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**A Review of Hazardous Chemical Species Associated with
CO₂ Capture from Coal-Fired Power Plants and
their Potential Fate during CO₂ Geologic Storage**

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ABSTRACT

Conventional coal-burning power plants are major contributors of excess CO₂ to the atmospheric inventory. Because such plants are stationary, they are particularly amenable to CO₂ capture and disposal by deep injection into confined geologic formations. However, the energy penalty for CO₂ separation and compression is steep, and could lead to a 30 – 40% reduction in useable power output. Integrated gas combined cycle (IGCC) plants are thermodynamically more efficient, i.e., produce less CO₂ for a given power output, and are more suitable for CO₂ capture. Therefore, if CO₂ capture and deep subsurface disposal were to be considered seriously, the preferred approach would be to build replacement IGCC plants with integrated CO₂ capture, rather than retrofit existing conventional plants.

Coal contains minor quantities of sulfur and nitrogen compounds, which are of concern, as their release into the atmosphere leads to the formation of urban ozone and acid rain, the destruction of stratospheric ozone, and global warming. Coal also contains many trace elements that are potentially hazardous to human health and the environment. During CO₂ separation and capture, these constituents could inadvertently contaminate the separated CO₂ and be co-injected. The concentrations and speciation of the co-injected contaminants would differ markedly, depending on whether CO₂ is captured during the operation of a conventional or an IGCC plant, and the specific nature of the plant design and CO₂ separation technology. However, regardless of plant design or separation procedures, most of the hazardous constituents effectively partition into the solid waste residue. This would lead to an approximately two order of magnitude reduction in contaminant concentration compared with that present in the coal. Potential exceptions are Hg in conventional plants, and Hg and possibly Cd, Mo and Pb in IGCC plants.

CO₂ capture and injection disposal could afford an opportunity to deliberately capture environmental pollutants in the gaseous state and co-inject them with the CO₂, in order to mitigate problems associated with solid waste disposal in surface impoundments. Under such conditions, the injected pollutant concentrations could be roughly equivalent to their concentrations in the coal feed.

The fate of the injected contaminants can only be determined through further testing and geochemical modeling. However, the concentrations of inadvertent contaminants in the injected CO₂ would probably be comparable to their ambient concentrations in confining shales of the injection zone. In general, the aqueous concentrations of hazardous constituents in distal parts of the injection zone, regardless of source, are likely to be limited by equilibrium with respect to coexisting solid phases under the acid conditions induced by the dissolved high pressure CO₂, rather than by the initial concentrations of injected contaminants. Therefore, even if a deliberate policy of contaminant recovery and injection were to be pursued, water quality in Underground Sources of Drinking Water (USDWs) would more likely depend on thermodynamic controls governing aqueous contaminant concentrations in the presence of high pressure CO₂ rather than those in the injected CO₂. The conclusions reached in this report are preliminary, and should be confirmed through more comprehensive data evaluation and supporting geochemical modeling.

1. INTRODUCTION

1.1 BACKGROUND

Carbon dioxide is a so-called “greenhouse” gas, and its increasing concentration in the atmosphere is believed to be a significant cause of global warming during the last 50 years. Because global warming is thought to be undesirable, several remedies have been proposed to limit the build-up of atmospheric CO₂. One proposed remedy is to capture and isolate carbon dioxide discharges from fossil fuel power plants and other stationary industrial sources. The injection of the captured CO₂ into deep sub-surface aquifers for storage and sequestration is currently favored as the most practical method for long-term isolation. However, the quantities of injected CO₂ would be enormous. A 1,000 MWE coal-fired power plant generates approximately 10,000 tonnes of CO₂ daily, and the combined production of all such plants would amount to 10⁷ tonnes/day in the United States alone. Furthermore, the energy requirements for capture and isolation by this means would be greater than 30% of the current electrical output, necessitating an offsetting increase in power generating capacity and injection of a further 3 x 10⁶ tonnes/day of CO₂.

The availability of suitable on-shore aquifers for storage and sequestration of such large quantities of CO₂ has yet to be rigorously evaluated, and the capacity of offshore aquifers for CO₂ storage is largely unknown. On-shore aquifer storage also raises the issue of protecting sub surface potable water supplies, formally known as Underground Sources of Drinking Water (USDWs). If the injected CO₂ were to migrate away from aquifers designated for long-term storage, USDW contamination would become a distinct possibility. The ingress of injected CO₂ in USDWs could have an adverse effect on water quality for the following reasons:

- Dissolution of CO₂ in the USDW could enhance the solubility of hazardous chemical constituents, causing them to exceed health-based limits (HBLs).
- Supercritical CO₂ is an excellent solvent for many organic compounds. These compounds could be present in the host saline aquifer, and could be dissolved and transported to the USDW.
- The injected CO₂ might contain hazardous chemical constituents incorporated either inadvertently during capture and compression, or deliberately as part of a broader pollution control strategy.

The third issue is of concern to the U.S. Environmental Protection Agency (EPA), and is the subject of the present review. The first issue is potentially important, and has already received attention in the literature (Jaffe, and Wang, 2003; Wang and Jaffe, 2005). The second issue is amenable to evaluation during field tests involving CO₂ injection and recovery, but will also require detailed laboratory and theoretical studies before its significance can be established. Because the scientific nature of this issue differs substantially from the third issue, it is not addressed in this report.

1.2 OBJECTIVES

EPA has asked the staff of the Lawrence Berkeley National Laboratory (LBNL) to conduct a preliminary literature survey to review the likely effects on groundwater chemistry by chemical

constituents dissolved in and introduced during the injection of supercritical CO₂, these constituents having been introduced, either accidentally, or deliberately during the capture of atmospheric CO₂ discharges from stationary power plants or industrial facilities. No prior studies have addressed this issue, and therefore the problem must be evaluated. This preliminary review addresses the question regarding the nature and magnitude of potential contaminants in CO₂ captured from current and future coal-burning power plants. Co-contaminants associated with CO₂ waste streams from oil or gas-fired power plants, petroleum refining, chemical processing industries, and natural gas recovery, while important, are omitted due to time and financial constraints.

The objectives of the review are to:

1. Postulate the most plausible processes used to separate CO₂ in coal-fired power plants
2. Identify the concentrations of contaminants likely to associated with CO₂ that has been compressed for injection disposal,
3. Speculate on the fate of contaminants during and following co-injection with CO₂.

The last objective can be divided into three sub-topics:

1. The impact of contaminants on injection well facilities, especially with respect to corrosion, precipitation, and reaction with tubing, casing and emplacement cements,
2. Reactions between the supercritical CO₂, contaminants and chemical constituents of the sub-surface environment of the injection zone, i.e., the formation brine and host rocks,
3. The consequences of inadvertent direct leakage of the injected waste stream as a gaseous phase into a shallower saline aquifer and/or a USDW with lower salinity.

1.3 SCOPE

The scope of this report can be divided into two main subjects:

- The identification of the chemical constituents resulting from combustion that might be co-injected with compressed CO₂
- The interactions of the co-injected chemical constituents with the injection facilities, the injection zone host rock, and groundwaters, both within the injection zone, and any distal aquifers into which the compressed CO₂ or reacted groundwaters might leak.

The first subject requires an understanding of current and future combustion processes, and potential CO₂ capture technologies either retrofitted to existing power plants, or those that could be developed in conjunction with current or future advanced integrated gasification combined cycle (IGCC) power plants. Accordingly, this review includes an *a priori* discussion of CO₂ capture technologies that could either be retrofitted to existing coal-fired power plants, or incorporated in IGCC power plant designs. The impact of future refinements in IGCC design on CO₂ capture is also considered. The application of CO₂ capture technologies to coal-fired plants is also likely to stimulate research and engineering into co-disposal technologies of other hazardous components in an attempt to lower pollution control costs and minimize the

environmental impacts associated with surface waste disposal. The precise identification of the co-contaminants, their concentrations and their chemical state(s) depends on plant design, choice of fuel, and the pollution control methods employed. Therefore, the injected co-contaminants can be characterized only in a general way. A survey of the relevant literature does, however, permit substantial refinement of the major issues, and helps define unresolved questions for further study.

In this report, the postulated concentrations of major and trace chemical pollutants are considered, and their most probable chemical states are identified from the published literature. With information concerning the identity, concentration and chemical state of co-contaminants gained from the evaluation of power plant design, it is then possible to speculate on the possible fate of these co-contaminants during and following injection. Because of the preliminary nature of the report, this discussion is qualitative in nature. Limitations regarding the ready availability of relevant thermodynamic and kinetic data preclude a quantitative evaluation of the fate of all chemical constituents at this time.

2. CO₂ CAPTURE FROM CURRENT AND FUTURE COAL-BURNING POWER PLANTS

2.1 INTRODUCTION

In the following paragraphs, I briefly summarize the range of CO₂ capture options currently available for modifying existing coal-fired power plants or foreseen when constructing new plants. The primary purpose of this summary is to anticipate how such technologies could affect the composition of contaminants likely to be associated with compressed CO₂ at the injection wellhead. I start with a discussion of potential modifications to conventional coal fired power plants. This is followed by discussion of IGCC power plant technology, representing an evolutionary step in more efficiently integrating CO₂ capture with power generation. Finally, I address the potential impact of novel technologies evaluated as part of the Carbon Dioxide Capture Project (CCP) (Thomas, 2005), which could be incorporated in IGCC power plants utilizing coal as a primary energy source. Under the CCP, several oil companies and other interested parties have sponsored engineering studies to investigate more efficient means of CO₂ separation from existing and future petrochemical processes. In most of these studies, natural gas was considered as a primary fuel source, and they are therefore not immediately relevant to electric generating facilities burning coal. They do, however, suggest future developments where parasitic energy losses associated with CO₂ capture and sequestration are minimized. Tax credits could also be made available to companies for avoiding or curtailing CO₂ emissions, which would provide a strong incentive to develop and adopt these novel technologies in new coal-fired power plant designs.

Among the novel technologies being considered by CCP is membrane separation of hydrogen from syngas after treatment to remove carbon monoxide through the water-shift reaction, and the impact of using pure oxygen rather than air for combustion. However, while significant research has been undertaken to evaluate more efficient means of capturing and compressing CO₂ in future plant designs, the issue concerning co-generated gaseous and volatile waste products that could be economically co-disposed of with compressed CO₂ has not been addressed. Thus, it becomes a matter of speculation regarding what co-generated wastes might become candidates for co-injection. For the purposes of this study, scenarios are considered where the maximum possible concentrations of co-contaminants are considered for injection.

2.2 CONVENTIONAL COAL FIRED POWER PLANTS

No domestic coal fired power plants have been modified to capture CO₂ from the effluent stack gases. However, technologies to accomplish such an objective are under active consideration (Nsakala *et al.*, 2001; Eimer, 2005). Nsakala *et al.* (2001) report on the results of an engineering feasibility study sponsored by a consortium of energy companies together with the U.S. Department of Energy (DOE) National Energy Technology Laboratory and the Ohio Coal development Office to evaluate three such alternative recovery technologies:

1. Coal combustion in air followed by CO₂ separation using a commercially available methyl ethanolamine (MEA) absorption/stripping process
2. Coal combustion with O₂ firing, with flue gas recycle and direct compression of the waste stream

3. Coal combustion in air with post combustion oxygen removal and CO₂ separation using tertiary amines

Each of the technologies was evaluated against a baseline case with due consideration of CO₂ tax credits and the impact on plant performance and power generating cost. The baseline case is the American Electric Power (AEP) Conesville Unit #5, located in Ohio. This unit produces 463 MW of electric power at its maximum continuous rating, and is representative of a large number of coal-fired units currently in use. Flue gases from the unit are treated to remove most, but not all of the contained gaseous oxides of sulfur (SO_x), primarily sulfur dioxide, and nitrogen oxides (NO_x) in a flue gas desulphurization system. The vented stack gases contain approximately 15 volume percent of CO₂. The three alternative technologies were simulated using a proprietary computer model belonging to ALSTOM Power Inc.'s US Power Plant Laboratories. The computer model was initially calibrated against the performance of the reference unit, and then used to model the three alternative technologies. It should be noted that all three alternative CO₂ separation technologies seriously degrade the net thermal efficiency and power output of the unit, as summarized in Table 1. The losses are primarily associated with auxiliary power requirements to operate either the CO₂ separation system, or alternatively the air separation unit, and compression of the separated CO₂. The three alternative technologies are briefly summarized in the following paragraphs.

Table 1. Performance of Existing and CO₂ Capture Study Cases of the AEP Conesville Unit #5

Quantity	Units	Current Plant	MEA CO ₂ Recovery	O ₂ fired, Direct CO ₂ Compression`	MEA/MDEA CO ₂ Recovery
Steam Cycle Parameters					
Total turbine generator output	kW	463478	331422	463056	431290
Total auxiliary power	kW	29700	70665	183365	89738
Net plant output	kW	433778	260757	279691	341551
Overall Plant Performance Parameters					
Net plant efficiency (HHV)	-	0.350	0.210	0.231	0.229
Normalized efficiency (HHV)	-	1.000	0.601	0.659	0.654
Overall Plant Emissions					
Carbon dioxide emissions	kg/h	470806	16878	28105	48877
Specific carbon dioxide emissions	kg/kWh	0.906	0.054	0.084	0.120
Avoided carbon dioxide emissions	kg/kWh	0.000	0.852	0.823	0.787

Summarized from data provided in Table 1 of Nsakala *et al.* (2001)

2.2.1 MEA CO₂ Recovery

One of the best-established technologies for separating CO₂ from other gases is through absorption by selected chemical compounds of the ethanolamine group. In the process selected in the present case, a 20 wt.% aqueous solution of monoethanolamine (MEA) contacts the flue gases in an absorption unit after cooling removal of water. The CO₂ combines with the MEA, which is then heated and flashed, releasing the CO₂ as a gas, which is then dried and compressed. The MEA is further treated to strip the residual CO₂ and recycled. The MEA is poisoned by SO₂, necessitating two upstream FGD absorbers, rather than the base case single unit, to remove all but residual SO₂. (to 10 dppmv). The presence of oxygen and residual SO₂ is tolerated through proprietary additives to the MEA solution. The produced CO₂ is relatively pure. See Table 2.

2.2.2 O₂ Fired Direct CO₂ Compression

Modification of the unit to operate on pure oxygen has the advantage of permitting a large enrichment of CO₂ and substantial decrease in N₂ content, such that direct compression of the flue gas after FGD treatment is feasible. In the design, an auxiliary air separation unit produces oxygen, and two-thirds of the flue gas is recirculated. The remaining flue gas is compressed, and 94 vol% of the CO₂ separated as a liquid between -30 and -45 °C at 24 bars. The fluid is then heated to 28 °C and compressed to 138 bars. The final CO₂ product contains significant impurities, as can be seen by inspection of Table 2. Notable is the presence of residual oxygen, which would prevent transmission of the product through standard high-pressure pipelines.

Table 2. Predicted CO₂ Fluid Compositions from CO₂ Capture Study Cases of the AEP Conesville Unit #5

Study Case	Temp., °C	Pressure, bar	Composition, vol. percent			
			CO ₂ ,	N ₂	O ₂	SO ₂
MEA CO ₂ recovery	28	138	99.95	0.05	-	-
O ₂ fired direct CO ₂ compression	28	138	94	1.2	0.93	0.0215
MEA/MDEA CO ₂ recovery	28	138	99.97	0.03	-	-

2.2.3 MEA/MDEA CO₂ Recovery

Lower energy consumption is achieved during absorbent regeneration by using a combination of MEA and methyldiethanolamine (MDEA) instead of MEA alone. As for the MEA CO₂ recovery process, the system is installed downstream of the FGD unit. However the MEA/MDEA mixture cannot tolerate the presence of oxygen, and therefore residual oxygen must be removed before CO₂ recovery. This is achieved through conversion of the excess oxygen to CO₂ and water using natural gas over a De-Oxy catalyst upstream of the absorption unit. CO₂ is recovered from the MEA/MDEA solvent, as when using MEA alone, and compressed in the normal manner. A very pure product is obtained, as shown in Table 2.

2.2.4 Discussion

Nsakala *et al.* (2001) restricted their analysis of CO₂ separation technologies to only three options. Another option would be O₂ fired direct CO₂ compression cycle without incorporating the FGD step, removing excess O₂ through conversion to CO₂ and water using natural gas over a De-Oxy catalyst, and directly compressing the CO₂ and contained SO_x and NO_x gases. Because essentially no stack gases would be vented to the atmosphere, it would appear superfluous to go to the trouble of stripping SO_x and NO_x gases using a FGD unit, when direct injection of all waste gases could be achieved expeditiously. Such an alternative process may not be feasible on either technical or economic ground, but further analysis is beyond the scope of this report.

The most sobering aspect regarding CO₂ capture from conventional coal-fired power plants, is the substantial energy penalty required, amounting to between 30 and 40 percent of the net power output. The resulting shortfall in energy production, would have to be offset by building additional energy capacity. If this capacity were to be implemented through construction of more coal-burning plants incorporating CO₂ capture and subsurface disposal, then the design objectives would be to maximize net specific power output for a given quantity of captured CO₂. The most promising system integration would probably be in conjunction with IGCC technology. The coal gasification stage in IGCC plants results in a waste gas stream composition that is quite different from conventional combustion, and its treatment and separation could result in injected gas compositions, which could also differ. These issues are discussed in the following section.

