DELIVERABLE 3.6
REPORT ON THE SPECIFICATION AND VALIDATION OF PURIFIED GAS

GECO

GEOTHERMAL
EMISSION
CONTROL

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SUMMARY

Carbon dioxide (CO_2) recycling is a method to reduce carbon emissions from the geothermal sector and to generate additional value. Two different gas separation and purification technologies have been developed within the GECO project as part of Task 3.1. Task 3.3. Deliverable 3.6 addresses the potential end-use of this gas in Iceland, which depends on its purity and possible industrial consumers. Although the cost of carbon capture and purification often hinders its utilization, there are already examples CO_2 utilization from geothermal power plants, such as methanol production and microalgae cultivation in Iceland and greenhouse food production, both in Iceland and New Zealand.

The aim of this deliverable is to provide the specification and validation methods of purified geothermal gas required for potential CO_2 utilization technologies. D3.6 is structured in the following chapters:

- Chapter 1 provides a general overview of carbon capture, utilization, and storage technologies, with a focus on utilization.
- Chapter 2 describes the available CO_2 utilization technologies in Iceland, and when possible, their gas purity specifications and potential contaminants.
- Chapter 3 focuses on the implementation of the two gas purification technologies at the Hellisheiði geothermal power plant and predicted gas compositions of the purified CO_2. This purified gas was then matched with potential end-users.
- Chapter 4 proposes the sampling procedure and analytical methods of components of interest to validate the CO_2 produced from the gas purification technologies.
- Finally, Chapter 5 summarizes the main findings of this study and describes future steps to be taken.

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1. INTRODUCTION

The purpose of GECO is to develop clean and cost-effective technologies for non-carbon and sulphur-emitting geothermal energy across Europe and the world. The carbon dioxide (CO_2) is a potential commercial by-product from geothermal power plants. Carbon dioxide recycling can generate direct financial benefits for the power plant while reducing its emissions and cooling processes. Within the GECO project, usable CO_2 will be generated by two different gas separation and purification methods, described in T3.1; the potential end use of this gas in Iceland depends on its purity and possible industrial consumers. Although cost of carbon capture and purification often hinders its utilization, there are already some examples using CO_2 from geothermal power plant emissions, such as methanol production and microalgae cultivation in Iceland and greenhouse food production, e.g. in Iceland and New Zealand. These cases can provide knowledgefor future expansion of CO_2 utilization from other geothermal sources.

1.1 Deliverable Objectives

The aim of this deliverable is to provide the specification and validation methods of purified geothermal gas required for potential CO_2 utilization technologies. The following objectives will help achieve this:

- Map the CO_2 utilization technologies currently available in Iceland (Ch. 2)
- Specify, when possible, the gas purity of CO_2 required for possible industrial consumers in Iceland (Ch. 2)
- Identify any potential trace elements or components in geothermal gas that might impact its utilization (Ch. 2)
- Match the purified gas from two gas separation and purification technologies developed within GECO to potential end-users (Ch. 3)
- Propose methodology for gas analysis to validate the gas purity during the testing of both purification technologies at the Hellisheiði geothermal power plant (Ch. 4)

This report is a product of T3.3 as well as the deliverables D3.1 and D3.2 (T3.1), in which the two gas purification technologies were described. The two technologies and the purity of gas produced will be tested in WP5.

