Removal of Hydrogen Sulfide and Recovery of Carbon Dioxide from Geothermal Non-Condensable Gas Using Water

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Abstract

A collaboration of geothermal power plant operating companies in Iceland is developing a water absorption technology that enhances the selectivity for hydrogen sulfide removal from non-condensable gas (NCG) that is rich in CO_2. Cool water is used to absorb the H_2S on a once-through basis, and the H_2S-containing water would then be injected into a suitable underground reservoir. Operation of the absorption at significantly elevated pressure (~5 bar or higher) is required in order to allow for water to have a reasonable solubility for the H_2S. Two varieties of this technology were considered, one in which a flash of the absorption column bottoms is used to increase the H_2S absorption selectivity, and one in which a reboiler is applied to the absorption column bottoms. Process simulations were used to estimate the performance of this concept for six geothermal power plants in Iceland, with the reboiled method preferred due to the availability of low-value heat from hot brine. In addition to H_2S removal, the recovery of CO_2 products from the NCG (after the H_2S is removed) was also considered. Conceptual designs were developed for recovery of low purity CO_2 gas and higher purity liquefied CO_2 products.

Keywords: noncondensable gas, NCG, H_2S abatement, hydrogen sulfide removal, CO_2 recovery, Iceland

1   Background

The removal of hydrogen sulfide (H_2S) from non-condensable gas (NCG) from geothermal facilities in Iceland has been the subject of intensive study in recent years. A group of geothermal operating companies in Iceland – Orkuveita Reykjavíkur, HS Orka, and Landsvirkjun – formed a collaborative group, referred to here as the SulFix team, to investigate, test, and implement H_2S removal technologies as well as technologies for the recovery and use of CO_2. Some of the previous work by the SulFix team[1] has focused on the use of water as an absorbent, and the recovery of H_2S-rich and CO_2-rich streams separately, followed by the disposal of these streams separately by injection into a suitable underground reservoir. The SulFix team has also investigated the bulk removal of the majority of both the H_2S and CO_2 using water, and the disposal of that mixed stream by injection.

Six geothermal power plants – Nesjavellir, Hellisheiði, Reykjanes, Svartsengi, Bjarnarflag, and Krafla – are operated and/or planned in Iceland by the member companies of the SulFix team. These facilities do not currently have H_2S abatement systems in place. A summary of the NCG characteristics at these facilities is given in Table 1.

Table 1. Characteristics of NCG for Each Geothermal Facility.							
Characteristic	Units	Nesjavellir	Hellisheiði	Reykjanes	Svartsengi	Bjarnarflag	Krafla
Gas Flow Rate	kg/s	1.381	1.204	0.54	1	0.18	1.1
H_2S Content	mass%	26.06	32.56	3.52	1.61	46.00	6.89
CO_2 Content	mass%	42.68	64.56	95.82	97.86	49.98	72.09
H_2 Content	mass%	1.04	0.39	0.02	0.03	3.56	0.32
N_2 Content	mass%	24.07	1.99	0.64	0.48	0	15.06
O_2 Content	mass%	6.08	0.38	0	0	0	5.27
CH_4 Content	mass%	0.06	0.116	0.01	0.01	0.28	0.02
Ar Content	mass%	0	0	0	0.02	0.17	0.36
H_2S Flow Rate	ton/day	31.1	33.9	1.64	1.38	7.15	6.54

There are many technologies available for the removal of H_2S from NCG. A technology screening study was performed for the Bjarnarflag facility in 2011, and was the subject of a paper presented at a previous GRC conference[2]; general information regarding the technologies that can be applied for H_2S removal from NCG can be found in that paper. This earlier paper concluded that the use of water scrubbing, followed by injection of the water, was the preferred

method for the removal of the H_2S from the NCG at Bjarnarflag. The use of water for this task is strongly dependent upon location-specific factors: the availability of plentiful cold ground water for use and the capability to inject the water loaded with H_2S and CO_2 (commonly referred to as "sour water") in a nearby injection well.

