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Non-Condensable Gas Composition Impacts on Carbon Capture and Water Injection

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ABSTRACT

Non-condensable gas streams from geothermal plants vary, but usually contain flammable species such as hydrogen, hydrogen sulfide, and/or methane in addition to carbon dioxide. Air ingress from direct-contact condensers and leaks in the vacuum areas of the geothermal plant introduce oxygen (air) into this gas mixture. Carbon dioxide capture projects that remove carbon dioxide from the non-condensable gas stream can concentrate the remaining species enough that the non-condensable gas stream exiting the carbon dioxide capture process is an explosive gas mixture. Somewhat similarly, water injection into the geothermal formation from external water sources can, over time, reduce the quantity of non-condensable gas associated with the geothermal steam. When this smaller quantity of non-condensable gas is mixed with the air introduced into the process through direct contact condensers or leaks, the non-condensable gas stream can become explosive. This paper examines the flammability of different common non-condensable gas species and the minimum oxygen concentration required to support combustion of these species. The impact of these non-condensable gas characteristics on carbon dioxide capture and water injection are reviewed. Potential solutions for managing the risk of explosive non-condensable gas mixture are also presented.

1. Introduction

Geothermal steam contains various non-condensable gas (NCG) species that vary by site depending on the characteristics of the reservoir. Typical NCG contains CO_2, H_2S, H_2, N_2, CH_4, NH_3, and/or Ar, but other species can also be present at low levels (Energy Sector Management Assistance Program, 2016). The NCG may be handled differently depending on the type of geothermal power plant, the species present in the gas, and local environmental regulations.

Figure 1 shows a general overview of a typical geothermal power plant equipped with NCG treatment. Steam from the turbine flows to a main condenser where cooling tower water condenses the steam. A direct-contact condenser (DCC) is shown in the figure. In a DCC, the cooling tower water contacts the steam directly. The direct contact results in a lower main-condenser temperature (and better steam turbine efficiency) than if the cooling water had flowed through a heat exchanger. Despite the low pressure of condensation, the large water flow rate sprayed into the DCC may result in the absorption of a significant amount of any H_2S that is present in the steam especially if there is also ammonia present. Because the water coming from the cooling tower is also saturated with air, most of this dissolved air may be stripped into the NCG.

In contrast to plants that use DCCs, some facilities use surface condensers. In a surface condenser, the cooling water passes through a heat exchanger and does not come into direct contact with the condensing steam. Although a surface condenser plant is slightly less efficient than a plant with a DCC (all else being equal), use of a surface condenser does greatly reduces absorption of H_2S into the condensate and also eliminates the issue of air from the cooling water being stripped into the NCG. This paper focuses primarily on plants equipped with DCCs, but conclusions may still apply to surface condenser plants in some instances.

Although the configuration of plants varies, the NCG from the condenser is typically drawn off by vacuum ejectors or vacuum pumps to maintain a vacuum for the turbine discharge. The ejectors discharge into an inter-condenser. The inter-condenser is another direct-contact condenser where water is used to condense much of the steam that remains after the main condenser. The NCGs are pumped from the inter-condenser to slightly-above atmospheric pressure using another ejector or pump, and the gas is directly contacted with water one final time in the after-condenser. The water from all the condensers is sent to the cooling tower. Turbine seal gland steam is often routed to one of the condensers or may be handled separately.

Depending on the local environmental and safety requirements, the condensate and/or NCG may need to be treated to remove H_2S and other species which may be present in the NCG (mercury, VOC, etc.). Removal of H_2S from the NCG is commonly referred to as primary H_2S abatement, while H_2S removal from the condensate is known as secondary H_2S abatement.

Several different technologies are used for H_2S abatement, but many plants with DCCs require both primary and secondary H_2S abatement, because in these types of plants, particularly when there is ammonia in the NCG, H_2S tends to be present in significant quantities in both the condensate and the NCG. Often “burn and scrub” technology is used for primary H_2S abatement with iron chelate added to the cooling water for secondary H_2S abatement. This combination integrates well when roughly 50% of the H_2S goes with the NCG and 50% with the condensate, since elemental sulfur produced by the iron chelate reaction with the water-dissolved H_2S (as sulfides) can react with SO_2 absorbed (as sulfites) in the scrubber after the burner, forming soluble thiosulfate salts (Bedell & Hammond, 1987).

On the other hand, many plants with H_2S in their steam, especially those equipped with surface condensers and those with no ammonia in their NCG, may only require primary H_2S abatement. In addition to burn and scrub, common technologies used for primary H_2S abatement include the redox processes and once-through pressurized water scrubbing. H_2S abatement technologies used in geothermal applications are documented in the literature (Mamrosh, McIntush, Beitler, Markusson, & Einarsson, 2012) (Benn, McIntush, Beitler, Mamrosh, & Hileman, 2010) (McIntush, Mamrosh, Beitler, & Kitz, 2017) (Rodriguez, Harvey, & Asbjornsson, 2014).

It is becoming increasingly necessary or desired to capture CO_2 from the NCG to lower CO_2 emissions to the atmosphere. CO_2 isolated from NCG can be sequestered by injection or can be purified and sold, assuming a market is available (Energy Sector Management Assistance Program, 2015). In some geological formations in Iceland, the abundance of cool groundwater allows CO_2 to be scrubbed from the NCG (at elevated pressure) and the water is then injected underground where the CO_2 dissolved in water reacts with basalts and other rock formations to form solid carbonates that permanently sequester the CO_2 (Carbfix Iceland ohf., 2021). H_2S dissolved in water can also react with the rocks to be permanently sequestered (Clark, et al., 2020).

CO_2 recovered from NCG may also be compressed into a dense-phase of intermediate purity for use in enhanced oil recovery applications. Alternately, the CO_2 could be captured and processed to supplement CO_2 concentrations in greenhouses or to produce a refrigerated-liquid CO_2 product of beverage quality, among others (Energy Sector Management Assistance Program, 2015).

Many NCG streams include CO_2 as the highest-concentration component, but the NCG may be a mixture of numerous components. Other components often include flammable gases such as hydrogen, H_2S, and methane, and oxygen is often introduced to the NCG as a result of the plant configuration. The isolation of CO_2 from NCG streams can concentrate the remaining species enough that the NCG stream exiting the treatment system can be an explosive gas mixture.

NCG composition and flow rate can also change over time, further complicating this issue and potentially resulting in problems associated with oxygen in the NCG years after the plant is built. One example is water injection into a geothermal formation. In this instance, water from an outside source is pumped into the formation to help maintain the steam production rate of the formation. Over time, this can reduce the quantity of NCG associated with the geothermal steam, resulting in the NCG concentration in the steam becoming lower. It may also shift the composition of the NCG. This can cause further issues with CO_2 removal projects, or it can become an issue with the NCG overall if the NCG composition and flow rate shift significantly.

