Purification of Geothermal Gases for Use in Pilot and Demonstration Scale Facilities

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ABSTRACT

Geothermal non-condensable gases (NCGs) represent a promising and underutilised source of CO_2 and CH_4 that has potential application in horticulture and microbial cultivation, among other industries. However, these gas streams contain H_2S and mercury that can inhibit microbial and plant growth or compromise biomass safety. Effective removal of these substances is essential, yet many existing treatment technologies are prohibitively expensive, overly complex, or generate excessive solid or liquid waste—making them unsuitable for small-scale applications.

This study draws on work conducted during the conceptual design phases of a pilot-scale photobioreactor utilising geothermal CO_2 and CH_4 to grow extremophilic microbes, and of a geothermal CO_2 supply for glasshouse CO_2 enrichment. The facilities considered are a 1000 L pilot-scale bioreactor, and a 1 hectare, venlo-style glasshouse. This study reviews purification technologies currently in use, assesses their viability at the relevant scales, and presents practical and low-cost approaches for purifying geothermal gases that are less well-known than systems for large-scale purification.

The results demonstrate the technical feasibility of purifying geothermal gases for a pilot scale bioreactor without costly infrastructure, high chemical consumption, or the generation of substantial solid or liquid waste. The CO_2 supply for a 1-ha glasshouse requires H_2S removal on the order of 0.1 tonne/day, nearing the threshold where systems producing elemental sulphur are often recommended. Optimal process selection must therefore consider several factors specific to the glasshouse site. This study aims to support the development of sustainable bioproduction systems that utilise geothermal NCGs and the findings are generally applicable to pilot-scale and demonstration-scale efforts in gas purification and conversion.

1 INTRODUCTION

Geothermal power generation typically produces a stream of non-condensable gases (NCGs) that is mainly CO_2, with smaller amounts of H_2S, CH_4, N_2, and trace impurities such as mercury and volatile organic compounds (VOCs). In New Zealand, standard practice has been to vent most of these gases directly to the atmosphere. This approach overlooks the potential value these gases could provide if captured and used productively.

Liquid carbon dioxide is expensive in New Zealand relative to prices internationally. The high CO_2 concentrations in geothermal NCGs make them attractive as a local source for glasshouse horticulture (ESMAP 2022), where supplementation can boost plant growth and yields, or for use in bioreactors to produce microbial biomass (Paci, et al. 2021). In microbial cultivation, the CH_4 in the NCGs can also be used to grow methanotrophs. Recent research has highlighted the benefits of co-culturing methanotrophs and microalgae, suggesting the presence of CH_4 can improve overall project economics. Both applications offer opportunities to convert a currently vented waste stream into valuable products. However, some constituents limit direct use without treatment due to their toxicity or potential to inhibit microbial or plant growth.

Development of new uses of geothermal NCGs can be expected to follow a phased approach, typically starting at pilot scale, moving through demonstration, and eventually reaching commercial scale. However, there is little published information on gas treatment processes at the smaller, early stages of development, including their costs and practical constraints. This lack of information adds risk and uncertainty, discouraging investment. In the New Zealand context, environmental regulations generally allow direct venting of H_2S, which alters the cost–benefit balance of treatment options. As a result, methods designed for H_2S emission abatement at large scale may not be most cost-effective for smaller-scale applications where limits are less stringent.

There is an existing body of literature on the purification of geothermal gases for CO_2 production at power station scale (Chaves 1996, Kiptanui 2015, Padilla 2007) and a number of reviews focused on H_2S removal. Studies on H_2S removal generally provide technology recommendations based on sulphur-loading ranges. Below about 0.1 tonnes S per day, reviews point to liquid or solid scavengers and basic alkaline scrubbing as the simplest, lowest-CAPEX options (Sanopoulos and Karabelas 1997, Mamrosh, McIntush and Fisher 2014b, Rodríguez, Harvey and Ásbjörnsson 2014). For intermediate loads (0.2–15 tonnes S per day), biological or liquid-redox processes such as THIOPAQ or LO-CAT, which produce recoverable elemental sulphur, are recommended (Padilla 2007, Mamrosh, McIntush and Fisher 2014b, Pudi, et al. 2022). When sulphur exceeds 20 tonne/day, economic analyses consistently favour absorption/Claus systems, because scale drives down unit costs and sulphur sales can offset the operating costs (Mamrosh, et al. 2019, McIntush, et al. 2016).

This study examines two near-term opportunities for small-scale use of geothermal gases: (1) supplying a 1000 L pilot bioreactor for microbial cultivation and (2) enriching a 1 ha glasshouse with CO_2. Their CO_2 demand differs by 2–3 orders of magnitude. For a 1-ha glasshouse, the CO_2 demand is around the 2 tonne/day, putting the required H_2S removal rate at around 0.1 tonne/day. This is close to the threshold for favouring processes producing elemental sulphur over simpler processes requiring less capital investment. The pilot-scale bioreactor requires H_2S removal at less than 10 kg /day, well below the ranges considered in previous reviews.