When compared to other solvents used to remove H_2S from gases, such as alkanolamines, water is a relatively poor solvent for H_2S. In order to achieve significant absorption of H_2S from a gas, a large amount of water is required and/or the absorption process must take place at high pressure. The availability of large amounts of cold water (lower temperature is also beneficial for H_2S absorption) allows for the effective removal of H_2S from the NCG at relatively moderate pressures.

When water is used to absorb H_2S from NCG in a conventional absorption system, such as in a packed tower, a large fraction of the CO_2 is also absorbed into the water. H_2S has roughly three times the solubility of CO_2 in pure water, so some selectivity for H_2S removal over CO_2 is achieved naturally because of the solubility difference, but because the concentration of CO_2 in NCG is usually higher than that of H_2S, the amount of CO_2 absorbed may still be higher than desired. The co-absorption of these species results in an overall greater requirement of water to remove a given amount of H_2S, and results in the sour water being loaded with both H_2S and CO_2. The injection of water containing both CO_2 and H_2S may have an effect on some subsurface chemistry; in some cases the subsurface chemistry may result in the preference to not inject CO_2 with the H_2S.

The selective removal of H_2S from NCG that contains a large amount of CO_2 is possible with a number of technologies. For the absorption of H_2S using water, the SulFix team and Trimeric Corporation have been developing a technology that allows significant selectivity to be achieved. In addition to limiting the amount of water used in the absorption and removing the need to inject CO_2-rich water, the selective absorption technology also results in the capability of recovering a CO_2-rich product for use.

For some cases, the NCG remaining after H_2S removal will be composed primarily of CO_2; nitrogen, oxygen, hydrogen, argon, methane, residual H_2S, and some other gases may also be present in minor amounts. The recovery of a CO_2 product from this CO_2-rich gas stream can be approached in a number of ways, depending upon the anticipated use of the product and the amount of other gases present in the CO_2.

This paper focuses on the selective removal of H_2S from NCG using water, and the subsequent recovery of a CO_2-rich gas product.

2   The Selective Removal of H_2S from NCG Using Water

H_2S and CO_2, both of which are often referred to as "acid gases", are only sparingly soluble in water at atmospheric pressure. Even at elevated pressure, the solubility of these gases in water is not very high; thus, it is uncommon to use water to absorb these gases in commercial-scale gas treating systems. Alkanolamines and some physical solvents are more commonly used for the absorption of acid gases. The alkanolamine and physical solvents are commonly used in acid gas absorption processes where the solvent is regenerated, releasing the acid gases as a concentrated stream, and the solvent is recycled to absorb more acid gas. Water can be used in a similar fashion, but due to the lower solubility characteristics of water, a much higher recirculation rate is required than with the alkanolamines and other physical solvents.

For cases where water can be used to absorb H_2S in a "once-through" manner, rather than needing to be regenerated and reused, and where the water can then readily be disposed of by injection into a suitable underground reservoir, it is logical consider the use of water as an absorbent for H_2S.

The need for the selective, or semi-selective, removal of H_2S from gas streams containing CO_2 is a common issue in gas treating, and some alkanolamines, physical solvents, and the process technologies that use these solvents are designed in order to enhance or tune the selectivity for H_2S removal. It is also possible to enhance the selectivity of a water scrubbing process. A number of different approaches can be taken to increase the selectivity of a solvent for the absorption of H_2S, such as exploitation of the relatively slow rate at which CO_2 absorbs into aqueous solution, chemical modification of the solvent to enhance H_2S absorption or retard CO_2 absorption, or altering the absorption process scheme to yield a net gain in selectivity.

In this project, alterations to the absorption process scheme are being considered as a way of increasing the overall selectivity of the absorption process. The water loaded with CO_2 and H_2S from the bottom of the absorption column is subjected to either a lower-pressure flash or to an elevated temperature partial vaporization (reboiler) in order to remove a large fraction of the CO_2 that has been absorbed by the water in the absorption column. The vapor stream from the flash or the reboiler, which would be rich in CO_2, would be returned to the bottom of the absorption column. This process arrangement allows for substantial improvement in the capability of water to absorb H_2S from the feed NCG while minimizing (but not eliminating) CO_2 absorption. The rest of this section describes this concept in more detail, and provides the results of process simulations that were used to characterize it.