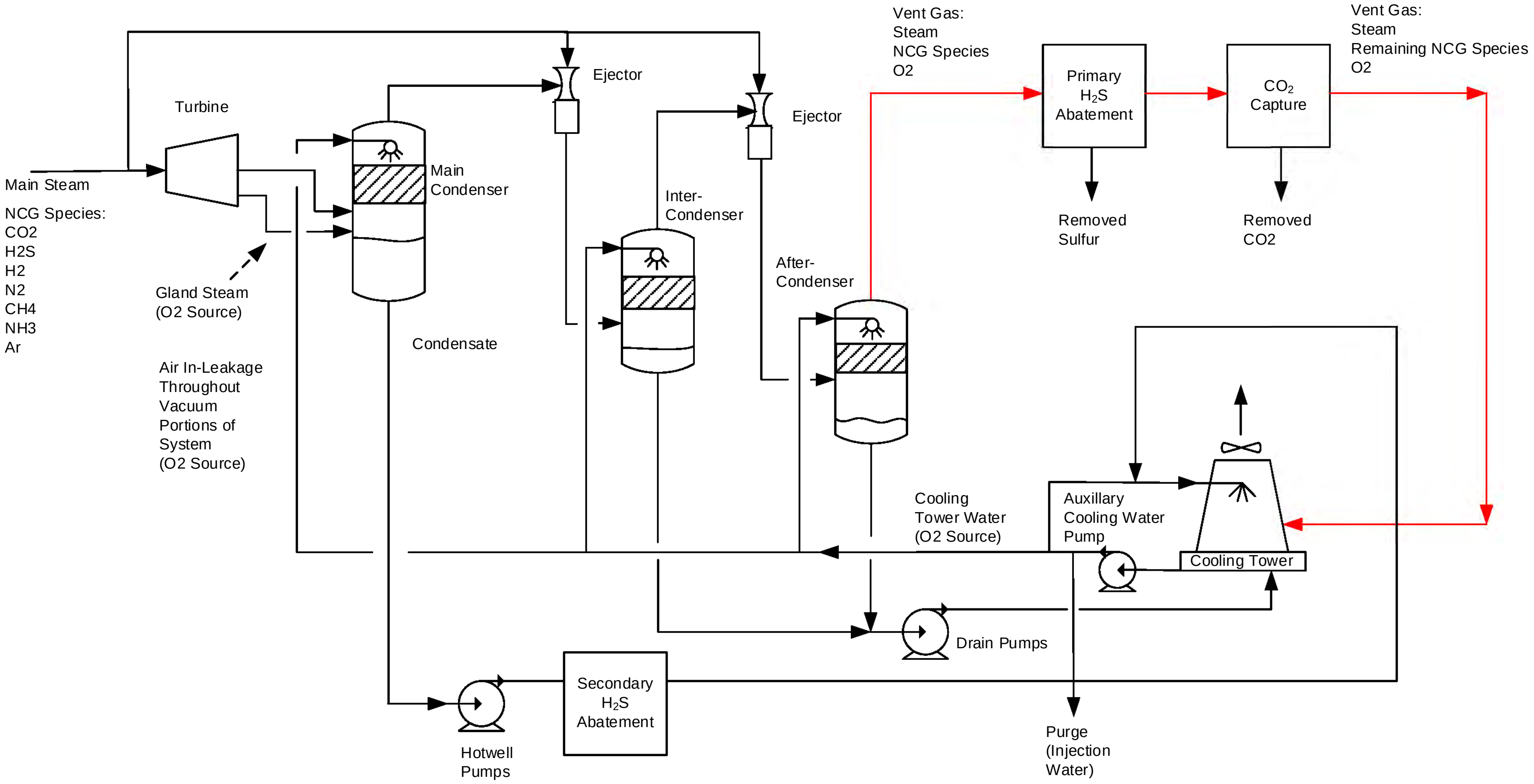


Figure 1. Example Geothermal Power Plant with H_2S Abatement and CO_2 Capture

2. Lower/Upper Flammability Limits and Limiting Oxidant Concentration for Common NCG Species and the Impact of Inert Gas Species

NCG composition varies greatly from one geothermal power plant to another and can even change from one steam producing well to another, but there are some components present at most locations. The main flammable components of NCG are typically hydrogen, hydrogen sulfide, methane, and ammonia. Common inert gas species include carbon dioxide and nitrogen.

This paper uses some terms and acronyms concerning flammable gases that, while familiar to most readers, may not always be interpreted the same. These terms and their definitions as used in this paper are:

- Lower Flammability Limit (LFL) – The LFL of a gas species or mixture is the minimum fraction of a flammable gas required for the gas to burn when mixed with air. LFL and Lower Explosive Limit (LEL) are used interchangeably (Crowl & Louvar, 1990).
- Upper Flammability Limit (UFL) – The UFL of a gas species or mixture is the maximum fraction of a flammable gas that can be present for the gas to burn when mixed with air. UFL and Upper Explosive Limit (UEL) are used interchangeably (Crowl & Louvar, 1990).
- Limiting Oxygen Concentration (LOC) – The LOC is the minimum fraction of oxygen in a gas mixture required for a combustion reaction to generate enough energy to heat the entire mixture of gases (including the inerts) to the extent required for the self-propagation of a flame. Other terms such as Minimum Oxygen/Oxidant Concentration or Minimum Oxygen for Combustion (MOC) may also be used (Crowl & Louvar, 1990).
- Explosive Gas Mixture – Although different terminology is sometimes used, an explosive gas mixture is a gas in which a mixture of fuels and oxygen are already present, and the gas only needs an ignition source to burn, deflagrate, or explode.

Table 1 shows a hypothetical NCG gas composition, which does not represent any particular geothermal power site, but which should be representative enough to support conclusions drawn in this paper.

Table 1. Hypothetical NCG Composition on a Dry Basis.

Gas Species in NCG	**Composition of NCG Upstream of DCC**	**Composition of NCG Downstream of DCC**
Carbon Dioxide (CO_2)	75.16%	63.91%
Hydrogen (H_2)	11.66%	9.91%
Hydrogen Sulfide (H_2S)	9.91%	8.43%
Methane (CH_4)	1.09%	0.93%
Ammonia (NH_3)	2.18%	0.00%
Nitrogen (N_2)	0.00%	13.29%
Oxygen (O_2)	0.00%	3.53%

Some geothermal facilities may have NH_3 present in the steam supplied to the turbines, but the NH_3 generally partitions almost entirely into the liquid water phase (i.e., the main condenser condensate) and is not be present in a meaningful amount in the NCG exiting the condenser. N_2

may also be present in small amounts, but for the purposes of this analysis, it is assumed to be zero upstream of the main condenser. N_2 and O_2 are noted in the third column of Table 1; these are a result of air ingress into the process. The oxygen may be higher than shown in Table 1 (e.g., 5 – 7 % O_2), if the gland steam from the seal system is added to the geothermal steam condenser system. The NCG will also be saturated with water at the conditions of the last condenser.

2.1 Hydrogen

H_2 is the gas species in NCG that has the widest flammability range in air as well as a low LOC, as shown below in Table 2 (in volume percent).