The two cases also have different contexts and objectives, affecting technology selection for the purification process. In the pilot-bioreactor case, the priority is to generate enough biomass for product testing and to gather data for the next techno-economic assessment; scalability is secondary, so the gas-clean-up train can employ simple, possibly non-commercial processes. The glasshouse scenario, by contrast, is intended to demonstrate an integrated geothermal CO_2 supply—encompassing sour-gas compression, mercury removal, bulk and polishing H_2S removal, and short-term storage—to reduce investment risk for larger deployments that have not yet been proven in New Zealand. Potential phytotoxic effects from other trace species, though possible, are relatively unlikely and are not the primary focus.

By outlining expected gas requirements, reviewing current practice worldwide, and estimating costs for treatment technologies, this paper aims to provide practical guidance for stakeholders considering small-scale geothermal gas utilisation.

2 REPRESENTATIVE SMALL-SCALE NCG CONSUMERS

Microbial cultivation in New Zealand carries far more technical and market uncertainty than glasshouse horticulture. Pilot-scale work is therefore essential to prove technical feasibility and generate enough biomass for product testing. Because the treated geothermal gas is fed almost undiluted and comes into direct contact with the culture medium, the potential for trace impurities to inhibit growth or accumulate in the biomass is a key concern. For these reasons, this study adopts a 1000 L photobioreactor as a realistic pilot scale. Operated continuously, it could yield roughly 200 kg/yr (dry wt), sufficient for laboratory analyses and limited product trials. The size is consistent with precedent: a spirulina pilot in Siena, Italy, used 1110 L of culture volume (Paci, et al. 2021), and the ongoing Xphiles project, funded by the Tauhara North No.2 Trust and the Ministry of Primary Industries, targets a 1000 L bioreactor.

While photoautotrophic microalgal or cyanobacterial cultures are expected to be the primary revenue earners, co-cultivation with methanotrophs can be advantageous in some settings: methanotrophs consume the CH_4 component of the geothermal gas alongside the CO_2 required by the phototrophs and help prevent the build-up of explosive CH_4–air mixtures in the reactor headspace. Gas demand at the 1000 L scale is modest relative to the geothermal resource, allowing the pilot to draw a steam/NCG mixture directly from production lines or well-heads instead of relying on low-pressure NCG vents from a power plant.

2.1 CO_2 demand and impurity limits

Table 1 summarises the CO_2 demand for the glasshouse and photobioreactor cases. Glasshouse demand varies diurnally and seasonally. The inclusion of buffer storage with a capacity on the order of one day's consumption is assumed. Although CO_2 liquefaction is unlikely to be economical at this scale, cost data from overseas installations indicate that low-pressure double-membrane gasholders (operating just above atmospheric pressure) provide a reasonable buffer-storage solution. Peak daily consumption for a glasshouse is typically about twice the daily mean across the year, and the purification system is therefore sized for that peak. Actual gas consumption ultimately depends on factors such as crop or microbe selection and the specific glasshouse or bioreactor design.

Table 1. CO_2 demand and impurity limits in the feed gas, i.e., the gas entering the glasshouse and bioreactor.

	Units	Glass-house	Bio-reactor
Peak CO_2 demand	kg/day	3000	10
Mean CO_2 demand	kg/day	1500	10
Annual CO_2 demand	tonne/yr	548	3.65
H_2S limit	mg/kg	1.9	-
Hg limit	mg/kg	1.3	-

The calculations to determine the gas demand and limits in Table 1 are complex and the full details are omitted for the sake of brevity. However, the basis of the calculations is discussed below.

2.1.1 Basis of glasshouse feed gas specifications

Daytime enrichment to 600–1000 ppm CO_2 is often desirable to accelerate crop growth and improve yields for certain crop types. This study targets 800 ppm during daylight hours, and the CO_2 supply rate to achieve this for a tomato crop was determined using the python package GreenLight Plus. The glasshouse concentration depends on the CO_2 supply rate and on the ventilation rate, as well as uptake by the crop. When vents are fully open, with ventilation rates potentially exceeding 20 ACH (Air Changes per Hour), achieving 800 ppm CO_2 is impractical and the CO_2 supply rate is limited to 30 $g/m^2/hr$. Impurity concentrations peak on the coolest days, when vents are mostly closed.

H_2S and elemental mercury (Hg^0) are the chief impurities that must be removed. Worker safety limits H_2S to 5 ppm but plant sensitivity requires more stringent limits. Damage is often observed above 0.3 ppm and has been observed below 0.1 ppm (Dunstall and Graeber 1997). We therefore set 0.03 ppm as the ceiling in the glasshouse atmosphere. This limit, combined with the worst-case low ventilation scenario, define the maximum H_2S concentrations permissible in the incoming CO_2 stream. Geothermal NCG contains mercury mainly as elemental vapour (Hg^0). Deposition of mercury in the glasshouse and its accumulation is a concern, although there is high uncertainty regarding the extent to which this may occur, and phytotoxic data related to concentrations in glasshouse atmospheres are scarce. Without mercury removal, concentrations are predicted to be close to WorkSafe NZ's 8h TWA of 0.025 mg/m^3 when glasshouse ventilation rates are at their lowest, requiring some degree of mercury removal. Upstream reduction of the mercury concentration to less than 1 $\mu g/m^3$ may be necessary to protect the H_2S removal train and avoid contamination of process waste streams.

