.0	32.5	1.3	4.2
10	56.1	41.2	0.7	2.0
15	53.5	44.7	0.4	1.4

the gas cleanup system temperatures and pressures. It may be assumed that all Hg present in coal will pass through the gas cleanup system and may interact with the SOFC anode.

### 3.1.8. Phosphorous (Class II)

The operational temperature and pressure of the gas cleanup system was found to have a small influence on the partitioning and phase equilibrium behavior of phosphorous. At a gas cleanup temperature of 200 °C and pressures of 5, 10, and 15 atm the condensed phase (NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>(s) was found to account for 98.1, 100, and 100% of the total phosphorous in the system, respectively. The dominant vapor phase form of phosphorous found in the system was (P<sub>2</sub>O<sub>3</sub>)<sub>2</sub>(g), however trace amounts of PH<sub>3</sub>(g) were also found to form at varying amounts based upon the temperatures and pressures.

### 3.1.9. Potassium (Class III)

The operational temperature and pressures found in a warm gas cleanup system did not effect the partitioning of potassium between the gas and solid phase and were found to effect the equilibrium composition very little. Three condensed equilibrium potassium compositions were found to form: KCl(g), K<sub>2</sub>CO<sub>3</sub>(s), and KHCO<sub>3</sub>(s). K<sub>2</sub>CO<sub>3</sub>(s) was found to be the dominant species formed at almost all temperatures and pressures. Trace amounts of KCl(s) were found to form at nearly all temperature and pressures studies except for 200 °C at 10 and 15 atm and 500 °C at 5, 10, and 15 atm. The third species KHCO<sub>3</sub>(s) was found to be the only condensed potassium specie at 200 °C at 1 and 5 atm. Although potassium is found with a much higher loading compared to the other trace species shown in Table 2 it should not pose a threat to SOFC anode operation since the condensed solid species are predicted to have a high removal efficiency.

### 3.1.10. Selenium (Class II)

The gas cleanup system temperature and pressure were both found to effect the equilibrium partitioning of selenium. At the lower operational temperatures of 200 and 300 °C selenium was found only to form the condensed phases CdSe(s) and PbSe(s). The percentage of CdSe(s) at 200 and 300 °C was found to be 1.0, 0.8, 2.0, and 7.0% at 1 and 15 atm, respectively. At temperatures of 400 and 500 °C selenium was found to partition between the condensed and gas vapor phases. PbSe(s) was the only condensed compound found at 400 and 500 °C at all pressures. Table 4 presents the equilibrium forms and percentages of Se found at the temperatures of 400 and 500 °C.

Table 4  
Equilibrium forms of Se at 400 and 500 °C

Temperature (°C)	Pressure (atm)	PbSe(s) (%)	H <sub>2</sub> Se(g) (%)	AsSe(g) (%)	PbSe(g) (%)
400	1	97.7	1.2	1.1	0.0
400	5	99.2	0.5	0.3	0.0
400	10	99.4	0.4	0.2	0.0
400	15	99.6	0.3	0.1	0.0
500	1	0.0	42.8	26.7	30.5
500	5	56.4	26.7	9.7	7.2
500	10	71.4	19.4	5.7	3.5
500	15	77.5	16.0	4.2	2.3

### 3.1.11. Sodium (Class III)

The operational temperature and pressure of the warm gas cleanup system did not effect the partitioning of sodium. Only two condensed solid sodium phases were found: Na<sub>2</sub>CO<sub>3</sub>(s) and (Na<sub>2</sub>O)(CrO<sub>3</sub>)(s). Na<sub>2</sub>CO<sub>3</sub>(s) was found to be the dominant specie formed at all temperatures and pressures except for 200 °C and 1 atm where only (Na<sub>2</sub>O)(CrO<sub>3</sub>)(s) was formed. Sodium is not considered to be a threat to SOFC anode operation since the condensed phases of the element will readily be removed at a high level of efficiency.

### 3.1.12. Vanadium (Class II)

The warm gas cleanup temperatures and pressures were not found to effect the partitioning of vanadium in coal syngas. The trace element was found to form only the condensed solid phase species V<sub>2</sub>O<sub>3</sub>(s) and V<sub>3</sub>O<sub>5</sub>(s). The vanadium oxide specie was found to form at 200 °C at 5, 10, and 15 atm while V<sub>2</sub>O<sub>3</sub>(s) was found to form at all other temperatures and pressures. The vanadium oxides should have a high degree of capture from the coal syngas stream and will not pose a threat to SOFC operation.

### 3.1.13. Zinc (Class II)

Zinc is a trace element found in coal syngas at higher levels than compared to most trace species contained in the reformed fuel. The temperature and pressure of the warm gas cleanup system was found not to effect the partitioning or equilibrium composition of the trace element. ZnO(s) was found as the favored equilibrium composition of zinc. Since condensed solid phase species are anticipated to have a high removal efficiency from the coal syngas stream zinc should not pose any complications towards the operation of SOFC anodes.

