

GEOTHERMAL CARBON DIOXIDE FOR USE IN GREENHOUSES

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INTRODUCTION

Geothermal fluids often contain carbon dioxide, which is a very effective growth stimulant for plants in greenhouses. Studies have shown that as CO₂ concentration is increased from a normal level of 300 ppm (mmol/kmol) to levels of approximately 1000 ppm crop yields may increase by up to 15% (Ullmann's Encyclopedia of Industrial Chemistry, 1989). It is suggested that geothermal greenhouse heating offers a further opportunity for utilization of the carbon dioxide present in the fluid. The main difficulty is that plants react adversely to hydrogen sulphide which is invariably mixed, at some concentration, with the CO₂ from geothermal fluids. Even very low H₂S concentrations of 0.03 mg/kg can have negative effects on the growth of plants (National Research Council, 1979). Therefore, an appropriate purification process for the CO₂ must be used to avoid elevated H₂S levels in the greenhouses. The use of adsorption and absorption processes is proposed.

Two purification processes have been modelled using the ASPEN PLUS software package, using the Geothermal Greenhouses Ltd. operation in Kawerau New Zealand as an example. A greenhouse area of 8000 m², which would create a demand for approximately 20 kg CO₂ per hour, was chosen based on a proposed expansion at Kawerau. The Kawerau operation currently takes geothermal steam (and gas) from a high temperature 2-phase well to heat an area of 1650 m². Bottled carbon dioxide is utilized at a rate of about 50 kg per day, to provide CO₂ levels of 800 mg/kg when the greenhouse is closed and 300 to 350 mg/kg whilst venting. In England and the Netherlands, CO₂ levels of 1000 mg/kg are often used (Ullmann's Encyclopedia of Industrial Chemistry, 1989) and similar concentrations are desired at Kawerau, but current costs of 0.60 NZ\$/kg for bottled CO₂ are too high (Foster, 1995).

H₂S LEVELS

Plants are very sensitive to elevated H₂S levels in the air. Small concentrations of 0.03 mg/kg (0.04 microg/liter) result in damage to some plants while other plant species (e.g., lettuce and sugar beets) show growth stimulation. However, all plants show deleterious effects at higher H₂S concentrations of 0.3 mg/kg (0.4 microg/liter) (National Research Council, 1979). In this study a hydrogen sulfide concentration of 0.03 mg/kg is considered acceptable if 1000 mg/kg CO₂ is added to the greenhouse atmosphere. The required CO₂ purity is, therefore, 99.997%. An H₂S content of 30 mg/kg or 40 ppm (mmol/kmol) in the CO₂, or less, has to be achieved by the purification process.

Because individual plant species respond differently, higher H₂S concentrations might be tolerable. In many

geothermal areas the characteristic "rotten-egg" odor of H₂S can be detected, indicating concentrations of 0.01 to 0.2 mg/kg H₂S; higher than the concentrations where negative effects on plant growth have been observed. It is likely, therefore, that many crops currently grown in geothermal greenhouses are H₂S tolerant species, requiring less intensive CO₂ purification. The effects of hydrogen sulfide on greenhouse staff are less problematic; since, the concentrations are well below those set for US industry at 15 mg/m³ (10 mg/kg) for an 8-hr workday and a 40-hr work week.

Non-condensable gas is typically present at 1 to 10 wt% in geothermal steam. Carbon dioxide is usually the main component, with hydrogen sulfide the next most important (approximately 1 to 5% of the CO₂ concentration). Minor components are nitrogen, ammonia, hydrogen, methane, and other gases. In this work, a geothermal steam composition of 98.6 mol% H₂O, 1.4 mol% CO₂ and 0.03 mol% H₂S was assumed. All other components were neglected. The values are typical for the main steam pipeline at Kawerau (Geothermal & Nuclear Sciences Ltd., 1992). The steam condition was assumed to be 12 bar (absolute) at saturation conditions.

ABSORPTION

An absorption process is suggested for recovery of CO₂, which will first require cooling of the fluid stream to condense the steam fraction. This heat could be used to warm the greenhouse. The water fraction remaining in the gases depends on the condensation pressure and temperature. Normally a low water fraction is an advantage, but the required heat transfer area increases enormously as full condensation is approached. Sizing of the heat rejection system is, therefore, critical to the success of such an operation and sensitivity to this parameter has been investigated.