1.2 Carbon Capture, Utilization, and Storage

Carbon capture, utilization, and storage (CCUS) technologies can reduce and remove CO_2 from the atmosphere and from point sources, which account for 50% of the global emission budget. The process consists of separating CO_2 and either transporting to a storage location for long-term isolation from the atmosphere or recycling of CO_2, for example, into valuable chemicals [1]–[5]. The capture of carbon is as yet still the most energy-intensive and expensive step [2]. The different technologies and applications of the CCUS process are summarized in Figure 1-1. Applications for CO_2 utilization technologies will be the focus of this report.
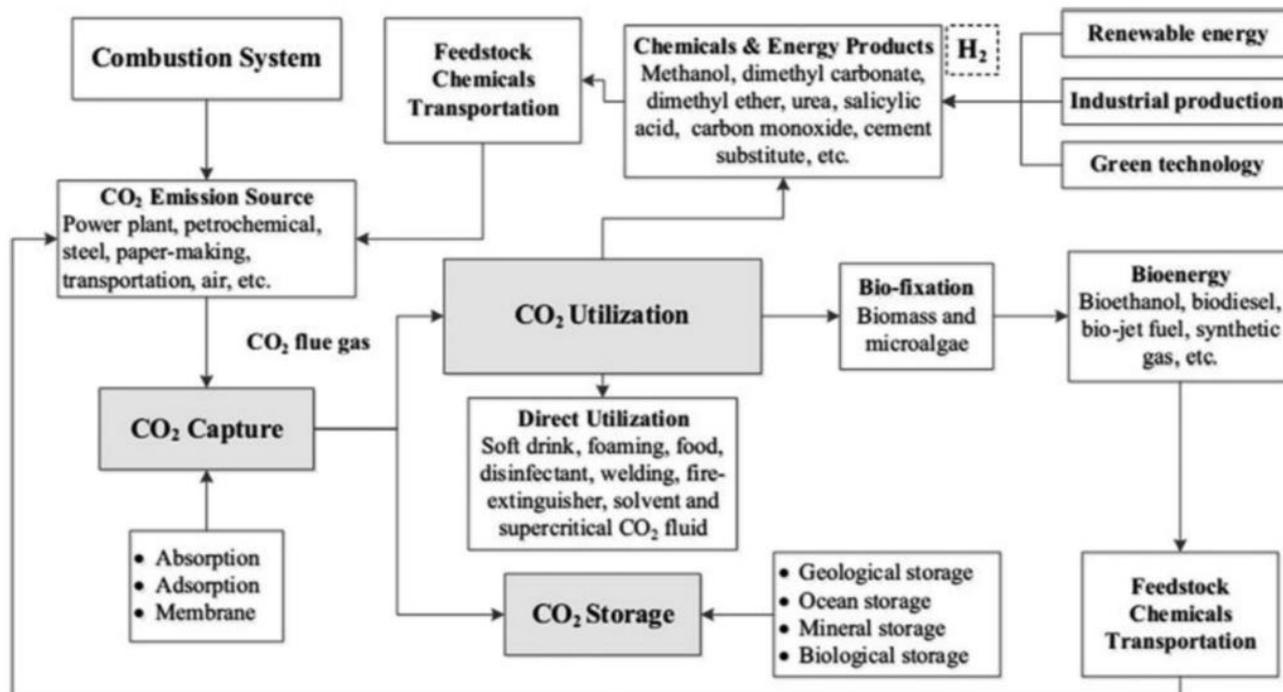
Figure 1-1. Emerging energy and industrial structures with zero carbon dioxide emission. Taken from [6].

1.2.1 CO₂ Capture

Carbon capture technologies can remove CO_2 directly from a point source's flue gas streams (post-combustion), before the gas is combusted to generate power (pre-combustion), or directly from the air (direct air capture; DAC). The types of gas separation technologies are absorption, adsorption, or membrane. Absorption involves both physical and chemical solvents, in which the CO_2 is absorbed to and then subsequently removed from. It has a high energy requirement for solvent regeneration. Adsorption also selectively removes CO_2 using either high-temperature or low-temperature materials but those are not yet cost-effective for large-scale operations. The last type of gas separation uses membranes that are more energy efficient and environmentally friendly [2], [5], [7].

1.2.2 CO₂ Utilization

By capturing and utilizing carbon, annual CO_2 emissions could be reduced by at least 3.7 Gt, which is equal to approximately 10% of the world's annual emissions [6], [8]. Moreover, the revenue generated from the utilized CO_2 can offset capture and implementation costs [8], [9]. However, costs depend largely on the purity of the CO_2 produced and the capture process as well as the energy requirement in CO_2 conversion [8]–[10]. The available CO_2 recycling technologies do not allow for its long-term storage (days to years) [10]; long-term storage methods are described in Section 1.2.3.

Technologies can be separated into two main groups: (a) the direct use of CO_2 (including bio-fixation), or (b) the conversion of CO_2 to energy and chemical products. Several industries already utilize CO_2 directly, such as beverage, food, foaming, disinfectant, welding, fire extinguishing, solvents, extractants, and biomass cultivation (e.g. microalgae). Phase changes can also be involved, e.g. supercritical CO_2 [6], [8].

Microalgae show significant storage potential: 1.8 tons of CO_2 can be fixed per ton of microalgae, but their large-scale cultivation is expensive [6], [9]. In addition, no chemical transformation is needed

during their cultivation [10] and the bio-fixation of CO_2 is accompanied with precipitation of $CaCO_3$. Furthermore, it is better to use the flue gas directly from the emission source as nutrients are consumed during the process. CO_2 concentration levels above 20% reduce productivity so high-quality CO_2 is not necessary. It is imperative to carefully manage the pH throughout cultivation; other factors to consider include the amount of CO_2, nutrients, temperature, and light source [6], [9].

The concept behind utilizing CO_2 to produce materials in the chemical industry was first developed in the 1970s [10]. Now decades later, several technologies exist to create value-added chemicals at a profit. Around 130 Mt CO_2 are used annually to manufacture urea, salicylic acid, cyclic carbonates and polycarbonates, with urea consuming most of the CO_2 industrially [11]. This contribution in reduction, however, is not large enough, but CO_2 conversion to energy products is believed to be an alternative for consuming more CO_2. While the production of products such as methanol, dimethyl carbonate, dimethyl ether, and carbon monoxide (CO) is promising, the big challenge is the competition with fossil fuels [6].