2.1   Characteristics of Selective H_2S Scrubbing using Water

Two methods for increasing the selectivity of H_2S absorption in once-through water scrubbing were investigated: a reboiled absorption column and an absorption column with bottoms liquid flashes. Using the gas feed composition basis shown in Table 2 and Table 3, both methods were

explored using process simulation software. Figure 1 shows a schematic of the reboiler method and Figure 2 shows a schematic of the flash method.

Case studies were created for both methods, with key variables changed. The absorber column in all of the case studies had 30 theoretical stages with a water feed of 36 kg/s at 20°C (30 theoretical stages is greater than needed to achieve a reasonable separation, but was chosen as a basis to demonstrate difference between different operating conditions). Table 2 shows the results from a case study for selective absorption of H_2S using a reboiled absorber column with a cross exchanger for heat recovery. The first column of the table shows the inlet gas composition and flow rate, cases 1-6 show the gas conditions out of the absorber at varying reboiler temperatures; for comparison, the first column shows the resulting gas conditions out of the absorber with no reboiler. Without a reboiler, the absorber removes nearly 100% of the H_2S and 55% of the CO_2; while high H_2S removal is desired, high CO_2 removal is not desired. As the reboiler temperature increases, the H_2S removal is estimated to decrease slightly and the CO_2 removal decreases more rapidly, resulting in the increasingly selective removal of H_2S.

Higher reboiler temperatures are associated with higher heat duty requirements. At the Icelandic geothermal power plants, the heat source for the reboiler would be either steam or hot brine. The economic viability of this process concept probably depends upon the ability to supply a large portion of the required reboiler heat by cross exchange. As shown in Figure 1, the bottoms stream is first cross-exchanged with the hot liquid from the reboiler separator; this scheme is possible because the water from the bottom of the column is still fairly cool (typically 21 – 22°C) even when the vapor return from the reboiler is over 100°C.

Table 2 is restricted to a single water feed flow rate and temperature, and a limited range of reboiler temperatures. These conditions are just shown as an example, and a wider range of conditions could be envisioned. In general, an increase in the feed water flow rate and a decrease in the feed water temperature temperature will increase the removal efficiency for both H_2S and CO_2. The selectivity for H_2S removal is achieved via the manipulation of the reboiler temperature.

Table 2

Stream Description	Feed Gas (NCG)	Treated Gas from Absorption Column						
		No Reboiler	Case 1	Case 2	Case 3	Case 4	Case 5	Case 6
Reboiler Temp, C		NA	60	80	100	110	115	118
Steam feed, kg/s		NA	0.82	0.83	0.86	0.88	0.89	0.91
Cross Exchange Duty, KJ/s		NA	4,441	7,440	10,421	11,891	12,610	13,016
Reboiler Duty KJ/s		NA	1,526	1,544	1,597	1,641	1,666	1,703
Total kg/s	0.400	0.138	0.209	0.244	0.269	0.281	0.287	0.290
H_2S mole%	24.9	0.02	0.06100	0.2020	0.5900	0.9610	1.21	1.37
CO_2 mole %	48.3	45.1	56.00	59.80	61.90	62.60	62.9	63.0
H_2S removal %		99.96	99.8	99.5	98.3	97.2	96.4	95.5
CO_2 removal %		55	29	17	8	5	3	0.6

Case Study for Selective Absorption of H_2S Using a Reboiled Absorber Column
30 theoretical stages, 5 bar operating pressure
Water feed at 36 kg/s and 20°C

Table 3 shows the results from a case study for selective absorption of H_2S using flash of the absorption column bottoms liquid. Multiple flash stages were considered: 1, 2, and 3, with the pressure of each flash decreasing. The final stage pressure for each case is shown in the table. The gas from each flash (which will be rich in CO_2) is compressed, combined with the other flash stages and sent back to the bottom of the column.

The first column of Table 3 shows the inlet gas conditions, cases 1-3 show the gas conditions out of the absorber with a differing number of flash stages; for comparison, the first column shows the resulting gas conditions out of the absorber with no flash.