Absorption is the uptake of gases by a liquid solvent. The equilibrium solubility determines the distribution of the absorbed material between the liquid and vapor phases. Depending on its volatility, the solvent can also appear in the vapor phase. During physical absorption, the absorbed molecules become polarized but remain chemically unchanged. In chemical absorption, a chemical conversion takes place. Equilibrium between the phases is determined by general thermodynamic principles and was predicted using theoretical models available within the ASPEN PLUS package. As yet, no comparison with between predicted and experimental data has been made; but, experience with other simulations indicates that accuracy greater than 80% can be expected for the equilibrium prediction.

In an absorber, gas and liquid are brought in contact counter currently. The solvent removes one or more

components from the gas mixture, more or less selectively. Normally, the laden solvent is withdrawn from the bottom of the absorber column and freed of the absorbed gas in a recycling system. It is then returned to the absorber. In most cases reversible processes are used and the dissolved components are released chemically unchanged.

PHYSICAL AND CHEMICAL ABSORPTION

The pressure dependence of physical and chemical absorption is significantly different. Typical equilibrium lines are shown in Figure 1, where loading capacity is presented as a function of the dissolved component. Physical absorption processes generally follow Henry's Law, so the liquid mol fraction of a component depends strongly on partial pressure (line b, Fig. 1). In chemical absorption, however, the equilibrium line is sharply bowed. After chemical saturation of the solvent, only weak physical absorption takes place. At low partial pressure the absorption capacity of the chemical solvent is much higher than that of the physical solvent; whereas, at higher partial pressure the opposite applies.

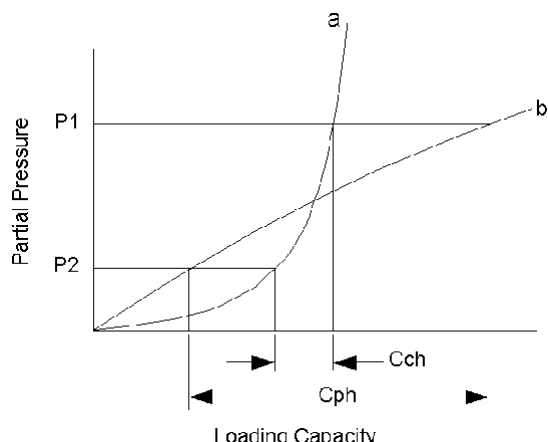


Figure 1. Equilibrium lines for chemical and physical absorption (Ullmann's Encyclopedia of Industrial Chemistry, 1989).

The strong pressure dependence of physical solubility can be utilized for solvent regeneration; since, pressure reduction releases most of the absorbed gas. However, if the dissolved components are chemically bound, less gas is released ($\Delta c_{ch} < \Delta c_{ph}$) and reboiling is almost always needed for regeneration of a chemical absorbent. Heat required for reboiling could be provided by hot geothermal fluids in this case.

In a physical absorption process, the solvent circulation rate is nearly proportional to the quantity of the gas to be cleaned. In contrast, the solvent circulation rate for a chemical process is proportional to the quantity of gas to be removed. This means chemical absorption processes are most economical with low levels of impurity; whilst, physical processes are more suitable for bulk removal of impurities. Examples of both processes have been investigated. The main difficulty is to find an appropriate absorbent that selectively absorbs H_2S .

THE PHYSICAL ABSORPTION PROCESS

Water was selected as the absorbent for the physical process, since it is cheap and freely available and H_2S and CO_2

have different solubilities in water. Unfortunately, although H_2S is considerably more soluble than CO_2 , both gases are only slightly soluble in water. Relatively high circulation rates are, therefore, required. Solubility decreases with increasing temperature, so absorption should take place at a low temperature. Despite the low solubility and high flow rates in this small scale application, a relatively simple process is required, and the use of water is considered appropriate.

The flow sheet of an absorption process with water is shown in Figure 2. After condensation and cooling to $120^\circ C$, the steam/gas fraction is separated in a flash tank at 10 bar and fed into the base of the absorber column; while, the separated water is removed for further use or disposal. Cool water fed into the top of the column absorbs the H_2S and some CO_2 as it passes downward, and purified CO_2 flows from the top of the absorber.