2.1.2 Basis of bioreactor feed gas specifications

The CO_2 demand for a 1000 L bioreactor producing primarily photoautotrophic microalgae is calculated on the basis of the target growth rate of the microalgae. CO_2 demand per unit of biomass produced has been measured for many commercially produced microalgae or can be estimated based on ultimate analysis of the biomass and assumptions regarding the source of the biomass carbon.

Venting of gases from the headspace of bioreactors is inevitable and increases the gas demand. Excess gases produced in the bioreactor, typically O_2, as well as impurities in the gas supplied to the bioreactor, need to be stripped. For the purposes of this study, conservative assumptions have been made regarding the CO_2 utilisation given that a pilot-scale bioreactor is considered. Little information is available on H_2S and Hg limits for bioreactors. As a conservative estimate, it can be assumed that all Hg entering the bioreactor is assimilated by the microbes and limits can be calculated based on limits placed on mercury in food. Some microalgae are known to be highly tolerant of H_2S and the limits may then be determined by effects on the palatability of the biomass. For the purposes of this study, it is assumed that as much Hg and H_2S should be removed as possible, while keeping costs below NZ$10 k per year.

2.2 NCG Composition and Flow Rates

Table 2 shows the NCG composition assumed in this study. This composition is representative of the gas vented from power stations in the Taupō Volcanic Zone (TPZ).

Table 2. NCG Composition.

Gas	Units	
CO_2	% (wt/wt)	95
H_2S	% (wt/wt)	4.0
CH_4	% (wt/wt)	0.50
N_2	% (wt/wt)	0.46
NH_3	ppm (wt/wt)	200
VOCs	ppm (wt/wt)	150
Ar	ppm (wt/wt)	60
Hg	ppm (wt/wt)	1

Table 3 shows the assumed mass flow rates entering the gas purification system in order to meet the CO_2 demand of the glasshouse and bioreactor.

Table 3. Mass flow rates assumed to enter the gas treatment system. Note that the last four rows are presented in g/day.

Gas	Units	Glasshouse		Bioreactor
		Mean	Peak	
CO_2	kg/day	2000	4000	100
H_2S	kg/day	84	168	4.2
CH_4	kg/day	10.5	21.1	0.53
N_2	kg/day	9.7	19.3	0.48
NH_3	g/day	420	0.84	0.021
VOCs	g/day	320	630	16
Ar	g/day	126	250	6.32
Hg	g/day	2.1	4.2	0.11

Given the very low gas flow rates to the 1000 L pilot bioreactor, substantial CO_2 loss is acceptable if it allows a simpler, cheaper purification train. In a phototroph–methanotroph co-culture, deliberately scrubbing some CO_2 may be desirable to raise the CH_4:CO_2 ratio. Accordingly, we assume that up to 90 % of the incoming CO_2 could be lost in the treatment system without compromising pilot objectives.

At the larger, 548 tonne/yr glasshouse scale, some CO_2 losses can be tolerated, particularly if the alternative is venting of the NCGs from the power station, but the cost of compressing and transporting surplus CO_2 becomes significant. For this assessment, the glasshouse purification train is allowed to lose no more than 25% of the CO_2; technologies with higher losses are deemed unattractive.

3 CURRENT PRACTICES FOR THE TREATMENT AND USE OF GEOTHERMAL NCGS

There are two approaches that can be taken to purifying CO_2 from the NCG gas mixture:

1. Remove unwanted gases to reduce their concentrations to acceptable levels.
2. Extract CO_2, leaving behind the unwanted gases.

The unwanted gases include those that may inhibit growth, be harmful to workers, or bioaccumulate and pose a risk to consumers.

The most cost-effective approach depends on the gas composition. In this study, where CO_2 makes up approximately 95% of the NCG stream by mass, extracting the CO_2 (approach 2) is likely to require more energy than removing the unwanted gases (approach 1). In addition, CO_2 extraction technologies are not 100% selective, and further process stages would likely be required to remove H_2S from the enriched CO_2 stream. In some cases, removing the impurities may be more expensive that extracting the CO_2, taking into account practical constraints, available technologies, and waste disposal. This can be the case for impurities that are inert and have low vapor pressures, such as nitrogen and argon. These gases are not toxic to the plants, microalgae, or bacteria and so do not necessarily need to be removed. This study therefore only considers the removal of unwanted gases (approach 1).