2.3 STATE-OF-ART IGCC COAL-FIRED POWER PLANTS

IGCC and related Natural Gas Combined Cycle (NGCC) power plants provide a substantial improvement in thermodynamic efficiency over that possible with conventional steam turbine powered electric generation. The reason is that the combustible gases generated by the IGCC, or input directly in the case of NGCC systems, are used to drive a combustion turbine as a first stage, and the exhaust gases used to boil water for steam turbine generation as a second stage. The greater thermodynamic efficiency is achieved through the combined operation of Brayton (gas turbine) and Rankine (steam turbine) cycles, as illustrated in Figure 1. The thermal efficiency for NGCC plants currently approaches 60% as demonstrated by the 480 MWe single gas turbine system installed at the Baglan Bay Power Station in South Wales (General Electric, 2004, 2005). The H System™ turbine, supplied by General Electric operates at a maximum temperature of 1,400 °C (Valenti, M., 2002). Even greater improvements, with a thermal efficiency higher than 70% could be achieved with a gas turbine operating with a hydrogen-oxygen mixture at temperatures as high as 1,700 °C (Hisa *et al.*, 1999). However, a cost-effective technology required for turbine operation at such temperatures has not yet been developed.

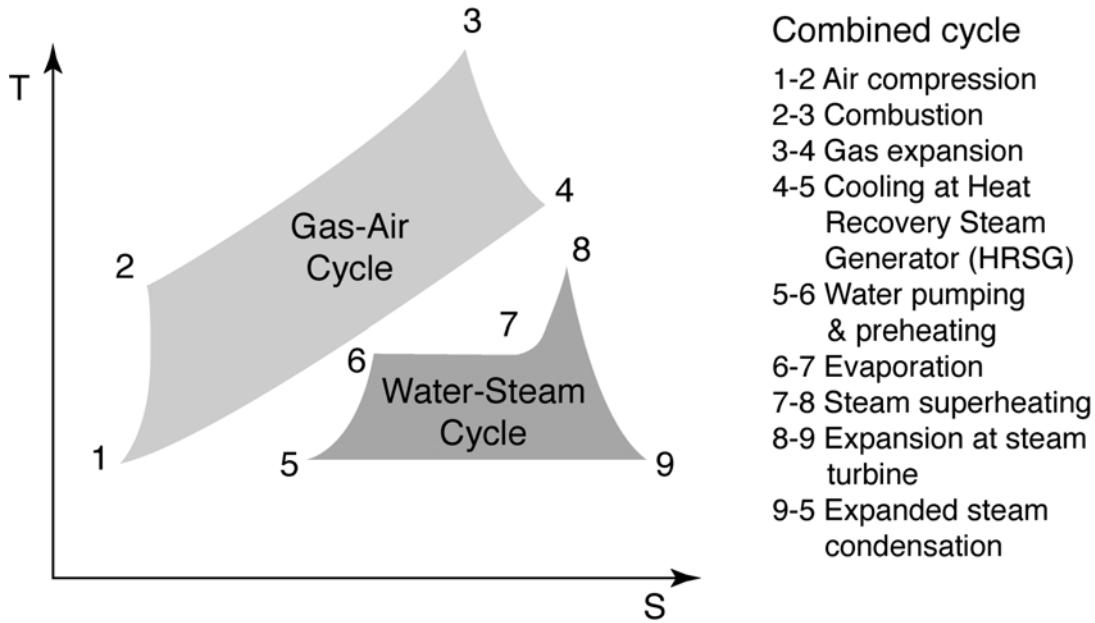
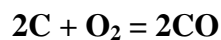


Figure 1. A temperature-entropy diagram to illustrate the increased thermodynamic efficiency of integrated gasification combined cycle (IGCC) power plants (after Treviño Coca, 2003)

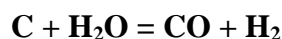
Increasingly stringent pollution control requirements, e.g., see Carlin (2002), and the potential need for CO₂ capture and sequestration greatly favors IGCC technology over existing power plant designs (Ratafia-Brown *et al.*, 2002). However, the capital and operating costs of NGCC systems are much less than coal-fired IGCC systems. Furthermore, coal-fired IGCC plants are predicted to be only marginally more cost effective than current state-of-the-art pulverized coal (PC) burning power plants (Leonard *et al.*, 2003). As a consequence, few IGCC plants have been built worldwide, despite their higher efficiency. However, the United States possesses abundant coal reserves with stable production costs, whereas natural gas supplies are being pinched by increasing demand and are subject to increasing price volatility. As a consequence, the calorific cost of coal as a fuel is approximately three times less expensive than natural gas, and, fuel costs for IGCC plants are substantially lower than for NGCC plants.

The basic method for coal gasification in IGCC plants has been in use since the middle of the nineteenth century when it was used to produce “town gas” for lighting purposes. Originally, coal was subjected to a three-stage treatment:

1. Pyrolysis, where coal was heated in a retort and decomposed, leaving a coke residue, and producing tars and oils, various gases, which were treated and processed to recover by-products including methane
2. Combustion, where the coke was burned in air to produce CO with complete consumption of oxygen:



3. Gasification, where steam was injected into the red-hot coke, which was reduced to CO plus H₂:

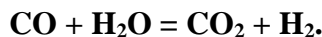


Because step 2 is exothermic, but step 3 is endothermic, steps 2 and 3 had to be alternated, while coke was continuously added. After treatment to remove pyrolysis by-products, the methane, from the pyrolysis, and CO and H₂ from steps 2 and 3 were combined, and stored in large tanks, or gasholders and distributed for domestic consumption.

In a modern IGCC plant, all three processes are combined in a single reactor, where comminuted coal is burned with restricted quantities of air or pure oxygen and steam. The reactor design and operating parameters can vary depending on the characteristics of the fuel. According to Trevino Coca (2003), the three most common are:

1. Moving bed (400-1,100 °C, 10-100 bar)
2. Fluidized Bed (800-1,050 °C, 10-25 bar)
3. Entrained (1,200-1,600 °C, 25-40 bar)

The gaseous products for each reactor design will vary, depending on the equilibrium distribution of gases in the reaction:



Higher temperatures favor a gas stream composed dominantly of CO and H₂, whereas at higher pressures, CO and H₂ concentrations are reduced, and steam concentration increases while CO₂ content remains nearly constant (Trevino Coca, 2003). The higher temperatures of fluidized bed and entrained reactant reactors lead to almost complete destruction of pyrolysis products.

The effluent from the coal gasification stage consists of a mixture of CO, CO₂, H₂O, H₂, together with other gaseous contaminants such as H₂S, COS, HCN, N₂ and NH₃, and entrained particulates. Before the gas is burned in a combustion turbine, it is cleaned up to remove the contaminants through application of the water shift reaction and acid gas removal (AGR), as described in Section 3.2.2, below, and particulates. The purified syngas stream is then combined with compressed air and ignited to drive the combustion turbine. The exhaust gases pass through a steam boiler to generate steam (see Figure 1) before being discharged to the atmosphere, as is current practice.

2.4 FUTURE REFINEMENTS TO COAL-FIRED IGCC POWER PLANTS.

IGCC plants are particularly suited for modification to allow capture of CO₂. The CCP has investigated several technological aspects of power plant cycles with the goal of maximizing CO₂ capture, while minimizing the unit cost. Although the emphasis was placed on NGCC plants, many of the more promising technologies, could, with minor modification, be applied to systems generating syngas from coal. The most promising technologies are summarized below. The technologies represent alternative approaches to cost effective carbon dioxide capture, and are not necessarily suitable for integration.

1. Effective integration of MEA CO₂ separation technology in NGCC power plants (Choi *et al.*, 2005).
2. Surface catalyzed water shift reaction to convert substantially all by-product CO to H₂ plus CO₂ (Mundschau *et al.*, 2005). Catalysis is optimal at pressures up to 35 bar and

a temperature of 700 K. A typical catalyst consists of a mixture of 90 wt% Fe_3O_4 and 10 wt% Cr_2O_3 .

3. Membrane separation of H_2 from the reformed gas stream, as per 1., above (Mundschau *et al.*, 2005). Membranes composed of composite metal foils of Group IVB – VB metals and their alloys, e.g., Nb, Ta, V and Zr, operating at about 30 bar and between ≈ 625 and ≈ 700 K, appear to be most promising.
4. Post AGR and water shift reaction separation of CO_2 using refrigeration to produce a liquid CO_2 product and H_2 gas turbine fuel (Holysh, 2005).
5. Simultaneous water shift reaction and CO_2 separation using a hydrotalcite absorbent (Allam *et al.*, 2005). The incentive for this approach is that the absorption of CO_2 promotes the conversion of CO into $\text{H}_2 + \text{CO}_2$.
6. Utilization of O_2 rather than air for turbine combustion, in order to avoid exhaust gas separation of N_2 and NO_x from CO_2 through cryogenesis (Miracca *et al.*, 2005).
7. An alternative separation of O_2 from compressed air at 20 bar and < 1075 °C using mixed conducting membranes rather than cryogenesis (Bucker *et al.*, 2005). This technology essentially allows pure oxygen to react with the combustible gas to generate a pure $\text{CO}_2 + \text{H}_2\text{O}$ effluent, which, in turn is used to heat the O_2 -depleted air to 1025 °C for expansion in a turbine.

3. THE BEHAVIOR OF GASEOUS AND VOLATILE POLLUTANTS IN CONVENTIONAL AND IGCC POWER PLANTS

3.1 INTRODUCTION

Gaseous and volatile pollutants can be divided into two broad categories, (1) those relating to nitrogen, sulfur and the halogens, and (2) a large number of inorganic trace elements, i.e., those elements present in coal with a concentration no greater than 100 µg/g (Weber *et al.*, 1996), and (3) residual organic compounds due to incomplete combustion. Because of their importance, pollution controls relating to nitrogen and sulfur species are discussed first. Their behavior is dependent on the state of oxidation during combustion. In contrast, the halides, principally F and Cl, are insensitive to oxidation state, and therefore their behavior in both conventional and IGCC plants is somewhat similar.

3.2 NITROGEN AND SULFUR

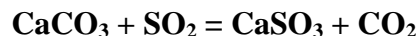
The sulfur present in coal occurs as pyrite (FeS₂), and as thio functional groups associated with the organic matter. Nitrogen, also associated with the organic matter, occurs as azo or amino functional groups.

3.2.1 Conventional Coal-fired Plants

3.2.1.1 Sulfur

During combustion, the pyrite is first converted to pyrrhotite (Fe_{1-x}S) with release of S₂(g), and then fuses, eventually being oxidized, primarily to SO₂, leaving an initial residue of magnetite (Srinivasachar and Boni, 1989). Thio groups and any volatilized sulfur are likewise oxidized to SO₂. A small proportion of the SO₂ is oxidized further to SO₃ through reaction with atomic oxygen, but SO₃ is hygroscopic and reacts with H₂O to form H₂SO₄. As the temperature of the flue gas falls, the dew point of H₂SO₄ is exceeded, and it condenses as an acid mist (Bionda, 2002). Both above and below the acid dew point, (SO₃ + H₂O) is adsorbed onto particulate material (PM) of the fly ash and particulate condensates, and is largely removed from the flue gas prior to emission. Because SO₂ is readily converted in the atmosphere to SO₃ and eventually acid aerosols, it is believed to be a significant contributor to acid rain (Carlin, 2002). Gaseous SO₂ is also believed to be responsible for tree damage in northeastern America and in northern Europe.

Legislation has been adopted to restrict SO₂ emissions from coal-burning power plants (Carlin, 2002). To meet these requirements, various SO₂ emission controls have been adopted. For example, limestone can be added to the coal during combustion, leading to the following reaction:



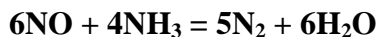
The CaSO₃ concentrates mainly in the residual bottom ash. Pulverized limestone can also be injected into the flue gases following combustion, where the same reaction takes place. Alternatively, the flue gases can be treated after PM removal by wet scrubbing in a flue gas desulphurization (FGD) plant using suspended particulate limestone. During this process, the

precipitated sulfite is oxidized to sulfate, and gypsum is precipitated, which can be recovered for production of wallboard.

3.2.1.2 Nitrogen

During the early stages of combustion, nitrogen functional groups break down and are released as HCN, NH₃, or N₂. The first two then undergo further oxidation to NO and small amounts of N₂O. The chemistry is complex and not fully understood. However, surface catalysis involving the fly ash particulates is involved (Kramlich and Linak, 1994; Pels *et al.*, 1995). The discharge of nitrogen oxides to the atmosphere is undesirable, because NO contributes to ozone destruction in the stratosphere, to ozone pollution in the lower atmosphere, and to the formation of acid rain (Carlin, 2002). Stratospheric ozone reacts with NO to produce NO₂ and O₂. Photolysis splits the NO₂ into NO plus atomic oxygen, which reacts with O₂ to form ozone. However, the net effect of NO is to deplete ozone levels in the stratosphere. In the lower atmosphere, similar reactions proceed, but with net production of ozone. In both the troposphere and stratosphere, NO₂ is further oxidized to N₂O₅, which reacts with water vapor to produce a nitric acid aerosol, HNO₃·3H₂O, which contributes to the formation of noctilucent clouds in the stratosphere, and acid rain in the lower atmosphere. N₂O is a greenhouse gas, which is about 270 times more effective than CO₂ in causing global warming. In the stratosphere, it reacts with atomic oxygen to form NO, which, in turn contributes to ozone destruction (Kramlich and Linak, 1994).

The oxides of nitrogen are collectively referred to as NO_x. Recently enacted legislation restricts NO_x emissions from stationary power generators to a greater extent than previously (Bitler, 1999; Carlin, 2002; U.S. Environmental Protection Agency, 2002). Accordingly, coal-fired power plants operate with pollution control equipment to remove NO_x. Current control technologies include the use of ammonia to convert NO_x to nitrogen:



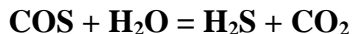
which can be performed through either selective catalytic reduction (SCR) or selective non-catalytic reduction (SNCR). Excess NH₃ used to abate NO_x is vented to the atmosphere as “slippage”, which can have adverse environmental consequences. Alternatively, NO can be catalytically oxidized to NO₂ and then absorbed by potassium carbonate. The loaded potassium carbonate can be regenerated using a reducing gas to convert the absorbed NO₂ to N₂ (Bitler, 1999).

3.2.2. IGCC Power Plants

The behavior of sulfur and nitrogen during combustion in IGCC plants differs from that of conventional power plants. Because of the reducing conditions imposed by complete consumption of oxygen, contaminating sulfur is reduced to H₂S and COS, and some of the nitrogen component is reduced to NH₃ and HCN.

In the IGCC power plant operated by ELCOGAS at Puertollano, Spain (Trevino Coca, 2003), the synthesis gas stream is filtered to remove entrained ash, and then scrubbed with water to strip HCl, HF, NH₃ and HCN, and partially strip CO₂ and H₂S. The pH of the solution is controlled through the addition of a 15 wt.% solution of sodium hydroxide. Part of the scrubbing solution is sent to a desorption system where H₂S, COS and HCN are separated in an acid column, and

NH₃ in an alkaline column. These gases are initially sent to a catalytic hydrolysis reactor where COS is converted into H₂S and CO₂ and HCN to NH₃ plus HCOOH, thus:



The gases then pass through an absorption column where a 50 wt percent aqueous solution of MDEA, is used to remove H₂S and CO₂ at 33 °C. The MDEA is then regenerated at 98 °C and the approximately 1:1::H₂S:CO₂ gas mixture sent to a Claus unit for H₂S conversion into sulfur. The cleaned synthesis gas is then fed to a gas turbine where it is burned using compressed air. To minimize NO_x formation the synthesis gas is enriched in nitrogen and steam added prior to ignition. The partial compositions of the input and output gas streams are given in Table 3. After heat is recovered from the turbine exhaust to drive a steam turbine, the exhaust vapor is discharged to the atmosphere.

Table 3. Compositions of Influent and Effluent IGCC Combustion Turbine Gases

Component	Influent Composition, Vol.%, dry basis	Effluent Composition, Vol.%, dry basis
CO	60.61	-
H ₂	22.08	-
N ₂	12.46	73.20
CO ₂	3.87	19.66
O ₂	-	6.0
Ar	1.03	1.14
S (as H ₂ S)	0.0016	-
SO ₂	-	0.00087
NO _x (as NO ₂)	-	0.0073
Particulates (mg/Nm ³)	-	7.5

Calculated from data given in Trevino Coca (2003).

3.3 FLUORINE AND CHLORINE

Fluorine and Chlorine form volatile HF and HCl during combustion, although tenuous evidence suggests that F₂ and Cl₂ might also form (Weber *et al.*, 1996). Both volatiles combine with water at lower temperatures to form corrosive acids. In conventional plants most of volatile HF and HCl is stripped during wet scrubbing by pollution control equipment to remove SO_x or NO_x from the flue gases, or during alkali scrubbing of the syngas in IGCC plants. Some HCl can also combine with NH₃ introduced to control NO_x by SCR or SNCR in conventional plants, or prior to cleaning of syngas in IGCC plants, in each case with formation of NH₄Cl. This salt is eventually removed by adsorption on PM or by scrubbing.