1.2.3 CO_2 Storage

The types of carbon storage possibilities are geological, ocean, mineral, and biological. The first option, geological storage, has been extensively researched [12] and has many natural and industrial analogues [13]–[15]. CO_2 can be stored underground for long periods of time by injecting into deep geological formations, such as depleted oil and gas reservoirs, coal formations, and saline formations. The injected CO_2 becomes less mobile over time as a result of multiple trapping mechanisms, structural and stratigraphic trapping followed by solubility and mineral trapping [1]. Ocean storage entails transporting CO_2 via pipelines or ships to an ocean storage site and injecting at depths greater than 1,000 m into the ocean's water column or at the sea floor [16], [17]. CO_2 would subsequently dissolve and disperse in the deep ocean waters [1]. Mineral carbonation is the fixation of CO_2 as stable carbon minerals upon the reaction with metal oxide bearing materials, like silicate minerals, whether ex situ or in situ [15], [18]. In situ carbonation, successfully demonstrated in the USA [19], [20] and Iceland [21], [22], involves the direct injection of CO_2 into the subsurface, where it reacts with the silicate minerals in, for example, mafic and ultramafic rocks [18]. Afforestation and reforestation, soil carbon sequestration, bioenergy with CCS, and biochar are examples of different types of biological storage, where CO_2 is stored by continual or enhanced biological processes [23], [24].

2. CO_2 UTILIZATION IN ICELAND

Iceland has been utilizing geothermal resources for electricity generation and district heating for almost a century; 61% of the country's energy supply is from geothermal sources. Their government is also set to increase the utilization of renewable energy resources, like geothermal or hydropower, not only for power generation, but also direct uses and the transport sector [25]. The following sections detail examples of utilizing CO_2 emitted from geothermal power plants or sources.

2.1 Microalgae

There are two examples of microalgae cultivation in Iceland by Blue Lagoon Ltd and Algaennovation, which fall into the direct use of CO_2 category of CO_2 utilization. Blue Lagoon Ltd. has been cultivating the microalgae *Cyanobacterium aponium* for their skincare products [26] and had run experiments to test productivity differences between commercial 99.99% (4N) CO_2 and geothermal gas from the Svartsengi geothermal power plant (run by HS orka). The latter was slightly diluted with atmospheric air (~8%) to a composition of about 90% vol CO_2 and 2% vol hydrogen sulphide (H_2S), but originally had 97% vol CO_2 (Table 2-1). The pH of the geothermal fluid was on average 7.9 but was lowered to 7.5 by the constant injection of CO_2 (whether pure or geothermal) through the automatic control of its flow into a closed photobioreactor. Experiment results showed similar productivity between both types of gases and no detrimental effects by H_2S on the equipment. The Blue Lagoon Ltd has been using the geothermal gas from Svartsengi without purification instead of purchasing the bottled CO_2 gas since this study [27].

Table 2-1. Chemical composition in vol% of geogas and pristine geothermal NCG **[27]**.

Component [vol%]	Geogas	Geothermal NCG
CO_2	89.61	96.56
H_2S	2.01	2.17
N_2	5.94	0.54
O_2	1.62	< 0.01
Ar	0.08	0.01
H_2	0.71	0.71
CH_4	0.02	0.02

Algaennovation is planning to cultivate high omega-3 algae using geothermal gas from the Hellisheiði geothermal power plant. The algae would be used as a feedstock for fish larvae, crustaceans, and mollusks. They would be using the gas stream after purification from the burn and scrub method, further described in Chapter 0. Like the Blue Lagoon Ltd., Algaennovation would be controlling factors such as the pH, CO_2 levels, nutrient concentrations, and minimizing concentrations of H_2S.

2.2 Methanol

There is one example of CO_2 conversion into fuel products in Iceland, the production of methanol by Carbon Recycling International (CRI), an Icelandic-American company. This renewable methanol, or Vulcanol, is sold commercially to clients in Europe and China, and delivered by sea. Methanol can be

used directly as a blend component for standard petrol or a feedstock for biodiesel from esterified vegetable oil or animal fats. Since 2012, CRI has operated a pilot plant that used the CO_2 emissions of non-condensable gases (NCG) in the steam from the Svartsengi geothermal power plant run by HS Orka. The hydrogen (H_2) required in the process is also produced locally by electrolysis of water. 1.7 million liters of methanol are produced annually, with plans to expand up to 5 million liters from about 6000 tons of CO_2 [25].

CRI states that they have minimum requirements for their methanol production so that further purification is limited, shown in
Table 2-2. They also require the feed gas be free of particulate matter and tars, but it may be delivered saturated with water at temperatures below 40 °C.

Table 2-2. CO_2 purity specification at CRI plant boundary (methanol loop).

Contaminant	Maximum concentration at CRI boundary limit
N_2 [vol%]	71.9
O_2 [vol%]	11.1
$H_2S + SO_2$ [ppm]	14.7
Cl & other halogens [ppb]	0.08
Fe, Ni (carbonyls) [ppb]	1.3
As, Hg [ppb]	0.4

2.3 Food and Beverage Industry

Since 1986, a facility at Hæðarendi in Grímsnes, South Iceland, has produced commercial liquid CO_2 derived from geothermal fluid of two gas-rich wells. The gas discharged from both wells is nearly pure CO_2 (Table 2-3), but it is further purified at the production site. About 3000 tons of CO_2 are produced annually, which accounts for a large share of the Icelandic market. CO_2 is sold by ÍSAGA, a chemical distributor now owned by Linde, to carbonated beverage and other food manufacturers as well as greenhouses around Iceland to enrich the atmosphere [25].