3.1 Technologies for H_2S removal

H_2S removal would almost certainly be the most expensive process in the gas cleaning system due to the quantities present. There are numerous existing reviews of H_2S removal technologies (Sanopoulos and Karabelas 1997, Padilla 2007, Rodríguez, Harvey and Ásbjörnsson 2014, Pudi, et al. 2022). Here we provide a brief summary of the most widespread technologies, and of those technologies that may be appropriate at small scale, despite lacking widespread adoption.

The first three methods described (liquid-redox, THIOPAQ, and the Claus process) produce elemental sulphur. The remaining methods typically produce significantly greater quantities of sulphur-bearing waste, or vent concentrated H_2S gas to atmosphere. Although the liquid-redox and THIOPAQ processes produce a sulphur-cake that has been used in organic agriculture, sale of this product is unlikely to generate significant revenue. If there are no interested parties then it may be necessary to pay for its disposal, as was found to be the case in Iceland (Rodríguez, Harvey and Ásbjörnsson 2014).

3.1.1 Liquid-redox methods

Liquid-redox processes (e.g. Stretford, LO-CAT, Sulferox) are the most widely deployed H_2S-removal technologies in geothermal plants (Chaves 1996, Sanopoulos and Karabelas 1997). Each follows the same two-stage pathway: the feed gas is first scrubbed with an alkaline liquor that absorbs H_2S as HS^- (Padilla 2007), after which the dissolved sulphide is oxidised in solution to elemental sulphur. Their chief attraction is that they run close to ambient temperature and pressure (Sanopoulos and Karabelas 1997).

Stretford has fallen from favour because its vanadium catalyst raises significant environmental and waste-disposal concerns (Padilla 2007). LO-CAT, often described as a simplified and more environmentally friendly Stretford variant (Chaves 1996), substitutes ferric-iron complexes stabilised by proprietary organic chelants for the vanadium. Several other systems (e.g. Sulferox, VALKYRIE, SULFCAT) are also based on stabilised ferric iron. Liquid-redox systems can routinely cut outlet H_2S to ≤ 10 ppm (Sanopoulos and Karabelas 1997), yet the management of waste streams remains a key disadvantage (Chaves 1996).

3.1.2 THIOPAQ

The THIOPAQ process, developed by Paques B.V. in 1993 for biogas desulphurisation, is described in the literature both as a liquid-redox system (Padilla 2007) and as a biological treatment technology (Kiptanui 2015). Recent vendor data places the number of installed units above 300, primarily for biogas upgrading applications. The process operates in two stages: H_2S is first absorbed into an alkaline liquor in a packed tower, after which Thiobacillus in an aerobic bioreactor oxidise the dissolved sulphide to elemental sulphur, a product that can be used in fertiliser blends. Because the hydroxide in the scrubber liquor is regenerated, chemical consumption is minimal and operating costs are comparatively low (Padilla 2007). THIOPAQ routinely achieves ≥ 99.5 % H_2S removal, with outlet concentrations of ≤ 25 ppm (Kiptanui 2015), and the manufacturer states that feed streams containing 1000–200000 ppm (20 %) H_2S can be handled. Additional benefits often cited include low capital cost, modest control requirements, and a reduced risk of plugging relative to Stretford or LO-CAT.

The THIOPAQ process has not been proven in geothermal but is mature in biogas processing and has been previously identified as a promising option for geothermal NCGs based on cost considerations (Kiptanui 2015, Padilla 2007).

3.1.3 Claus process.

The Claus process is the most widely used route for producing elemental sulphur from H_2S–rich gas streams in the natural-gas and refining industries (Chaves 1996). It is a high-temperature, gas-phase process. An H_2S-enriched feed, typically ≥ 25 % H_2S after pre-concentration using an absorption/regeneration loop, is combusted to SO_2, which then reacts catalytically with the remaining H_2S to yield elemental sulphur and water. Geothermal uptake has been minimal; the only commercial installation reported is at the Yanaizu-Nishiyama power station in Japan (Padilla 2007).

3.1.4 Scrubbing with chemical solvents

In New Zealand, environmental regulations generally allow geothermal power stations to directly vent H_2S along with the other NCGs, which alters the cost–benefit balance of treatment options. Literature focussed on H_2S removal from geothermal NCGs elsewhere in the world is typically targeted at abating H_2S emissions and therefore do not consider this option.

Concentrating the H_2S can be achieved by scrubbing it from the NCGs in an absorption column followed by its release from the solvent in a stripping/regeneration column. Scrubbing with chemical solvents has been the dominant technique for purifying fuel gases since the 20th century (Pudi, et al. 2022) and is often used upstream of the Claus process. Alkanolamines are the most widely deployed chemical solvents for acid-gas removal. Compounds such as monoethanolamine (MEA), diethanolamine (DEA) and methyl-diethanolamine (MDEA) reversibly bind H_2S and, to a lesser extent, CO_2 through acid–base reactions that form protonated amine–bisulphide or carbamate species. Regeneration demands heat. A lean–rich exchanger recovers part of the sensible load but the latent heat tied to steam generation is lost. In geothermal plants, available low-grade heat may be able to supply much of the reboiler duty, reducing operating costs.