The importance of the presence of chloride during coal combustion lies in its ability to complex with hazardous trace constituents to form volatile chloride complexes, thus potentially increasing the volatility of the affected elements. This subject is discussed in greater detail in the following section.

Summary of the Fate of Minor Gaseous Components

Table 4. Fate of Minor Gaseous and Volatile Compounds

Element	Conventional Power Plant	Coal-fired IGCC Plant
N	Reaction between oxygen and nitrogen during combustion produces gaseous nitrogen oxides (NO _x), primarily NO and NO ₂ . Most are removed in the FGD circuit, or through catalytic process.	During syngas production, most nitrogen is converted to N ₂ , HCN and NH ₃ . Water shift reaction would convert HCN to CO ₂ + NH ₃ . Most NH ₃ would be removed by acid washing of syngas prior to combustion, or in water condensate prior to CO ₂ compression.
S	Converted mainly to SO ₂ with minor SO ₃ (SO _x) during combustion. FGD circuit removes most SO _x . Some is adsorbed on fly ash. Limestone addition to the feed helps remove SO ₂ .	Converted primarily to H ₂ S and COS. The water shift reaction converts COS to H ₂ S + HCOOH (+ CO ₂) H ₂ S can be stripped from the syngas prior to combustion by MEA separation with CO ₂ and subsequent conversion to S by the Claus process. If H ₂ is separated from the syngas after water shift treatment, H ₂ S could be compressed and co-injected with CO ₂
F	Some volatilized as HF. Balance adsorbed by fly ash or incorporated in bottom ash. HF is stripped from flue gas by the FGD circuit.	Some volatilized as HF. Balance adsorbed by ash or glass product. HF can be stripped from flue gas during alkaline wash of syngas prior to combustion, or during condensation of steam prior to CO ₂ separation and compression
Cl	Some volatilized as HCl. Balance adsorbed by fly ash or incorporated in bottom ash. HCl is stripped from flue gas by the FGD circuit.	Some volatilized as HCl and possibly CHCl ₃ . Balance adsorbed by ash or glass product. HCl can be stripped from flue gas during alkaline wash of syngas prior to combustion, or during condensation of steam prior to CO ₂ separation and compression. Possible reaction with NH ₃ with condensation of NH ₄ Cl during inter-cooling of syngas prior to combustion.

3.4 VOLATILE TRACE ELEMENTS

The Clean Air Act Amendments (CAAA) of 1990 identified 189 hazardous air pollutants (HAPs), of which, eleven are trace elements likely to be discharged from stack gases of a coal-fired utility. They include As, Be, Cd, Cr, Co, Hg, Mn, Ni, Pb, Sb, and Se. In addition, several other elements are worthy of consideration, because of their impact on the environment. They include Ba, regulated by the Resource Conservation and Recovery Act (RCRA), B and Mo, regulated by Irrigation Water Standards, and V, which, as V₂O₅, is very toxic, and regulated compound, (Weber *et al*, 1996). The behavior of several other trace elements in coal during combustion has been reviewed in the literature, i.e., Ga, Ge, P, Sn, U and Zn.

The concentrations of all trace elements listed above in various coal types are compiled in Table 5. Not all of these elements are necessarily volatile under conditions relating to deep injection co-disposal with a compressed CO₂ carrier fluid at temperatures below 100 °C even though these same elements might adversely affect the environment if released with stack gases

Table 5. Volatile and Trace Element Constituents of Coal

Element	Middle Kittanning Parent Coal (Miller et al., 1998)	Unspecified (Mojtahedi et al., 1990)	Unspecified (Wilde and Halbrook, 1977)	Sub-bituminous Coal (Frandsen et al., 1994)	Bituminous Coal (Yan et al., 1999)	Black Thunder (Bool and Helble, 1995)	Washed Pittsburgh No. 8 (Bool and Helble, 1995)	Falkirk, ND, lignite (Weber et al., 1996)	Pennsylvania/Ohio blend, bituminous (Weber et al., 1996)	Pittsburgh No. 8, bituminous (Weber et al., 1996)	Illinois No. 5 and 6 blend, bituminous (Weber et al., 1996)	Illinois-Indiana Basin, bituminous (Weber et al., 1996)	Lee ranch, NM, sub-bituminous (Weber et al., 1996)	Illinois blend, bituminous (Weber et al., 1996)	Big Sky (PRB), sub-bituminous (Weber et al., 1996)	Rochelle coal (Radian Corp., 1995)
Volatile Concentrations in Coal, Wt% dry basis																
C	81.64	69.3		54.8	57.69	69.83	78.11	59 ±2.2%	70 ±2.1%	72 ±0.82%	71 ±2.8%	70 ±2.7%	61 ±1.9%	70 ±0.85%	68 ±2.0%	70
H	5.16	4.2		6.3	2.88	5.73	4.70	4.5 ± 24%	4.9 ±4.5%	5.0 ±4.7%	5.1 ±11%	4.8 ±4.0%	4.8 ±7.7%	4.9 ±5.8%	4.8 ±14%	4.6
N	1.48	1.15		1.2	0.97	0.92	1.41	0.89 ±20%	1.4 ±3.2%	1.4 ±3.2%	1.4 ±4.1%	1.3 ±3.7%	1.1 ±4.9%	1.3 ±5.4%	1.0 ±8.6%	0.99
S	1.11	1.1 – 1.9		0.3	0.82	0.51	1.92	1.1 ±3.5%	3.0 ±2.4%	3.3± 4.0%	2.9 ±4.8%	3.5 ±4.5%	0.65 ±16%	3.4 ±6.8%	1.2 ±5.3%	0.28
O	5.14	5.57		33.8	5.73	17.07	6.27									
Ash		18.9		3.6		5.94	7.58	17 ±2.7%	13 ±0.68%	12 0.56 11 0.72	13 ±0.66%		21 ±0.66%	12 ±1.5%	12 ±1.68%	6.7
F				.01				0.0057 ±7.7%	0.0081 ±7.8%	0.0058 ±7.8%	0.0080 ±9.8%	0.0110 ±15%	0.0080 ±17%	0.0097 ±16%	0.0044 ±14%	0.0076
Cl				0.03				0.40 ±25%	0.14 ±61%	0.085 ±25%	0.12 ±29%	0.074 ±31%	0.039 ±58%	0.064 ±23%	0.03 ±46%	0.0039
Trace Element Concentrations in Coal, ppm dry basis																
As	3.20	33	9.6	1	15	3.8	1.4	7.6 ±44%	26 ±39%	9.4 ±36%	3.5 ±29%	2.7 ±38%	1.7 ±39%	2.4 ±24%	1.2 ±40%	0.98
B	14.68		102	50				130 ±35%	71 ±18%	72 ±16%	170 ±22%	210 ±15%	77 ±17%	230 ±15%	83 ±34%	32
Ba	138.43		130					570 ±35%	76 ±27%	31 ±21%	49 ±14%	49 ±22%	310 ±45%	47 ±38%	370±53	370

Element	Middle Kittanning Parent Coal (Miller et al., 1998)	Unspecified (Mojtahedi et al., 1990)	Unspecified (Wilde and Halbrook, 1977)	Sub-bituminous Coal (Frandsen et al., 1994)	Bituminous Coal (Yan et al., 1999)	Black Thunder (Bool and Heible, 1995)	Washed Pittsburgh No. 8 (Bool and Heible, 1995)	Falkirk, ND, lignite (Weber et al., 1996)	Pennsylvania/Ohio blend, bituminous (Weber et al., 1996)	Pittsburgh No. 8, bituminous (Weber et al., 1996)	Illinois No. 5 and 6 blend, bituminous (Weber et al., 1996)	Illinois-Indiana Basin, bituminous (Weber et al., 1996)	Lee ranch, NM, sub-bituminous (Weber et al., 1996)	Illinois blend, bituminous (Weber et al., 1996)	Big Sky (PRB), sub-bituminous (Weber et al., 1996)	Rochelle coal (Radian Corp., 1995)
Be	4.19		0.92	1				0.72 ±17%	2.4 ±12%	1.3 ±16%	1.4 ±22	1.6 ±16%	1.3 ±8.4%	1.3 ±11%	0.42 ±18 %	0.27
Cd	0.21	2.4	0.78	0.05				0.079 ±39%	0.085 ±39%	0.11 ±32%	0.51 ±58%	1.0 ±58%	0.56 ±140%	0.58 ±35%	0.06 ±63%	0.1
Co	14.68	8.2	9.6	5				2.1 ±46%	7.0 ±28%	5.5 ±31%	4.4 ±40%	3.6 ±21%	4.1 ±25%	3.9 ±29%	0.86 ±43%	1.9
Cr	27.26		15	30		10	4.5	8.1 ±13%	20 ±21%	16 ±19%	21 ±14%	35 ±4.3%	6.6 ±14%	28 ±9.9%	4.4 ±19%	4.7
Cu		154	15					9.3 ±30%	21 ±13%	8.5 ±20%	13 ±15%	11 ±18%	15 ±49%	11 ±18%	9.5 ±22%	11
Ga				5												
Ge			6.9	5												
Hg	0.02	2.0	0.27	0.1	0.1	0.099	0.11	0.15 ±17%	0.26 ±20%	0.13 ±25%	0.085 ±26%	0.11 ±74%	0.080 ±9.1%	0.10 ±10%	0.084 ±17%	0.11
Mn	20.98		49					120 ±17%	27 ±11%	18 ±10%	29 ±13%	34 ±14%	77 ±20%	41 ±24%	150 ±19%	9.9
Mo	6.30		7.5					4.0 ±88%	4.5 ±46%	1.9 ±47%	5.8 ±48%	7.9 ±54%	2.1 ±97%	8.3 ±52%	7.9 ±55%	0.55
Ni		16	12	25				7.3 ±50%	28 ±38%	14 ±15%	18 ±25%	19 ±14%	6.8 ±18%	18 ±16%	5.1 ±90%	1.6
P			71	50												300
Pb	19.18	18	5.9	25				3.3 ±64%	14 ±34%	6.0 ±44%	8.5 ±39%	13 ±30%	8.9 ±23%	9.1 ±35%	5.2 ±27%	1.3
Sb	4.26		0.15	1		0.23	0.16	0.75 ±37%	2.1 ±12%	0.64 ±7.6%	0.62 ±25%	0.79 ±35%	1.7 ±44%	0.49 ±5.9%	0.47 ±5.0%	0.12
Se	1.58		1.7	1	2.5	0.88	0.93	0.80 ±34%	2.6 ±24%	1.9 ±26%	2.2 ±26%	3.2 ±38%	1.2 ±34%	2.9 ±21%	0.84 ±28%	3.4

Element	Middle Kittanning Parent Coal (Miller et al., 1998)	Unspecified (Mojtahedi et al., 1990)	Unspecified (Wilde and Halbrook, 1977)	Sub-bituminous Coal (Frandsen et al., 1994)	Bituminous Coal (Yan et al., 1999)	Black Thunder (Bool and Heible, 1995)	Washed Pittsburgh No. 8 (Bool and Heible, 1995)	Falkirk, ND, lignite (Weber et al., 1996)	Pennsylvania/Ohio blend, bituminous (Weber et al., 1996)	Pittsburgh No. 8, bituminous (Weber et al., 1996)	Illinois No. 5 and 6 blend, bituminous (Weber et al., 1996)	Illinois-Indiana Basin, bituminous (Weber et al., 1996)	Lee ranch, NM, sub-bituminous (Weber et al., 1996)	Illinois blend, bituminous (Weber et al., 1996)	Big Sky (PRB), sub-bituminous (Weber et al., 1996)	Rochelle coal (Radian Corp., 1995)
Sn			4.8	5												
Sr	10.49															200
U			1.3													
V	25.17	28	33	25				17 ±8.7%	34 ±14%	31 ±14%	39 ±15%	46 ±9.4%	26 ±6.1%	37 ±12%	9.4 ±9.3%	13
Zn	56.63		272	100		11.0	4.6									7.9

Over the last 15 years, a significant number of studies have been conducted to determine the behavior and fate of volatile trace elements during combustion of coal. These studies were in response to stricter regulations governing HAPs due to CAA Amendments of 1990, as discussed above, and included both laboratory, pilot plant and operating facility evaluations. A characteristic of these studies, and in particular, those conducted on pilot plant and operating facilities, is the overall lack of accuracy in achieving satisfactory mass balances between the fuel input, and emerging waste streams. This lack of accuracy can be ascribed to several causes:

- The low concentrations of many of the trace elements in the feed
- Flaws in sampling methods
- Flaws in the analytical methods
- Non-uniformity of the feed
- Collection of data at times differing from the time of combustion of the analyzed feed
- Non steady state operation.

Even with the analysis of the same coal samples by different laboratories, as illustrated in a round-robin study reported by Weber *et al.* (1996), substantial discrepancies arose between the analytical results from different laboratories, in part due to differing analytical methods used. These problems have serious consequences in the management of air pollution by HAPs, and have stimulated the Electric Power Research Institute (EPRI) to sponsor ongoing research under their PISCES (Power Plant Integrated Systems Chemical Emissions Studies) program to improve analytical methods and accountability.

The difficulties indicated in the foregoing paragraphs obviously impact the current analysis. Furthermore, the large variability of operating parameters, and pollution control technologies between individual coal-fired utilities makes any form of generalization regarding the fates of individual trace elements even more challenging. As an illustration, consider the partial listing of variables inherent in current state of the art coal fired power plants:

- The nature of the fuel, whether soft brown coal or bituminous coal, or refinery coke
- The efficiency of combustion
- The concentrations of minor elements in the solid fuel, which would constitute the residual ash or slag after combustion, but which would affect the behavior and fate of gaseous and volatile products of combustion
- The concentrations of minor elements that would lead to the formation of gaseous or volatile products upon combustion, and which could affect the volatilization, gasification and transport of hazardous trace constituents, e.g., S, N, Cl, F.
- The combustion method, i.e., whether moving bed, fluidized bed, entrained flow, etc.
- The nature of the feed, i.e., pulverized or as a coal-water slurry
- The nature and configuration of burners in the furnace
- The temperatures attained during combustion, especially in relation to the stages of combustion, i.e., volatilization and char formation

- The physical nature of char and ash formed during combustion
- The presence of additives to control combustion, and capture gaseous or volatile pollutants, e.g. limestone for SO₂ removal, NH₃ for NO_x control or water for temperature control
- Post-combustion techniques for the removal of SO_x, e.g., flue gas desulphurization (FGD) through injection of pulverized limestone in the flue gas, or through wet scrubbing
- Post-combustion techniques for the removal of NO_x, e.g. selective catalytic or non-catalytic NO_x abatement

With respect to IGCC plants, a corresponding set of variables also applies, including those cited above with respect to fuel type, the type of gasification system, i.e., moving bed, fluidized bed, or entrained flow, and the use of additives, e.g., limestone to slag particulate waste in entrained flow gasifiers. In addition, differing technologies can be used to clean up the syngas prior to combustion in a gas turbine. Finally, by the time conventional power systems are replaced by IGCC systems, various advanced technologies, currently under development, may be incorporated as standard practice, as noted in Section 2.4.

The literature covering the fate of trace elements during combustion reflects the variability in plant design and operating conditions enumerated above. It is difficult to reconcile the disparate observations in order to formulate a coherent description of trace element behavior. Furthermore, current analytical procedures to measure trace element concentrations in the gaseous and particulate matter phases are of questionable reliability and reproducibility. Research and development is actively underway to improve analytical methods for stack-gas emissions, e.g., see EPRI (2005). Despite these limitations literature studies can be used in a qualitative sense as a basis for making preliminary predictions relevant to the purpose of this report. In the following section, the behavior of a number of trace elements, either under oxygen-rich or oxygen-poor combustion conditions, is considered.

3.4.1 The Volatilization of Trace Elements during Combustion: Experimental Determination

The fate of trace elements during coal combustion has been studied several times. The findings of three such studies under differing operating conditions are presented here.

1. A (2 MMBtu) research boiler (Falcone Miller *et al.*, 1998) operating at ambient pressure with excess air. The trace element distribution in the gaseous state was measured at 140 and 160 °C. Operating conditions replicate in some measure, those of a full scale coal-burning utility.
2. A laboratory-scale pressurized fluidized bed combustor operating at 5, 7 and 10 bar in the presence of excess air. The trace element distribution in the gaseous state was measured between ≈650 and ≈750 C, (Mojtahedi *et al.*, 1990).
3. A commercial IGCC facility operated by Louisiana Gasification Technology Inc. (LGTI) at Plaquemine, Louisiana. The gasifier is a proprietary design of the high temperature entrained-flow slagging type. Operating parameters were not disclosed, but probably fall into the range for entrained systems, i.e., 1,200-1,600 °C, 25-40 bar.

Trace element distribution in the raw syngas is estimated from measurement of their partitioning between the slag and other monitored waste streams in the facility, (Radian Corporation, 1995).

The concentrations of trace elements in waste streams can be reported in different ways. Ideally, for the purposes of this study, the concentrations of trace elements should be reported in relation to the concentration of carbon in the coal feed, as it is presumed that the motivating parameter will be the molar concentration of a given trace element in a mole of CO₂. However, studies conducted in response to the regulatory requirements of CAAA (1990), commonly report the fate of HAPs in terms of µg/Nm³ flue gas, lb/MMBtu, % of concentration originally in the coal, or as an “emission factor”. Transformation of data reported in these differing units to molar concentrations, usually requires conversion factors employing data that were not reported as part of the study. For reasons of time and economy, the fate of trace elements in the cited three studies are reported in terms of the percentage of each element in the original coal.