Table 2-3. Gas composition in vol% of samples taken by ÍSOR from Hæðarendi **[28]**.

Sample #	20150242	20150243
Well	HE-7	HE-2
CO_2	99.34	99.47
H_2S	0.034	0.026
N_2	0.561	0.441
O_2	< 0.001	0.007
Ar	0.010	0.008
CO	0.001	< 0.001
H_2	0.007	0.006
CH_4	0.053	0.042

Each facility producing CO_2 for the food and beverage industry, like ÍSAGA and Hæðarendi, has a documented system for quality management following the model in the ISO 9000, Quality management, or ISO 22000 (HACCP) series of standards, and preferably certified. According to the European Industrial Gases Association, the CO_2 supplied to the beverage and food industry should meet the specifications given in Table 2-4. Possible impurities found in natural wells and geothermal sources are also listed in Table 2-5. It is important to note that the raw gas composition from a natural well/geothermal source will vary with time and this should be taken into account [29].

Greenhouses in Iceland are currently purchasing their CO_2 from ÍSAGA, which originates from the two CO_2-rich wells at Hæðarendi, to stimulate plant growth. A New Zealand study from 1997 notes that the use of geothermal CO_2 is possible, if a purification process is used to reduce the initial H_2S content. Plants and vegetation are very sensitive to elevated H_2S levels in the air. Although some plant species can handle small H_2S concentrations of 0.04 mg/l, all show negative effects at higher H_2S concentrations of 0.4 mg/l. Thus, a required CO_2 purity should be 99.997% and a minimum H_2S concentration of 40 ppm in the CO_2 [30].

Table 2-4. CO_2 specifications for food and beverage grade CO_2 **[29]**.

Component	Concentration
Assay	$\geq 99.9\%$ v/v
Moisture	≤ 20 ppm v/v
Ammonia	≤ 2.5 ppm v/v
Oxygen	≤ 30 ppm v/v
Oxides of nitrogen (NO/NO$_2$)	≤ 2.5 ppm v/v each
Non-volatile residue (particulates)	≤ 10 ppm w/w
Non-volatile organic residue (oil and grease)	≤ 5 ppm w/w
Phosphine[***]	≤ 0.3 ppm v/v
Total volatile hydrocarbons (calculated as CH$_4$)	≤ 50 ppm v/v of which ≤ 20 ppm v/v non-methane hydrocarbons
Acetaldehyde	≤ 0.2 ppm v/v
Aromatic hydrocarbon	≤ 0.02 ppm v/v
Carbon monoxide	≤ 10 ppm v/v
Methanol	≤ 10 ppm v/v
Hydrogen cyanide[*]	≤ 0.5 ppm v/v
Total sulphur (as S)[**]	≤ 0.1 ppm v/v
Taste and odour in water	No foreign taste or odour
Appearance in water	No colour or turbidity
Odour and appearance of solid CO$_2$ (snow)	No foreign odour or appearance

[*] Analysis necessary only for carbon dioxide from coal gasification sources

[**] If the total sulphur content exceeds 0.1 ppm v/v as sulphur then the species must be determined separately and the following limits apply:

Carbonyl sulphide	≤ 0.1 ppm v/v
Hydrogen sulphide	≤ 0.1 ppm v/v
Sulphur dioxide	≤ 1.0 ppm v/v

[***] Analysis necessary only for carbon dioxide from phosphate rock sources.

Table 2-5. Possible trace impurities from natural wells/geothermal sources **[29]**.

Component
Aldehydes
Benzene
Carbon monoxide
Carbonyl sulphide
Cyclic aliphatic hydrocarbons
Dimethyl sulphide
Ethanol
Ethers
Ethyl acetate
Ethyl benzene
Hydrogen sulphide
Ketones
Mercaptans
Mercury
Methanol
Radon
Sulphur dioxide
Toluene
Volatile hydrocarbons
Xylene

