



NATIONAL ENERGY TECHNOLOGY LABORATORY



Trace Species Partitioning as Affected by Cold Gas Cleanup Conditions: A Thermodynamic Analysis

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Acronyms and Abbreviations

AsH ₃	Arsine	MDEA	Methyldiethanolamine
atm	Atmosphere (14.696 psi)	MEA	Monoethanolamine
Be	Beryllium	N ₂	Nitrogen
C ₂ H ₄	Ethylene	Na	Sodium
C ₂ H ₆	Ethane	NH ₃	Ammonia
C ₄ H ₁₀	Butane	NETL	National Energy Technology Laboratory
C ₆ H ₆	Benzene	Ni	Nickel
Cd	Cadmium	Ni ₃ P ₂	Nickel phosphide
CH ₄	Methane	NiAs	Nickel arsenide
CO	Carbon monoxide	NiSb	Nickel antimonide
CO ₂	Carbon dioxide	O ₂	Oxygen
COS	Carbonyl sulfide	Pb	Lead
Cr	Chromium	PH ₃	Phosphine
CS ₂	Carbon disulfide	ppmv	Parts per million volume
DEA	Diethanolamine	psi	Pounds per square inch
DIPA	Diisopropylamine	psia	Pound per square inch absolute
DGA	Amineoethoxyethanol	psig	Pound per square inch gage
DOE	Department of Energy	Sb	Antimony
ft	Foot, Feet	scfd	Standard cubic feet per day
gal	Gallon	Se	Selenium
H ₂	Hydrogen	SO ₂	Sulfur dioxide
H ₂ O	Water	SOFC	Solid oxide fuel cell
H ₂ S	Hydrogen sulfide	V	Vanadium
HCl	Hydrochloric acid	vol%	Volume percent
HCN	Hydrogen cyanide	Zn	Zinc
Hg	Mercury	°C	Degrees Celsius
IGFC	Integrated gasification/fuel cell	°F	Degrees Fahrenheit
K	Potassium		

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1. Introduction

Generation of synthesis gas (syngas) by coal gasification produces volatile metal and organic trace species that must be removed or captured using high-throughput gas cleanup processes. The thermodynamically predicted partitioning of trace syngas species in warm gas cleanup systems was an early focus of integrated gasification-fuel cell (IGFC) system design, and the partitioning behavior is well documented [1]. Less information is available describing how the volatile materials will behave in traditional low temperature gas cleanup environments, such as those present in the Selexol or amine gas treatment processes. Although conventional low-temperature gas cleanup is technically mature [2], early IGFC designs anticipated that entropic losses would arise in integrated power generation applications due to cooling the syngas from the gasifier conditions (1200–1600 °C) and then re-heating to fuel cell operating conditions. Near-term IGFC processes anticipate the use of low temperature gas cleanup, which warrants reconsideration of the trace species partitioning in the conventional cleanup processes. This technical note considers a thermodynamic analysis of trace material partitioning in a simplified low temperature syngas cleanup process.

2. Background

Conventional low-temperature gas cleanup processes consist of two primary types, Selexol and amine gas treatment. The process operating conditions of both are considered in the thermodynamic analysis; though the cleanup system configuration is generalized to permit broad analysis of trace material behavior. In both Selexol and amine gas treatments, process gas is equilibrated at the temperature and pressure of the cleanup unit without consideration of the chemical or adsorption processes that may occur in the operating systems due to interaction with the cleanup sorbent and/or reactant.

1.1 Selexol Process

Selexol is an acid gas removal solvent used to separate H₂S and bulk CO₂ from natural and synthesis gas streams produced by gasification processes. Selexol is composed of a mixture of dimethyl ethers of polyethylene glycol. The Selexol process can be tailored to selectively remove either H₂S or CO₂ by adjusting the process operating conditions [3]. Selexol also removes water, COS, mercaptans, ammonia, hydrogen cyanide, and metal carbonyls. The relative solubilities of select gases in Selexol are shown in Table 1, where K is the solubility equilibrium constant.