The gas laden absorbent is then flashed at 3 bar, releasing mainly CO_2 , which is recycled into the absorber column by the compressor. Without recycling, much of the CO_2 would be lost with the H_2S . Flash regeneration alone is not sufficient to achieve the required CO_2 purity so a steam heated regeneration column is used as a final stage. At $133^\circ C$, almost all the absorbed CO_2 and H_2S are released in this column and a water purity of 0.5 ppb H_2S is achieved. Heat needed for regeneration could be supplied using the heat exchanger in which the inlet steam is condensed; however, low cost steam is available and direct injection of steam seems appropriate. Finally, the water stream is recycled to the absorber after rejecting heat to the greenhouse.

Unfortunately, the process as presented cannot reduce the H_2S to 40 ppm, due to a limitation on the purity of the regenerated water. This process can remove H_2S from the CO_2 down to 400 ppm so residual H_2S must then be removed using an appropriate adsorption process. It is possible to achieve a CO_2 purity of 99.997 % (40 ppm H_2S) with a more complex absorption process using water, but the high water flow rates and heat loads are unlikely to be economical.

Production of approximately 20 kg/hr CO_2 requires an inlet steam flow of 1200 kg/hr (~ 40 kg/hr CO_2). After initial separation 37 kg/hr CO_2 is passed to the absorber, where 22 kg of CO_2 are recovered, at a water flow rate of 4000 kg/hr. About 0.5 kg/hr of H_2S is removed, reducing H_2S content from 1.4% to 400 ppm. Unrecovered CO_2 is removed with the H_2S . The predicted power requirement is 4.3 kW, made up of water pump power (3.3 kW - efficiency 30%) and gas recycle compressor power (1.0 kW - efficiency 72%). The CO_2 recovery rate increases if the flash tank pressure is reduced (or temperature increased); but, water circulation rates and compressor power increase significantly. Regeneration requires 800 kg/hr steam to heat the circulating water to $133^\circ C$ so approximately 1250 kW_{th} of heat is removed from the steam in total. It is anticipated that a reasonable proportion of this heat can be used in the greenhouse.

One major constraint is the need to condense inlet steam in the presence of very high levels of non-condensable gases. This would require a large heat exchanger area and careful attention to heat exchanger design. A range of higher condensing temperatures have, therefore, been considered; with

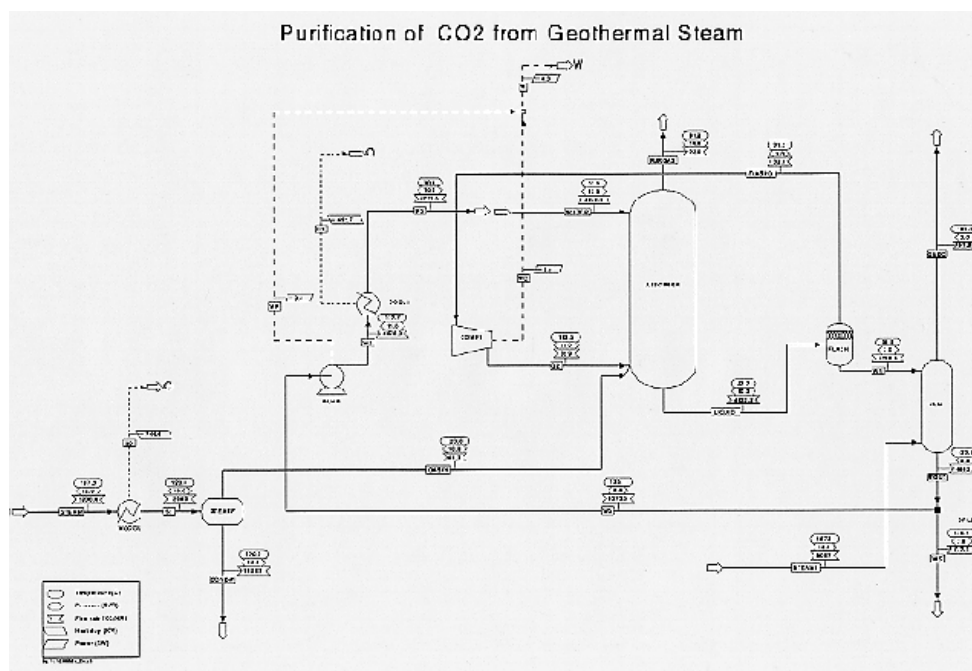


Figure 2. Flow sheet arrangement for absorption process with water.

absorber inlet temperature varied between 24 and 50°C. The influence on the required water flow rate, electrical power requirement, flow rate of regeneration steam, and water cooling load can be seen in Figure 3. Production of purified CO₂ increases by about 10% as the temperature increases from 24 to 50°C.