3. CCU AT HELLISHEIÐI GEOTHERMAL POWER PLANT

Carbon storage using the CarbFix method [31] has been successfully demonstrated at two sites at the Hellisheiði geothermal power plant (run by ON Power) in SW Iceland (Figure 3-1): (a) CarbFix - a pilot site with pure CO_2 and CO_2-H_2S test gas injections in 2012 [21], [32] and (b) CarbFix2 - an industrial site where there is a continuous CO_2-H_2S gas injection since 2014 [22], [33]. The geothermal power plant operates about 35 production wells, where the discharged two-phase fluids are separated, and the subsequent steam fed into the seven turbines of the power plant [34]. About 50,000 tons of a geothermal gas mixture is emitted from these turbines [22].
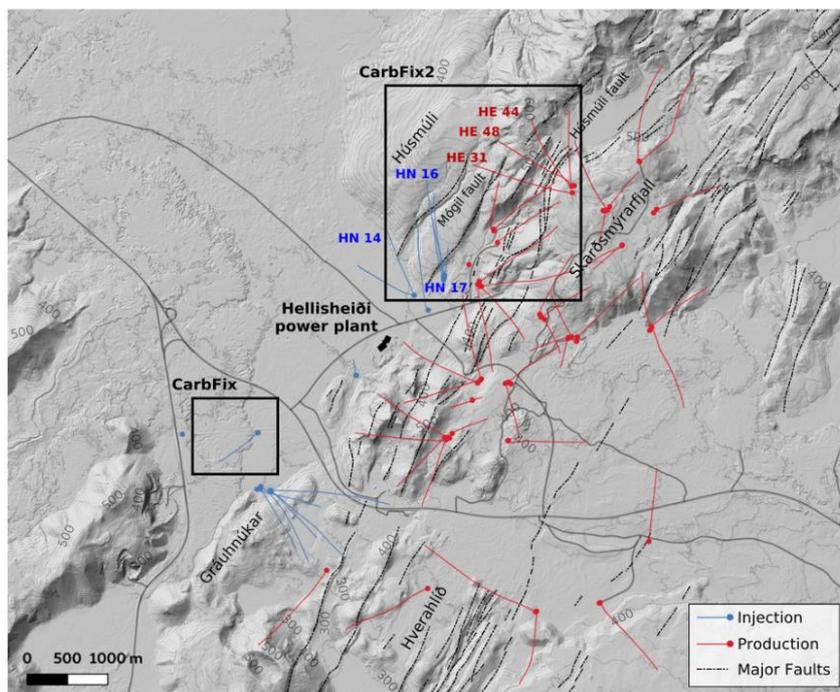
Figure 3-1. Map of the CarbFix and CarbFix2 sites at the Hellisheiði Geothermal Power Plant in SW Iceland; production wells are in red and injection wells in blue. Modified from **[33]**.

Since June 2014, a portion of the geothermal gas from the turbines is diverted to a specific capture and re-injection process, following the CarbFix technology. CO_2 and H_2S are dissolved into condensate water from the power plant [34], as these acidic gases are much more soluble in water than the other geothermal gases, In addition, the condensate is cooled from around 45 °C to 15 °C to further increase the solubility [35]. The condensate is sprayed into the top of a 12 m absorption column with 6 m packing (scrubbing tower) under controlled pressure, temperature, and water and gas flow rates and interacts with an exhaust gas stream [34]. This dissolves the CO_2 and H_2S while the less soluble, non-acidic gases (e.g. H_2, nitrogen N_2, argon Ar, methane CH_4) are vented into the atmosphere. The scrubbing tower is currently optimized to recover 56% of the CO_2 and 97% of the H_2S from the exhaust stream [22], thus the remaining CO_2 and H_2S is presently also emitted. Table 3-1 shows the gas compositions before and after the scrubbing tower. Cases 1 and 2 refer to range of concentration over extended operational period of the plant. The gas-charged condensate from the CarbFix scrubbing tower is then re-injected back into the geothermal reservoir to mineralize as carbonates and sulphides [22], [33].

Table 3-1. Composition in vol% of geothermal gas before and after the CarbFix scrubbing tower.

Component	Before	After	After
[vol%]		Case 1	Case 2
CO_2	57.5	61.7	53.5
H_2S	22.0	0.60	3.0
H_2	14.3	30.1	33.1
O_2	1.0	1.0	1.7
N_2	5.0	5.5	8.4
CH_4	3.7	0.24	0.26

3.1 Gas purification technologies

Two additional gas capture technologies, in order to purify the remaining geothermal gas that is currently vented to the atmosphere from the scrubbing tower, have been developed within the framework of GECO (T3.1). These technologies will be installed at Hellisheiði and testing conducted later in the project (WP5) with the aim to commercialize the purified gas for possible industrial consumers.

An **amine-based low temperature purification technology** was developed by CIRCE. It consists of an amine-based absorption stage, where H_2S levels can be reduced below 1 ppm using a selective solvent. The sweet gas (about 64% CO_2) is then sent to a compression and liquefaction stage to obtain a CO_2 liquid stream at 60 bar and -55 ℃. Fixed bed adsorbents are also used to remove primarily water. The resulting CO_2 liquid stream will have a purity of 99.5% while the gas phase is rich with H_2 (about 80% H_2, 12% CO_2) and small amounts of H_2S, N_2, and CH_4. Further details can be found in D3.1 and D3.7.

A second **purification technology, burn and scrub**, was developed by Reykjavík Energy (OR). The flammable species are removed and H_2S converted into sulphur dioxide (SO_2) with an incinerator. Then, the SO_2 is scrubbed from the gas stream using water. The resulting gas stream would contain approximately 30% CO_2 and 70% N_2. The composition of CO_2 could potentially be up to 70% and liquefied with an oxygen generator. Further details can be found in D3.2 and D3.8.