3.4.1.1 Research Boiler Operation

The purpose of the study described by Falcone Miller *et al.* (1998) was to trace the volatility of trace elements during and following combustion of coal. The coal was of the bituminous type from the Middle Kittanning seam from Pennsylvania (Table 5), and was fed to the boiler either in pulverized form (PC), or as a coal-water slurry fuel (CWSF). The trace elements monitored were those identified in Title III of the CAA Amendments of 1991; As, Be, Cd, Cl, Co, Cr, F, Hg, Mn, Ni, P, Pb, Sb and Se. In addition, the elements B, Ba, Mo, Sr, V and Zn were also included in the analyses.

Both the PC and CWSF were burned with excess air. Combustion efficiency was 97.5 and 96.8% and residual oxygen was 5.3 and 4.6% for PC and CWSF respectively. Temperatures were measured at the boiler exit (930, 850 °C), the baghouse inlet (160, 140 °C) and baghouse outlet (114, 105 °C) respectively for PC and CWSF.

The total flue gas concentration and the concentration in the gaseous state for the above listed Title III elements at the baghouse inlet are presented in Table 6 in terms of the percentage of the initial concentration in the coal. At the measured operating baghouse inlet temperatures, 160 and 140 °C, respectively for PC and CWSF feeds. The order of volatility for the trace elements is, for PC: B > Hg > Se > Zn > Pb > V..., and for CWSF: (Cd) > B > Hg > Se > Pb = Zn > As > Sb = Co... It is noteworthy that only B, Hg and Se were found to be present in the gaseous state in other than trivial concentrations. Although other elements were present in the gaseous state at concentrations equal to or less than one tenth of one percent, the significance of these values could be debated. The findings indicate that even the most volatile of elements, B, Hg and Se, were already substantially partitioned into either the bottom or fly ashes. It is generally understood that those elements, which volatilize at combustion temperatures, are preferentially sorbed onto particulates with falling flue gas temperatures, and that only a small proportion are released to the atmosphere in operating coal-fired power plants (Weber *et al.*, 1996).

Table 6. Selected Trace Elements in Flue Gas exiting a 2 MMBtu Research Boiler¹

Element	Total Flue Gas Concentration at the Baghouse Inlet compared with the Quantity Present in Coal Charge, wt.%		Concentration in Gaseous State at the Baghouse Inlet compared with the Quantity Present in Coal Charge, wt.%	
	PC2 (≈160°C)	CWSF3 (≈140°C)	PC (≈160°C)	CWSF (≈140°C)
As	15.9	13.9	0.00	0.11
B	57.9	12.6	28.97	5.26
Ba	6.0	1.3	0.00	0.01
Be	25.2	9.3	0.00	0.07
Cd	5.3	99.0	0.00	21.98
Co	18.5	9.3	0.00	0.09
Cr	26.2	10.6	0.00	0.08
Hg	28.5	7.9	3.51	4.80
Mn	7.9	5.0	0.10	0.04
Mo	37.1	7.6	0.00	0.08
Pb	19.9	11.9	0.00	0.12
Sb	6.6	9.3	0.09	0.09
Se	22.5	7.6	0.29	0.26
Sr	63.6	4.3	0.00	0.03
V	33.8	12.6	0.00	0.10
Zn	12.6	12.6	0.16	0.12

¹Calculated from data presented in Falcone Miller *et al.* (1998)

²Pulverized Coal

³Coal-Water Slurry Fuel

3.4.1.2 Pressurized Fluidized Bed Combustion

Mojtahedi *et al.* (1990) used a pressurized fluidized-bed combustion facility, rated at 130kW thermal when burning solid carbonaceous fuels, to measure the concentrations of certain trace elements in the gaseous state emerging in the flue gas from the combustor. The fuels used were peat and coal with and without admixed finely or coarsely ground limestone. The trace elements investigated were As, Cd, Co, Cu, Hg, Ni, Pb, V and Zn. The chemical analysis of the coal is given in Table 5. For sampling purposes, a small gas stream was extracted from the duct immediately downstream of the combustor.

Gaseous phase concentrations, in terms of the percentage of the trace element present in the original fuel, were calculated from the data provided in the paper, and are presented in Table 7. Only the results for a coal feed with admixed fine and coarse limestone at 5, 7 and 10 bar respectively are presented. Because the gas stream was sampled immediately following combustion rather than after passage through a boiler, as in the research boiler study described above, the flue gas temperature was much higher, i.e., between 650 and 750 °C.

Table 7. Selected Trace Elements exiting a Pressurized Fluidized Bed Combustor in the Gaseous State¹

Element	Flue Gas Concentration ² in the Gaseous State, Percentage of Quantity Present in Coal Charge		
	5 bar, 651-678°C	7 bar, 707°C	10 bar, 741-749°C
As	2.89 – 3.92	3.01	2.11 – 2.23
Cd	2.07 – 4.96	4.13	1.24 – 1.65
Co	4.8 - 86	6.7	0.61 – 2.8
Cu	0.57 – 1.10	0.43	0.30 – 0.57
Hg	8.46 – 10.4	18.9	7.46 – 4.98
Ni ³	265 - 432	382	59 - 145
Pb	1.27 – 0.22	3.09	0.77 – 1.66
V	0.99 – 1.63	1.17	0.32 – 0.60
Zn ⁴	0.55 – 0.78	0.70	0.27 – 0.48

¹Calculated from data presented in Mojtabedi *et al.* (1990)

²Based on calculations assuming complete oxidation of carbon in the coal in the presence of excess air. Corrections not made for oxidation of S, N and H

³Ni values are meaningless, because of contamination by stainless steel sampling equipment.

⁴Concentration of Zn in the coal feed not given in reference. An estimated value used in the calculation, based on the average concentrations in coal analyses given in Table 3.

Note that some approximations were made as a matter of expediency in calculating the data in the above table. However, these approximations have no material effect on the conclusions drawn in the analysis in this report.

Not all elements in the research boiler study were analyzed in the PFBC effluent flue gas. Furthermore, operating conditions differed, and the volatility of some elements were likely affected by the addition of limestone. Therefore, a strict comparison with the results of the previous study is not possible. Nevertheless, results are qualitatively comparable, in that the major fraction of all trace elements measured, had already partitioned into the ash phase even at temperatures between 650 and 750 °C. The trace elements in order of volatility are (Co) > Hg > As > Cd > Pb > V > Cu > Zn. As expected, Hg persisted in the gaseous phase. Co is a suspect outlier analysis, which might have been affected by contamination from stainless steel parts used in the test equipment.

3.4.1.3 Coal Gasifier

Radian Corporation was commissioned by the U.S. Department of Energy to undertake a study of the fate of trace elements in an IGCC plant operated by Louisiana Gasification Technology Inc. (LGTI) at Plaquemine, Louisiana. This plant consumes 2,200 tons of coal per day and generates 161 MW of electric power using two gas turbines. The syngas feed to the turbines is supplemented with natural gas. The publicly released version of the resulting report (Radian Corporation, 1995) is heavily redacted, and information of critical importance to the current evaluation has been withheld.

The gasifier is a proprietary design of the high temperature oxygen-blown, entrained-flow slagging type, in which the coal is fed as a water-based slurry. Operating parameters are not disclosed, but probably fall into the range for entrained systems, i.e., 1,200-1,600 °C, 25-40 bar (see Section 2.3, p. 10). A comprehensive suite of trace and minor elements was analyzed at several points throughout the IGCC system. Those investigated include As, Ba, B, Be, Cd, Cr, Co, Cu, Mn, Hg, Mo, Ni, P, Pb, Se, V and Zn in addition to S, K and Cl. A chemical analysis of the Rochelle coal from Wyoming, and used in the study, is given in Table 5. The trace and minor element distribution in the raw syngas, sampled downstream of the gasifier at a temperature of about 540 °C, and analyzed, was not disclosed. The particulate matter (char) removed from the syngas stream at about 230 °C was also analyzed, but not disclosed. However, an approximate determination of the effluent stream can be made by comparing the percentage distribution of the respective trace elements in the slag, and calculating by difference the percentage fraction in the present in the gasifier effluent (as gas and entrained char). The results of this calculation are presented in Table 8, and compared with the percentage fractions in the gas turbine exhausts, which also contain traces of contaminants introduced with the natural gas.

Table 8. Distribution of Trace elements in an IGCC Plant¹

Element	Slag, %	Raw Syngas (by Difference), %	Gas Turbine Exhaust, %
As	45	55	4.3
Ba	120	-	<0.1
B	81	19	n.d.
Be	93	7	n.d.
Cd	15	85	56
Cr	120	-	1.1
Co	100	0	0.6
Cu	97	3	2.5
Mn	99	1	0.6
Hg	1.4	98.6	23
Mo	100	0	25
Ni	180	-	4.9
P	100	0	1.7
Pb	16	84	4.2
Sb	65	35	n.d.
Se	49	51	3.3
V	100	0	0.13
Zn	44	54	12
S	0.79	99.21	46
F	23	77	1
Cl	16	84	n.d.

¹Data taken from Radian Corporation (1995)

The partitioning of trace elements between the bottom ash (or slag) and the gaseous phase should be quite different in a coal gasifier, when compared with that from either the research boiler, or the pressurized fluidized bed combustor. In the latter cases, combustion occurs in the presence of excess oxygen, whereas in the former case, oxygen supply is restricted to ensure optimum production of CO and H₂. Trace element volatility would be enhanced, as reducing conditions are favorable to the formation of volatile reduced gaseous species of the trace elements, such as hydrides and carbonyls. The estimates in Table 8, despite the characteristically poor mass balance closures, suggest that major fractions of some trace elements partition into the gaseous phase (although an unknown fraction would also be associated, or could have condensed on suspended particulates). From Table 8, the order of volatility of the trace elements is Hg > Pb > Cd > As > Zn > Se > Sb > B > Be > Cu > Mn. This volatilization sequence can be compared with that quoted from the work of Kalfadelis and Magee (1975) for another coal gasifier: Hg > Se > Pb > Cd > As > Sb > Be > Ni > V, given in Table 9. With the exception of Se, the two sequences are comparable. The relatively lower volatility of anionic species such as Se, when compared with heavy metals in the LGTI plant, might be attributed to the addition of limestone to the coal slurry feed. Although not disclosed in the report, there is strong evidence that limestone was added as a flux to aid in the formation of a liquid slag (Trevino Coca, 2003). The slag contains 16 wt.% Ca, whereas the ash residue of coal combustion alone would have contained only 0.16 wt %. The increased concentration of Ca would cause the preferential partitioning of As, Se, Sb and B, as calcium salts in the slag (Bool and Helble, 1995; Anonymous, 1998).

3.4.2 The Volatilization of Trace Elements during Combustion: Theoretical Calculations

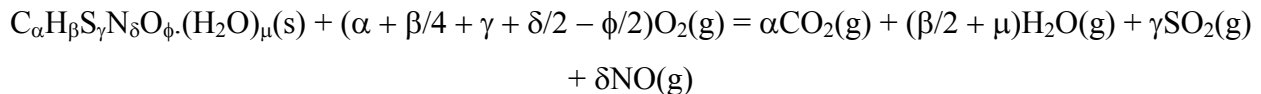
Several studies have been reported, in which calculations have been made to determine the predicted equilibrium distribution of gaseous and volatile species at given temperature, pressures and, in two studies, the stoichiometric ratios of oxidant, e.g., Frandsen *et al.* (1994), Yan *et al.* (1999). Frandsen *et al.* (1994) summarize earlier studies of equilibrium distributions and sources of thermodynamic data. The equilibrium thermodynamic calculations can be presented graphically, as the molar percentage distribution of species versus temperature. As such, they provide valuable insights regarding the principal species likely to be responsible for the volatility of a given trace element, and what the fate of the volatile species might be when the flue gas or syngas streams are subject to various processing steps to remove contaminants, and ultimately to compress waste carbon dioxide. Such calculations are, however, at best semi-quantitative in nature for the following reasons:

- Not all species may have been incorporated in the model, because, either they have not been identified, or no thermodynamic data exists for the omitted species
- The quality of the thermodynamic data used is variable, and subject to uncertainties
- A standardized pressure is used in all calculations. Syngas production can occur under a variety of plant design conditions.
- The model omits reactions involving adsorption or secondary phase formation through interaction of the trace element with chemical components in the ash or with sorbing additives, e.g., see Scotto *et al.* (1994) and Linak *et al.* (1995), or with other minor chemical components of the coal, e.g. Cl or S.

- The fundamental assumption, that the system is at thermodynamic equilibrium, does not occur in reality, where most of the participating reactions are subject to kinetic constraints.
- The identities and amounts of contaminants likely to be co-disposed with captured CO₂, depend on many operational factors.

Apart from the large number of variables associated with current practice, consideration must also be given to the impact of plant modifications associated with future attempts to more efficiently capture CO₂ from existing conventional fossil-fuel fired power plants. Finally, future plant designs, in which CO₂ capture is integral to power generation would raise yet another set of variables.

As noted in the preceding sections, the volatility of trace elements can, depending on the chemistry of a particular element, be strongly dependent on the oxidation state of the system. In a more recent investigation Frandsen *et al.* (1994) formalized the extent of oxidation, by defining the stoichiometric ratio of oxygen to combustibles, λ , as the air excess coefficient. It is assumed that coal of a given molar composition, reacts with oxygen according to the following equation:



The stoichiometric air requirement is given by:

$$L_{\min} = (\alpha + \beta/4 + \gamma + \delta/2 - \phi/2)/Y(O_2)$$

Where

$Y(O_2)$ is the mole fraction of oxygen in the air. The air excess coefficient, λ , is now defined as

$$\lambda = L/L_{\min}$$

The λ parameter has been used in several modeling studies to describe the oxidation state of the system, and is referred to further below.

Wilde and Holbrook (1977) calculated the equilibrium distribution of gaseous species for selected trace elements under conditions expected at “the outlet of a coal gasifier” at 1,000 °C and 1.5 atm pressure, but the specific oxygen stoichiometry assumed in the calculations is not given. The composition of the coal used in the calculations is given in Table 5. The trace elements investigated include As, B, Ba, Be, Cd, Co, Cr, Cu, Ge, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, U, V and Zn. The authors conveniently listed the participating species for each trace element, and compared the calculated species distribution with experimental results, where available, from a coal gasifier investigation by Kalfadelis and Magee (1975). The results are reproduced in Table 9. Agreement between experimental and model equilibrium values is, as the authors point out, “seen to be semi quantitative”. In most cases, model equilibrium calculations over-predict volatilization, with the exception of V and Ni. Over prediction of volatility is to be expected, as sorption and chemical reactions with ash are not taken into account. However, under prediction suggests the omission of complexing agents, or important volatile species from the thermodynamic database.

Table 9. Volatilization of Trace Elements During Coal Gasification¹

Element	Participating Model Species			Species Present, Low O ₂ , λ = 0.6, P = 1.5 atm, T = 1000 °C		Quantity Volatilized, Percentage of Inventory	
	s	l	g	Sp.	%	Calc.	Obs.
As		As ₂ O ₃ As ₂ O ₃	As ₄ AsCl ₃ AsN HAsO ₃ H ₃ AsO ₄ As ₂ AsH ₃ As AsO	AsN HAsO ₃ H ₃ AsO ₄ As ₂ AsH ₃ As AsO	30 27 23 15 3.1 0.44 0.24	100	65
B		B ₂ O ₃	B ₂ O ₃ BO BO ₂ B ₂ (OH) ₄ B ₂ O ₂ BH ₂ BH ₃ B(OH) ₂ BCl ₃ H ₂ BO ₃ HBO ₂	H ₂ BO ₃ HBO ₂	62 38	100	n.m ²
Ba	BaO BaSO ₄	BaCl ₂ Ba	BaS BaH Ba BaCl BaO BaCl ₂	BaSO ₄ (s) BaCl ₂	94 4	4.0	n.m.
Be	Be BeO BeS Be ₃ N ₂		Be(OH) ₂	Be(OH) ₂	100	100	18
Cd	CdS CdO	CdCl ₂	Cd(CH ₃) ₂ CdCl Cd(OH) ₂ CdO CdCl ₂ CdH Cd	Cd	100	100	62
Co	CoO CoS CoCO ₃ Co		CoCl CoCl ₄ CoCl ₂ CoCl ₃ Co CoO CoH	Co(s) CoH	59 41	41.2	n.m.
Cr	Cr Cr ₂ (SO ₄) ₃ Cr ₂ O ₃		Cr CrN CrO ₃ CrO H ₂ CrO ₄ CrCl ₂ CrO ₂	Cr ₂ O ₃ (s)	0	0.0	n.m.