Gas solubility decreases at higher temperatures; so, the absorber flow rate and regenerator steam flow both increase with temperature. Pump power increases correspondingly, although higher pump efficiency is predicted for larger pumps; hence, the change in power curve slope at 32°C. The cooling load also increases; but, due to an increased temperature difference, the heat transfer area is reduced. Purified CO₂ production increases slightly at higher temperatures; since, less CO₂ is absorbed with the H₂S.

TEMPERATURE OF GAS INLET STREAM

The heat exchanger area required for condensing the inlet steam depends on the outlet temperature. Lower temperatures require disproportionately larger areas; as, the non-condensable gas partial pressure rises in the condenser. Sensitivity to this parameter was tested by varying temperature in cooler from 70 to 170°C.

As the water saturation temperature is approached (10 bar - 180°C), the steam fraction increases significantly, heating the bottom stage of the absorber column (Fig. 4). The increased temperature reduces CO₂ absorption and production of purified gas increases. More gas is recycled, increasing compressor power slightly. The cooling load reduces and the required heat exchanger area is greatly decreased due to the a higher temperature difference and higher water fraction in the non-condensable gases. Because the electricity costs increase significantly for a small increase in purified gas flow, it is advisable to reduce the gas inlet temperature as far as possible within economic limits imposed by the cooling load.

REQUIRED CARBON DIOXIDE PURITY

The purity achieved in the absorption process determines the costs for the second purification stage, which is an adsorption process. Water flow rates decrease significantly if higher H₂S levels in the purified CO₂ are specified. Compressor and pump power also reduce (Fig. 5). For example, the power requirement decreases from 4.3 to 2.9 kW if a CO₂ purity of 99.90% instead of 99.96% is acceptable. Furthermore, the flow rate of purified CO₂ increases if higher H₂S levels are specified; since, less CO₂ is absorbed with the H₂S. Increasing the H₂S level from 200 to 1500 ppm provides over 50% more CO₂. Obviously it is important to carefully evaluate the required CO₂ purity for the first stage.

SIZE OF ABSORBER AND REGENERATION COLUMN

The vessel sizing option of the ASPEN PLUS program has been used to estimate vessel size. For the base process described, an absorber column size of 1.5 m height and 0.27 m diameter with a random packing of 1-inch plastic pall rings would be sufficient. Pressure drop in the column is negligible due to the very low gas flow rate. The regeneration column requires a larger diameter (0.47m), due to the higher flow rate, once again assuming random packing with 1-inch plastic pall rings. A packing height of 1 to 1.5 m is expected to be sufficient. These values show that the vessels are relatively small and pipes could probably be used to construct the columns, keeping costs down.

CHEMICAL ABSORPTION PROCESS USING MDEA

Chemical absorption of unwanted hydrogen sulfide was also investigated. Several solvents are available, and aqueous amine solutions have been used extensively in the oil and gas industry (Ullmann's Encyclopedia of Industrial Chemistry, 1989). In this horticultural application selective removal of H₂S is important. Good selectivity is shown by tertiary