Table 2. Flammability Limits in Air and Limiting Oxygen Concentration for Hydrogen (Zabetakis, 1965) (National Fire Protection Association, 2019 Edition).

Gas Species	LFL	UFL	LOC
Hydrogen (H_2)	4.0%	75%	4.6%

The flammability of H_2 is affected by the presence of inert gases, for the purposes of this paper defined as nitrogen and carbon dioxide. Figure 2 shows a flammability diagram for a mixture of hydrogen, inert gases, and air.

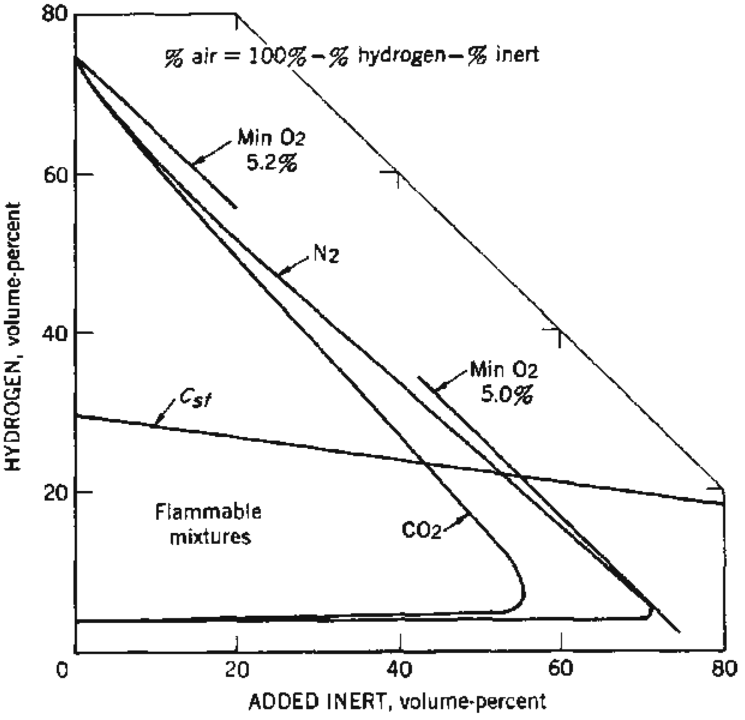


Figure 2. Flammability Diagram of Hydrogen-Inert-Air Mixtures (Zabetakis, 1965).

The LOC (“Min. O_2”) shown in Figure 2 is different from the LOC (4.6%) shown in Table 2; the value shown in Table two is more recent data from *NFPA-69 Standard on Explosion Prevention Systems, 2019 ed.* (National Fire Protection Association, 2019 Edition). Two conclusions can be drawn from Figure 2, and these conclusions also apply to the other flammable gas species.

1. The type of inert gas present impacts the mixture’s flammability. If the gas mixture has 60% or more CO_2, it should not be able to burn regardless of the hydrogen and oxygen concentrations.
2. The fractions of hydrogen and carbon dioxide also determine how flammable the gas mixture might be. In other words, if the mass flow of CO_2 and H_2 is decreasing over time, but the mass flow of air remains constant, then the fraction of CO_2 and H_2 in the resulting mixture will decrease and could lead to the gas becoming flammable. The “nose” on the graph in Figure 2 illustrates this phenomenon. A mixture that has a hydrogen fraction close to the LFL of hydrogen (4.0%) will require a high fraction of CO_2 or N_2 for the gas to not be flammable. Conversely, a mixture that has a hydrogen fraction close to the UFL of hydrogen (75%) requires a much smaller fraction of CO_2 or N_2 for the gas to not be flammable.

It is important to note that the values in Table 2 and Figure 2 are at ambient pressure and temperature. Changes to pressure and temperature affect the flammability of a gas.

2.2 Hydrogen Sulfide

Hydrogen sulfide (H_2S) is another flammable gas commonly found in NCG, and it has a flammability range almost as wide as hydrogen. In addition to being flammable, H_2S is a toxic and odorous gas at even low (ppm) concentrations. As a result, it is often deemed necessary to remove H_2S from NCG. Table 3 shows the flammability limits (in volume percent) for H_2S mixed with air.

Table 3. Flammability Limits in Air and Limiting Oxygen Concentration for Hydrogen Sulfide (Zabetakis, 1965) (Pahl & Holtappels, 2005) (National Fire Protection Association, 2019 Edition).

Gas Species	LFL	UFL	LOC
Hydrogen Sulfide (H_2S)	3.9-4.3%	63%	6.4-10.0%

Figure 3 shows a flammability diagram for mixtures of H_2S, CO_2, and air. Figure 3 shows that similar conclusions can be drawn for H_2S that were drawn for hydrogen: that mixtures with concentrations of H_2S close to the LEL (3.9-4.3%) require a higher fraction of CO_2 to be present to avoid the gas being flammable. The LOC shown in Table 3 does not agree with that shown in Figure 3, because Table 3 has also been updated to reflect more current experimental results (National Fire Protection Association, 2019 Edition).

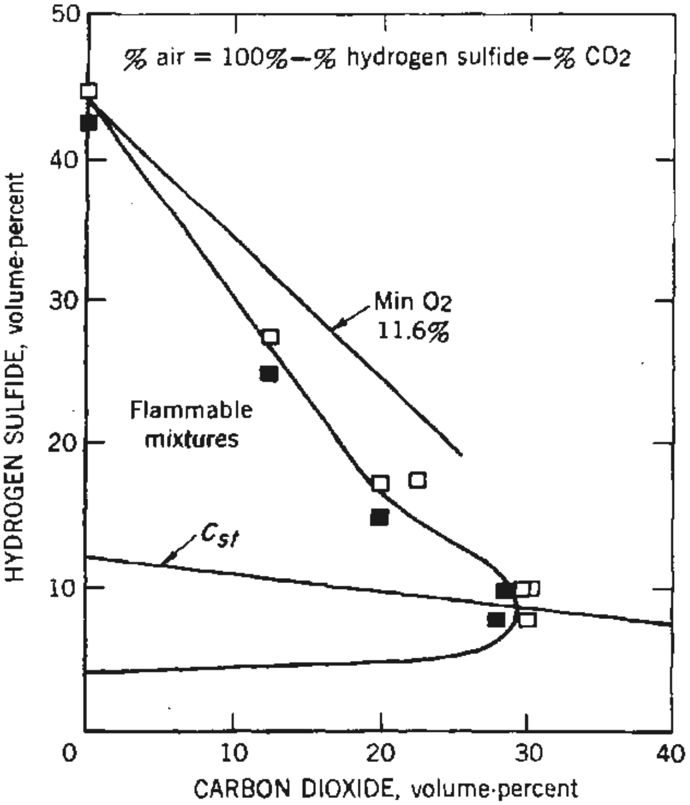


Figure 3. Flammability Diagram of Hydrogen-Carbon Dioxide-Air Mixtures (Zabetakis, 1965).