Element	Participating Model Species			Species Present, Low O ₂ , λ = 0.6, P = 1.5 atm, T = 1000 °C		Quantity Volatilized, Percentage of Inventory	
	s	l	g	Sp.	%	Calc.	Obs.
Cu	CuO Cu ₂ O Cu	CuCl	CuCl ₂ Cu ₂ CuO CuH Cu CuCl	Cu(s) CuH Cu CuCl	59 41 7 1.9	53.4	n.m.
Ga							
Ge	GeS		Ge GeCl ₂ GeH GeCl ₄ GeH ₄ GeO GeS	GeO GeS	91 9	100	n.m.
Hg		HgCl ₂	HgO HgCl HgH HgCl ₂ Hg(g)	Hg(g)	100	100	96
Mn	Mn ₃ O ₄ MnS Mn ₂ O ₃ MnO	MnCl ₂	MnCl ₂ MnH MnO MnCl Mn	MnO(s) Mn	100 0.03	0.03	n.m.
Mo	MoO ₂ Mo	MoO ₃	Mo MoO ₂ MoO ₂ Cl MoCl MoO H ₂ MoO ₄ MoO ₃ MoCl ₄ H ₂ MoO ₄ MoCl ₂	H ₂ MoO ₄ Mo(s) MoCl ₂	73 16 11	100	n.m.
Ni	NiO NiO ₂ Ni	NiCl ₂	Ni NiCl Ni(CO) ₄ NiCl ₂	Ni(s)	100	0.015	24
P			P ₂ PO ₂ PCl PSCl ₃ PS POCl ₃ PH PCl ₅ PO P ₄ O ₁₀ PCl ₃ PH ₂ PH ₃ P PO ₂ PCl PSCl ₃ P ₄ O ₆	P ₄ O ₆	100	100	n.m.

Element	Participating Model Species			Species Present, Low O ₂ , λ = 0.6, P = 1.5 atm, T = 1000 °C		Quantity Volatilized, Percentage of Inventory	
	s	l	g	Sp.	%	Calc.	Obs.
Pb	PbS Pb ₃ O ₄	PbO Pb	PbCl ₂ Pb ₂ PbCl ₄ PbO PbH Pb PbS PbCl	Pb PbS PbCl	73 27 0.21	100	65
Sb		Sb Sb ₂ S ₃ Sb ₂ O ₃	Sb ₄ SbCl ₂ SbO SbH ₂ SbCl ₃ Sb ₂ SbCl H ₃ SbO ₄ Sb HSbO ₃	SbCl H ₃ SbO ₄ Sb HSbO ₃	51 45 3.2 0.60	100	33
Se			Se ₂ SeO SeO ₂ Se(CH ₃) ₂ CSSe CSe H ₂ Se COSe Se	H ₂ Se COSe Se	97 2.9 0.22	100	74
Sn	SnO ₂ Sn(SO ₄) ₂ SnO	Sn	Sn SnCl ₂ SnCl SnCl ₄ SnS SnO SnH	SnS SnO SnH	95 3.7 1.2	100	n.m.
Sr							
U	U(CO ₃) ₂ U USO ₄ UO ₂	UCl ₃	UCl ₂ UCl ₃ UCl ₄	UO ₂ (s)	100	0.0	n.m.
V	V VN VS VCl ₂ VO V ₂ O ₄	V ₂ O ₅ V ₂ S ₃	H ₂ VO ₃ VO VCl ₄ V VN VOCl ₃ VO ₂ VCl ₂	V ₂ S ₃ (l)	100	0.0	3.0
Zn	ZnO ZnCO ₃	ZnCl ₂	ZnH ZnCl ₂ ZnO Zn	Zn	100	100	n.m.

¹Data compiled from Wilde and Halbrook (1977). This reference does not indicate the oxygen mass factor, γ, used in the calculation of the distribution of volatile species. It is assumed that γ < 1.0 for consistency with the coal gasification process.

²n.m. = not mentioned.

Frandsen *et al.* (1994) also investigated the equilibrium distribution of specific trace elements between 100 and 1,600 °C and 1.5 atm air during combustion of coal of a given stoichiometric composition in the presence of two different concentrations of oxygen, where $\lambda = 1.2$ and 0.6, representing, respectively, the operating conditions in a conventional coal-fired utility where air is present in excess, and conditions with restricted oxygen access typical of those occurring during coal gasification. The composition of a sub-bituminous coal, including the trace elements, is summarized in Table 5. Frandsen *et al.* (1994) considered the following trace elements: As, B, Be, Cd, Co, Cr, Ga, Ge, Hg, Ni, P, Pb, Sb, Se, Sn, Ti, V and Zn. Calculations were performed using a Gibbs free energy minimization routine together with a supporting database of 800 gaseous, liquid and solid species drawn from standard reference sources. However, the participating species were not identified, so it is not possible to assess the limitations of their thermodynamic analyses.

To illustrate thermodynamic calculations of species distributions, the results of the study by Frandsen *et al.* (1994) for B and Cd, and the results of the study by Yan *et al.* (1999) for As and Hg are presented in the following sections. All four trace elements are noted for their volatility under either oxidizing or reducing combustive conditions.

3.4.2.1 Arsenic

The equilibrium distribution of As species with temperature for both oxidizing ($L = 1.2$) and reducing ($L = 0.6$) are illustrated in Figures 2a and 2b, respectively. Under oxidizing conditions, As is volatilized as oxide species above 500 °C. Below that temperature, condensation will take place. Under reducing conditions, volatilization occurs at a much lower temperature, about 300 °C, and a more complex array of gaseous species forms, including As_4 , hydrides, and AsO above 600 °C. Below 300 °C, As condenses as a sulfide of arsenic, As_2S_3 . Under reducing conditions, a small concentration of AsSe(g) also forms. This illustrates the potential for volatile trace elements to react with each other, thereby enhancing the volatility of both. Such conditions can be identified only if the theoretical analysis permits interactions between trace elements. The equilibrium behavior of As under both oxidizing and reducing conditions is qualitatively in agreement with experimental observation, detailed in the previous section.

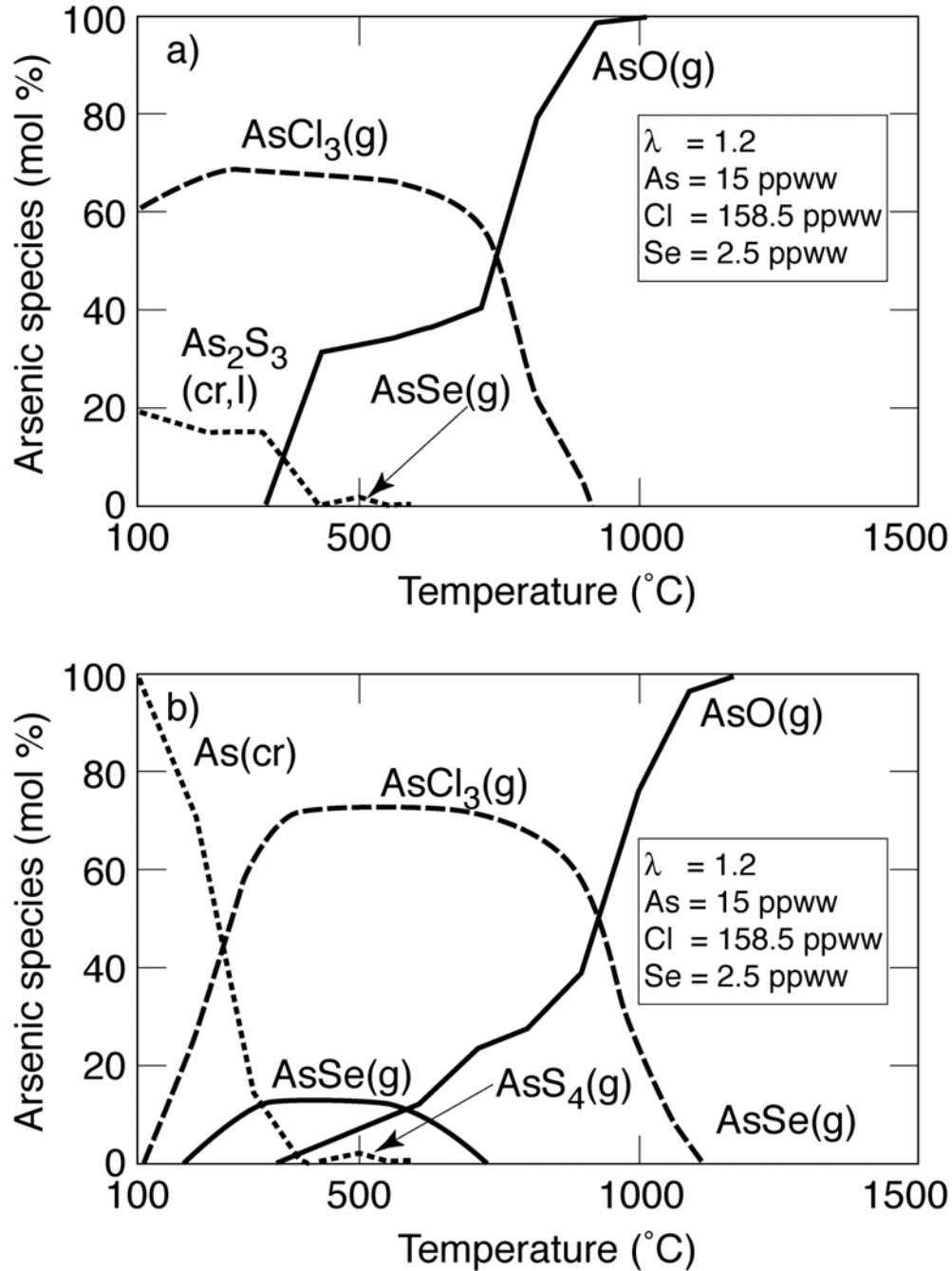


Figure 2. Equilibrium distribution of arsenic species as a function of temperature at 1 bar pressure, (a) under oxidizing conditions, and (b) under reducing conditions (after Yan *et al.*, 1999)

3.4.2.2 Boron

The equilibrium distribution of B species with temperature under oxidizing conditions ($\lambda = 1.2$) is illustrated in Figure 3. Boron volatilizes at about 100 °C, primarily as boric acid gas (H_3BO_3). Above 1,000 °C, the gaseous boric acid dehydrates to HBO_2 , and above 1,400 °C, a minor concentration of BO_2 , not illustrated in Figure 3, begins to make its appearance. Under reducing

conditions ($\lambda = 0.6$), the behavior is similar. The distribution of the minor species $\text{H}_3\text{B}_3\text{O}_6(\text{g})$ differs somewhat, and $\text{BO}_2(\text{g})$ does not form over the temperature range investigated.

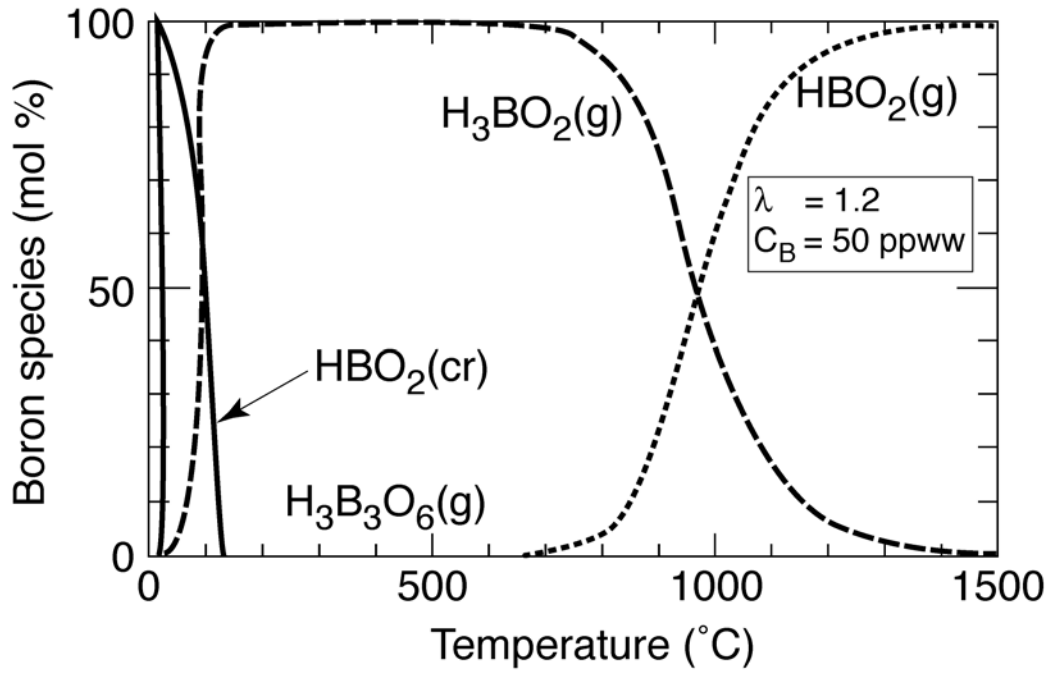


Figure 3. Equilibrium distribution of boron species as a function of temperature at 1 bar pressure under oxidizing conditions (after Frandsen *et al.*, 1994)

3.4.2.3 Mercury

The equilibrium distribution of Hg species with temperature under oxidizing conditions ($\lambda = 1.2$) is illustrated in Figure 4a. Above 100 °C, significant volatilization can take place as the mercuric chloride complex, $\text{HgCl}_2(\text{g})$. The extent of volatilization as a chloride is obviously dependent on the amount and availability of chloride species in the coal feed. At 500 °C HgCl_2 dissociates with the formation of native mercury vapor, and $\text{HCl} + \text{O}_2$ gas. A small fraction also forms the volatile oxide, HgO . Under reducing conditions, only elemental mercury vapor is formed above 500 °C (Figure 4b). Under reducing conditions, a small percentage of $\text{HgSe}(\text{g})$ also forms.

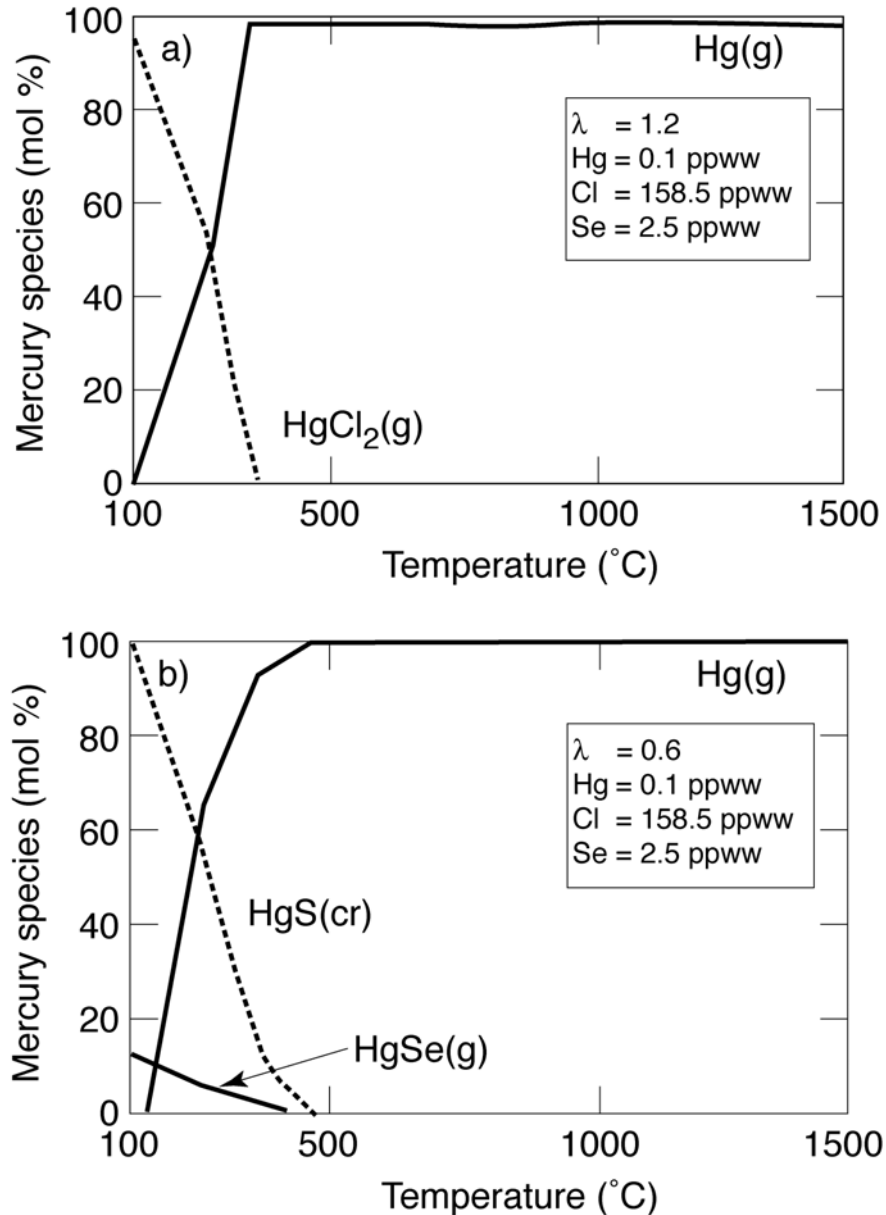


Figure 4. Equilibrium distribution of mercury species as a function of temperature at 1 bar pressure, (a) under oxidizing conditions, and (b) under reducing conditions (after Yan *et al.*, 1999)

3.4.2.4 Cadmium

The equilibrium distribution of Cd species with temperature under oxidizing conditions ($\lambda = 1.2$) is illustrated in Figure 5. The chemistry of Cd under these conditions is somewhat analogous to that of Hg, except that volatilization of CdCl_2 occurs at 500 °C instead of 100 °C. At about 900 °C, CdCl_2 also decomposes with the formation of $\text{Cd}(\text{g})$ and a small fraction of $\text{CdO}(\text{g})$. Under reducing conditions, $\text{CdS}(\text{cr})$ is stable to about 400 °C. Above this temperature, Cd, like Hg, volatilizes as $\text{Cd}(\text{g})$. As with Hg, no volatile Cl complexes with Cd are formed under reducing conditions.