## 3.2. Vapor specie interactions with Ni-YSZ anode—ARA study

The initial evaluation of the effect of warm gas cleanup temperatures and pressures showed that 7 elements in 14 vapor species (listed in Section 3.1) can be emitted from the cleanup system and passed on to the fuel cell. Table 5 presents the trace elements and their respective concentrations that were found after passing through warm gas cleanup conditions. These species may interact with the Ni-YSZ anode of the SOFC. These fourteen species were evaluated to determine what interactions

Table 5  
Trace specie concentrations after warm gas cleanup

Component	Concentration (ppmv)
Sb	0.07
As	0.6
Cd	0.011
Pb	0.26
Hg	0.025
P	1.91
Se	0.15

with the SOFC anode materials (Ni(s), ZrO<sub>2</sub>(s), and Y<sub>2</sub>O<sub>3</sub>(s)) were possible. The analysis was performed for both the inlet and outlet edges of the SOFC anode (the latter assuming 85% of the fuel has been utilized). These evaluations showed that As, Sb, and P trace vapor species found in coal syngas may react with Ni over the operational temperature range of 700–900 °C. The following sections will review the possible interactions associated with these trace vapor species.

### 3.2.1. Anode coal syngas trace specie equilibrium calculations

Gibb's free energy minimization calculations were first used to determine if any interactions existed between the SOFC anode and the residual trace species found in the coal syngas after passing through a warm gas cleanup system. Since the actual operational parameters of proposed warm gas cleanup systems have not yet been determined the highest trace specie levels found from the results in Section 3.1 were used, regardless of temperature or pressure at which they occurred. Table 5 presents the trace specie concentrations that were used in the anode equilibrium calculations.

Because the oxidation potential changes through the anode as fuel compounds are oxidized during operation, two anode studies were performed—one that examined anode inlet edge

Table 6  
Outlet edge syngas composition

Component	Composition (vol%)
H <sub>2</sub>	4.6
CO	4.0
CO <sub>2</sub>	36.5
N <sub>2</sub>	3.0
H <sub>2</sub> O	51.9

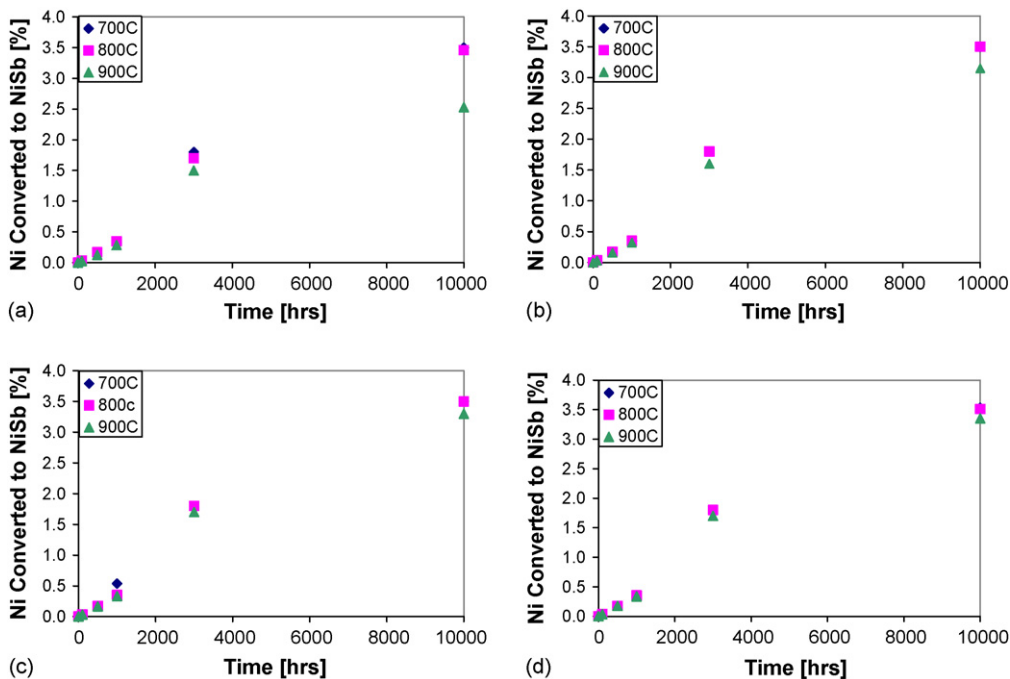


Fig. 1. Ni converted to NiSb(s) at inlet edge of the SOFC at 1 atm (a), 5 atm (b), 10 atm (c), and 15 atm (d).

effects, and one that analyzed anode outlet edge effects. The bulk (major species) syngas composition used at the inlet of the SOFC anode is listed in Table 1. For the outlet edge, a syngas composition representing 85% fuel utilization was used with the trace specie concentrations listed in Table 5. This outlet bulk syngas composition is shown in Table 6.