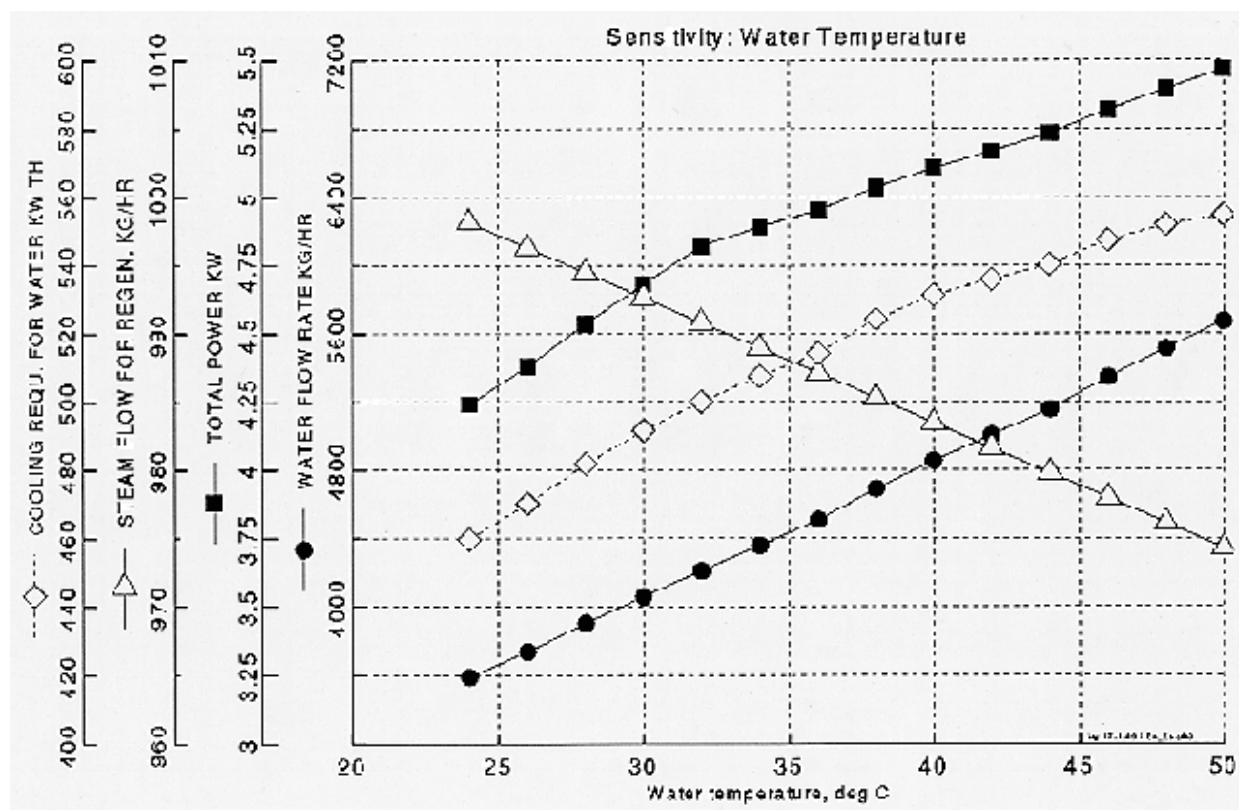


Figure 3. Influence of water temperature on mass flow rates, cooling load and power requirements.