3.2 Potential End-Users for CO_2

The CO_2 produced from the amine-based purification technology would be close to but not quite at beverage- and food-grade CO_2 quality as specified in Table 2-4. The predicted levels of H_2S and CH_4 is not below allowable concentrations and CO_2 levels would be just under the required $\geq$ 99.9%. Nevertheless, the Blue Lagoon's success in using geothermal sourced CO_2 with over 2% vol H_2S for microalgae cultivation indicates that this purified CO_2 could also be utilized for microalgae cultivation. As mentioned earlier, Algaennovation is also planning to utilize the gas stream from the burn and scrub purification technology at the Hellisheiði plant. Yet, if additional purification steps were taken to further reduce concentrations of H_2S and CH_4 in amine-based system, then the CO_2 could likely be sold at beverage- and food-grade quality to ÍSAGA. Of note is that most of the trace impurities for beverage- and food-grade CO_2 quality listed in Table 2-5 would not be expected in gas

from geothermal sources, but rather from natural gas wells. Thus, of those listed, only H_2S, SO_2, CO, and mercury (Hg) are expected.

The CO_2 produced from the burn and scrub method might have fewer customers for CO_2 utilization, as it would be diluted up to 70% with N_2. Greenhouses already dilute food-grade quality CO_2 with air, which is composed of 78% N_2, before adding to the greenhouse to boost plant productivity. Therefore, this CO_2 could potentially be directly utilized without additional air dilution by greenhouses. Microalgae cultivation companies, like Algaennovation, may also be able to utilize this CO_2-N_2 gas mixture, although further tests would be needed to determine any possible effects of N_2 on the microalgae and the optimal amounts for said gas mixture. There could be additional uses in the food industry if the CO_2 purity is up to 70% and liquefied.

4. METHODOLGY FOR VALIDATION OF PURIFIED GAS

To verify the purified CO_2 from the two gas purification technologies proposed in Section 3.1, sampling and subsequent analysis of relevant components would take place as described below. This is also summarized in Table 4-1.

As the Hellisheiði power plant has wet-steam wells (fluid withdrawn from > 100 °C liquid-dominated geothermal reservoir), both the liquid and vapor fractions need to be collected from the geothermal production wells. A detailed sampling procedure for wet-steam wells can be found in Arnórsson et al. [36] in which a Webre steam separator is used to collect the liquid water and steam phases separately (Figure 4-1). It is important to highlight that steam samples not be contaminated with liquid water, as also pointed out by Giroud [37] (and vice versa). This can be verified by analysing the steam condensate for sodium or potassium [36].
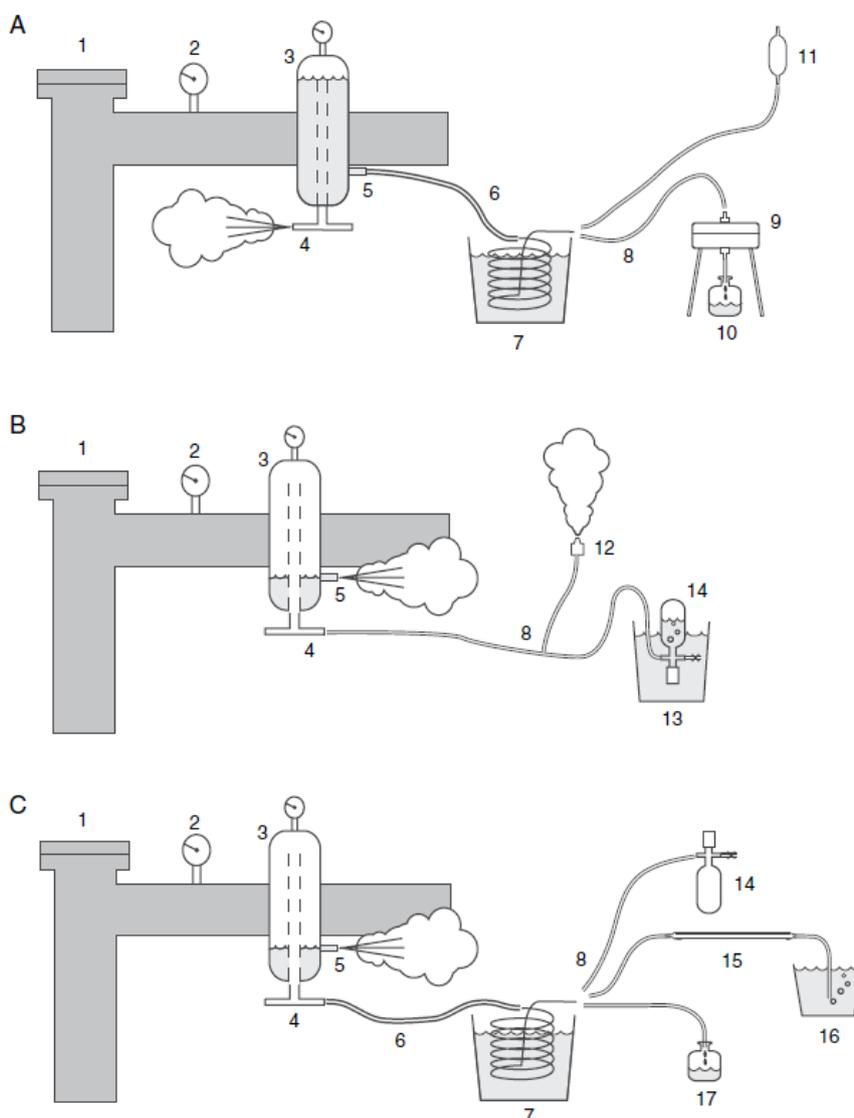
Figure 4-1. Equipment for the sampling of water and steam (gases) from a wet-steam well discharge using a Webre steam separator. Further explanation found in Arnórsson et al. **[36]**.
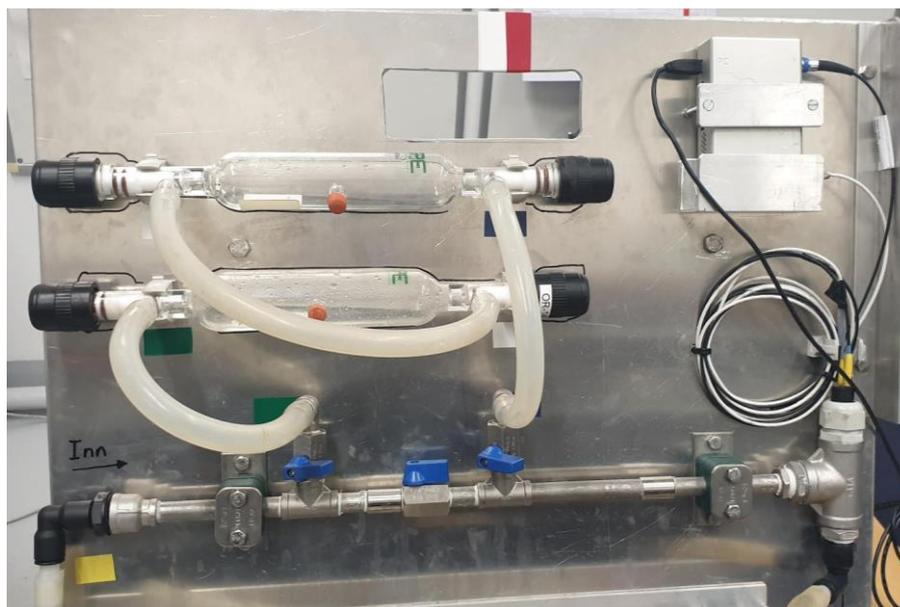
Figure 4-2. Gas sampling procedure from CarbFix scrubbing tower and burn and scrub purification technology. Taken by Reykjavik Energy (OR).