For these two anode studies, we arbitrarily analyze thin sections at the inlet and exit edges, respectively. The SOFC anode

sections are assumed to have an area of 1 cm<sup>2</sup>, with a 0.1 cm length in the direction of flow. The assumed anode electrode was made of a 50% porosity cermet with a 1:1 volume ratio of Ni(s) to 8YSZ. The coal syngas volume used in the calculation was based on an anode performance 0.5 A cm<sup>-2</sup>, operated over periods of 1, 100, 500, 1000, 3000, and 10,000 h. The equilibrium calculations were completed at temperatures of 700, 800, and 900 °C and pressures of 1, 5, 10, and 15 atm.

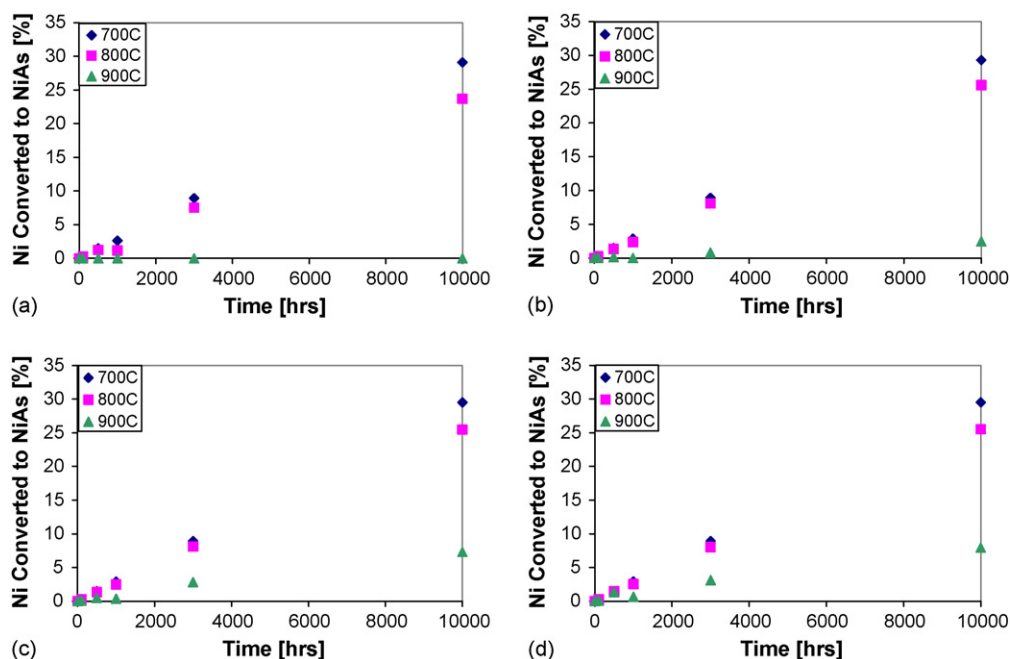


Fig. 2. Ni converted to NiAs(s) at inlet edge of the SOFC at 1 atm (a), 5 atm (b), 10 atm (c), and 15 atm (d).

Based upon the equilibrium calculations it was found that three of the trace species may form secondary Ni phases at anticipated SOFC operating conditions. These three trace species were Sb, As, and P. The three compounds that were found to form were NiSb(s), NiAs(s) at both the inlet and outlet edge of the SOFC and Ni<sub>5</sub>P<sub>2</sub>(s) at the inlet edge of the SOFC. The results for NiSb(s) formation at the inlet edge conditions are shown in Fig. 1.

The results for NiAs(s) formation at the inlet edge conditions are shown in Fig. 2.

From Figs. 1 and 2 it may be seen that much less Ni is converted to NiSb(s) than NiAs(s) which is due to the lower concentration of Sb trace species in the coal derived syngas when compared to As trace species as shown in Table 5. However the results do show that NiSb(s) and NiAs(s) may form simultaneously during SOFC operation. As compared to the formation of NiAs(s) the formation of NiSb(s) is not as readily influenced by operating temperature and pressure.

From Fig. 2 it may be seen that the amount of NiAs(s) formed at the inlet edge of the SOFC increases over time at all temperatures and pressures. Temperature is shown to have an effect on the amount of NiAs(s) formed at the inlet edge of the SOFC as the amount of Ni converted to NiAs(s) decreases as system temperature increases. Pressure is also shown to have an effect on the amount of NiAs(s) formed at the inlet edge of the SOFC. Although the effect of pressure is not as influential at operating temperatures of 700 and 800 °C it does have a clear effect at 900 °C as almost no NiAs(s) is formed at 1 atm but nearly 10% of the Ni is converted to NiAs(s) at 15 atm.