As with the reboiler cases, without flash the absorber removes nearly 100% of the H_2S (desired) and 55% of the CO_2 (not desired). As flash stages are added, the H_2S removal decreases slightly and the CO_2 removal decreases more rapidly resulting in the selective removal of H_2S.

While flashing the bottoms liquid to a lower pressure is a relatively inexpensive unit operation, the gases liberated in the flash, which contain mostly CO_2 with some H_2S, must be compressed to 5 bar in order to be returned to the absorption column.

The cases in Table 3 show a few cases where the flash pressure is varied from 0.5 to 2 bar, but the feed water temperature and flow rate are not varied. Note that the feed water flow rate and temperature have a significant effect on this system. In general, an increase in the water flow rate and a decrease in the temperature will result in an increase in the absorption efficiency of both CO_2 and H_2S. Manipulation of the flash conditions result in the selectivity for H_2S removal.

Table 3

Case Study for Selective Absorption of H_2S Using an Absorber Column with Bottoms Flash
30 theoretical stages, 5 bar operating pressure
Water feed at 36 kg/s and 20°C

Stream Description	Feed Gas (NCG)	Treated Gas from Absorption Column			
		No Flash	Case 1	Case 2	Case 3
No. Flash Stages		0	1	2	3
Last Stage Pressure, bar		NA	2	1	0.5
Compressor Power, kW		0	19	48	82
Total kg/s	0.400	0.138	0.227	0.287	0.342
H_2S mole %	24.9	0.021	0.11	1.2	13
CO_2 mole %	48.3	45.1	58	63	56
H_2S removal %		99.96	99.7	96.3	53.3
CO_2 removal %		55	23	2.5	0.004

The flash and reboiler techniques for increasing the H_2S absorption selectivity are different methods of achieving the same goal. From a capital cost perspective, the reboiler method will require the installation of rather large heat exchangers, while the flash method will require the purchase of gas compression. From an operating cost perspective, the reboiler method will consume either steam or hot brine (if available), while the flash method will typically require electricity to drive the compressors. The choice of the method to use for achieving selectivity may be dependent upon the situation and preference of the site at which the technology would be implemented.