2.3 Methane

In some geothermal plants, there is little or no methane present in the NCG, while in others, methane is a significant portion of the NCG. Table 4 shows the flammability limits (in volume percent) for methane mixed with air.

Table 4. Flammability Limits in Air and Limiting Oxygen Concentration for Methane (Crowl & Louvar, 1990) (National Fire Protection Association, 2019 Edition).

Gas Species	LFL	UFL	LOC
Methane (CH_4)	5.0%	15.0%	11.1-13.1%

Figure 4 shows the flammability envelope for methane mixed with air and different inert species. The figure illustrates that mixtures with methane will exhibit similar behavior to mixtures with H_2 and H_2S; as the gas approaches the LFL value, more inert gas will be necessary to avoid a flammable mixture and that CO_2 is a more effective inert gas for shrinking the flammability envelope of a flammable gas.

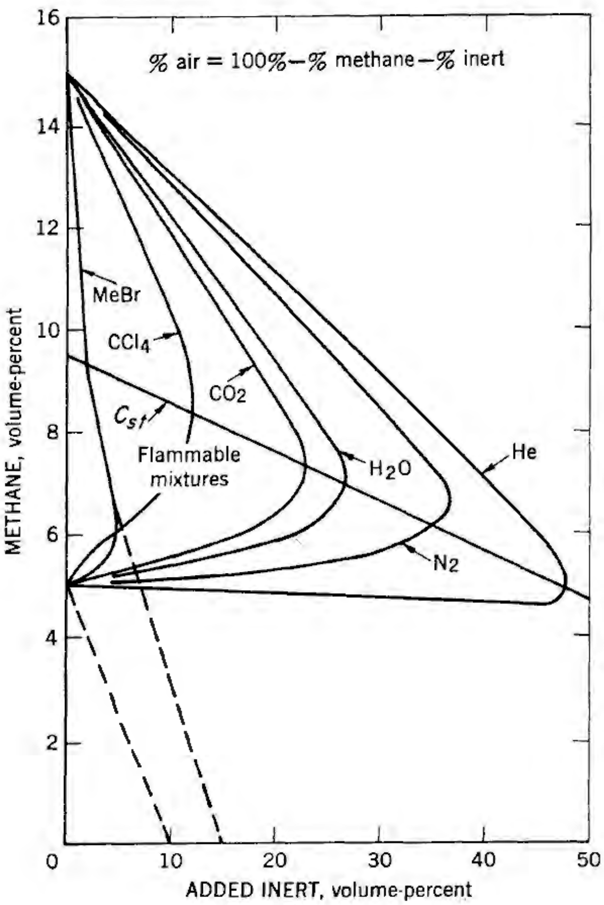


Figure 4. Flammability Diagram of Methane-Inert-Air Mixtures. (Zabetakis, 1965)

2.4 Mixtures of Flammable Gases

The use of only pure-component flammability properties to represent those of a mixture may be inaccurate, particularly if the mixture is not dominated by a single component. LOC and flammability limits for a mixture of flammable components tend to be proportional to the molar concentration of the mixture, whereas the presence of an inert gas serves to narrow flammability envelopes because of the quenching characteristics of inert gases.

The prediction of the LOC, UFL, and LFL for gas mixtures is not a well-established practice. Techniques are available to utilize pure-component flammability properties and mixture composition to predict the properties of a mixture, but these techniques are for approximation purposes only. Laboratory data is typically considered the standard for accurately defining these properties for gas mixtures. This section summarizes the methods used to estimate the flammability properties of gas mixtures.

LOC for gas mixtures is typically calculated based on the fuel components only, using the following equation (National Fire Protection Association, 2019 Edition):

$$LOC_{mix} = \frac{\sum_i x_i \times S_i}{\sum_i x_i \times \frac{S_i}{LOC_i}}$$

Where:

- LOC_{mix} is the LOC estimated for the gas mixture,
- x_i is the mole fraction of the individual flammable component *i* based on a **fuel-only** composition,
- S_i is the theoretical stoichiometric ratio of O_2 to fuel component *i*,
- and LOC_i is the known LOC for fuel component *i*.

This calculation assumes the presence of an inert diluent and air; different inert diluents have different effects on the LOC, and there are, for example, different LOC documented for flammable materials containing different inert diluents – usually nitrogen or CO_2. For geothermal NCG, CO_2 is the most common diluent and the LOC_{mix} would be calculated using LOC_i determined with CO_2 as the inert diluent.

Calculation of LFL and UFL for gas mixtures is more complicated, in that the amount of inert gas that is present must be taken into consideration in the calculation of the LFL_{mix} and UFL_{mix}. The estimation method is based on mole-weighted averaging, but upper and lower limits for “pseudo-mixtures” of the inert diluent with the individual flammable components are required as part of the calculation. Graphs showing the effect of UFL and LFL of the inert diluent on the individual flammable components are used to estimate the UFL and LFL of these pseudo-mixtures. The details of this calculation method are provided in a reference (Coward & Jones, 1952).

For the gas mixture given in Table 1, the LOC_{mix}, UFL_{mix}, and LFL_{mix} were estimated using these standard techniques. The results are shown in Table 5. The LOC_{mix} tends to be intermediary between the LOC of the flammable components. The UFL and LFL would normally also be intermediate between the values of the constituent gases, but the presence of the inert gas (CO_2) serves to narrow the range between the UFL and LFL for the mixture and may also shift the concentration range higher.

In the estimation of the LFL_{mix} and UFL_{mix}, the “flammable gas” concentration is considered to be that of the total fuel plus the added inert – hydrogen, hydrogen sulfide, methane, and CO_2 (everything except air). The value shown in Table 5 for “Total Fuel + Inert” (83.18 vol %) is the concentration that should be compared to the UFL_{mix} and LFL_{mix}. The estimates in Table 5 show that this mixture is too rich in fuel (total fuel + inert) to burn without additional air being added because 83.18% is greater than the UFL_{mix} of 49.3%. The oxygen concentration in the gas stream is 3.53%, and this is compared to the LOC_{mix} of 8.1%. The actual oxygen concentration of the gas is well below the LOC_{mix}, so there is not enough oxygen in this gas stream to support combustion in any case.

For this gas stream, the oxygen content is below the LOC_{mix} and the concentration of fuels plus inerts is above the UEL_{mix}, so this mixture is not explosive as-is because it is both too rich in fuel and too low in oxygen. (But it may burn if it is released to the atmosphere or additional air is added to the mixture.)

Table 5. Estimated Flammability Properties of Hypothetical NCG Mixture.

Gas Species in NCG	**NCG Comp vol %**	**LOC vol %**	**UFL vol %**	**LFL vol %**
Carbon Dioxide	63.91			
Hydrogen	9.91	4.6	75	4
Hydrogen Sulfide	8.43	10	63	4
Methane	0.93	13.1	15	5
Total Fuel + Inert	**83.18**			
Nitrogen	13.29			
Oxygen	**3.53**			
Mixture Predicted Properties		**8.1**	**49.3**	**18.5**

3. Sources of Oxidants in the Geothermal Power Process

The steam from geothermal reservoirs typically does not contain significant quantities of oxygen, and the nitrogen content of the steam is usually small. However, the NCG can contain significant oxygen and nitrogen which can come from various sources, including:

- Vacuum leaks
- Routing of gland steam to the condenser system
- Stripping of dissolved air from cooling tower water (DCCs only)

These sources are discussed in the subsections below.