The results for Ni<sub>5</sub>P<sub>2</sub>(s) formation at the inlet edge conditions are shown in Fig. 3.

From Fig. 3 it may be seen that Ni<sub>5</sub>P<sub>2</sub>(s) is the dominant species formed at the inlet edge of the SOFC anode. The results show that approximately 90% of the Ni contained at the inlet edge of the SOFC is converted to Ni<sub>5</sub>P<sub>2</sub>(s). System temperature and pressure are also shown to effect the amount of Ni<sub>5</sub>P<sub>2</sub>(s) that is formed. Pressure shows the greatest influence on the total amount of Ni(s) that is converted to Ni<sub>5</sub>P<sub>2</sub>(s) at the inlet edge of the SOFC anode. At a system pressure of 1 atm no Ni<sub>5</sub>P<sub>2</sub>(s) is shown to take place at 900 °C, however at a system pressure of 15 atm nearly 90% of the Ni(s) contained in the anode is converted to Ni<sub>5</sub>P<sub>2</sub>(s) at 900 °C. The cause of Ni<sub>5</sub>P<sub>2</sub>(s) to be the dominant species formed at the inlet edge of the SOFC anode is due to the fact that the coal derived syngas contains nearly 2 ppm of phosphorous trace species.

Overall the results presented in Figs. 1–3 show that nearly all of the Ni contained at the inlet edge of the SOFC will be converted to a secondary phase due to interactions with trace species in the coal syngas. A system operating temperature and pressure of 900 °C and 1 atm shows the least amount of Ni(s) conversion to a secondary species. This is caused by the reduction in the amount of Ni<sub>5</sub>P<sub>2</sub>(s) formation that takes place at this system operating temperature and pressure.

The thermodynamic equilibrium calculations that were completed at the outlet edge conditions revealed no significant changes in the amount of NiAs(s) and NiSb(s) formed as compared to the results presented in Figs. 1–3. However a very large change in the amount of Ni<sub>5</sub>P<sub>2</sub>(s) formed at the inlet edges versus outlet edges of the SOFC was found. In fact nearly no formation of Ni<sub>5</sub>P<sub>2</sub>(s) was found at the outlet edge of the SOFC regardless of system temperature or pressure. These results show that the conversion of the fuel species (H<sub>2</sub> and CO) to their respective products (H<sub>2</sub>O and CO<sub>2</sub>) does effect the interaction between

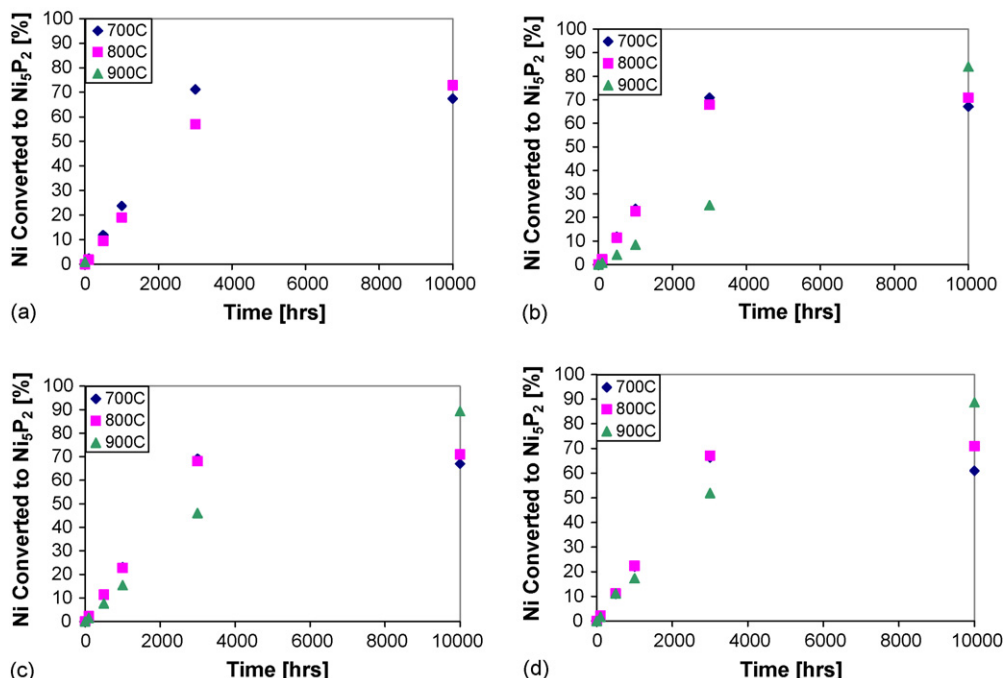


Fig. 3. Ni converted to Ni<sub>5</sub>P<sub>2</sub>(s) at inlet edge of the SOFC at 1 atm (a), 5 atm (b), 10 atm (c), and 15 atm (d).