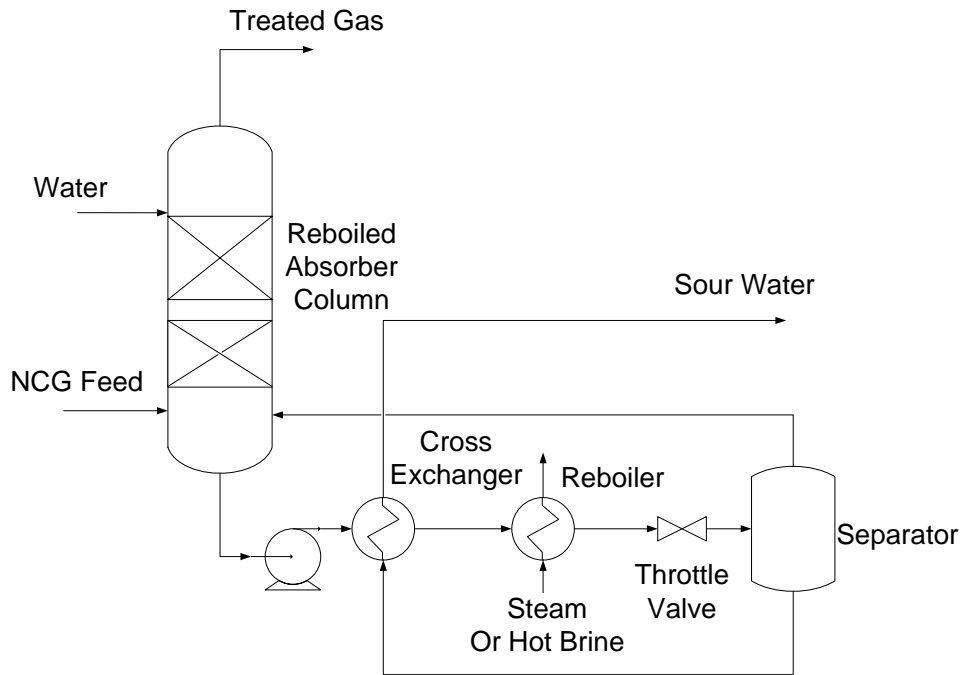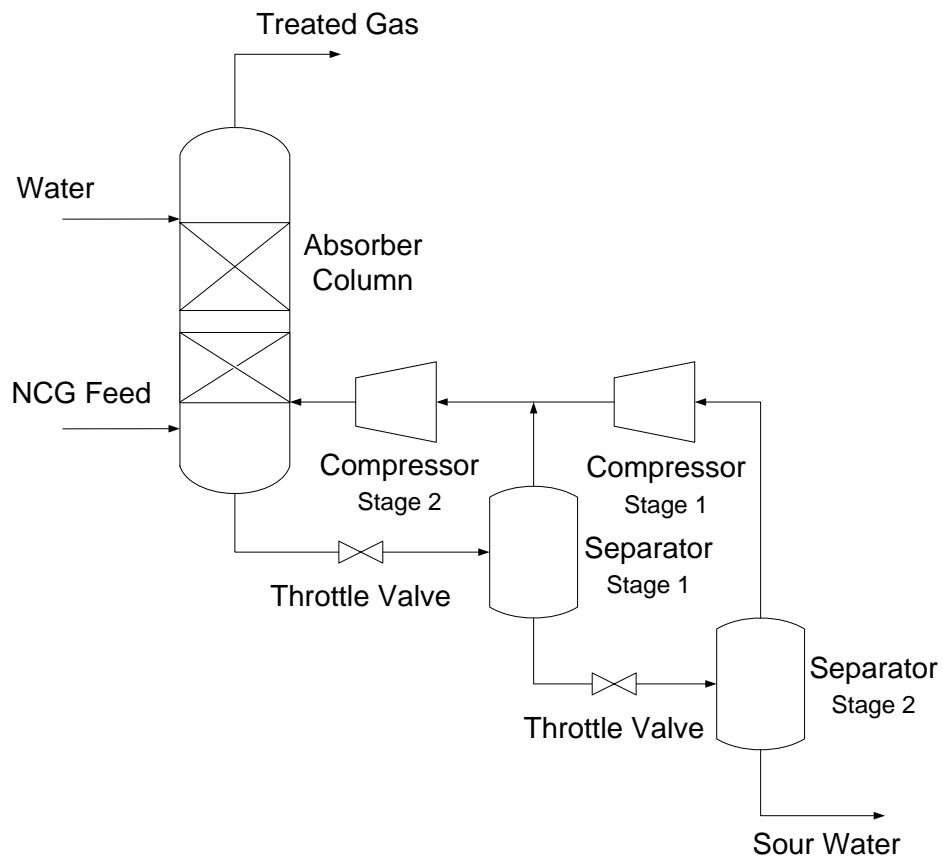**Figure 1. Conceptual Design for Selective H$_2$S Scrubbing Using a Reboiled Absorber Column**

Treated Gas

Water

Reboiled
Absorber
Column

Sour Water

NCG Feed

Cross
Exchanger   Reboiler

Separator

Throttle
Valve

Steam
Or Hot Brine

Figure 2. Selective H$_2$S Scrubbing Using an Absorber Column with 2-Stage Bottoms Flash

Treated Gas

Water

Absorber
Column

NCG Feed

Compressor
Stage 2

Compressor
Stage 1

Separator
Stage 1

Throttle Valve

Throttle Valve

Separator
Stage 2

Sour Water

2.2   Application of Selective H₂S Scrubbing to Different NCG Streams

After the two methods for achieving H₂S selectivity were considered by the SulFix team, it was decided to pursue further study of the reboiled method, primarily because of the preference to use hot brine or low value excess steam as the main utility requirement rather than electricity.

The reboiled selective scrubber for H₂S removal was then considered for the six different geothermal power plant sites, using process simulation software. The results of the study are shown in Table 4. Typical requirements for theoretical stages in the absorption column ranged from 15 to 20.