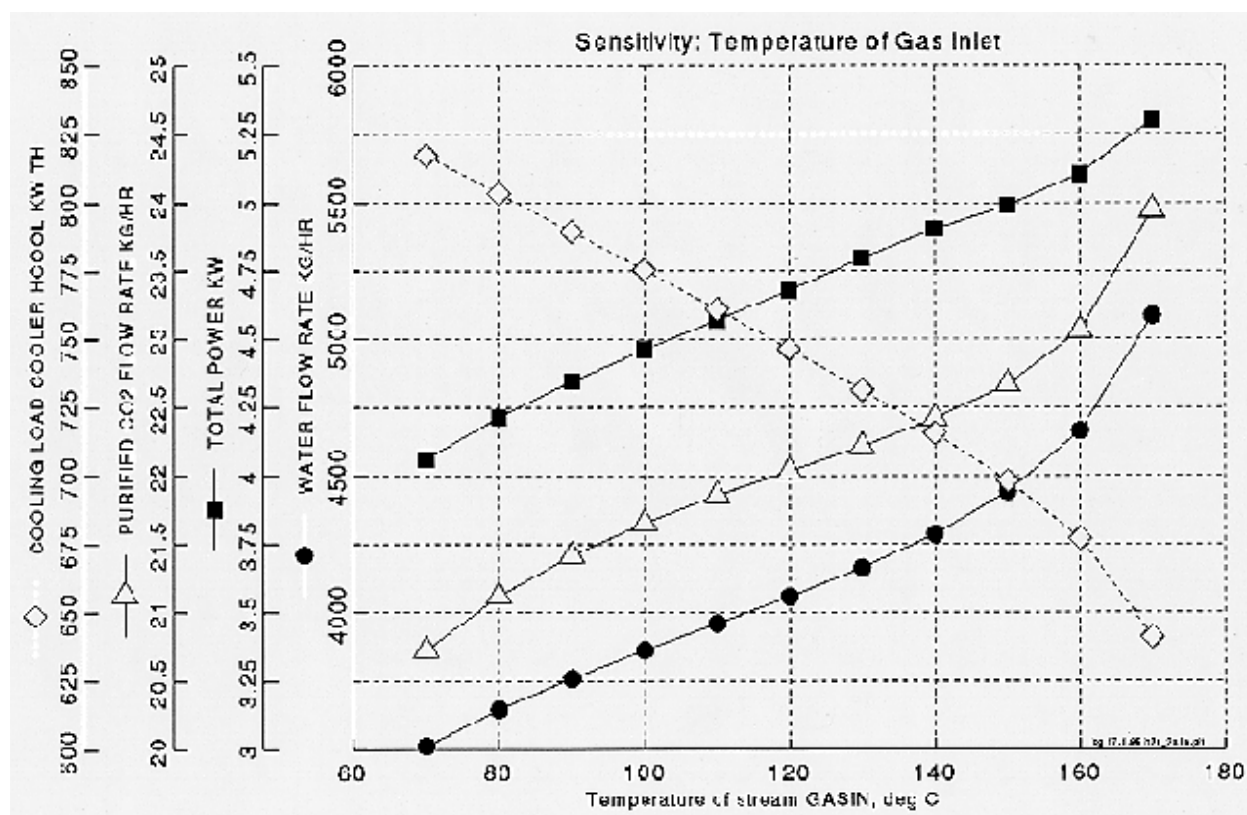


Figure 4. Influences of gas inlet temperature on water flow rate, power requirements, condenser cooling load, and purified CO₂ flow rate.

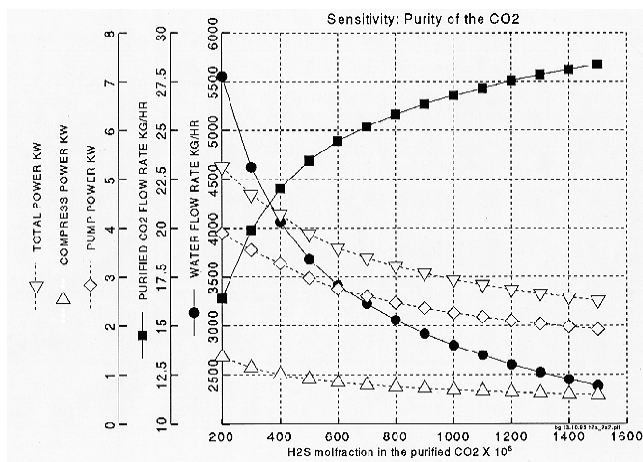


Figure 5. Influence of the specified H₂S fraction in the purified CO₂ on the absorption process.

alkanol-amines (Ullmann's Encyclopedia of Industrial Chemistry, 1989; Savage, et al., 1986), of which the most commonly used is an aqueous solution of n-methyldiethanolamine (MDEA). Chemical equilibria for the MDEA solvent were calculated using the ASPEN PLUS built-in data bank. Typically MDEA concentrations of 2.5 to 4.5 mol per liter are used for acid gas absorption (Kohl, et al., 1995). For this simulation a 4 M aqueous MDEA solution (27% by weight) has been chosen.

An H₂S concentration of 1000 ppm in the purified CO₂ stream has been specified for this process. Residual H₂S is then removed in an appropriate adsorption process, as for the physical absorption process. Although higher purities can be achieved, a very high heat duty is required for solvent regeneration. Furthermore, as CO₂ is absorbed with the H₂S it becomes difficult to selectively recover CO₂.