3.1 Vacuum Leaks

Air in-leakage is common in geothermal power plants. The steam is expanded to vacuum conditions in the turbine and condensed under vacuum. Not all of the components of the vacuum system are necessarily leak-free. Air in-leakage can occur in different areas of the power plant including valves, flanges, bolted connections, rupture disks, manways, vacuum transfer devices (e.g., pumps, ejectors, fans), instrument fittings, and any other equipment under vacuum. Air ingress has also been reported from drain float traps that did not close properly in the after-condenser and when the seal of an inter-condenser drain ran empty (Cyr, 2015). Corroded piping in vacuum service can also be a source of air in-leakage. Leaks of this nature should be monitored and repaired when possible at the plant.

3.2 Routing of Gland Steam to the Condenser System

Turbine shaft seals are another potential source of air to the NCG. In the turbine, the rotor extends from both the front and back of the turbine casing. The seals on the shaft represent a potential leak location, where steam could escape on the high-pressure side or air could leak in on the vacuum side. There are different types of seals that are used in the glands along the rotor that exit the turbine casing to minimize leaks. Labyrinth seals are one type, but others can be used as well. Labyrinths make small compartments that cause pressure drop along the rotor, but gland steam is also used to further prevent steam leakage or air ingress (Swapan & Debnath, 2019).

In the high-pressure turbine gland, steam can leak off under pressure. The leak-off steam is composed of the geothermal steam only, so it will contain NCG but not air since it operates at pressure. Excess leak-off steam may be routed to one of the condensers; this pressure leak-off steam can also be used as seal steam to the vacuum gland during normal operation.

The gland sealing the vacuum area is the area of concern for oxygen ingress. Typically, this gland is kept at a slightly higher pressure (but still vacuum) compared to the turbine vacuum and steam is added to keep air from being pulled into the turbine. Air and steam (with NCG) are swept out of the last section of seal in the gland to prevent steam from leaking to the atmosphere; this is also true of the last section of seal in the high-pressure gland. The steam and air leak-off can also go to the main condenser or to a separate gland steam condenser system. The presence of H_2S in the steam complicates the handling of the gland steam. H_2S-containing steam may not be allowed to leak to the atmosphere for safety and environmental reasons, while a separate gland steam condenser system may be complicated by the need to abate H_2S.

The turbine gland steam can contain a significant amount of oxygen and nitrogen from air. For example, one geothermal power plant estimated that the oxygen content of the NCG could be reduced in half (from approximately 5 mol% to 2.5 mol%) by rerouting the gland steam so that the gland steam did not flow to the steam condensers.

3.3 Direct-Contact Condensers

The other main source of oxygen ingress to the NCG is unique to plants that are equipped with direct-contact condensers. This type of condenser uses direct contact of cooling tower water with the turbine-exhaust steam. The cooling water feeding the DCC is saturated with air from the cooling tower. As that cooling water flows into the vacuum conditions of the condensers, most of that oxygen and nitrogen is stripped from the cooling water and ends up in the NCG.

The solubility of oxygen in water can be estimated using Henry's Law constants (Sander, 2015). The Henry's Law constant and temperature variance for oxygen are approximately:

$$H(298\text{ K}) = 1.3 * 10^{-5}\text{ mol/m}^3\text{ Pa or } 1.32 * 10^{-3}\text{ mol/kg atm}$$

$$d\ln(H) / d(1/T) = 1500\text{ K}$$

$$\text{Ln } H_2 = \ln H_1 - 1500 * (1/T_1 - 1/T_2)$$

Where 1 = standard conditions
2 = actual conditions

$$O_2\text{ solubility (mol/kg)} = H_2\text{ (mol/kg atm)}*\text{ Partial Pressure of } O_2\text{ (atm)}$$

At typical cooling tower conditions (~75°F and atmospheric pressure of 13.2 psia for example), the resulting oxygen content in the water is approximately 8 ppmw. At this concentration, about

125,000 gallon of water will add 1 pound of oxygen to the NCG. This amount of oxygen may seem negligible. However, the NCG content of most steam sources is small, and cooling water recirculation flow rates required for condensers is extremely large. Thus, when a direct contact condenser is used it typically ends up providing a large fraction of the oxygen in the NCG. One geothermal power plant estimated that approximately 70% of the oxygen in the NCG came from the cooling water and 30% from the turbine shaft seals. Each geothermal power plant is unique, however, and the oxygen content of the NCG and the source of the oxygen can vary considerably based on the design of the equipment in the process.

4. Integration of Carbon Capture into the NCG Treatment Process and Flammability Concerns

4.1 Carbon Dioxide Removal Limitations

Carbon capture projects are proliferating across the globe with increased public focus on carbon emissions. To meet carbon reduction goals, companies are investigating methods for reducing emissions at all of their production sites and this includes geothermal power production sites. The NCG emitted from these sites usually has a high mole fraction of CO_2, and in general, CO_2 removal processes are more cost-effective as the mole fraction of CO_2 in the gas increases. As a result, removing CO_2 from NCG is, at first glance, relatively attractive.

Most CO_2 removal processes that are commercially available today have a basis in the natural gas treating industry, and the removal processes are tailored to selectively remove the “acid gases” CO_2 and H_2S, while leaving the other components behind. In a natural gas treating application, selectively removing acid gases is beneficial, since it leaves the more valuable hydrocarbon species in the bulk gas. Applying these acid-gas removal technologies to carbon-capture projects on NCG streams can radically change the composition of the NCG residue gas. In the United States, a historical target for carbon capture projects is 90% removal of the CO_2, and generally both H_2S and CO_2 can be assumed to be removed by these processes. Table 6 shows the resulting NCG residue gas composition when all of the H_2S and 90% of the CO_2 is removed, considering the original NCG composition in Table 1. Table 7 shows the calculated LFL, UFL, and LOC for the NCG stream as it exits the CO_2 removal unit. (The data in the tables are in volume percent.)

Table 6. NCG Composition Before and After 90% CO_2 Removal on a Dry Basis.

Gas Species in NCG	**Composition of NCG Upstream of CO_2 Removal Unit**	**Composition of NCG Downstream of CO_2 Removal Unit**
Carbon Dioxide (CO_2)	63.91%	18.77%
Hydrogen (H_2)	9.91%	29.11%
Hydrogen Sulfide (H_2S)	8.43%	0.00%
Methane (CH_4)	0.93%	2.72%
Total Fuel + Inerts	**83.18%**	**50.60%**
Ammonia (NH_3)	0.00%	0.00%
Nitrogen (N_2)	13.29%	39.03%
Oxygen (O_2)	**3.53%**	**10.37%**

Table 7. LFL_{mix}, UFL_{mix}, and LOC_{mix} for NCG After Carbon Capture.