Table 4. Results of Selective H₂S Removal Evaluation for Different Sites

		Site					
		Nesjavellir	*Hellisheiði*	*Reykjanes*	*Svartsengi*	*Bjarnarflag*	*Krafla*
Inlet Gas to Scrubber							
Gas Flow Rate	kg/s	1.381	1.204	0.54	1	0.18	1.1
H2S Content	mass%	26.06	32.56	3.52	1.61	46.00	6.89
CO2 Content	mass%	42.68	64.56	95.82	97.86	49.98	72.09
H2 Content	mass%	1.04	0.39	0.02	0.03	3.56	0.32
N2 Content	mass%	24.07	1.99	0.64	0.48	0	15.06
O2 Content	mass%	6.08	0.38	0	0	0	5.27
CH4 Content	mass%	0.06	0.116	0.01	0.01	0.28	0.02
Ar Content	mass%	0	0	0	0.02	0.17	0.36
H2S Flow Rate	ton/day	31.1	33.9	1.64	1.38	7.15	6.54
Scrubber Performance							
H2S absorbed into water	%	99.78	99.93	99.00	95.03	99.87	99.67
CO2 absorbed into water	%	17.4	17.7	14.8	14.3	4.1	26.4
H2S in treated gas	ppmw	<600	<300	<1000	<1000	<300	<300
Water feed to H2S Scrubber							
Flow rate	kg/s	240	135	50	65	40	125
Feed Temperature	C	30	20	20	5	20	20
Water containing H2S and CO2 from scrubber to be injected (Sour water)							
Temperature	C	42	31	33	16	35	32
pH (@ temp)		4.0	3.9	4.1	4.1	4.1	4.0
Vapor Pressure (@ temp)	bara	1.2	1.9	1.4	1.4	0.9	1.7
Reboiler							
Temp	C	127	90	110	90	130	100
Duty	kJ/s	11,387	5,862	2,196	2,607	2,092	4,995
Heat recovery cross exchanger							
Duty	kJ/s	85,494	33,774	16,192	18,809	15,888	32,727

Results from each site vary based on the heating medium available (brine or steam), the composition and flow rate of the gas to be treated, the amount and temperature of the available feed water, the desired maximum height for an absorption tower, and the H₂S removal

requirements. Generally, hotter reboiler temperatures result in better selectivity for the removal of H_2S compared with CO_2; larger volumes of feed water, colder feed water temperature, and greater amount of contacting stages in the absorber result in better overall removal of H_2S.

The results of the simulation study showed that conditions at Bjarnarflag produce the best results with 99.9% H_2S removal and 4.1% CO_2 removal from the gas. Bjarnarflag has the lowest gas flow rate of any site but contains the highest concentration of H_2S at 46% in the gas stream. Water at 20°C is fed to the scrubber and the heating medium is able to reboil the bottoms stream to 130°C. Svartsengi has the lowest H_2S removal due to the lowest concentration of H_2S in the feed gas stream and a less stringent H_2S requirement at this site. This means the scrubber can run with a lower reboiler temperature (90°C) and lower water feed rate (65 kg/s) than some of the other sites, while still achieving the H_2S requirement. At each site at least 95% of the H_2S and less than 30% of the CO_2 is absorbed in this study. H_2S in the treated gas stream is removed down to approximately 300 ppm to 1000 ppm. Deeper removal of H_2S might require additional treatment.

2.3   Comments on Absorption Tower Design

In the design of packed columns for the absorption of H_2S from a gas stream, the sizing of the column typically requires a variety of data, such as the amount of H_2S that is to be removed, the characteristics of the absorbent (water), the type of packing to be used, and the flow rates and properties of the gas and the water. Additionally, the efficiency of the packing or trays to be used in the column to contact the liquid and gas phases must be known.

Although the removal of H_2S from gases using various aqueous solutions (e.g., caustic, alkanolamines) is extremely common, the removal of H_2S using only water is less common and the publically available data on this topic is typically limited to equilibrium conditions; little information appears to be readily available on the efficiency of packing and trays for H_2S removal by water. For the more common solvents, such as alkanolamines, the efficiencies of trays and packing for the absorption of H_2S are well documented and the performance of commercial-scale units can readily be predicted using manual calculations and process simulation tools.