The flow sheet for the simulated absorption process with MDEA is shown in Figure 6. This process is similar to that used for physical absorption with water with the following modifications:

- Inlet steam (and gas) is condensed at 2.5 bar and 100°C, as a lower absorber pressure is acceptable;
- Absorber column temperatures are higher and the MDEA solution enters the column at 70°C;
- Purified CO₂ is cooled to 60°C in a gas cooler and condensed water is separated out. This step was included for satisfactory simulation of the H₂S fraction in the purified CO₂, as the high water fraction in the absorber gas outlet results in a low H₂S mol fraction. In practice, this step may not be necessary;
- The flash tank is slightly heated to improve CO₂ recycling to the absorber; as, pressure reduction alone is not sufficient;
- Regeneration of the chemical solvent requires the use of a true reboiling process; where, the solvent is evaporated and stripped with its own vapor, rather than heating directly with steam containing H₂S, and

- Water lost from the solvent in the gas outlet stream is replaced by make-up water at a temperature of 30°C before recycling to the absorber.

Compared to the absorption process with water the main differences with MDEA are:

- Absorbent flow rate is substantially lower with 785 kg/hr required, compared to more than 4000 kg/hr;
- The pump and compressor are much smaller due to the lower flow rate and the reduced pressure differences. The power requirement is 0.4 kW, about 10% that of the water system, and capital cost will be lower;
- Regenerator heat loads are relatively high (780 kW) at the required purity (~50 ppm H₂S). This heat load could be met by condensing about 1200 kg/hr steam, so initial condensation of the inlet steam/gas mixture could supply the regenerator. Ultimately, most of this heat is rejected from the regeneration column at lower temperatures (~100°C) and much of it could be used in the greenhouse;
- The circulating solvent requires just 26 kW of cooling to achieve the required temperature of 70°C;
- The temperature of the purified gas is relatively high at 87°C, and
- Approximately 11 g/hr MDEA are lost in the waste gas outlet stream. Cooling the outlet stream and recycling the condensate can reduce this loss significantly. Only trace amounts of MDEA are expected in the purified CO₂. Condensed water from the purified CO₂ stream should be recycled as it contains 120 ppm MDEA.

The MDEA absorption process has the advantage of lower circulation rates, lower electricity demand, lower pressures, and higher cooling temperatures. The disadvantages compared with the water absorption system are a higher heat requirement, lower CO₂ purity and minor losses of MDEA.

ADSORPTION PROCESS FOR FURTHER PURIFICATION OF THE CO₂

Purities achieved with either of the absorption processes discussed are not sufficient for direct use of the CO₂ in greenhouses. Further purification is, therefore, required to reduce H₂S concentration from 400 or 1000 ppm to 40 ppm or less. Approximately 5 to 20 g/hr of H₂S has to be removed in this final step, so a simple solution is an adsorption process without adsorbent regeneration. The advantages of an adsorption process are high selectivity and a loading capacity that is almost independent of partial pressure.

Selective adsorption of H₂S can be achieved using activated carbon. The loading capacity of 50-min activated coconut-shell charcoal for H₂S is approximately 10 to 25 % by weight (i.e., 1 kg of activated charcoal can adsorb 100 to 250 g of H₂S) (Kohl, et al., 1995). Other activated carbon products are expected to have similar capacities. Assuming a loading capacity of 10%, approximately 25 to 100 g/hr