Table 1 - Relative Solubility of Various Gases in Selexol Solvent [4]

Component	K	Component	K
H ₂	0.03	NH ₃	11
CO	0.07	H ₂ S	21
CH ₄	0.15	CS ₂	55
C ₂ H ₆	1.00	SO ₂	214
C ₂ H ₄	1.11	C ₆ H ₆	605
CO ₂	2.30	H ₂ O	1683
C ₄ H ₁₀	5	HCN	2904

A typical Selexol process is operated at approximately 40 °C and between 300 and 2000 psia. The Selexol process is a physical adsorption process, making it relatively easy to regenerate the solvent at high pressure. Selexol can adsorb 5.2 ft³/gal/atm of H₂S and 0.56 ft³/gal/atm CO₂ at 20 °C [5]. A representative example of this total capacity is found in the Tejas Power Corporation (Texas) Selexol unit, which operates with a total feed gas throughput of 90 to 115 million scfd.

According to a study conducted by Dow Chemical Corporation [4], the Selexol process can be tuned to remove hydrocarbons through adsorption into the solvent or by creation of a secondary phase. The solubility of hydrocarbons in Selexol increases proportionally to molecular weight. Higher hydrocarbons (C₆+), including benzene, toluene, and naphthalene, are reduced from <300ppmv to undetectable quantities. Lighter hydrocarbons, including ethane, ethylene, and propane, are only partially removed. The solubility of hydrocarbons decreases when the water content within the solvent increases with the effect becoming more pronounced as molecular weight increases. The hydrocarbon saturation point is eventually reached after which the hydrocarbons form a separate phase on top of the Selexol solvent allowing the hydrocarbon phase to be decanted.

1.2 Amine Gas Treatment

Amine gas treatment is similar in operation and function to the Selexol process. This process uses aqueous alkylamines (amines) to remove H₂S and CO₂ from synthesis gas streams. There are several types of amines used for gas treatment including monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), diisopropylamine (DIPA), and aminoethoxyethanol (DGA), with MEA, MDEA, and DEA being the most commonly used. Similar to the Selexol process, amine gas treatment operates between 35 to 50 °C and between 75 to 3000 psia, depending on the desired removal selectivity [6].

The amine gas treatment process is based on the reaction of a weak base (alkylamines) with a weak acid (H_2S and CO_2) resulting in the formation of a water-soluble amine acid gas salt. For example, DEA reacts with H_2S to produce a DEA-sulfide salt as shown in Equation 1.



This process is reversible at elevated temperatures, which allows the amine to be regenerated and recycled. However, reaction with strong acid anions such as formate, acetate, thiosulfate, thiocyanate, and chloride can create “heat stable salts”. Once such salts form, the solvent cannot be regenerated at elevated temperatures. Heavy hydrocarbons can also degrade the solvent by condensing and causing foaming. At high concentrations, the hydrocarbons can change the solvent physical properties.

3. Model System

A simplified thermodynamic system is considered in the present effort to provide an initial approximation of the trace species partitioning in the traditional cleanup environment. The thermodynamic model considers only the temperature, pressure, and syngas species of the gas stream subjected to cleanup conditions, and does not explicitly include thermodynamic parameters for process chemicals used in the Selexol or amine gas treatment systems. Further, no interactions between synthesis gas and process chemicals are considered.

The thermodynamic system considered consists of two primary components—the gas cleanup system and the solid oxide fuel cell (SOFC)—as shown in Figure 1. Bulk synthesis gas compositions are obtained from a survey of 18 gasification units representing deployed systems. The synthesis gas stream is spiked with trace species to simulate a typical exposure, as described by Martinez, et al. [7]. The synthesis gas is typically composed of approximately 30% H_2 , 34% CO , 13% CO_2 , 9% N_2 , 11% H_2O , and 3% CH_4 with flows that are normalized to achieve comparable electrochemical performance from the SOFC. The results obtained can be scaled to any desired syngas flow rate. The trace species doping is summarized in Table 2.