For the absorption of H_2S using amines or caustic, the efficiency of trays and packing tend to be very good – the height of a transfer unit (HTU) of packing is often in the ~ 100 to 300 mm range. For systems in which the solubility of the species to be absorbed is very low, such as when water is the absorbent for H_2S, the efficiency of trays and packing tends to be much lower. For such systems, HTU may range as high as ~500 mm to 1500 mm. A limited search of the literature and other resources did not result in enough data to directly predict the HTU for this system. Another factor that makes estimating the packing efficiency particularly challenging for this system is the fact that two gas components are being absorbed concurrently and the gas volume changes substantially (due to the fact that the fractions of H_2S and CO_2 in the feed gas are very

high) as the gas goes up the absorption column. Some process simulation software have rate-based methods that are capable of estimating the mass transfer efficiencies of systems like this, but without validation against some pilot plant or commercial plant data, it is not certain that these simulation software predictions are accurate.

Based on the novelty of this selective H_2S absorption scheme and the lack of data on the efficiency of packing and trays for this system, the SulFix team decided that it was preferred to undertake a pilot-scale test of this concept prior to commercialization, with the goal of obtaining data on the efficiency of the absorption column and the reboiler system under conditions expected during commercialization of the technology.

2.4   Deep H_2S Removal

The water scrubbing technology being developed is not ideal for achieving deep (i.e., zero to low ppm) H_2S removal from the feed gas. For cases where very low H_2S is required in the treated gas, it may be more economical to add an additional H_2S removal method rather than trying to design the water scrubber to achieve this by itself.

For the NCG treatment at the SulFix team member geothermal power plants, the removal of H_2S down to low ppm levels prior to venting the NCG is not required. It is thought that removal of H_2S down to very low levels would only be required if it is desired to recover a CO_2 product; for many CO_2 products, the removal of H_2S down to very low levels could be required.

Many technologies are available for removing small amounts of H_2S from gases. For cases where the amount of H_2S to be removed is less than about a few hundred kilogram per day, it is most common to use "scavenger" technology. H_2S scavengers are solid or liquid chemicals that react irreversibly with H_2S, and are capable of removing the H_2S in the gas down to near zero ppm levels. The capital cost of scavenger systems is typically low due to the fact that the process will usually consist only of one or more vessels that contain the scavenger material. Operating costs tend to dominate the economics of the use of scavengers, because spent scavenger is typically disposed of, and is replaced with fresh material. A review of the typical scavenging options and their performance is contained in a reference.[3]

A common implementation of solid scavengers (such as SulfaTreat[*]) is to provide two fixed beds that are operated in parallel or in a lead-lag mode; with at least two fixed bed vessels, the system can be operated while one of the beds is changed out.

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[*] SulfaTreat is offered by the M-I SWACO division of Schlumberger. Other similar scavengers - based on metal oxide reactants - are available from other companies.

3   Options for CO_2 Recovery

Although the focus of this work is on improving the effectiveness of water for H_2S removal from H_2S, some consideration was also given to the potential for CO_2 recovery following the H_2S removal. The characteristics of NCG vary substantially by location, and the method used for CO_2 recovery, and the economic parameters of the recovery, will also vary. Therefore, the methods and conclusions discussed here may not apply to other situations.

A few important considerations for CO_2 recovery from NCG include:

- The amount of H_2S remaining in the CO_2 after the water scrubbing (or other bulk H_2S removal technology)

- The concentration of other components (e.g., hydrogen, helium, methane, nitrogen, oxygen, etc.) in the NCG

- Hazards associated with the NCG (e.g., flammability)

- The intended use of the CO_2, and its required purity

- Whether the CO_2 product should be available as a gas or liquid

For the SulFix team member companies in Iceland, two general categories of CO_2 products were identified:

- A liquefied, industrial-grade CO_2 product that would be transported from the site by tank truck.