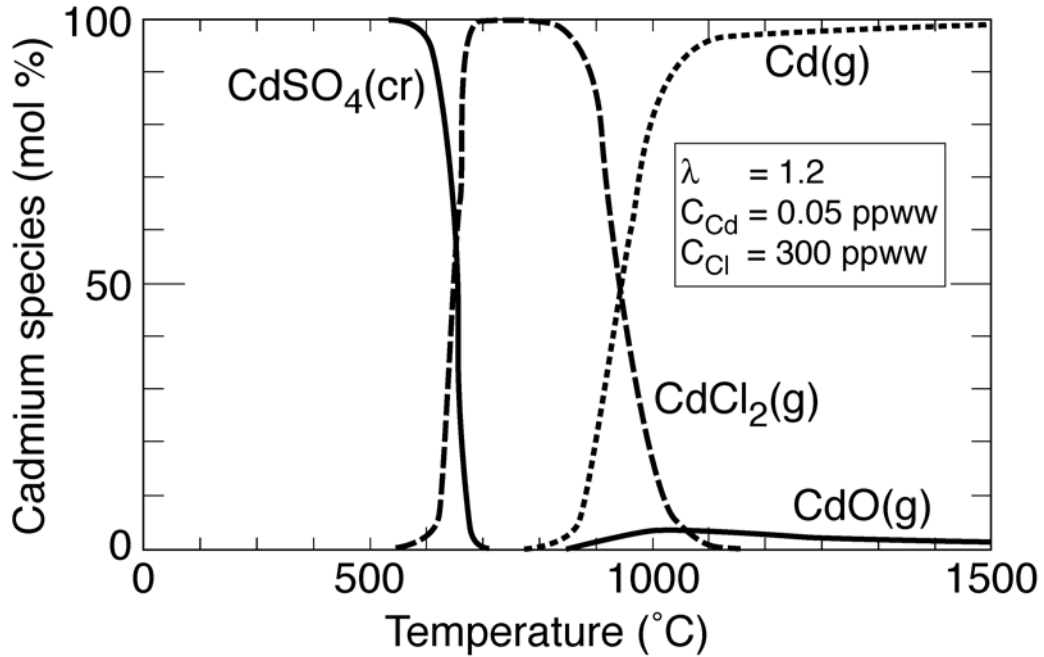


Figure 5. Equilibrium distribution of cadmium species as a function of temperature at 1 bar pressure under oxidizing conditions (after Frandsen *et al.*, 1994)

3.4.3 Summary Discussion Regarding the Fate of Trace Elements following Combustion

The volatilization of trace elements during combustion and subsequent behavior during treatment of the off-gases is complex and is generally influenced by the nature of the combustion process. The following processes are influential, and can be divided into two broad stages, volatilization due to increasing temperature, and condensation during falling temperature

Volatilization

1. Thermal decomposition of organic matter containing thio functional groups with which thiophilic elements might be associated.
2. The decomposition of pyrite, first by release of sulfur, then fusion and eventually oxidation. Trace elements substituting for sulfur in the pyrite lattice or contained in secondary evolved phases within the pyrite will be released at various stages depending on their affinity for either the condensed or gaseous phases.
3. Volatilization of some trace elements may be affected by their ability to form gaseous sulfur complexes, which will in turn be affected by the oxidation state of the system.
4. Several potentially hazardous trace elements can form volatile halide complexes. The degree of volatilization will generally depend upon the concentration of chloride in the feed, and upon temperature.
5. Some elements, especially metals, volatilize readily in the native state, e.g., As, Hg.
6. Some elements preferentially volatilize as oxides when combustion occurs with excess oxygen, e.g., P, As.

Condensation

1. Direct nucleation of a liquid or solid phase when falling temperature causes supersaturation of the volatile constituent.
2. Adsorption on suspended solid particulate material or pulverized additives.
3. Absorption in molten suspended particulate material (fly ash).
4. Reaction of the gaseous species with suspended solid particulate material to form a melt.
5. Reaction of the gaseous species with suspended solid particulate material injected into the flue gas to control sulfur emissions.
6. Absorption of a gaseous species by a pre-existing melt, such as results from the formation of a slag through the deliberate addition of a fluxing agent, e.g., lime.
7. Absorption of a volatile species by an aerosol, e.g. sulfuric acid mist, formed previously through nucleation (as in 1. above).
8. Dissolution in the aqueous phase during wet scrubbing of flue gas to remove SO₂.
9. Reaction with excess ammonia during SCR or SNCR of NO_x in the flue gas.
10. Selective dissolution during syngas cleaning, e.g. acid and alkaline washing, MEA removal of CO₂ and H₂S, etc.
11. Destabilization of volatile carbonyls during the syngas water shift reaction.
12. Surface catalyzed oxidation of volatile hydrides.

In conventional coal-fired power plants, it is claimed that well over 95% of the inventory of most hazardous trace elements are captured through various condensation processes, e.g., see Falcone Miller *et al.* (1998). The quantities could be even higher, because some of the volatile constituents have already condensed by nucleation and precipitation, but the particles that form are too small to be captured by conventional particulate removal technologies and are included in the total inventory of vented material, although they are in the non-volatile state. The kinetics of agglomeration of the nucleated particles with fly ash is also too slow to be a significant factor in their removal.

In IGCC plants, volatiles can be removed through a variety of processes and mechanisms, including those used to clean-up syngas. It is beyond the scope of this study to examine each potentially hazardous element individually, and in terms of the combustion process. However, a qualitative assessment can be made, based on practical and theoretical considerations. This assessment is presented in Table 10.

Table 10. Fate of Trace Elements Following Coal Combustion

Element	Conventional Coal-fired Power Plant			Coal-fired IGCC Plant		
	Volatilization	Condensation	Volatile Residue, % (1)	Volatilization	Condensation	Volatile Residue, % (2)
As	Calculated to volatilize as AsCl ₃ and AsO.	Could nucleate or condense on particulates within the boiler. Submicron particles can escape the baghouse. >99% is captured prior to stack gas emission.	<1 (0.31)	Calculated to volatilize as AsCl ₃ and AsO with minor AS ₄ and AsS Minor AsN and arsine (AsH ₃) may be present.	Syngas combustion would cause As species to oxidize and be removed during separation of water from the CO ₂ prior to compression. The reaction with H ₂ S could lead to removal of As as AsS or As ₂ S ₃ . If H ₂ is separated prior to combustion, AsN and AsH ₃ could remain in the compressed CO ₂ injectate.	4
B	Calculated to volatilize as B(OH) ₃ and HBO ₂ .	Less than 25% B would pass the baghouse. FGD could capture a significant fraction of the B.	<25	Calculated to volatilize as B(OH) ₃ and HBO ₂ , but some could be reduced to BH ₃ .	Boric acid would be stripped by the aqueous condensate prior to CO ₂ compression and injection. BH ₃ could remain in the compressed CO ₂ injectate.	n.d.
Ba	Possible minor volatilization as BaCl ₂ or BaO	Almost all Ba is partitioned in the bottom and fly ash and removed. Stack gas emissions are negligible.	<1 (0.26)	Calculated to volatilize as BaCl ₂ .	Most Ba would be trapped in the residual ash or slag. The remainder would be removed in the steam condensate prior to CO ₂ compression	3<1
Be		Most Be is trapped in the fly ash and removed. Stack gas emissions are negligible.	<<1	Calculated to volatilize as Be(OH) ₂	Most Be would be trapped in the residual ash or slag. The remainder would be removed in the steam condensate prior to CO ₂ compression.	-n.d.
Cd	Calculated to volatilize as Cd Calculated to volatilize as Cl ₂ and Cd(g)	Approximately 1% of the Cd inventory escapes the baghouse. The FGD circuit will strip most of this small fraction.	1	Calculated to volatilize as Cd(g).	The balance will partition in the ash or slag. Volatilized carry-over could react to form CdS and precipitate with steam condensate.	60

Element	Conventional Coal-fired Power Plant			Coal-fired IGCC Plant		
	Volatilization	Condensation	Volatile Residue, % (1)	Volatilization	Condensation	Volatile Residue, % (2)
Co	A very small fraction is volatilized, but the form is not known. Like Ni, probably volatilizes as CoCl_2 , CoO and Co(g)	This fraction is substantially removed prior to emission from the baghouse, and the residue is likely stripped by the FGD circuit. Almost all Co, $\approx 99\%$ partitions into the fly bottom ashes in the II state	$\ll 1$ (0.32)	Calculated to volatilize as CoH . Could form $\text{Co}_2[\text{CO}]_4$.	If H_2 is separated prior to combustion, CoH could remain in the compressed CO_2 injectate. The water shift reaction could destroy $\text{Co}(\text{CO})_4$ with formation of CO_2 and CoO . CoO would condense as a solid particulate, and be eliminated with the steam condensate.	0.6
Cr	Cr(VI) is a known carcinogen, and there is concern regarding the release of Cr in the VI state in stack gases. However, the oxidation state of Cr in stack gases is unknown.	Most Cr, $\approx 99\%$, partitions, most likely in the (III) state, into the fly and bottom ashes.	$\ll 1$	The relatively reducing conditions make it highly improbable that Cr(VI) compounds will be produced. Calculations indicate that no volatile Cr(III) species would form.	Almost all Cr would be partitioned as Cr(III) in residual ash or slag.	1
Cu	A small fraction is volatilized, but the form is not known. Possible species are CuCl_2 , CuCl , CuO and Cu(g)	Almost all Cu, $\approx 99\%$ partitions into the fly bottom ashes in the II state	1 (3.32)	Calculated to volatilize as CuH , Cu(g) and CuCl	Cu could be reduced to the metallic or (I) state, probably partitioning in the ash or slag. Possible reaction with H_2S to form precipitates of Cu_2S or CuS	3
Ga						-
Ge				Calculated to volatilize as GeO and GeS		-
Hg	Hg Calculated to volatilize in the native form, as HgO , but oxidizes as the temperature falls below 500 C to HgO , HgCl_2 or CH_3HgCl .	The FGD circuit could strip a substantial fraction of the Hg^{2+} component.	≤ 30	Calculated to volatilize as Hg(g) . Possible formation of HgH .	Depending on circuit design, most Hg could be stripped by H_2S and precipitated as HgS (cinnabar) in the water condensate prior CO_2 compression. With slow kinetics, however, HgH could be co-injected with CO_2 .	20
Mn	A small fraction of Mn is observed to volatilize during combustion, but the volatile species have not been determined,	Well over 99.5% is removed before release from the bag house, and much of the residue is likely to be stripped in the FGD circuit.	< 1 (0.26)	Calculated to be non-volatile. A small quantity of Mn(g) could form.	Most, if not all, is likely to be partitioned in the II state as an oxide component in the ash or slag.	0.6

Element	Conventional Coal-fired Power Plant			Coal-fired IGCC Plant		
	Volatilization	Condensation	Volatile Residue, % (1)	Volatilization	Condensation	Volatile Residue, % (2)
Mo	Mo is probably volatilized as one or more of the oxides, MoO, MoO ₂ or MoO ₃ .	Most, 97%, condenses or is adsorbed onto fly ash particulates prior to release from the bag house. Much of the remainder is likely to be stripped by the FGD circuit.	≈1	Calculated to volatilize as H ₂ MoO ₄ with minor Mo(g) and MoCl ₂ . Could also be mobilized as gaseous Mo(CO) ₆ .	Addition of limestone to the feed would favor Mo partitioning in the ash or slag. Volatile oxides would condense and dissolve in the steam condensate. During the water shift reaction, Mo(CO) ₆ would be oxidized to MoO ₃ and CO ₂ . The MoO ₃ would be stripped by the aqueous condensate prior to CO ₂ compression and injection.	30
Ni	Probably volatilizes as NiCl ₂ , NiO and Ni(g)	Almost all Ni, ≈99% partitions into the fly bottom ashes in the II state.	<1 (0.43)	Calculated to be non-volatile. Ni could also be mobilized as gaseous Ni(CO) ₄ .	The water shift reaction could destroy Ni(CO) ₄ with formation of CO ₂ and NiO. NiO would condense as a solid particulate, and be eliminated.	5
P	Calculated to volatilize as oxides, P ₂ O ₅ and PO ₂ and as PCl ₃			Calculated to volatilize as P ₄ O ₆	P oxides would dissolve in the steam condensate prior to CO ₂ compression.	2
Pb	Calculated to volatilize as PbO, PbCl ₂ and Pb(g).	although >99% is condensed prior to emission from the bag house. removal of the <1% residue probably takes place in the FGD circuit	<1 (0.31)	Calculated to volatilize as Pb(g), PbS and PbCl.	Pb volatiles could be quantitatively removed and precipitated as PbS during condensation and separation of the water prior to CO ₂ compression.	4
Sb	Calculated to volatilize as Sb ₂ O ₃ .	Condenses primarily on particulates within the boiler. Submicron particles can escape the baghouse. >99% is captured prior to stack gas emission.	<1	Calculated to volatilize principally as SbCl and H ₃ SbO ₄ with minor Sb, and HSbO ₃ . Stibnine (SbH ₃) might also form.	Sb would be oxidized and removed during separation of water from the CO ₂ prior to compression. The reaction of SbH ₃ with H ₂ S during H ₂ S separation could lead to removal of Sb as Sb ₂ S ₃ . However, if the reaction is slow, SbH ₃ could remain in the CO ₂ injectate.	n.d.

Element	Conventional Coal-fired Power Plant			Coal-fired IGCC Plant		
	Volatilization	Condensation	Volatile Residue, % (1)	Volatilization	Condensation	Volatile Residue, % (2)
Se	Calculated to volatilize as SeO, SeO ₂ or SeO ₃ .	Less than 1% Se escapes the baghouse, suggesting that most condenses on the fly ash. The remainder is likely to be stripped by the FGD circuit.	<1	Calculated to volatilize primarily as H ₂ Se with minor COSe and Se(g)	H ₂ Se would probably be removed with H ₂ S and incorporated into sulfur through the Claus process. Otherwise, a portion of the SeH ₂ could partition into the aqueous condensate, and the balance co-injected with CO ₂	3
Sn	Might volatilize to SnO and Sn(g)	Sn species would probably condense or be adsorbed by fly ash.	<1	Calculated to volatilize primarily as SnS, with minor SnO and SnH		-
Sr	Might partially volatilize as SrCl ₂	Less than 1% of the Sr inventory escapes the baghouse. The FGD circuit will strip most of this small fraction.	<<1	Might partially volatilize as SrCl ₂	Most Sr will partition in the ash or slag. Volatilized carry-over will be stripped during condensation of the water prior to CO ₂ injection.	-
U			<<1	Calculations indicate that no volatile U species would form.	U species would concentrate in the residual slag.	-
V		A negligible fraction of V escapes the baghouse. Almost all of the V inventory will be associated with the bottom and fly ashes.	<<1	Calculations indicate that no volatile V species would form. V has the potential to form V(CO) ₄	Most V would partition into the slag, especially if limestone were added to the feed. The water shift reaction could destroy V(CO) ₄ with formation of CO ₂ and V ₂ O ₅ , which would condense as a solid particulate, and be eliminated.	0.1
Zn	Probably volatilizes as ZnCl ₂	Somewhat more than 1% of the Zn inventory escapes the baghouse. The FGD circuit will strip most of this small fraction	≈1 (0.34)	Calculated to volatilize as Zn(g).	The balance will partition in the ash or slag. Volatilized carry-over could precipitate as ZnS through reaction with H ₂ S and be stripped during condensation of steam.	10

- (1) The values given in parentheses are those reported for 2003 by the Seminole Generating Station, a coal fired power plant operated by Seminole Electric Cooperative, Inc., and located in Putnam County in northeast Florida. (Seminole, 2003), and are given for comparison.
- (2) The volatile residue for a coal-fired IGCC plant is based on results presented in Table 9.

Several uncertainties in this assessment require that the findings be considered as tentative. As noted in Section 3.4.2, the volatilized species were identified in thermodynamic analyses that incorporated only those species for which thermochemical data were available at the time. Important species might therefore have been omitted. Furthermore, the thermochemical data may be subject to errors. The mechanisms and kinetics of many of the condensation reactions are poorly understood and remain unquantified. As a consequence, predictions of the persistence of some volatile species and their carry-over into the CO₂ injectate remain highly uncertain.

3.5 HAZARDOUS ORGANIC COMPOUNDS

Weber *et al.* (1996) conducted a series of round-robin chemical analyses of organic compounds in coal-fired power plant stack gases. The classes of organic compounds selected for analysis include aldehydes, volatile organic compounds (VOCs), semivolatile organic compounds (SVOCs), polycyclic aromatic hydrocarbons (PAHs), and chlorinated dioxins and furans. Analytical difficulties and concentrations at or below detection limits forced rejection of most of the collected data. Acceptable data for detected compounds in stack gases from between 2 and 8 power plants were compiled, and the median concentrations are reproduced in Table 11. Median ambient air concentrations for these same compounds, where available, are also reproduced in Table 11.