Gas from both the CarbFix scrubbing tower and the burn and scrub purification method will sampled through a needle valve from a pipe exiting at 6 bar-a and 1 bar-a, respectively, as shown in Figure 4-2. In the case of the scrubbing tower, the pressure would then be lowered to 1 bar-a. Silicon tubing connects first to a gas bottle and then to water bottle, used to observe the flow rate. Oxygen levels are monitored throughout to quality check the sampling procedure.

Evacuated Giggenbach bottles are used to obtain steam samples and contain a solution of either NaOH or KOH. The majority of the gas phase in geothermal steam is most often CO_2 and H_2S (> 90% by volume), which dissolves into the bottle's alkaline solution, while the remaining gases (H_2, CH_4, N_2, O_2, Ar) are concentrated in the head space above the solution. These are analysed by gas chromatography (GC), and the CO_2 and H_2S in the steam condensate are determined by titration. Of potential interest for beverage- and food-grade quality CO_2 (Table 2-4) is to also determine the CO content. However, the collection of CO using a hydroxide solution leads to its reaction with H_2S in the alkaline solution (unless cadmium (Cd) acetate is added to precipitate CdS to stop this reaction) and subsequently lower analytical values. Thus, it would be necessary to immediately separate the CO from the alkaline solution by transferring it to another evacuated sampling bulb [36]. If CO is collected with empty pre-evacuated bottles, a GC with a specific detector for reducing gases has to be used (by methanization). Samples taken for hydrocarbons would be also analysed by GC, although heavier hydrocarbon gases would require analysis by GC-MS (mass spectrometry) [38].

Both proposed gas purification technologies (and CO_2 utilization technologies) do not currently identify potential contamination from trace elements in steam that could impact subsequent utilization. Nevertheless, generally volatile components like H_2S, CO_2, and H_2 partition upon boiling within the well with the vapor phase having very low metal-transporting capacities [39]. If high concentrations of trace elements are detected, these could be considered as carry-over from the liquid phase to vapor during sampling, especially if they are not expected to partition significantly into the vapor phase. Steam samples from the nearby Nesjavellir geothermal power plant (also run by ON Power) were analysed with several elements above detection (e.g. aluminium, boron, chromium, manganese, strontium) [37]. Semi-volatile elements like chloride, boron, and silica in addition to non-metals and metalloids like

antimony, arsenic and selenium [39]–[43] may also be present in geothermal steam without any moisture or brine carry-over. However, the Hellisheiði plant uses a brine pH modification system to increase the pH and decrease scaling. This along with the system's operating pressure can strongly influence vaporous carry-over of said elements [39].