In contexts where H_2S emissions are to be avoided, the absorption/regeneration loop would need to be followed with chemical conversion of the H_2S, explaining the lack of attention this method has received in most other reviews. Safety considerations regarding release of a concentrated H_2S stream would need to be addressed and returning the H_2S to the power station to remix with the NCGs may be an alternative.

3.1.5 Scrubbing with physical solvents

Physical solvents such as Selexol, Rectisol, and Purisol absorb H_2S mainly through physical dissolution in a pressurised absorption column. Regeneration is usually achieved by lowering the pressure in a stripping column, and the energy demand is lower than for chemically reactive solvents. At pressures below about 20 bar g their H_2S loading capacity is lower than that of amine systems, which leads to larger equipment (Pudi, et al. 2022). The selectivity for H_2S over CO_2 is generally less than for chemical solvents.

3.1.6 Scrubbing with water

Water can also be used as the physical solvent. Water-washing is widely used in biogas upgrading for removing H_2S. H_2S has about three times the solubility of CO_2 in water. Process designs can reduce CO_2 loss to some extent and this option has been assessed in several studies (D. L. Mamrosh, K. E. McIntush and A. Douglas, et al. 2014, Dunstall and Graeber 1997, D. L. Mamrosh, K. E. McIntush and C. Beitler, et al. 2012). Larger absorption columns and larger absorbent flow rates are required compared to scrubbing with alkaline solution (discussed next) or other chemical absorbents. However, it may be appropriate for small-scale NCG purification where significant CO_2 losses can be tolerated and where it is desirable to minimise the handling of chemicals and waste streams.

3.1.7 Scrubbing with caustic

Sodium hydroxide scrubbers absorb H_2S, forming aqueous NaHS, a saleable product for paper, mining and tanning when purity is high (Mamrosh, McIntush and Fisher 2014b). To avoid Na_2S production and excessive NaOH consumption, NaOH concentration and liquid-to-gas ratio must be tightly controlled. Because the alkaline solvent is not regenerated, caustic scrubbing is usually limited to small H_2S loads (<0.1 tonne per day), though it can be economic up to 10 tonne per day where NaHS off-take exists (Mamrosh, McIntush and Fisher 2014b).

High CO_2 concentration raises NaOH demand through carbonate formation. Modern designs exploit the faster absorption of H_2S to minimise this. Saleable NaHS solutions contain 15–45 wt % NaHS with <3 wt % Na_2CO_3 and <4 wt % Na_2S. Achieving this quality often requires excess NaOH ($\geq$2:1 NaOH:H_2S) at moderate pH. If a single recirculating loop meets the removal target, capital costs are lower than for regenerative THIOPAQ or liquid-redox systems. However, where no NaHS buyer exists, waste disposal can dominate total cost.

3.1.8 AMIS method.

AMIS (Italian: Abatement of Mercury and Hydrogen Sulphide) removes H_2S by catalytically oxidising it with air to SO_2, which is then scrubbed with geothermal water and reinjected (Sabatelli, Mannari and Parri 2009). Developed by ENEL for its small (≈20 MW) unattended Tuscan plants, the three step system is:

1. Hg capture on selenium-impregnated ceramic or sulphur impregnated carbon at ≈70 °C.
2. Selective catalytic oxidation of H_2S to SO_2 at ≈240 °C; the reaction is exothermic, so no external heat is required.
3. Absorption of SO_2 in condensate/brine, forming soluble sulphites/thiosulphates that are reinjected; no reagents are consumed.

Field experience shows >95 % H_2S removal with negligible chemical usage (Baldacci, et al. 2005). However, this solution relies on agreeing upon reinjection logistics with a reservoir operator.

3.1.9 Solid scavengers

Most solid scavengers work by chemisorption where the scavenger reacts with the target substance to form a stable compound (Mamrosh, et al. 2019). Solid scavenger systems are widely used for both H_2S and Hg removal. The scavenger media typically has high internal porosity and fills large vessels that the gas passes through. Solid scavengers produce a sulphur-bearing solid waste in quantities that are an order of magnitude greater than the removed sulphur. For this reason, they are often used as a second stage polishing step for streams with more than trace amounts of H_2S.

Iron sponge is a traditional iron-oxide-based solid scavenger used for H_2S removal. The hydrated iron oxide is impregnated onto a high-surface-area support such as wood shavings (Mamrosh, et al. 2019). The material is usually 10-20% iron oxide by weight. Spent iron sponge usually contains iron sulphide (FeS) and some elemental sulphur. Pyrite (FeS_2) can also be formed if there is excess oxygen present. Iron sponge can be partially regenerated by exposure to air (oxidizing iron sulphide back to iron oxide and elemental sulphur), though this generates heat and requires careful management. Spent media is typically disposed of and replaced with fresh media. The spent media (containing iron sulphide, elemental sulphur, and potentially some mercury) may be considered hazardous waste due to flammability, toxicity and potential for H_2S release.