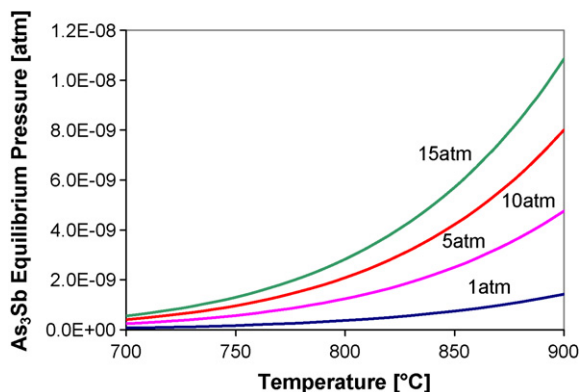
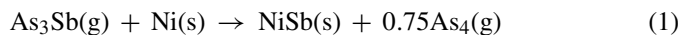


Fig. 4. Equilibrium pressures of  $\text{As}_3\text{Sb}$  associated with Eq. (1) over SOFC operating conditions.

$\text{Ni(s)}$  and phosphorous trace species found in the coal derived syngas. These results also indicate that the trace species in coal syngas will have a greater effect on the inlet edge of the SOFC when compared to the outlet edge of the SOFC since the maximum amount of  $\text{Ni(s)}$  found to convert to a secondary phase at the outlet edge of the SOFC was 35% after 10,000 h of operation. The following sections will review the possible reactions responsible for the formation of the secondary Ni phases found in the anode and the influence of fuel utilization on the formation of  $\text{Ni}_5\text{P}_2\text{(s)}$ .

### 3.2.2. Antimony trace species

One antimony trace vapor specie ( $\text{As}_3\text{Sb(g)}$ ) that was found to form over the gas cleanup system temperatures also showed the potential to interact with the SOFC anode based upon the equilibrium calculations presented in Sections 3.1.1 and 3.2.1. Further equilibrium calculations were also completed to determine the equilibrium partial pressure of  $\text{As}_3\text{Sb(g)}$  to form  $\text{NiSb(s)}$ . Eq. (1) represents the Sb trace specie reaction with Ni contained in the SOFC anode.



The equilibrium partial pressure of  $\text{As}_3\text{Sb(g)}$  was determined by calculating the partial pressure of  $\text{As}_3\text{Sb}$  while the reaction in Eq. (1) is in equilibrium based upon an  $\text{As}_4$  concentration of 0.15 ppmv which was determined from the calculations presented in Section 3.1.

Fig. 2 presents the equilibrium partial pressure curve for  $\text{As}_3\text{Sb(g)}$  at total system pressures of 1, 5, 10, and 15 atm.

From Fig. 4 it may be seen that the equilibrium pressure of  $\text{As}_3\text{Sb}$  increases with SOFC temperature (700–900 °C) and pressure (1–15 atm), respectively. These results show that Sb trace species may potentially pose a threat to the SOFC anode especially at lower temperature and pressure operations.  $\text{As}_3\text{Sb(g)}$  was found to account for 0.01 ppmv of the coal syngas after passing through warm gas cleanup conditions. This concentration leads to a  $\text{As}_3\text{Sb(g)}$  partial pressure of  $1.0 \times 10^{-8}$  to  $1.5 \times 10^{-7}$  atm in an SOFC system operating between 1 and 15 atm. At these partial pressures  $\text{As}_3\text{Sb(g)}$  should react with  $\text{Ni(s)}$  to form  $\text{NiSb(s)}$ . Experimental testing must be completed

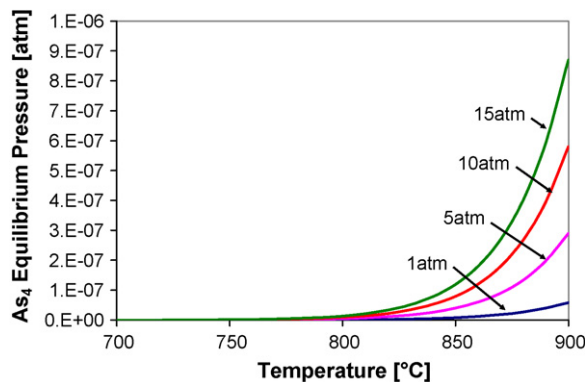


Fig. 5. Equilibrium  $\text{As}_4$  pressures associated with Eq. (2) over SOFC operating conditions.

to determine the kinetics associated with Eq. (1) and the effect  $\text{NiSb(s)}$  formation has on SOFC performance.