Lower Flammability Limit	6.8%
Upper Flammability Limit	56.4%
Limiting Oxygen Content	5.6%

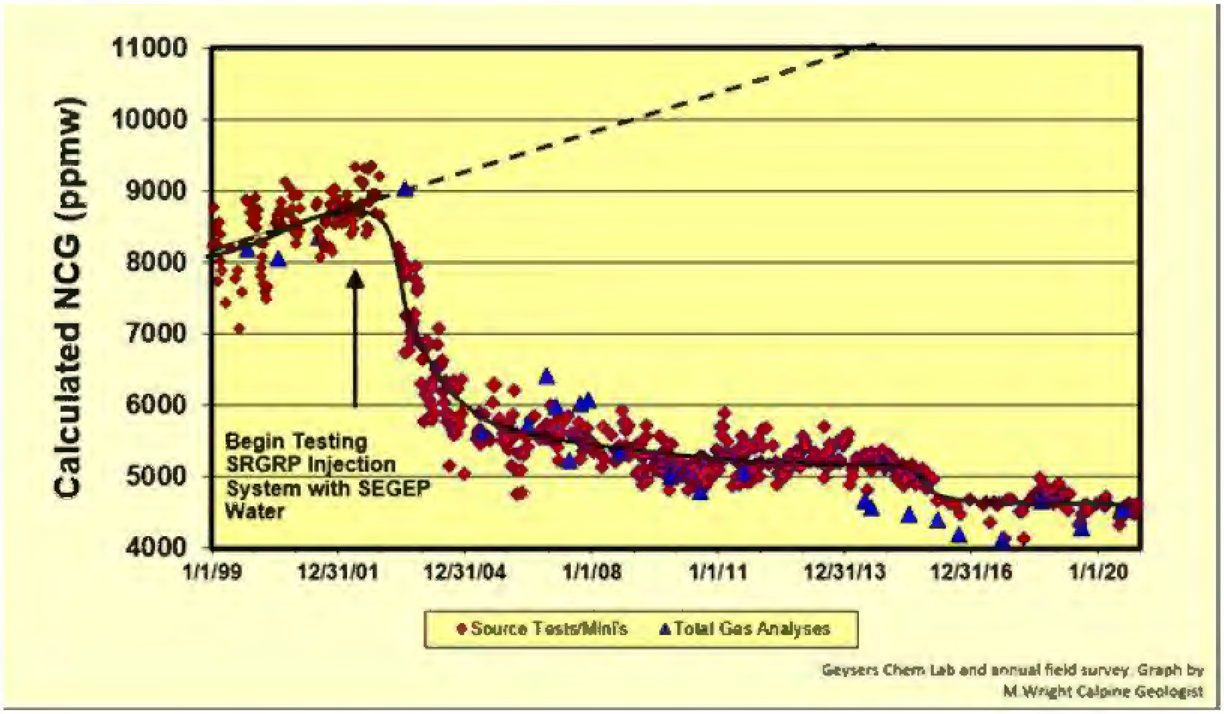
Table 7 shows that the NCG exiting the carbon capture process is now an explosive gas mixture, since the O_2 content is above the LOC of the mixture, and the concentration of flammable gases plus inerts is between the calculated LFL and UFL. It is generally considered prudent to avoid the formation of an explosive gas mixture inside of process equipment. To avoid an explosive mixture, changes would have to be made to the process. One example is to reduce the CO_2 capture percentage (to leave more CO_2 in the residue NCG as a diluent). Another example is to make changes that reduce the air ingress.

4.2 Water Injection Process Limitations

Some geothermal power plants inject water into the reservoir to replace the water (i.e. steam) that is condensed in the power plant. Since the condensing process usually involves the use of cooling towers, a portion of the steam condensed is lost to the atmosphere; blowdown from the cooling tower may be injected, along with water from other sources. At some areas of The Geysers, California, treated waste water has been injected into the steam reservoir since 2003. Figure 5 shows the steam flow-weighted average NCG concentration for steam flowing to all the interconnected plants in the north Geysers (Calpine Units 5/6, 7/8, 11, 12, and 17). As shown in the figure, the NCG concentration has dropped considerably since water injection began. The NCG concentration prior to water injection was on the order of 8,500 ppmw; after water injection was implemented, the NCG content decreased to about 4,500 ppmw.

The composition of the NCG has also changed over the years since water injection began, likely due to the solubility of some of the gases over others in the injection water. Figure 6 shows the change in hydrogen and CO_2 content of the NCG in Calpine Unit 8 at The Geysers. The CO_2 concentration has dropped from 65 vol% to 45 vol% in the NCG. On the other hand, the hydrogen concentration has increased from 15 vol% before wastewater injection to nearly 30 vol% currently. Moreover, the H_2S concentration has also reportedly decreased, so there is less H_2S that needs to be removed in the abatement system at the plant.

While the NCG conditions have changed over time with water injection into the reservoir, the air/oxygen ingress rate into the NCG has remained relatively constant, since most of the air comes from degassing of the cooling tower water that operates with an essentially fixed circulation rate. The turbine gland steam also contributes to the oxygen in the NCG. As a result, the ratio of air/oxygen to NCG had gone up over time.



Geysers Chem Lab and annual field survey. Graph by M.Wright Calpine Geologist

Figure 5. Steam Flow Weighted Average NCG Versus Time for Units 5/6, 7/8, 11, 12, and 17.

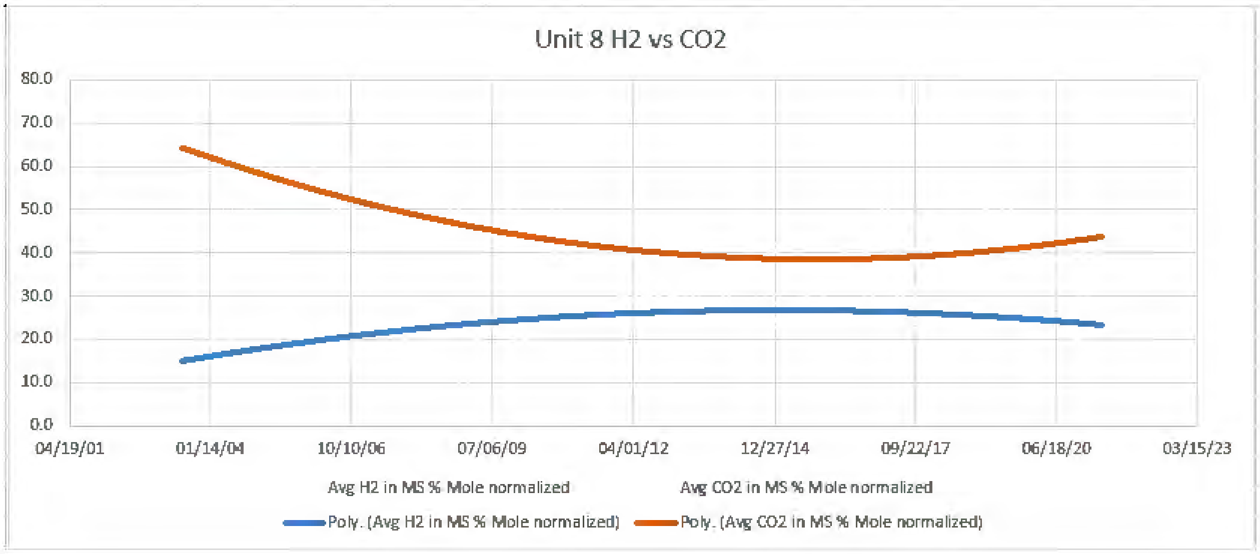


Figure 6. H_2 and CO_2 Content of NCG at Unit 8.