Numerous other solid scavenger products for H_2S removal are available. Many use metal oxides or potassium iodide on an activated carbon or inert, porous support. Advantages over iron sponge include easier change-out, reduced fire risk, and improved performance over certain humidity and temperature ranges.

3.1.10 Other H_2S removal technologies

There are many other processes for H_2S removal and sulphur recovery. These include the Wet Gas Sulphuric Acid process, XERGY process, the Fe-Cl hybrid process, and pressure swing adsorption. These processes were excluded from detailed consideration due to either being still being in development (Fe-Cl process) or due to lack of demonstration in geothermal (Wet gas Sulphuric Acid process, XERGY process, pressure swing adsorption), suggesting prohibitive costs or challenges in process control at the relevant scale.

3.2 Technologies for Hg removal

Solid scavenger systems are the predominant and most effective processes for elemental mercury removal from gaseous streams. The mercury reacts chemically with active sites on the solid sorbent, forming a stable, non-volatile compound.

Sulphur-impregnated activated carbon is one of the most common and widely used materials. The elemental mercury (Hg^0) reacts with the sulphur to form highly stable and insoluble mercury sulphide (HgS), commonly known as cinnabar. This chemisorption mechanism is effective even for trace mercury levels. The material has a high capacity for elemental mercury, is relatively cost-effective, and is a well-established technology. It can be sensitive to certain contaminants (e.g., heavy hydrocarbons), and the spent material requires careful disposal as hazardous waste. HgS is stable and regeneration is generally uneconomical.

Sulphur-impregnated activated carbon was trialled in the AMIS system but was replaced with a ceramic mass impregnated with Selenium (Baldacci, et al. 2005). The sulphur-impregnated activated carbon was reported to have a higher pressure drop and, in humid conditions, some hydrogen sulphide was oxidized to sulphur dioxide, causing downstream issues. Problems with temperature control of the activated carbon (due to reactions of H_2S and CH_4 with oxygen) have also been reported and water vapor can saturate the activated carbon and reduce the absorption efficiency.

4 TREATMENT OPTIONS AND COSTS AT SMALL SCALE

4.1 Costs of H_2S removal

In this section, cost estimates available from the literature are first scaled to assess the feasibility of downscaling established technologies to the scale required to supply CO_2 to the 1 ha glasshouse. Several other methods are then considered that, although are not cost-effective at large scale, may be appropriate at the scales considered in this study.

4.1.1 Scaling from Previous Cost Estimates

Reported costs of H_2S removal available in the literature have been scaled to provide order of magnitude estimates for a system to supply a 1 ha glasshouse. Capital costs were scaled by the H_2S removal rate using the six-tenths rule.

$$\frac{C_a}{C_b} = \left(\frac{A_a}{A_b}\right)^{0.6}$$

Technology	*Reference*	*Year*	*CEPCI ratio*	*Location*	*H2S content (%)*	*Operating*	*Capital costs*		
						Scaled and escalated operating cost (NZD/yr)	*From reference (NZD)*	*Capacity ratio*	*Scaled and escalated cost (NZD)*
LO-CAT	McIntush, 2016;	2016	1.47		0.16	$519,000	$10,855,000	0.0902	$3,760,000
LO-CAT	Kiptanui, 2015	2015	1.43	Kenya	1.59	$77,000	$33,400,000	0.0102	$3,050,000
THIOPAQ	Kiptanui, 2015	2015	1.43	Kenya	1.59	$60,000	$12,358,000	0.0102	$1,130,000
THIOPAQ	Padilla, 2007	2007	1.51	El Salvador	7.90	$25,000	$9,352,000	0.0247	$1,530,000
MDEA absorption	Dunstall, 1997	1997	2.05	New Zealand	1.63	$111,000			

Table 4. Operating and capital costs for various technologies when scaled to supply a 1-ha glasshouse. Adjusted for inflation and plant capacity from previous estimates.

The ratio A_a/A_b is referred to as the capacity ratio. Operating costs are scaled linearly with the H_2S removal rate. The scaled costs were indexed to 2025 using the Chemical Engineering Plant Cost Index (CEPCI). The results are shown in Table 4.

The costs in Table 4 should be interpreted with caution. More detailed adjustments could not be applied uniformly due to a lack of information in many of the sources. The costs can only be considered order of magnitude estimates. The earliest of the studies is from almost 3 decades ago and there have been relative changes in the cost of utilities, labour and chemicals over that period, as well as significant technology advancements and changes in engineering codes. The H_2S removal capacity has been scaled by two orders of magnitude in some cases and the six-tenths rule is unlikely to remain applicable for the very small capacity ratios. Some of the systems may not be available at such low capacities. Furthermore, plant location has not been accounted for.