### 3.2.3. Arsenic trace species

Four trace As vapor species,  $\text{As}_4\text{(g)}$ ,  $\text{AsH}_3\text{(g)}$ ,  $\text{AsSe(g)}$ , and  $\text{As}_3\text{Sb(g)}$  were shown to form in the coal syngas after passing through warm gas cleanup conditions. Of these trace species,  $\text{As}_4\text{(g)}$  and  $\text{AsH}_3\text{(g)}$  show the potential to react with Ni contained in the SOFC anode, i.e. the Gibb's free energy of the reactions is negative. Eqs. (2) and (3) represent the two As interactions that may take place with Ni in the SOFC anode.

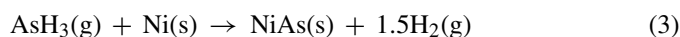
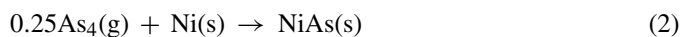


Fig. 5 presents the equilibrium concentrations (ppbv) of  $\text{As}_4\text{(g)}$  associated with Eq. (2).

From Fig. 5 it may be seen that the equilibrium pressure associated with  $\text{As}_4\text{(g)}$  ranges from nearly 0 to  $8.5 \times 10^{-7}$  atm. From the warm gas cleanup equilibrium calculations presented in Section 3.1 it was found that a maximum concentration of 0.15 ppmv of  $\text{As}_4\text{(g)}$  existed in the coal syngas. This concentration of  $\text{As}_4\text{(g)}$  accounts for a partial pressure of  $1.5 \times 10^{-7}$  to  $2.3 \times 10^{-6}$  atm over the operational pressure range of the SOFC, which are well above the equilibrium pressures of  $\text{As}_4\text{(g)}$  in Fig. 3.

Fig. 6 presents the equilibrium pressures associated with Eq. (3) at the inlet (a) and outlet (b) edge of the SOFC. Two sets of equilibrium pressure calculations had to be completed with  $\text{AsH}_3\text{(g)}$  since the  $\text{H}_2$  pressure in the coal syngas dramatically changes as it is consumed by the SOFC anode.

From Fig. 6 it may be seen that the equilibrium pressure of  $\text{AsH}_3\text{(g)}$  decreases from the SOFC inlet to outlet conditions. This is due to the decrease in the  $\text{H}_2$  pressure caused by the consumption of the fuel at the electrolyte interface. The  $\text{H}_2$  consumption shifts the reaction towards the products, therefore requiring less  $\text{AsH}_3\text{(g)}$  to form the product  $\text{NiAs(s)}$ . These results show that  $\text{NiAs(s)}$  formation would more likely take place as the fuel gas is consumed across the anode of the SOFC. However since the data presented in Section 3.1.2 showed that  $\text{As}_4\text{(g)}$  was the predominant arsenic specie formed the lowering of the equilibrium pressure of  $\text{AsH}_3\text{(g)}$  associated with Eq. (3) at the outlet edge of the SOFC should have little effect on the amount



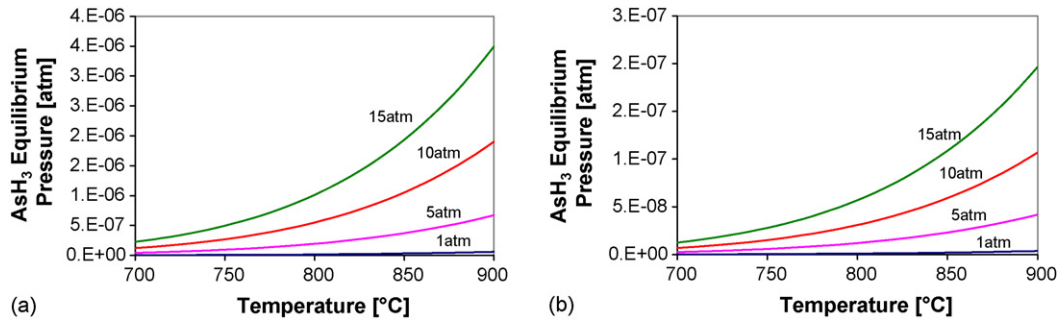


Fig. 6.  $\text{AsH}_3$  equilibrium pressures with Eq. (3) at SOFC inlet (a) and outlet (b) conditions.

of  $\text{NiAs(s)}$ . Evidence of this is presented in Fig. 1 which shows little change in the amount of  $\text{NiAs(s)}$  formed at the inlet and outlet edge of the SOFC.

### 3.2.4. Phosphorous trace species

Two trace phosphorous vapor species ( $(\text{P}_2\text{O}_3)_2$  and  $\text{PH}_3$ ) have been shown to form in the coal syngas after passing through warm gas cleanup conditions. Of the two trace species thermodynamic calculations were used to determine that  $\text{PH}_3(\text{g})$  shows the potential to react with Ni contained in the SOFC anode, i.e. the Gibb's free energy of the reaction was negative. Eq. (4) represents the phosphorous interactions that may take place with Ni in the SOFC anode.