The reported data show that the concentrations of most detected organic compounds are very low, and, with the exception of formaldehyde, acetaldehyde and chloromethane, they are roughly equivalent or below those found in the atmosphere. Analyses for chlorinated dioxins and furans indicated that stack gas emissions of these compounds were extremely low, being close to or below the limits of detection. It was therefore concluded that they are not significant atmospheric pollutants from the coal-fired plants included in the study.

The concentrations of organic compounds are reported in units of $\mu\text{g}/\text{Nm}^3$ of stack gas effluent. In column 4 of Table 11, these results are converted to ppbw in CO₂, assuming that the stack gas effluents contained an average of 15 wt% CO₂ (Nsakala *et al.*, 2001). Results show that the quantities are in all cases less than 1 ppmw of CO₂, and therefore, the concentrations of organic compounds in stack effluents of conventional coal-fired power plants are unlikely to be significant contaminants in separated CO₂ for deep subsurface injection. In fact, it would appear more likely that MEA source contaminants, compressor oil, and other incidental contaminants of the CO₂ separation and compression would more likely be found in injected CO₂.

Radian Corp (1995) have reported on the concentrations of detected organic compounds in the incinerator and stack gas emissions of a commercial IGCC facility operated by Louisiana Gasification Technology Inc. (LGTI) at Plaquemine, Louisiana. The combined emissions from both incinerator and turbine stack are reported in Table 12. The approximate concentrations of the reported organic compounds in a hypothetical CO₂ waste stream can be estimated on the basis that the plant consumes 2,200 ton/day coal containing 70 wt% carbon. The calculated concentrations in terms of ppbw are given in the last column of the table. Implicit in these calculated concentrations is the assumption that organic compounds in the natural gas, which was used in combination with the syngas to feed the combustion turbines did not materially affect the concentrations of organic compounds in the plant gaseous effluents.

Table 11. Hazardous Organic Compounds Generated during Combustion in a Conventional Coal-fired Power Plant (after Weber *et al.*, 1996)

Species	Median Stack Concentration, $\mu\text{g}/\text{Nm}^3$	Medium Ambient Air Quality Concentration, $\mu\text{g}/\text{Nm}^3$	Calculated Concentration in CO ₂ Injectate, ppbw
Aldehydes			
Formaldehyde	42	5	143
Acetaldehyde	150	3	509
Acrolein	11	15	37
Propionaldehyde	19	21	64
VOCs			
Benzene	10	6	34
Toluene	7	8	24
<i>m-p</i> -Xylene	2.3	6	7.81
<i>o</i> -Xylene	0.5	6	1.7
Ethylbenzene	0.4	3	1.4
Styrene	2	0.5	6.8
2-Butanone	13	-	44.
2-Hexanone	15	-	51
<i>n</i> -hexane	2	6.4	6.8
Chloromethane	75	1.5	255
Trichlorofluoromethane	3	1.2	10
Carbon disulfide	6	0.15	20
SVOCs			
Phenol	1.1	19	3.7
2-Methylphenyl	2.4	1.6	8.1
Acetophenone	1.4	-	4.8
Naphthalene	1	1.3	3.4
2-Methylnaphthalene	0.05	0.1	0.17
1- Methylnaphthalene	0.02	0.1	0.07
Acenaphthylene	0.01	-	0.03
Phenanthrene	0.13	-	0.44
Anthracene	0.008	-	0.03
Fluoranthene	0.08	-	0.27
Pyrene	0.04	-	0.14
Chrysene	0.015	-	0.05
Benz[<i>a</i>]anthracene	0.006	-	0.02
Acenaphthalene	0.03	-	0.10
Dibenzfuran	0.07	-	0.24

Table 12. Hazardous Organic Compounds in Combined Stack Emissions in an IGCC Plant (after Radian Corp, 1995).

Species	Combined Stack Emissions, lb/yr	Calculated Concentration in CO ₂ Injectate, ppbw
Aldehydes		
Formaldehyde	0.045	95.64
Acetaldehyde	0.0048	10.20
Benzaldehyde	0.0079	16.79
VOCs		
Benzene	0.012	25.50
Toluene	0.000053	0.11
Carbon disulfide	0.12	255.05
SVOCs		
Naphthalene	0.0011	2.34
2-Methylnaphthalene	0.00098	2.08
Acenaphthylene	0.000071	0.15
Benzo(a)anthracene	0.0000062	0.01
Benzopyrene	0.000015	0.03
Benzo(g,h,i)perylene	0.000026	0.06
Benzoic Acid	0.39	828.91

The results show that the concentration of no organic compounds in compressed CO₂ for sub-surface disposal from a typical IGCC plant would exceed 1 ppmw, and therefore, their presence can be ignored.

4. SUMMARY OF POLLUTANTS MOST LIKELY TO BE CO-INJECTED WITH CO₂

The preceding evaluation shows quite clearly that the concentrations of other chemical components accidentally incorporated in CO₂, when captured from conventional coal fired power plants, or from advanced coal-fired IGCC plants, will be at most, relatively insignificant. For minor volatile species of S, N, F, and Cl, the concentration in CO₂ from conventional power plants is unlikely to exceed 5% of the base concentration in the original coal feed, i.e. between 0 and 250 ppmv. For potentially hazardous trace elements, such as As, B, Ba, Be, Cd, Co, Cr, Cu, Ge, Hg, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Sr, U, V and Zn, with the possible exception of Hg, the percentage concentrations are currently predicted to be at least two orders of magnitude less in concentration than was originally present in the coal. However, given that the concentrations of most of these elements were only in the ppm range in the original coal, accidentally incorporated concentrations are unlikely to exceed the range from 0.01 to 10 ppmv. The consequences of co-injecting such low concentrations of potentially hazardous chemical constituents are examined further in the following section.

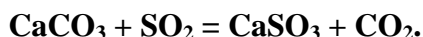
In current IGCC coal-fired power plants, the concentrations of minor volatile species could be somewhat higher, i.e., <700 ppmv. The concentrations of potentially hazardous trace elements could also be somewhat higher, in some cases rising to a much as 25% of the original concentration in the coal feed, the reason being that particulate removal during coal gasification is more efficient and at higher temperatures, decreasing the opportunity for sorption, and reducing conditions favor the stabilization of gaseous species that are less likely to nucleate and condense with falling temperature. It should be noted that advanced IGCC designs would probably result in very clean CO₂ separations, and CO₂ injected into the subsurface could be very pure, unless deliberate efforts at co-disposal of co-contaminants were to be implemented.

Uncertainties in the concentrations of both minor and trace constituents predicted to be co-injected with compressed CO₂ are substantial as noted elsewhere in this report and are almost certainly to be of the order of plus or minus one order of magnitude. Therefore, concentrations equivalent to 10% of the initial concentration in coal would represent a very conservative upper limit for all but the most volatile combustion products. Of these, gaseous nitrogen and sulfur species, and Hg would require special consideration.

CO₂ capture and injection disposal from conventional or advanced cycle fossil fuel power plants is likely to generate interest in alternative pollution abatement technologies, which would be more compatible with CO₂ separation and capture, and which would cost less than current abatement technologies. For example, the current cost of NO_x removal from current power plants is estimated to be about \$2,500/ton (Miracca *et al.*, 2005), whereas the cost of SO_x removal is estimated to range up to \$650/ton (Carlin, 2002). Furthermore, the separation of gaseous pollutants such as NO_x and SO_x from flue gases without the generation of solid waste for disposal in surface impoundments would alleviate environmental concerns regarding the leaching of fly ash impoundments. Undoubtedly, alternative separation and disposal technologies could be developed provided there exist sufficient economic, taxation and/or regulatory incentives. It is clearly beyond the scope of this report to anticipate such future separation technologies and their impact on contaminant loading of CO₂ injectates. The most conservative approach would be to assume that a “perfect” system of separation of gaseous contaminants will exist, and that all SO₂ and NO products of combustion, the quantity depending

on the bulk composition of the fuel feedstock, could be co-injected in solution with the supercritical CO₂ injectate. A somewhat more realistic approach would be to consider scenarios based on current technology. A simple example would suffice to illustrate the possibilities.

Conventional coal-fired power plants are required to abate SO₂ discharges, and this is accomplished through the use of FGD circuits. One approach involves the injection of dry pulverized limestone into the flue gas at elevated temperature, leading to the reaction:



The calcium sulfite product could be decomposed by calcining, thus:



and the SO₂ combined with the CO₂ following capture, and both gases compressed and co-injected. In limited concentrations, SO₂ could advantageously reduce ferric iron in host rock minerals, thereby making ferrous iron available for CO₂ sequestration as siderite.

With respect to NO (+ N₂O), recovery and concentration is somewhat more challenging. Perhaps NO could be adsorbed by customized zeolites, which could be regenerated through contact with supercritical CO₂ prior to injection. However, costs associated with such recovery techniques must be compared with current practices using SCR or NCSR where NO_x is reduced to N₂, which can be discharged into the atmosphere with no environmental consequences. However, NH₃ “slippage” during treatment to remove NO_x has adverse photochemical consequences (Bitler, 1999), and therefore capture technologies to eliminate the problem may provide a needed incentive.

IGCC plants possess advantages over conventional systems in that the primary gaseous sulfur compound of coal gasification is H₂S, which is readily separated using ethanolamine stripping technology. As noted elsewhere in this report, native sulfur can be recovered from the recovered H₂S using the Claus process. However, excess worldwide capacity no longer justifies recovery of sulfur, and it may therefore be more cost effective to co-inject H₂S with CO₂. Gaseous nitrogen species generated by coal gasification are also present in the reduced state, i.e. as NH₃, HCN and N₂. the water shift reaction will destroy HCN and concentrate most of the nitrogen species as NH₃, which can be readily removed by acid washing. Because NH₃ could be recovered and converted into a fertilizer, it would appear that there would be little incentive to co-inject ammonia with CO₂.

For the foreseeable future, combustion turbines of IGCC plants will utilize air rather than oxygen. Therefore the effluent gases will contain small concentrations of atmospheric nitrogen derived NO_x species. These species would have to be removed from the effluent stream prior to ethanolamine recovery of CO₂. NO_x elimination could be undertaken using SCR or SNCR technologies, or it is remotely possible that selective sorption of NO_x might be undertaken with subsequent co-disposal with the captured CO₂.

In the more distant future, technological developments may allow the operation of thermodynamically efficient hydrogen/oxygen fueled gas turbines at very high temperatures. If the hydrogen stream is derived from coal gasification with water shift reaction and separation of hydrogen using semi-permeable membrane technology (Mundschau *et al.*, 2005), then direct

compression of the waste stream might be undertaken following condensation of the associated excess steam. This stream would contain all sulfur and nitrogen species surviving or generated during the water shift reaction as well as volatile species of trace elements such as potentially persistent hydrides of As, Se, Sb and Hg. Metal carbonyls, such as Ni(CO)₄ would be unlikely to be present as they would have been destroyed during the water shift reaction. Volatile chlorides and fluorides would partition into the steam condensate, as would any other water-soluble species. Furthermore, insoluble sulfides of transition and heavy metals, such as NiS, NiS₂, ZnS, PbS, AsS, As₂S₃, Sb₂S₃, etc are also likely to nucleate as solid particulates and be removed from the CO₂ waste stream prior to compression and disposal.

In summary, if a deliberate policy of volatile contaminant disposal were adopted, IGCC plants could yield waste streams containing substantially all of the contained sulfur in the original coal feed, a significant percentage of nitrogen species, and minor to significant percentages of the original inventory of trace elements in the coal, depending on the circuit configuration and advanced state of technology.

Tables 13a and b summarize the gaseous species and their concentrations present in captured and compressed CO₂ under two conditions: (1) Incidental inclusion under normal operating conditions, and (2) Where a deliberate policy of maximum co-injection of minor volatile contaminants (Table 13a) and trace volatile contaminants (Table 13b) is implemented to eliminate co-disposal with surface solid wastes. The latter values are fictive in that separation of the listed constituents, even using the most efficient separation procedures, would never attain 100%. However, the calculated concentrations of most of the trace elements are very small, and therefore of limited significance. Of those trace elements with the highest listed concentrations, i.e., B, Ba, P and Sr, the last three would have minimal impact if co-disposed with solid wastes. Furthermore, it would be technologically infeasible to convert Ba and Sr into gaseous species at ambient temperatures. Boron, however, is of more than passing interest. At ambient temperatures, it would condense as B(OH)₃, and therefore would not normally be readily available for sub-surface injection. Its conversion to a gaseous form such as diborane (B₂H₆) would economically impractical. However, its co-disposal with fly ash in surface impoundments could result in leaching and transport into surface waters (Narasimhan *et al.*, 1992). Alternative capture technologies for B might become necessary in the future, but in any case, subsurface co-injection with captured CO₂ would not be a serious alternative.

Table 13a. Gaseous Contaminant Concentrations Injected with Compressed CO₂, either Incidentally, or deliberately for Maximum Decontamination of Solid Waste

Species	Contaminant Concentration, ppmv			
	Conventional Power Plants		IGCC Power Plants	
	Incidental	Maximum	Incidental	Maximum
Minor Species				
SO₂	<250	1500	<50 - 700	-
H₂S	-	-	-	1500
NO	≈15	1425	<400	-
N₂O	≈0.1	75	-	-
F	≈7	70	7	70
Cl	≈2	20	n.d.	20

Table 13b. Gaseous Trace Contaminant Concentrations Injected with Compressed CO₂, either Incidentally, or Deliberately for Maximum Decontamination of Solid Waste

Species	Contaminant Concentration, ppmv		
	Incidental		Deliberate
	Conventional Power Plants	IGCC Power Plants	Conventional and IGCC Power Plants
As	0.0022	0.0097	0.224
B	12.6983	n.d.	50.793
Ba	0.4623	0.0462	46.226
Be	0.0005	n.d.	0.514
Cd	0.0002	0.0085	0.015
Co	0.0006	0.0033	0.553
Cr	0.0016	0.0171	1.551
Cu	0.0297	0.0743	2.970
Ga	0.0000	-	-
Ge	0.0000	-	-
Hg	0.0028	0.0022	0.009
Mn	0.0309	-	3.092
Mo	0.0010	0.0246	0.098
Ni	0.0047	0.0229	0.468
P	1.6619	2.8252	166.191
Pb	0.0011	0.0045	0.108
Sb	0.0002	n.d.	0.017
Se	0.0074	0.0244	0.739
Sn	0.0000	-	-
Sr	0.0392	-	39.166
U	0.0000	-	-
V	0.0044	0.0057	4.379
Zn	0.0207	0.2488	2.074

Notes. All calculations are based on the chemical analysis for Rochelle coal reported by Radian Corporation (1995), reproduced in Table 5. The incidental concentrations of trace elements from conventional coal-fired power plants are based on attenuation factors reported in Table 10. Those for IGCC power plants are based on the estimates given in Table 8. The latter values are approximate, and probably minimal, because natural gas was co-injected with syngas as feed to the combustion turbines in the IGCC plant under study.

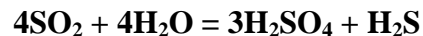
5. FATE OF CONTAMINANTS FOLLOWING INJECTION: GENERAL DISCUSSION

In this section, brief discussions are given regarding the potential fates of both major and trace contaminants co-injected with compressed CO₂. In common with the remainder of this report, the conventional and IGCC power plant contaminants are treated separately.

5.1 CONVENTIONAL POWER PLANT CONTAMINANTS

5.1.1 SO₂

The estimated concentration of SO₂, when deliberately recovered and incorporated with CO₂ in the injectate, ranges from 0.15 – 2 vol.%. Upon injection, the SO₂ would partition into the pore waters, as SO₂ is extremely soluble in the aqueous phase. Preliminary modeling studies to evaluate the fate of SO₂ co-injected with CO₂ in deep saline aquifers have recently been conducted by Xu *et al.*, and reported (Xu *et al.*, 2005a). In the subsurface environment, at a total pressure of less than 500 bar, and temperature about 75 °C, SO₂ is unstable with respect to its reaction products with the aqueous phase and will decompose:



The resulting sulfuric acid will attack almost all host rock minerals with the exception of quartz, leading to dramatic changes in the mineralogy, and the precipitation of secondary sulfates and hydroxy-sulfates, and amorphous silica. The H₂S generated will reduce Fe(III) to Fe(II) and precipitate pyrite and other minor sulfides. Modeled localized porosity changes within the formation adjacent to the well bore suggest that formation sealing is not likely to be an issue (Bryant and Lake, 2005). However, limitations in the current model preclude an expression of serious concern without further research to address these limitations.

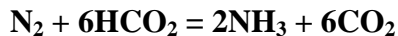
The primary limitation of our current modeling (Xu *et al.*, 2005a) is that it does not take into account the kinetics of the reaction cited above, which is expected to be slow at the temperatures and pressures of concern. The literature on the kinetics of SO₂ disproportionation is very limited. However, it is expected that sulfurous acid (H₂SO₃) will initially dominate water-rock interactions, leading to the precipitation of secondary sulfites such as hannebachite (CaSO₃·0.5H₂O) and orschallite (Ca₃(SO₃)₂SO₄·12H₂O).