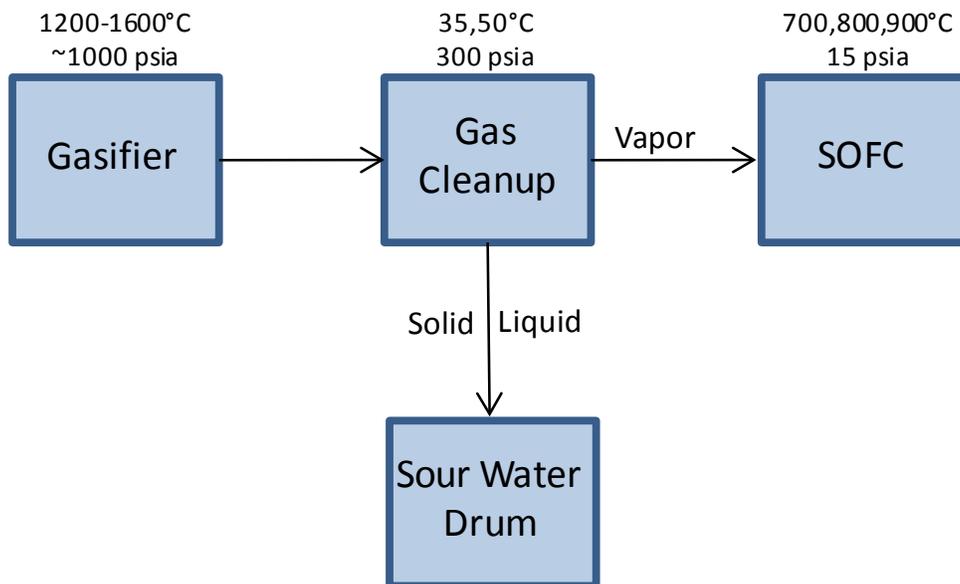


Figure 1 - Block flow diagram of syngas movement from gasifier to SOFC.

Table 2 - Summary of Trace Species Doped into Syngas Mixture [1]

Component	Concentration [ppmv]	Component	Concentration [ppmv]
AsH ₃	0.60	K	0.00
HCl	1.00	Se	0.15
PH ₃	1.91	Na	0.00
Sb	0.07	V	0.03
Cd	0.01	Pb	0.26
Be	0.03	Zn	9.00
Cr	6.00	H ₂ S	10.00
Hg	0.03	COS	0.10

The bulk synthesis gas is equilibrated at the conditions of a typical Selexol or amine gas treatment system, specifically at temperatures of 35 °C and 50 °C and a pressure of 300 psia. An analysis at near-atmospheric conditions (20 psia) was also completed to determine if there are any contaminant partitioning effects due to the operating pressure of the adsorption vessel, however the differences are not significant. The source synthesis gas equilibrated under these conditions is partitioned between solid/liquid and gas phases, with solid/liquid phases exhausted from the process and gas phases passing to the solid oxide fuel cell system.

The gas phase materials are then equilibrated at the temperature and pressure conditions of the fuel cell following the methodology of Martinez et al. [7] to evaluate the reaction with the nickel-based SOFC anode. SOFC operating temperatures tested were 700, 800, and 900 °C, and operating pressure was 1 atm. If the steam quantity in the source syngas is insufficient to suppress solid carbon formation in the equilibrated mixture, then steam is added iteratively until coke formation is zero; this would be necessary in a real IGFC system as well [8]. Any trace species that are predicted to exit the cleanup system as volatile species and arrive at the SOFC are then equilibrated with nickel in the simulation to determine the extent of the interaction.

The thermodynamic software, FactSage v6.1, was used to generate thermodynamic predictions for bulk and trace species that will pass through cold gas cleanup conditions. The source code was adapted from code previously used at NETL and is described in detail by Martinez et al [7]. It is critical to emphasize that the simplified thermodynamic model used here produces the equilibrium composition of the gas and does not account for kinetic barriers to generation of the equilibrium composition. This feature is not expected to impact the predictions of trace species partitioning, as many species simply condense at the gas cleanup conditions. More detailed contaminant partitioning predictions will require a complex, thorough kinetic analysis of trace material interactions with the synthesis gas constituents and process chemicals.

4. Results/Discussion

At cold gas cleanup conditions, the syngas equilibrates to primarily become CH₄ and CO₂ by the methane-steam reforming and water-gas shift reactions. That is, the steam content of the syngas stream is converted to CH₄, CO₂, or condensed in all cases by greater than 98% and in some cases completely. It is critical to note that this is an equilibrium calculation (Gibbs' free energy minimization) and that conversion of syngas to CH₄ of the predicted magnitude is not likely due to the kinetic barriers to formation. When the gases are reheated prior to reaction in the SOFC, typical values for CH₄ and CO₂ are predicted. Also note that in practice the gas stream will be cooled before injection in the cleanup unit. Therefore, the condensed steam that is expelled as sour water, along with any solid precipitates that form at these conditions, is removed prior to gas treatment; this is consistent with previous reports [9]. According to the thermodynamic model, all quantities of the trace species; lead, cadmium, arsenic, zinc, chromium, vanadium, and beryllium; are quenched into the discharged sour water.