Since the flammability envelope of hydrogen is very wide, the combination of i) higher O_2 relative to NCG and ii) higher NCG flammability content has resulted in the NCG leaving the last condenser having high fuel and oxygen concentration such that it close to, or occasionally in, the explosive mixture range. Also, the reduction of NCG supplied to the plant has reduced the vent gas flow rate. For plants that use a burner to combust the NCG, the lower NCG flow may be less than the design point of the burner combustor nozzles such that the velocity of the gas entering the burner may sometimes be less than the flame velocity. This can cause “burn-back” or the propagation of the burner flame back upstream of the burner into the feed gas line. In such plants, modifications to the burner system may need to be considered, and additional safety devices (e.g., flame/deflagration arrestors, monitoring, etc.) may need to be installed to minimize the risk when handling this stream.

This example of water injection changing the NCG conditions over time is important to consider when evaluating the potential for carbon capture from NCG. When removing CO_2 from NCG, the other species present in the NCG will increase proportionately, and the possibility that the NCG characteristics may change over time (e.g., due to injecting water into the steam reservoir) must also be taken into account. The presence of oxygen is a key issue; if oxygen could be excluded from the NCG, then an explosive gas mixture could not be formed.

5. Process Options to Mitigate Potential Explosive Gas Mixtures

The removal of the bulk of the CO_2 from geothermal NCG may result in the residue gas containing high concentrations of combustible gases and oxygen such that the residue gas may be in or near the explosive region. Consideration must therefore be given to mitigating the risk of such mixtures. General mitigation methods include:

- Modification of the condensing and NCG treatment processes to reduce the probability of explosive gas mixtures being present.
- Designing the NCG handling system to safely handle explosive gas mixtures when they are present.

The following sections discuss these issues and the mitigation methods that might be considered.

5.1 Modification of Condensing and NCG Treatment Processes

Given that the first consideration should be to avoid producing a gas in the explosive range, the modification of existing systems and NCG treatment processes should always be considered. The key parameters that play into the formation of an explosive gas mixture are straightforward:

- Fuel concentration. For a gas to burn the fuel concentration must be between the UFL and LFL.
- Inert diluent. The presence of an inert diluent, considered as part of the fuel, serves to narrow the flammability limits, making it easier to keep the gas concentration above the UFL or below the LFL.
- Oxygen. If the oxygen concentration can be kept below the LOC, then the mixture cannot ignite without additional air being added.

Flammability parameters – LOC, UFL, LFL – are difficult to predict with great accuracy, and gas compositions in processes often vary. If these flammability parameters are determined by the calculation methods described earlier, a significant margin for error must be assumed; experimental determination of these limits is preferred.

It is common to set conservative targets for operations as they relate to the flammability limits (Cunliffe, 2001) (The Linde Group, 2021) (Zlochower & Green, 2021) (Mentasti & Crippa, 2013) (US Code of Federal Regulations), and different targets may be used depending upon various details, such as the continuity of the process operation and the existence of a continuous monitoring system.

A maximum permissible oxygen concentration (MPOC) may be set by comparison to the LOC. A generally-accepted rule is the MPOC should be two percentage points below the LOC (e.g., if the LOC were 6% O_2, then the MPOC by this rule of thumb would be 6% - 2% = 4% O_2) (Cunliffe, 2001). But, other rules may be applied such as when “the plant is NOT continuously monitored, the plant shall not operate at any level higher than 60% of the Limiting Oxygen Concentration.” The reference continues “If the Limiting Oxygen Concentration is below 5 per cent, the plant shall not operate above 40% of the Limiting Oxygen Concentration” (Cunliffe, 2001).

Additionally, NFPA 69 specifies that the fuel concentration only reach 25% of the LFL value, or 60% of the LFL for gaseous systems with automated in-line sensors and controls (National Fire Protection Association, 2019 Edition) (Zlochower & Green, 2021); regulations that apply to inerting vent gases in the maritime industry using flammable gases specify safety factors that can be applied to the UFL, such as raising the flammable content to 170% of the UFL or 10 percentage points higher (US Code of Federal Regulations). Using safety factors such as these are a long-standing practice in many areas.

The concentration of oxygen may be the parameter most amenable to change in geothermal NCG. Lowering the air ingress into the NCG can serve two purposes: reducing the oxygen concentration below the LOC_{mix} and/or reducing the dilution of the fuel portion of the NCG such that it is above its UEL_{mix}, and thus is too rich to burn. Changing the routing of gland steam can result in a significant reduction of oxygen from the NCG. Proper mechanical maintenance of vacuum systems is also important.

Dealing with oxygen originating from cooling water in direct-contact condensers in an existing plant is more challenging. The cooling water is likely saturated with air (oxygen and nitrogen) in the cooling tower, and given the warm, vacuum conditions in the condenser, it is usually assumed that nearly all of the oxygen in the cooling water is stripped into the NCG. This can increase the fraction of oxygen in the NCG significantly.

In the design of new facilities, consideration should be given to the effect of the DCC on the flammability properties of the NCG. For NCG known to be fuel-rich, a DCC may be a risky choice. For existing plants with DCCs, considering changes which might result in fuel-enrichment in the NCG, such as CO_2 recovery, should be carefully weighed, and may not be practical.

There is little that can practically be done regarding the fuel content of the NCG, so in the consideration of CO_2 recovery, the change in LEL, UEL, and LOC of the NCG residue gas must be carefully analyzed. Because the fuel content of the NCG is fixed (other than the potential removal of H_2S prior to CO_2 recovery), the main issue that can be adjusted is the amount of oxygen that is allowed into the NCG. it may also be possible to add large enough amounts of air, to dilute the concentration fuel (plus inerts) to below the LEL_{mix}.

Changes that may be considered form limiting air ingress to the NCG are highly dependent upon the mechanical details of the geothermal facility; some of the more direct options for reducing oxygen in the NCG include:

- Replace DCC with surface condenser. This would prevent air ingress to the NCG due to cooling water saturation with air.
- Add a tempered water loop. Two cooling water loops would be established. One loop would circulate water from the DCC to a new surface heat exchanger. The other loop would circulate water from the new surface exchanger to the cooling tower. This arrangement would prevent air ingress to the NCG due to cooling water saturation with air.
- Fix leaks in equipment in the parts of the condenser system that are under vacuum.
- Reroute gland steam. Gland steam handling can be complicated if the steam contains H_2S. Gland steam from the vacuum portion of the seal may contain oxygen from air, and avoiding adding it to the condenser system can substantially reduce O_2 in the NCG.