Nevertheless, the results indicate which technologies warrant consideration at the scales considered in this study. The capital cost of the liquid-redox process is likely prohibitive for a 1 ha glasshouse. Operational costs also appear to be higher than alternatives such as the THIOPAQ process. Although the THIOPAQ system has not been implemented in NZ, discussions with PAQUES and information on their website suggests THIOPAQ systems are available at this scale.

4.1.2 Scrubbing with NaOH

Table 5 shows minimum operating costs for bulk removal of H_2S with NaOH scrubbing. This estimate assumes an ideal stoichiometric reaction of NaOH with H2S and negligible scrubbing and reaction of CO_2. This is unrealistic, given the high CO_2 concentration and relatively small scale of the system, limiting the sophistication of the control systems, and complexity of the process. The cost of caustic for the glasshouse system, including delivery, is assumed to be NZ$2/kg on a dry basis. The cost of caustic for the bioreactor, which requires two orders of magnitude less, is assumed to be NZ$10/kg.

For the glasshouse case, the minimum annual cost of the caustic in Table 5 compares favourably with operating costs of other processes. However, actual NaOH consumption could be an order of magnitude higher and a simple single-loop absorber design is unlikely to be sufficiently selective for H_2S. Utility costs associated with the system are expected to be comparatively low. The main labour costs are expected to be related to maintaining the NaOH supply and handling of the NaHS solution.

	Units	**Glass-house**	**Bio-reactor**
Peak H2S removal	kg/day	170	0.84
Peak NaOH consumption	kg/day	200	0.99
Mean H2S removal	tonne/yr	31	0.31
Mean NaOH consumption	tonne/yr	36	0.36
NaOH annual cost	NZD/yr	$72,000	$3,600
NaHS daily volume*	L/day	1066	5.3

Table 5. Minimum NaOH consumption and cost for bulk removal of H_2S by scrubbing with NaOH. *Assumes an NaHS concentration of 20% by weight. For the glasshouse, daily NaOH volumes are for periods of peak CO_2 demand.

Producing a saleable NaHS solution is not feasible at this scale, given the CO_2 concentration in the NCGs. Disposal of the NaHS is likely to incur significant costs and can easily exceed the costs of the NaOH. Disposal via a hazardous waste contractor is likely to be cost-prohibitive. The HS- ion would most likely need to be further oxidised in an additional process to form a sulphate liquor that could be cheaply disposed of, incurring additional chemical costs.

For the bioreactor, the cost of NaOH scrubbing may be acceptable. NaOH consumption is likely to be at least double that given in Table 5 and spent solution volumes could be an order of magnitude larger. The cost of waste disposal would need to be considered to evaluate the relative cost performance of this process.

4.1.3 Scrubbing with water

To assess the performance and costs associated with water scrubbing, bubble column simulations were conducted using Python. The equations below were solved for the mass flow rate of each species in the gaseous and aqueous phases using the solve_bvp function in the SciPy package:

$$\frac{d\dot{m}_{g,i}}{dz} + \lambda_i = 0 \quad , \quad \frac{d\dot{m}_{aq,i}}{dz} - \lambda_i = 0$$

$$\lambda_i = k_{L,i} a A (C_{aq,eq,i} - C_{aq,i})$$

At each position along the column, the mass transfer rate per unit volume for species i is given by (λ_i/A). Back-mixing was neglected. The product $(k_{L,i}a)$ and the gas hold-up were estimated using the correlations of Akita and Yoshida, 1974. CoolProp was used for pure component properties. Equilibrium dissolved gas concentrations $(C_{aq,eq,i})$ were calculated using Henry's law. The gas-charged liquid is circulated to an ambient pressure degassing tank where it is assumed that vapour-liquid equilibrium is reached with the released gases at 1 atm absolute, before the water is returned to the top of the bubble column.

For the glasshouse supply, to achieve H_2S removal exceeding 75%, CO_2 losses generally exceeded one-third. This was the case over a range of column heights from 3-8 m, for a range of operating pressures (5-16 bar gauge), and a range of water flow rates. However, for the bioreactor, the CO_2 losses may be acceptable, and the equipment sizing was found to be appropriate for a low-cost system. Table 6 show the mass flow rates and mass fractions at the inlet and outlet of two 2 m high bubble columns in series, operating at 7 bar gauge.

	in	BC1 out	BC2 out
Mass flow rates (kg/day)			
CO2	100	46.8	19.7
H2S	4.21	0.45	0.07
CH4	0.53	0.51	0.49
N2	0.48	0.48	0.47
Mass fractions			
CO2	0.950	0.967	0.948
H2S	0.040	0.009	0.003
CH4	0.005	0.011	0.024
N2	0.005	0.010	0.022

Table 6. Mass flow rates and mass fractions entering and leaving two bubble columns in series.