The trace species that remain in the gas phase are carried downstream to the SOFC. The mass of volatile sulfur, chlorine, selenium, antimony, mercury, and phosphorus partitioning to the gas phase depends mostly on the amount of water vapor. When less steam is present in the effluent gas, more sulfur, chlorine, and phosphorus remain vaporized and pass through the gas cleanup system to the SOFC. When more steam is present, more antimony and mercury pass through cold gas cleanup. Partitioning of contaminant material is shown in Figure 2 where the relative amount of trace species passing through is depicted as a function of steam content in the syngas at cold gas cleanup conditions. In practice, greater or lesser steam concentrations may be controlled by system design.

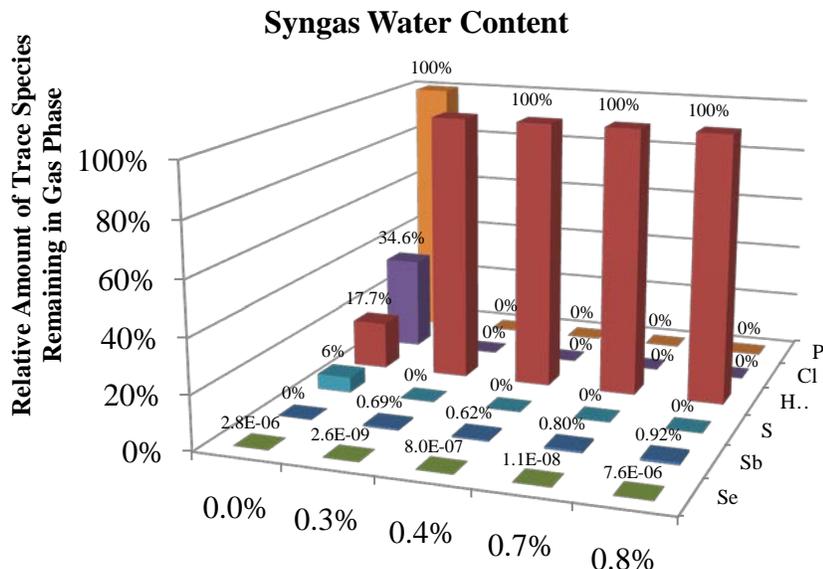


Figure 2 - Effect of steam content on the relative amount of trace species that passes through the cold gas cleanup process. The values are an average of the different gasifiers analyzed.

When the cleanup unit is simulated thermodynamically at near-atmospheric conditions (20 psia), slightly more steam passes through. This increases the amount of mercury and antimony that pass through the system, which is consistent with the trend. However, the amounts are not significantly increased and do not affect the SOFC performance downstream.

Based on individual trace species input, a maximum of 7.4% sulfur, 51% chlorine, 0.0045% selenium, 1.8% antimony, 100% mercury, and 100% phosphorus pass through. Cross reference of Figure 2 with Table 2 will provide concentration estimates of remaining trace material in the syngas after cleanup (e.g. Sb is 0.92% of 0.07 ppm). Evaluation of absolute concentration of trace material in the syngas depends on the specific gasification and cleanup system, and absolute concentrations are not necessary to validate the general conclusions of the present analysis.

Of those materials passing through cleanup, phosphorus poses the largest threat to SOFC operation due to the formation of non-conductive nickel phosphide phases. The phosphorus only passes through when steam is not present in the gas stream after cold gas cleanup. These results are obtained from a purely thermodynamic analysis of syngas behavior under traditional gas cleanup operating conditions. Additional trace material can be expected to be removed due to adsorption by the solvents. In practice, the presence of the process chemicals (Selexol or amine) will cause additional sulfur to be eliminated, further sweetening the syngas. In the amine gas treatment system, chlorine will also likely be incorporated into the solvent.

Under this simple thermodynamic analysis, a majority of trace coal species will be quenched out with the liquid water into the sour water. This leaves trace to ultra-trace quantities of coal contaminant species in the syngas effluent. With the exception of phosphorus, these trace species (or their quantities) are not predicted to pose any deleterious effect to SOFC operation. Mercury is not predicted to interact with nickel at SOFC operating conditions.