Other, less obvious methods could be considered for dealing with this issue, such as:

- Deaerate the cooling water after the cooling tower and before the DCC.
- Control cooling water flow rate to condensers to avoid using more than necessary.
- Dilute the NCG with an inert gas.
    - Recycle CO_2 recovered from the NCG.
    - Add some other inert gas (N_2).
    - Slip some steam around the final condenser.
    - Recycle flue gas from an H_2S abatement incinerator

5.2 Handling Explosive Gas Mixtures

Handling explosive gas mixtures is usually considered an unacceptable risk, and it is common in most of the processing industries to adjust process concepts and designs as necessary to avoid the generation of an explosive gas mixture. However, there are situations in which the generation of such a mixture cannot reasonably be avoided, and there are situations where there is a high degree of uncertainty or variability in the composition and conditions of gas streams being produced. Additionally, there are processes where avoidance of the issue is a moot point, such as in the generation of chemicals that are unstable and/or do not require an oxygen source (e.g., acetylene, ethylene oxide) to ignite or explosively decompose.

Examples of industries where designs are put in place to handle explosive gas mixtures which may possibly be present include pulp / paper (TAPPI, 2014) (U.S. Chemical Safety and Hazard Investigation Board, 2018) (Lin, 2021) and steel degassing (Zoellig, Grob, & Schiller, 2014). Gas mixtures in the explosive range are sometimes defined as “Zone 0”. Design for handling such gases are the most stringent, typically requiring multiple redundant safety features and intrinsically safe equipment (Davies & Heidermann, 2013), as shown in Figure 7. By definition, a gas in the explosive composition range only requires that an ignition source be present for the gas to ignite. Therefore, when designing systems for handling of gases which may be in the explosive composition range, elimination of any possible ignition source and provision of adequate venting for an ignition event are essential. Good design practice may also logically include minimization of pipe length and the volume of systems containing such mixtures, with the mixture neutralized or destroyed (e.g., burned in a controlled fashion) as quickly as possible.

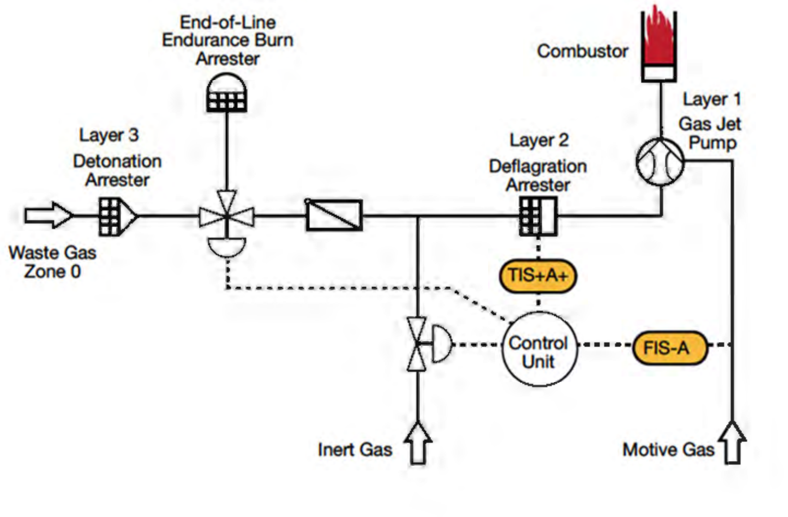


Figure 7. Example of Design to Handle and Destroy an Explosive Gas Mixture (copied from (Davies & Heidermann, 2013))

In plants equipped with burn and scrub systems, there is a built-in ignition source – the burner. Given that the destruction of the NCG by controlled combustion is desired, the presence of that ignition source may be deemed acceptable assuming that sufficient care is taken (such as shown in Figure 7) to prevent propagation of the flame upstream and that other safeguards (e.g., hydraulic barriers) are implemented to control any ignition that occurs.

Other ignition sources apart from the burner may also be present in the vent gas piping, such as static and friction. Additionally, as mentioned in Section 1, in some geothermal plants with DCC's iron chelate may be added to the cooling water for secondary H_2S abatement (Bedell & Hammond, 1987). The same (or similar) iron chelates are also used in some of the redox primary H_2S abatement processes (e.g., LOCAT, SulFerox, Sulfint, Valkyrie). One ignition source that has been theorized to possibly be present in geothermal NCG treatment units using iron chelates is pyrophoric iron sulfides. Iron sulfide (FeS_x) may, depending upon its exact molecular formula, surface area, particle size, and crystalline form, be pyrophoric – that is, iron sulfide may combust spontaneously when exposed to air at ambient temperatures. Pyrophoric iron sulfides are a well-known issue in the gas treating industry (Spooner, Sheilan, & van Hoorn, 2006).

It has been proposed that iron chelates in cooling water may be carried into NCG vent piping by entrainment from the direct contact condensers. Once in the vent piping, the iron sulfides may form a layer combined with other solids, such as elemental sulfur. Iron sulfides can be produced by the reaction of iron with H_2S or with elemental sulfur (Clark & Dowling, 2016). Elemental sulfur can be formed in the vent piping or be carried in by entrainment with cooling water, and there can react with iron to form iron sulfides. Theoretically, when the pipe surface coating is disturbed (e.g., by changes in flow rate, startup, etc.), pyrophoric iron sulfides could be exposed to the oxygen-containing NCG, resulting in an ignition source. At a few plants where iron chelate was in use for secondary H_2S abatement, piping sections removed from NCG systems and left laying on the ground exposed to the air have been seen to heat up and eventually catch on fire. This observation is consistent with the theory that pyrophoric iron sulfide layers can be a source of ignition in these systems.

Although evidence of pyrophoric iron sulfide seems to have been found in only a limited number of instances, geothermal power plants which use iron chelates, particularly those with direct-contact condensers, should be aware of the potential for the formation of pyrophoric iron sulfides in vent gas piping.

6. Conclusions

This paper presented an overview of the flammability issues related to NCG at geothermal power plants, and how this issue relates to the recovery of CO_2 from the NCG. Oxygen in the NCG often results from air in-leakage from turbine glands and other sources, as well as the oxygen that is stripped from the cooling water with direct-contact condensers. When CO_2 is captured from the NCG, the concentration of flammable species increases and the oxygen present in the stream can make the gas an explosive mixture. In cases with water injection to the reservoir, the NCG may be flammable due to the lower NCG content and relatively constant amount of oxygen in the stream from the air that is stripped from the cooling water and turbine glands. The NCG characteristics can limit the amount of CO_2 that can be captured to avoid having the treated gas be an explosive mixture. Examples of industries where designs are put in place to handle gas mixtures were presented, along with a summary of good safety practices and potential methods for reducing the oxygen in the NCG.

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