Little is known about the trace element composition of geothermal steam from the Hellisheiði power plant. Trace elements from steam vents at other geothermal areas in Iceland have been analysed by collecting the steam into a series of condensation traps with a gas pump at the end of line to control the flow for 3-4 hours. The traps consisted of two 1-liter polypropylene bottles, a Teflon safety trap, and two Teflon traps with Teflon chips and NaOCl; the condensate in the polypropylene bottles was combined, filtered and acidified, and the condensate in the Teflon traps degassed, oxidized using UV light, then filtered and acidified. These samples were then analysed by inductively coupled plasma mass spectroscopy (ICP-MS) [44].

Mercury is of interest to food- and beverage-grade quality CO_2 but can be difficult to measure due to its volatility. One proposed method to determine Hg is to add an oxidizing agent, such as $KMnO_4$, to the sample for analysis, which is carried out by reduction, gold amalgamation of the element Hg, heating, and flameless atomic absorption spectroscopy (AAS) [45]. However, Hg can also be analysed by atomic fluorescence spectroscopy (AFS), thereby eliminating the use of chemicals/additives and complicated digestion procedures, as described above, which are also time consuming [46], [47]. Moreover, vapor analysers have developed to obtain a sample on-site, which can be combined with a portable AFS to allow for the immediate analysis of Hg [48]–[50].

SO_2 is another component of potential interest, however low concentrations are expected. As it stands, a disadvantage of using Giggenbach bulbs with NaOH is that the sulphur species (primarily H_2S and SO_2) would be dissolved in the NaOH fluid and do not readily differentiate. Thus, a sample could be taken without NaOH, to be able to determine both H_2S and SO_2 [45]. Alternatively, the total sulphur can be analysed by gravimetry by using $BaCl_2$ to precipitate $BaSO_4$ after the oxidation of the solution; the speciation into SO_2 and H_2S is obtained by the average oxidation state of sulphur assuming that the content of elemental sulphur and sulphuric acid is negligible. In order to either preserve the original H_2S content, or measure it directly, a second container filled with Cd^{+2} or arsenic-spiked alkaline solution could be used [38], [51]. Other methods would be either to analyse the total sulphur by inductively coupled plasma atomic emission spectroscopy (ICP-AES) or to analyse SO_4 after oxidation by ion chromatography (IC).

Table 4-1. Proposed analytical methods for components of interest (*or possible interest) for CO_2 utilization.

Component	Phase	Container	Analytical Method
CO_2	Steam Condensate	Gas bottle	Titration
H_2S	Steam Condensate	Gas bottle	Titration
H_2	Gas	Gas bottle	GC
O_2	Gas	Gas bottle	GC
N_2	Gas	Gas bottle	GC
CH_4	Gas	Gas bottle	GC
Ar	Gas	Gas bottle	GC
CO	Gas	Gas bottle w/out NaOH	GC
SO_2 (Total S)	Steam Condensate	Separate gas bottle or container	ICP-AES or IC
Metals & metalloids*	Steam Condensate	Plastic bottle or condensation traps	ICP-MS
NH_3	Steam Condensate	Plastic bottle	Spectroscopy or Ion Selective Electrode
Hydrocarbons (C2-C4)	Gas	Gas bottle w/out NaOH	GC-MS
Heavier Hydrocarbons	Steam Condensate	Gas bottle w/out NaOH	GC-MS
Hg	Gas	Vapor Analyzer	AFS

5. CONCLUSIONS

This deliverable presents specifications and validation methods of purified geothermal gas from two gas purification technologies for potential CO_2 utilization technologies. A literature review was conducted of current CO_2 utilization technologies, and which technologies were available in Iceland in addition to the different gas purity specifications, identifying also potential contaminants. Based on this, the predicted CO_2 produced from the two gas purification technologies developed within the GECO project were matched with potential end-users. Lastly, sampling and analytical methods were proposed to validate the purity of the CO_2.

The main findings of this work are:

- Current CO_2 utilization technologies in Iceland consist of methanol production, microalgae cultivation, and production of high-quality CO_2 for the beverage and food industry, including greenhouse food production.
- The predicted CO_2 from the two gas purification technologies (amine-based absorption and burn & scrub) could be utilized for microalgae cultivation and food production in greenhouses. If further purification steps are taken, then the purified gas could potentially be sold to ÍSAGA as food- and beverage-grade quality CO_2, like the CO_2 produced from Hæðarendi, or as liquid CO_2.
- The proposed analytical methods to validate potential components of interest in the purified CO_2 for further utilization are summarized in Table 4-1, mainly by titration, GC, and ICP for major and minor components as well as a portable AFS for Hg.

Future steps involve the sampling and analysis of geothermal gas before and after the two gas purification technologies to validate the purity of the CO_2 and its potential end-users. In addition, there is limited knowledge of trace elements in geothermal steam from Icelandic power plants and whether this would be of concern for CO_2 utilization technologies. Therefore, obtaining the trace element composition of gases from the Hellisheiði and Hæðarendi production wells, the CarbFix scrubbing tower, and purification technologies could help evaluate whether certain elements would negatively impact its utilization as a higher quality CO_2, for example, in the food and beverage industries. The results from this work could be of use for future development of CO_2 utilization technologies in the rest of the geothermal industry.

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