In all cases in which phosphorus passes through cold gas cleanup, the equilibrium reaction with nickel produces nickel phosphide species (predicted as Ni_5P_2). Following the assumptions and analysis of Martinez et al., after 3000 h the anode deactivation due to the formation of this non-conductive phase ranges from 0 to 47% as shown in Figure 3A. At warm gas cleanup conditions, syngas from each of the analyzed gasifiers results in secondary phase formation when reacted with the SOFC anode. The total deactivation at these conditions is up to 61%, as shown in Figure 3B. Clearly, the impact of phosphorus is great enough to require removal upstream. This can be perhaps be accomplished by ensuring that a small quantity of steam remains in the synthesis gas under cleanup system operating conditions. For the simulation executed at near-atmospheric conditions (20 psia), a trace amount of NiSb is formed. However, the amount is not significant enough to cause additional nickel deactivation.

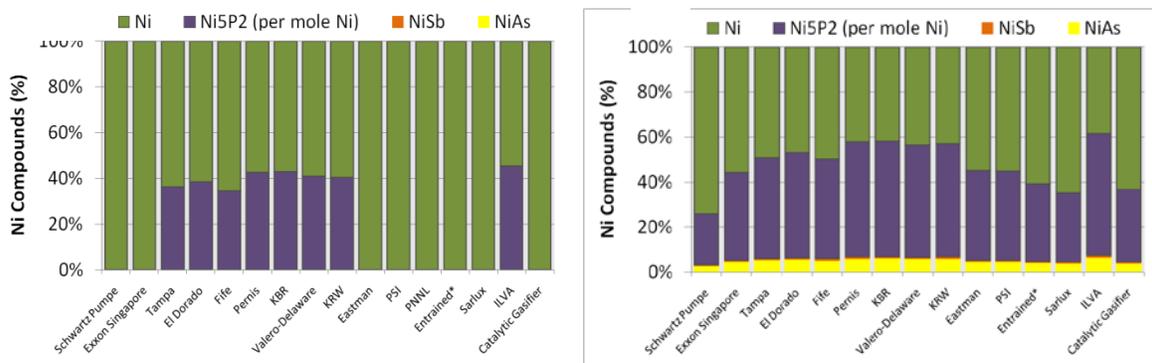


Figure 3 – A) Percent of nickel in SOFC anode converted to secondary phases after cold gas cleanup. In this case, the lack of arsenic and the minimal amount of antimony does not lead to formation of the corresponding nickel phase. B) The same comparison taken from Martinez et al. from simulations after warm gas cleanup conditions. In this case there is sufficient arsenic and antimony to produce secondary phases with nickel.

5. Conclusions

Trace species contained in synthesis gas derived from coal gasification can be removed from the process stream using traditional low temperature gas cleanup systems including Selexol and amine gas treatment. This study uses a simplified thermodynamic model to generate a conservative first approximation of gas cleanup effectiveness based on the temperature and pressure conditions of the cleanup system. A concentration estimate of volatile trace material passing through the cleanup system is necessary to evaluate possible impacts to downstream processes, including power generation with a nickel-based solid oxide fuel cell.

In the cleanup system, partitioning of trace species between sour water waste streams and process gas depends upon operating conditions, which dictate the thermodynamic state of the system. In traditional gas cleanup systems operating between 35 and 50 °C and 300 psia, a substantially lower concentration of volatile trace coal species passes to the solid oxide fuel cell compared to warm gas cleanup operation. Trace species such as arsenic, beryllium, cadmium, chromium, lead, vanadium, and zinc are condensed or quenched in the liquid water that is formed in the traditional cleanup processes. Trace species antimony, chlorine, mercury, phosphorus, selenium, and sulfur partition between sour water waste and process gas phases.

Of the elements that pass through the cleanup processes to the solid oxide fuel cell, only phosphorus is known to have a deleterious effect on nickel-based SOFC performance. Thermodynamic predictions and experimental observations show that mercury will not interact with nickel at SOFC operating conditions. The study indicates that a thermodynamic driver exists for phosphorus precipitation and eventual removal from the cleanup system, as long as sufficient water exists in the cleanup process. Phosphorus reaction chemistry inside the cleanup system must be investigated to develop phosphorus knock-out processes, or to assure that kinetic limitations are not present that will impede realization of the predicted thermodynamic state. At near-atmospheric pressure (20 psia) a very small amount of NiSb is likely to be formed in the SOFC, but not enough to deactivate the anode any more than at 300 psi.

The trace coal species content in syngas after cold gas cleanup is very low and current technical projections indicate that thermodynamic drivers exist that support syngas cleanup. Targeted cleanup system design efforts will mitigate deleterious impacts to the SOFC and facilitate achievement of system performance goals.

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