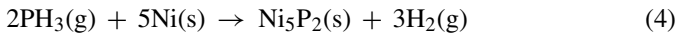


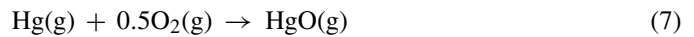
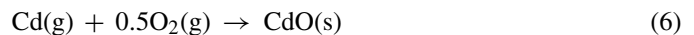
Fig. 7 presents the equilibrium partial pressures (atm) of  $\text{PH}_3(\text{g})$  associated with Eq. (4) at the inlet (a) and outlet (b) conditions.

From Fig. 7 it may be seen that the equilibrium concentration associated with  $\text{PH}_3(\text{g})$  actually decreases with fuel utilization. However as the previous equilibrium calculation showed no formation of  $\text{Ni}_5\text{P}_2(\text{s})$  was found in the outlet edge of the SOFC anode where as  $\text{Ni}_5\text{P}_2(\text{s})$  was found to be the dominant secondary Ni phase found at the inlet edge of the SOFC anode. The cause for this change in the formation amount of  $\text{Ni}_5\text{P}_2(\text{s})$  is related to the formation of the second phosphorous trace specie ( $(\text{P}_2\text{O}_3)_2(\text{g})$ ). As the fuel is consumed at the electrolyte interface oxygen is added in the form of  $\text{H}_2\text{O}(\text{g})$  and  $\text{CO}_2(\text{g})$ . The addition of these oxide species increases the partial pressure of  $\text{O}_2(\text{g})$  in the system from approximately  $1 \times 10^{-22}$  to  $2 \times 10^{-19}$  atm.

This increase in oxygen partial pressure allows for the oxidation of phosphorous to  $(\text{P}_2\text{O}_3)_2(\text{g})$  and inhibits the formation of  $\text{PH}_3(\text{g})$  therefore reducing the amount of  $\text{Ni}_5\text{P}_2(\text{s})$  formed in the anode of the SOFC at the outlet edge.

### 3.2.5. Trace metal species

Three trace metal species (Pb, Cd, and Hg) were found in the vapor phase of the trace coal syngas mixtures in warm gas cleanup temperature and pressure conditions. These trace metal vapors could potentially effect the SOFC operation by oxidizing in the anode atmosphere of the SOFC due to the oxygen available in the system from the electrochemical oxidation of the fuel species, shown as Eqs. (5)–(8).



Oxidation of the trace metal vapor species could potentially effect the anode in two manners. First the diffusion of gas species through out the anode could potentially be inhibited if the oxidized species were to deposit in the anode. Second if the trace metal species were to deposit in their oxidized forms at the electrolyte interface the electrochemical oxidation of the fuel species could be altered. In order to determine the potential for the oxidation of these trace species the  $\text{O}_2$  partial pressure in equilibrium with the coal syngas that has gone through 85% fuel utilization was calculated using the Gibb's free energy minimization routine

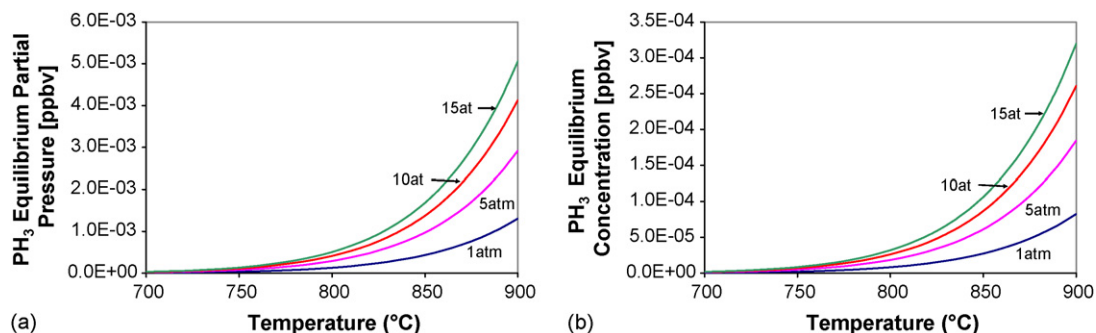


Fig. 7.  $\text{PH}_3$  equilibrium pressures with Eq. (4) at SOFC inlet (a) and outlet (b) conditions.