The water flow rate through each bubble column is 9.5 L per minute requiring modest pump powers on the order of 1 kW. The degassing tanks, sized for a 2-hour residence time, are less than 2.5 m^3. The modelling results suggest water scrubbing may be an attractive option, although a small polishing stage using a solid scavenger would likely be required.

4.1.4 Solid scavengers

The most common solid scavengers for H_2S removal use iron oxide on a porous substrate such as activated carbon. Cost estimates received for one such scavenger, Purafil Puracarb suggest a media cost of NZ$90 per kg H_2S removed. Prices available online suggest products such as SulfaTreat may achieve costs less than NZ$10 per kg of H_2S removed, although these costs have not been confirmed in NZ. Ease of handling related to the change-out of spent scavenger is often emphasized in the marketing by suppliers of H_2S scavengers. According to discussions with suppliers, this largely accounts for differences in cost of the various products.

Costs associated with H_2S removal using solid scavengers are given in Table 7. A scavenger cost of NZ$40 per kg H_2S removed is assumed. Approximated media consumption is calculated assuming replacement when the scavenger has adsorbed H_2S equal to 10% of their mass and media volumes consumed assume a media bulk density of 0.8.

For the 1 ha glasshouse, the annual cost of the scavenger would be over NZ$1M. The labour costs associated with the change-out of the scavenger can also be high and waste disposal can be challenging. However, it may be reasonable as a polishing stage, with over 95% of the H_2S first removed in a bulk removal stage.

	Units	Bioreactor	Glasshouse
H2S removal	kg/day	4.21	84.2
Annual cost	NZD/yr	$61,000	$1,230,000
Scavenger consumption	kg/day	42.1	842
	L/week	368	7370

Table 7. Costs and quantities associated with H_2S removal using a solid scavenger. Values apply to complete H_2S removal with no prior bulk H_2S removal. Daily quantities for the glasshouse case apply to the year-average day.

The costs for the bioreactor case may be acceptable. The scavengers are highly selective and conservative assumptions stated earlier regarding CO_2 losses in the treatment system may not be applicable. If an order of magnitude less H_2S needed to be removed, the scavenger cost is approximately NZ$6000/yr, and the weekly quantities that had to be handled (~40 L) are very manageable.

4.2 Cost of Hg removal

The mass rates of mercury removal are 4-5 orders of magnitude less than for H_2S. Even considering a 1-2 order of magnitude difference in the cost of Hg scavenger materials, the scavenger purchase cost and labour associated with of Hg removal using solid scavengers is likely to be at least an order of magnitude less than the H_2S removal. The capital cost for the system is also likely to be comparatively low, although vessels may need to be sized for bed lives of several years to meet specifications such as minimum empty bed contact times. Waste disposal costs would likely exceed the scavenger purchase cost and would need to be considered. A solid scavenger solution for mercury removal is likely to be significantly cheaper than the H_2S removal system at all the scales that have been discussed.

5 CONCLUSIONS

H_2S removal is likely to be the most expensive process in geothermal gas purification systems for supplying glasshouse CO_2, or for supplying bioreactors with mixtures of CO_2 and CH_4.

In addition to the H_2S removal rate, selection of the bulk H_2S removal should consider the availability of operators on site, the cost of utilities, the presence of consumers for the sulphur-bearing products (e.g., elemental sulphur-cake, NaHS), the cost of waste disposal, possibilities for reinjection of the sulphur-bearing waste, and the acceptability of venting or returning a purified H_2S stream.

For a 1 ha glasshouse consuming on the order of 1 tonne/day of CO_2, established technologies such as LO-CAT are likely to cost over NZ$3M and operating expenses are expected to exceed NZ$50k/yr. Operating costs for a solid scavenger system are likely to be on the order of NZ$1M/yr while scrubbing with NaOH is likely to cost over NZ$100k/yr, even with an optimised system. Both processes produce significant quantities of sulphur-bearing waste, with disposal costs that potentially outweigh the purchase cost of chemicals.

Processes that vent the H_2S gas to atmosphere or return it to the power station in a concentrated stream are attractive due to having low chemical consumption and zero waste disposal. However, new consents may be required to vent a small, dense plume rich in H_2S, as opposed to the large, comparatively dilute plumes currently released by geothermal power stations. Estimating the costs of an absorption/regeneration loop to concentrate and vent the H_2S requires detailed modelling similar to that done by Dunstall and Graeber, 1997. Such modelling was beyond the scope of this study, but these processes warrant further investigation. The availability of low-grade heat for stripping the H_2S from alkanolamines may significantly reduce the process utility costs and should be investigated.

For operations consuming up to 100 kg/day CO_2, a solid scavenger, water scrubbing, or NaOH scrubbing is recommended. The performance of absorption columns at this scale is challenging to predict accurately but the reviewed literature and preliminary calculations indicate sufficient H_2S selectivity, acceptable chemical consumption, and relatively low equipment costs. Solid scavenger costs can be estimated with high certainty, while the operation costs of systems utilising absorption columns have greater uncertainty.

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