5.1.2 NO_x

The primary NO_x components formed during oxidative combustion of coal are NO with minor N₂O. Traces of NO₂ could also form in the stack gases following combustion. Because these NO_x species are derived primarily from the nitrogen containing functional groups in the original coal, an estimate of the maximum quantity formed can be estimated from the composition of the coal (See Tables 5 and 13a).

A modeling study of the co-injection of NO and NO₂ with CO₂ in deep saline aquifer is the subject of a companion report (Xu and Apps, 2005b). NO is an oxidizing agent, and would be reduced in stages by organic matter in the aquifer:





where HCO_2 is taken as symbolic of organic matter in general. The kinetics of these reactions have not been studied, and therefore, Xu and Apps (2005b) assume local equilibrium as a limiting case where the reactions are considered to be infinitely fast. In fact, the conversion of N_2 to NH_3 is likely to be very slow in the absence of nitrogen fixing biota. Limitations in the availability of organic matter, may induce alternative decomposition pathways, including reaction with co-injected SO_2 , either directly, or through the agency of the H_2S decomposition product. The end product, NH_3 , will hydrolyze to form $\text{NH}_4^+ + \text{OH}^-$. The NH_4^+ will substitute in the inter-layer positions of clays with the formation of tobelite, the ammonium analogue of illite, should NH_4^+ migrates to distal regions beyond that where sulfurous/sulfuric acid destruction of smectitic and illitic clays occurs in the vicinity of the injection well.

5.1.3 Hg

Regardless of the form of residual Hg in the compressed CO_2 , it will eventually react with H_2S , the disproportionation product of SO_2 , to produce the highly insoluble mineral cinnabar, HgS . Although some Cl^- and HS^- complexes in the aquifer pore water may mobilize Hg, it is expected that Hg in solution will remain at concentrations at or below HBLs.

5.1.4 Hazardous Trace Elements

With perhaps a couple of exceptions, the hazardous trace elements can be divided into three classes as a matter of convenience: Sulfosalts (P, As, Sb, Se), transition metals (Cu, Ni, Co, Zn), and heavy metals (Cd, Mo, Pb). The exceptions are Be and B. Under oxidizing conditions, and at elevated temperature, all of these elements would initially be present as either oxides or chlorides, or in the native form (Table 9). Upon cooling to ambient temperature, these species would nucleate as fine particles and would be separated from the captured CO_2 or dissolve in the steam condensate. Therefore it would be expected that the cited trace elements would be present at negligible concentrations, and have no impact on the chemistry of the injected formation.

5.2 IGCC POWER PLANT CONTAMINANTS

5.2.1 H_2S

During syngas formation, most of the sulfur present in coal is converted to H_2S , and small concentrations of COS are converted to H_2S by the water shift reaction. The impact of injecting H_2S as a co-contaminant with CO_2 on the chemistry of a saline aquifer has been investigated by Xu *et al.* (2005a). The most significant response to the presence of H_2S is the precipitation of pyrite through sequestration of Fe(II) from chlorites, and reduction of Fe(III) in iron oxides, i.e., hematite and goethite. Because H_2S is quite soluble in the aqueous phase, a substantial fraction of that co-injected with CO_2 will partition into the formation waters. The fate of that fraction remaining miscible with CO_2 fluid requires further study. Excess H_2S accompanying CO_2 , and penetrating a USDW, could prevent the solubilization of heavy metals such as Pb. However, the solubility in the groundwater of some trace elements could be enhanced through the formation of sulfide complexes, as is postulated for Ag, As, Au, Hg and Sb (Bessinger, 2000).

In recent years, acid gas injection, primarily mixtures of CO₂ and H₂S, with H₂S concentrations ranging from 2 - 84% has become common practice in the Canadian provinces (Bachu *et al.*, 2005), apparently with no adverse consequences. However, H₂S is highly toxic, and would, furthermore, impart an undesirable odor to water recovered for potable purposes.

5.2.2 Nitrogen Species

During coal gasification, nitrogen is released as NH₃, HCN and N₂. The water shift reaction converts the HCN to NH₃. The NH₃ would be substantially removed with the steam condensate as NH₄Cl and NH₄OH. The residual N₂ could be separated, depending on the IGCC plant design, or, if present in minor quantities, could be co-compressed with the CO₂. Co-injected N₂ would preferentially remain in the CO₂ fluid phase. However, ambient conditions are such that it could eventually be reduced to NH₃ and be incorporated as NH₄⁺ in the interlayer positions of smectitic or illitic clays in the host rock. The transformation from N₂ to NH₃ would likely be very slow in the absence of biotic catalysts, as noted above. However, inorganic surface mediated catalytic reactions cannot be ruled out.

5.2.3 Hg

The behavior of Hg would be analogous to that of Hg in the effluent steam from a conventional power plant. However, the possible metastable persistence of HgH, may result in higher concentrations of Hg in the compressed CO₂. Ultimately, Hg will be immobilized as HgS, which has a very low solubility in the aqueous phase.

5.2.4 Hazardous Trace Elements

As with conventional power plant effluents, the hazardous trace elements can be conveniently divided into three classes: Sulfosalts (P, As, Sb, Se), transition metals (Cu, Ni, Co, Zn), and heavy metals (Cd, Mo, Pb). The exceptions are Be and B.

Gaseous hydrides and nitrides of the sulfosalts may persist metastably in the captured CO₂ and be co-injected. The behavior of these species following injection requires further evaluation. P would eventually oxidize to phosphate. As and Sb would react with H₂S to form AsS, As₂S₃, Sb₂S₃. Arsenic could also co-precipitate with pyrite as a solid solution with S. All sulfosalts with the exception of P could precipitate with transition metals, present as in the formation rocks of the CO₂ injection zone, or co-introduced as hydrides with the injected CO₂. Because the concentrations of the sulfosalts would be trivial in comparison with H₂S, it is expected that most would substitute for S in secondary sulfide minerals. However, this conjecture requires further review. In any case, the concentrations of the sulfosalt elements in injection zone pore waters are expected to be very low, and may be dominated by native concentrations of these elements.

Although the concentrations of volatile transition metal hydrides formed during coal gasification are expected to be negligible (Table 9), they may persist metastably, and be co injected with the CO₂. Their partitioning between the CO₂ fluid phase and ambient pore waters requires further review. As noted in the previous paragraph, the transition metals are most likely to react with excess H₂S and precipitate as sulfides, possibly in solid solution in pyrite. The predicted concentrations of transition elements in pore waters are likely to be determined ultimately, and subject to kinetic constraints, not by the co- injection of these elements with CO₂, but rather by

the impact of dissolved CO₂ on the aqueous solubility of these elements already present in the injection zone formation host rocks and confining shales. As noted in Section 5.2.1, above, due consideration should be given to potential aqueous sulfide complexation of some hazardous trace elements, and enhanced transport resulting there from.

5.3 DISCUSSION

Under normal circumstances, it can be expected that the process of CO₂ separation from the combustion or gasification of coal will lead to a two-three order of magnitude reduction in the concentrations of minor and trace elements co-existing with carbon in the coal feed. Exceptions to this general rule would be Hg, and possibly Cd, Mo and Pb in effluents from IGCC plants. The reducing conditions inherent in coal formation tend to favor the concentration and fixation of siderophilic and thiophilic elements, and as a consequence, such elements, including most of those specifically identified as trace elements in coal, tend to become enriched by up to 3 orders of magnitude when compared with normal sediments. Similar concentrations are commonly observed in so-called black shales, which are normally enriched in organic matter, and form under reducing eutrophic conditions in closed or stagnant marine basins and fresh water lakes. Therefore, their partitioning into the solid waste residues during combustion or gasification offsets the process of trace element concentration in coals. The net result would be roughly zero enrichment of trace and minor elements in CO₂ when compared with the concentrations expected in the confining shales of a typical deep saline aquifer. Given that the confining shales of many deep saline aquifers are commonly enriched in carbonaceous material, and could also be similarly enriched in trace elements, and given that the volume of shale containment beds is usually five times that of permeable sandstone aquifers into which CO₂ would be injected, it is reasonable to assume that the masses of co-injected trace elements would not significantly impact *in situ* masses of trace elements in confining shales.

The essential difference between the co-injected trace elements, and those already present is that the latter are already immobilized, whereas the former must undergo suitable transformations in a CO₂-rich environment before immobilization can be achieved. As noted in the preceding sections, the oxidative or reductive capacity of the CO₂ depends on the presence of co-contaminants such as H₂S, SO₂ or NO, which, however, would normally be present in only trace concentrations. The deliberate addition of excess H₂S could greatly aid in the immobilization of most co-injected trace elements, subject to the possible offsetting impact of aqueous sulfide complexation in the case of As, Hg and Sb. However, the increased acidity due to high-pressure CO₂ would increase the aqueous concentration of many trace elements, regardless of their origin.

It is the author's expert judgment that the presence of incidental co-contaminants in a CO₂ injectate would not adversely affect water quality in USDWs. However, if they were to do so, the contribution of contaminants from *in situ* sources, caused by dissolution through increased acidity due to the presence of high pressure CO₂, would be equally important. Much depends on the kinetics of hazardous trace element leaching from confining shales by CO₂-rich groundwater, and the time frame considered relevant to USDW contamination.

If it is assumed that advantage would be taken to decontaminate surface waste residues of coal combustion, i.e., fly ash and slag, then, at a maximum, the concentrations of co-contaminants in the CO₂ could exceed *in situ* aquifer concentrations by up to three orders of magnitude. Such

high concentrations may or may not be significant, depending on the fate of the co-contaminants in injection zone. It would be expected that the contaminants would eventually approach saturation concentrations equivalent to those attained due to dissolution of these same trace elements from the confining shale beds in the presence of high pressure CO₂. Therefore, the source of such contaminants would be irrelevant, and inherent to subsurface CO₂ disposal and sequestration rather than the inclusion of trace contaminants in the injected CO₂.

The preceding qualitative arguments should be bolstered by a comprehensive evaluation of trace element concentrations in typical shales and sediments, which could be used as a basis for comparison with the projected concentrations of those same elements in the injected CO₂ (± H₂S). The precipitation of elevated concentrations of hazardous constituents in the injection zone would be dependent on the kinetics of species transformation under reducing conditions in the injection zone, the state of alteration of the host rocks due to the presence of CO₂, SO₂, H₂S, NO, etc, the rate of disproportionation of SO₂, and interactions with dissolved components of the host rock and with co-contaminants. Interactions leading to precipitation, co-precipitation, adsorption and ion exchange could all play a part in ultimately controlling the aqueous phase concentrations of hazardous constituents. It is possible that the hazardous constituents would upon injection, partition into the aqueous phase and separate chromatographically around the injection well, leading to localized elevated concentrations, although with limited mobility.

Geochemical modeling to evaluate the impact of the injected CO₂ on the concentrations of trace elements in the aqueous phase is virtually a necessity, given the complexity of the subsurface chemistry and the multiplicity of elements under consideration. Preliminary attempts have already been undertaken in a restricted manner with respect to Pb in a potable aquifer (Jaffe and Wang, 2003; Wang and Jaffe, 2005). Such modeling evaluations go beyond the scope of this report, and for this reason, a definitive conclusion cannot be reached at this point. However, the current evaluation does suggest that the potential role of co-contaminants in adversely affecting water quality in USDWs is small.

6. CONCLUSIONS

The evaluation conducted in this report permits the following conclusions:

- The substantial parasitic energy losses (approximately 30–40%), associated with the retrofitting of CO₂ capture facilities on existing coal fired power plants, make it highly unlikely that such modifications will be implemented in the foreseeable future.
- Alternative IGCC power plant designs, even when using existing state of the art technology, are thermodynamically far more efficient than current conventional power plants, and therefore produce less CO₂ per unit of power output than conventional plants.
- IGCC plants are readily adapted for CO₂ capture, and therefore represent an attractive opportunity for CO₂ capture and sequestration.
- Despite the advantages of coal-fired IGCC technology, few IGCC plants have been built in the United States until now, because the higher capital cost of their construction is not justified, when compared with cheaper NGCC plants, despite the price volatility of natural gas.
- If CO₂ capture and geologic sequestration from coal-fired power plants were implemented, consideration would have to be given to the major technological changes in domestic power generation that such a policy would induce, including the necessary construction of IGCC and/or nuclear power plants to compensate for the approximately 30% energy shortfall due to CO₂ capture and injection.
- With respect to the co-injection of combustion derived contaminants with CO₂, two factors must be taken into consideration: (1) the very different chemical state of contaminants derived from conventional coal fired power plants when compared with those from IGCC plants, due, respectively to combustion with oxygen excess or with restricted oxygen, and (2) the opportunities afforded by CO₂ capture, to co-inject hazardous contaminants that would ordinarily be disposed of into surface waste impoundments.
- If the sulfur and nitrogen bearing gaseous contaminants of combustion are disposed of by conventional means in both conventional and IGCC plants, only small amounts of these constituents would likely be co-injected with CO₂ in the deep subsurface, and their impact in corroding the injection zone host rocks and modifying ground water composition would be minor.
- If advantage is taken of CO₂ capture and geologic sequestration to co-inject sulfur and nitrogen gaseous products of conventional combustion, then major chemical changes in the injection zone can be expected upon injection of SO₂. The injection of NO_x species is expected to be less consequential, but nitrogen chemistry, particularly in association with injected SO₂, is not well-understood and requires further review.
- If advantage is taken of CO₂ capture and geologic sequestration to co-inject sulfur and nitrogen gaseous products of coal gasification, then consideration must be given to the consequences of H₂S injection in amounts that could saturate the pore water of the injection zone. It is not immediately clear to what extent residual H₂S might

be transported with the migrating CO₂ fluid phase, and what the chemical consequences might be, especially in relation to the fate of hazardous trace elements. Nitrogen bearing gaseous species are not expected to be injected in other than minor or trace amounts. Their persistence in the subsurface environment is not known, and their impact in contaminating potable water supplies requires further review.

- Many hazardous trace elements in coal are volatilized during combustion. However, with some isolated exceptions, the volatile species either nucleate as solid or liquid particles, or are adsorbed on particulates (fly ash) upon cooling, and residues remaining in the gaseous state generally constitute at most only a few percent of the original inventory in the coal. This condition applies, whether during conventional combustion or coal gasification.
- In IGCC plants, the separated and compressed CO₂ may contain residual metastably persisting hydrides of several hazardous trace elements. It is expected that the concentrations of these elements in the compressed CO₂ fluid will be very low if co-injected with CO₂,
- The concentrations of hazardous volatile organic species in the gaseous effluents from both conventional and IGCC plants are extremely low, and will not be significant contaminants in injected CO₂.
- Under normal conditions, trace elements co-injected with CO₂ would be at concentrations comparable to or less than expected in the confining shale beds of the injected aquifer. Most are likely to partition into the pore water of the injection zone and precipitate as secondary sulfides. Their average concentrations could be less than the native concentrations of these elements in the host rock. However, the injection process could lead to localized concentration zones around the injection well due to chromatographic separation processes.
- Chemical reactions involving the co-injected trace elements are likely to lead to saturation concentrations in distal regions of the injection zone, which could be similar to those expected through interaction of the CO₂ with the confining shale beds.
- Hazardous trace element contamination of USDWs is more likely to be due eventually to the impact of CO₂ promoted dissolution from confining shale beds, than to their presence in the injected CO₂. However, the leaching of hazardous trace elements from confining shale beds is expected to be slow. Given the information at hand, expert judgment leads to the general conclusion that the incidental inclusion of contaminants with captured CO₂ would, if injected, have minimal impact on the water quality in USDWs.

7. RECOMMENDATIONS

In preparing this report for submission, several technical issues remain incompletely researched, for lack of time or resources. These issues are important in developing confidence in some of the conclusions presented, and in finalizing recommendations regarding the development and promulgation of technical regulations governing CO₂ injection disposal from coal-fired power plants. They include the following:

1. More quantitative estimates should be made on the range of concentrations of co-contaminants expected in captured CO₂ under conditions of incidental and deliberate inclusion (Table 12).
2. A copy of the unredacted report on the fate of trace elements in the LGTI plant (Radian Corp., 1995) should be obtained, and critical information regarding the concentration of hazardous volatile elements in the gasifier effluent extracted for further evaluation.
3. Henry's Law behavior of volatile gases, including SO₂, NO_x, trace metal hydrides and nitrides, should be evaluated with respect to CO₂ fluid/saline brine partitioning at the temperatures and pressures expected in the injection zone of a well dedicated to CO₂ sequestration.
4. The kinetics of dissolved SO₂ disproportionation, NO_x reduction, and trace element hydride and nitride decomposition should be researched, summarized, and evaluated.
5. The concentrations of hazardous trace elements in CO₂ sequestration well injection zone host rocks should be researched, summarized, and compared with the amounts of the same elements introduced through CO₂ injection.
6. Modeling should be conducted to predict the equilibrium concentrations of hazardous trace elements in saline aquifers under both ambient CO₂ partial pressures and elevated partial pressures characteristic of conditions during CO₂ injection disposal.

Fulfillment of the tasks recommended above, should allow completion of the issue under consideration.

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