Table 7  
Oxygen partial pressures associated with coal syngas and Eqs. (5)–(8)

$T$ (°C)	$p_{O_2}$ (syngas)	$p_{O_2}$ (Eq. (5))	$p_{O_2}$ (Eq. (6))	$p_{O_2}$ (Eq. (7))	$p_{O_2}$ (Eq. (8))
700	1.60E–17	9.80E–15	8.50E–07	7.50E+15	5.42E–17
710	3.10E–17	2.70E–14	2.10E–06	1.10E+16	9.77E–17
720	5.10E–17	7.30E–14	5.10E–06	1.50E+16	1.74E–16
730	1.10E–16	1.90E–13	1.20E–05	2.10E+16	3.07E–16
740	2.00E–16	5.00E–13	2.90E–05	2.90E+16	5.34E–16
750	3.70E–16	1.30E–12	6.70E–05	4.10E+16	9.21E–16
760	6.60E–16	3.20E–12	1.50E–04	5.60E+16	1.57E–15
770	1.20E–15	7.70E–12	3.40E–04	7.70E+16	2.65E–15
780	2.10E–15	1.90E–11	7.50E–04	1.00E+17	4.42E–15
790	3.70E–15	4.40E–11	1.60E–03	1.40E+17	7.31E–15
800	6.40E–15	1.00E–10	3.50E–03	1.90E+17	1.20E–14
810	1.10E–14	2.40E–10	7.30E–03	2.50E+17	1.94E–14
820	1.90E–14	5.30E–10	1.50E–02	3.40E+17	3.13E–14
830	3.20E–14	1.20E–09	3.10E–02	4.40E+17	4.99E–14
840	5.30E–14	2.60E–09	6.30E–02	5.80E+17	7.88E–14
850	8.80E–14	5.60E–09	1.30E–01	7.60E+17	1.24E–13
860	1.50E–13	1.20E–08	2.50E–01	1.00E+18	1.92E–13
870	2.40E–13	2.50E–08	4.90E–01	1.30E+18	2.97E–13
880	3.80E–13	5.20E–08	9.40E–01	1.70E+18	4.54E–13
890	6.20E–13	1.10E–07	1.80E+00	2.10E+18	6.91E–13
900	9.80E–13	2.20E–07	3.40E+00	2.70E+18	1.04E–12

along with the  $O_2$  partial pressures associated with Eqs. (5)–(8) and the maximum concentrations of the metal vapor species as discussed above. A fuel utilization of 85% was used as described in the previous calculations. The results from these calculations are shown in Table 7 below.

From Table 7 it may be seen that even at the highest required fuel utilizations for SOFC anodes all four trace metal species show no tendency to oxidize in the anode environment. Also the calculations showed that Ni(s) is the most readily oxidized metal specie in the SOFC environment and previous testing has shown no formation of NiO(s) in the SOFC anode at 85% fuel utilizations so oxidation of trace metal species in the SOFC anode should not be an issue. (These calculations only consider the bulk  $O_2$  concentrations.)

#### 4. Conclusions

Although the feasibility of operating SOFCs with a clean coal syngas has been proven feasible the effect of trace species contained in coal syngas has not been investigated. Thermodynamic evaluations were used in this paper as a first level means to predict the partitioning between the gas and condensed phase and form of trace species contained in coal syngas since experimental testing of each trace specie is not feasible. The thermodynamic investigations presented in this paper yielded the following conclusions:

(1) Many of the trace species in coal syngas will not reach the SOFC anode. In particular the elements Be, Cr, K, Na, V, and Z all formed condensed phase species under warm gas cleanup conditions and should be efficiently removed at high levels. Except for potential upset conditions within the gasifier and cleanup systems these elements are not considered to pose any threat to the anode of the SOFC.

- (2) Thermodynamic evaluations showed that Sb, As, Cd, Pb, Hg, P, and Se vapor phase forms were found in the coal syngas at warm gas cleanup conditions and will allow these elements to possibly form secondary phases in the SOFC anode. Past trace specie concentration measurements from coal syngas validate these results [17,20–22].
- (3) No secondary phase formations between the vapor specie forms and oxide components ( $ZrO_2(s)$  and  $Y_2O_3(s)$ ) were found.
- (4) No phase formations between Se vapor species and Ni were found.
- (5) Sb, As, and P vapor phase species were shown to have the potential to form secondary phases with Ni in the SOFC anode even with such low trace concentrations found in the coal syngas.
- (6) Oxidation of the fuel species was shown to have a large effect on the amount of secondary Ni phases formed in the anode of the SOFC. The increase in the oxygen partial pressure at high fuel utilizations was found to inhibit the formation of  $PH_3(g)$  thereby reducing the amount of secondary Ni phase formation.
- (7) The oxidation of the trace metal vapor species Cd, Hg, and Pb were also investigated and shown not to be feasible.

The results presented in this paper revealed that most trace species contained in coal syngas should form a condensed phase and have a high removal efficiency. However of particular interest the Sb, As, and P vapor phase species do show the ability to secondary phases with Ni(s) contained in the SOFC anode. Since the thermodynamic evaluations do not yield any information towards the kinetics or any associated electrochemical interactions experimental testing should be pursued to determine if the trace vapor species identified in this paper do pose a problem for SOFCs.

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