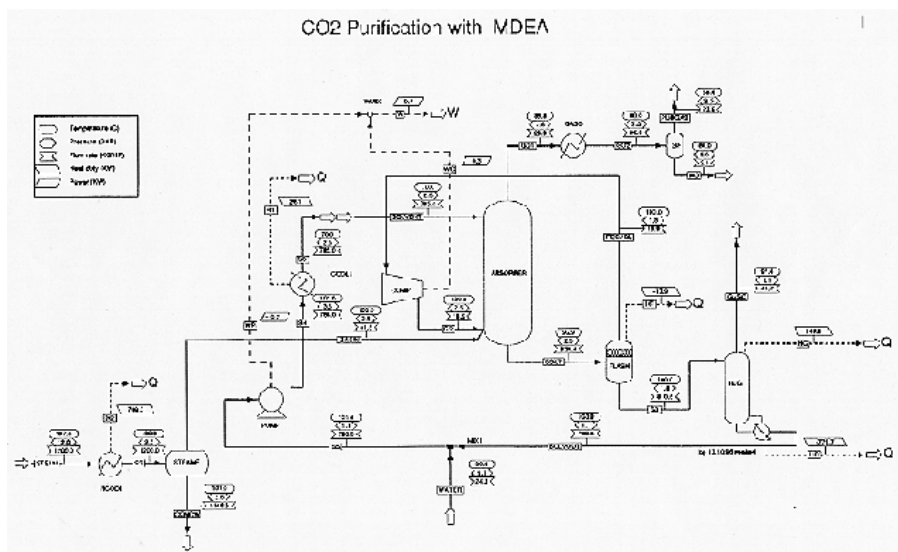


Figure 6. Flow scheme for chemical absorption with MDEA solution.

activated carbon would be required for final purification of CO_2 that had been pre-treated in one of the absorption processes. The costs of activated carbon products are 0.70 to 5.50 \$US/kg (Encyclopedia of Chemical Technology, 1992). Material costs for this adsorption process are, therefore, relatively low. However, the operating cost involved in exchanging the activated carbon filters should be considered.

Assuming electricity costs of 0.07 \$US/kWh and a cost of 3.5 \$US/kg activated carbon, the total costs are approximately 0.40 \$US/hr for the process with water and 0.35 \$US/hr for the process with MDEA. The costs for both methods are similar because the achieved purity with the MDEA process is lower than that achievable with the water process, increasing the activated carbon consumption. The value of the purified gas is approximately 8.4 \$US/hr or 70,000 \$US/year, which is many times greater than the costs calculated above (approximately 3,500 \$US/year).

The required quantity of activated carbon depends on the purity achieved by the absorption process and an economic optimum for the combination of both processes requires careful further study.

CONCLUSION

The use of geothermal carbon dioxide for growth stimulation of plants is possible, if a purification process is used to reduce the initial hydrogen sulfide content. Alone, an absorption process using water or aqueous MDEA is not feasible at the required purity. However, both processes are suitable for bulk removal of H_2S and it is possible to remove residual H_2S with an activated carbon adsorption process.

Power requirements for purification of 20 kg CO_2 /hr are relatively small: 4.3 kW for physical absorption with water and 0.4 kW for chemical absorption with MDEA. Activated carbon consumption is approximately 20 to 100 g/hr. Running costs are approximately 0.40 \$US/hr for the physical process with water and 0.35 \$US/hr for the chemical process with MDEA. The product value is about 8.4 \$US/hr; so, either of these combination processes appear economically attractive compared to current use of bottled CO_2 .

REFERENCES

- Encyclopedia of Chemical Technology, 1992. "Carbon (activated), Kirk - Othmer," vol. 4, p. 1022, 4th ed., John Wiley & Sons, New York.
- Foster, B., 1995. Personal communication. Geothermal Greenhouses Ltd, Kawerau, New Zealand.
- Geothermal & Nuclear Sciences Ltd, July 1992, June 1992. "Gas Analysis of Steam at Tasman Lumber, Kawerau."
- Kohl, A. and F. Riesenfeld, 1995. "Gas Purification," 4th Ed, Gulf Publishing Co., Houston, London, Paris, Tokyo.
- National Research Council, 1979. "Hydrogen Sulfide," Sub-committee on Hydrogen Sulfide, Committee on Medical and Biologic Effects of Environmental Pollutants, University Park Press, Baltimore.
- Savage, D.; Funk, E.; Yu, W. and G. Astarita, 1986. "Selective Absorption of H_2S and CO_2 in Aqueous Solutions of Methyldiethanolamine," Ind. Eng. Chem. Fundam, p. 326-330.
- Ullmann's Encyclopedia of Industrial Chemistry, 1989. "Carbon Dioxide." 5th ed., vol. A5, p. 165 - 183, VCH Verlagsgesellschaft, Weinheim, New York.
- Ullmann's Encyclopedia of Industrial Chemistry, 1989. "Absorption Processes." 5th ed., vol. A12, p. 249 - 260, VCH Verlagsgesellschaft, Weinheim, New York.
- Ullmann's Encyclopedia of Industrial Chemistry, 1989. "Hydrogen Sulfide." 5th ed., vol. A13, p. 467-485, VCH Verlagsgesellschaft, Weinheim, New York.