- A lower purity CO_2-rich gas product that would be transported by pipeline to local users, such as greenhouses.[4]

Many other grades of CO_2 may exist, and many other uses of the CO_2 are possible. It was considered preferable to produce a marketable CO_2 product prior to considering other disposition options for the CO_2, or direct venting.

3.1   *Lower purity CO_2-Rich Gas Product*

If there is a local use for a CO_2-rich gas product, it is possible that a CO_2-rich NCG can be used directly after it has been treated for H_2S removal. However, there may be some gas components that must be removed prior to a specific use. For example, for use in a greenhouse it may not be desired to transport and use a flammable gas mixture, so CO_2-rich gases rich in hydrogen and/or methane may have to be further treated. Various separation techniques could be used to remove the unwanted gas species from the mixture, but for producing a low purity CO_2 product at the lowest cost, it may be feasible to remove the flammable species by combustion with oxygen from air. The addition of the air needed to support the combustion results in the dilution of the product gas with nitrogen, unless pure oxygen is used rather than air.
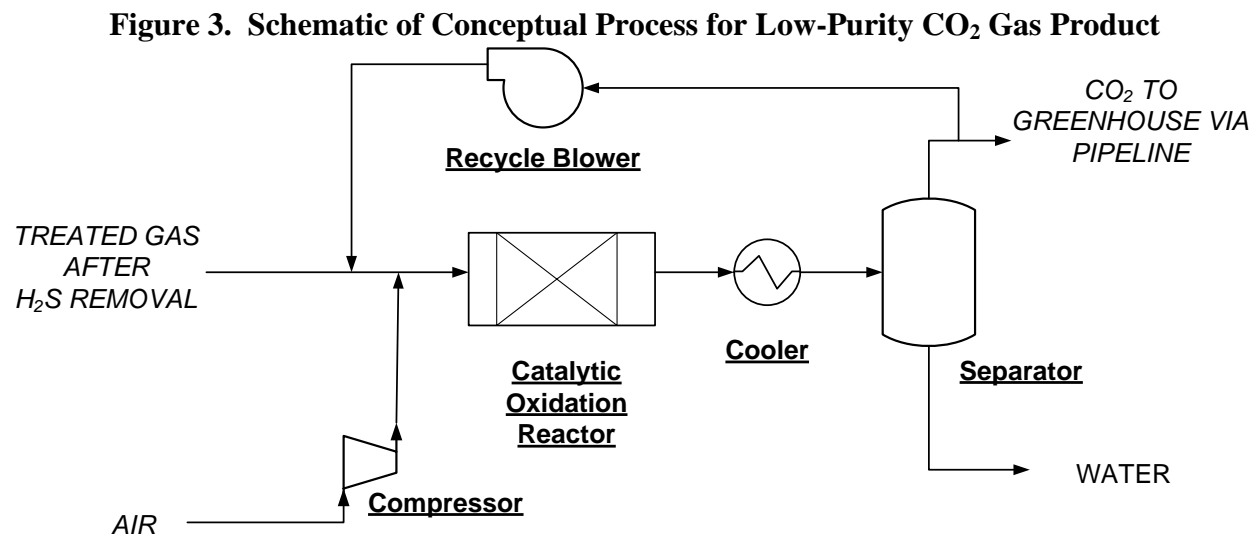
Figure 3 shows a schematic of a conceptual process to combust NCG that has been treated for H_2S removal. In one case that was considered, a stream which has been reduced in H_2S concentration would have a composition of approximately:

   81 mole % CO_2
   13 mole % H_2
   5 mole % N_2
   1 mole % O_2
   <1 mole % others

By the use of catalytic oxidation, with a partial recycle of the product gas to control the catalytic reactor temperature, the above gas stream can create a gas product of approximately:

   79 mole % CO_2
   < 1 mole % H_2
   19 mole % N_2
   <1 mole % O_2
   <1 mole % others

The applicability of this technology is very specific to the composition of the NCG, and the purity requirement for the recovered CO_2. Different technologies and different approaches may be required in other situations.

Figure 3. Schematic of Conceptual Process for Low-Purity CO_2 Gas Product

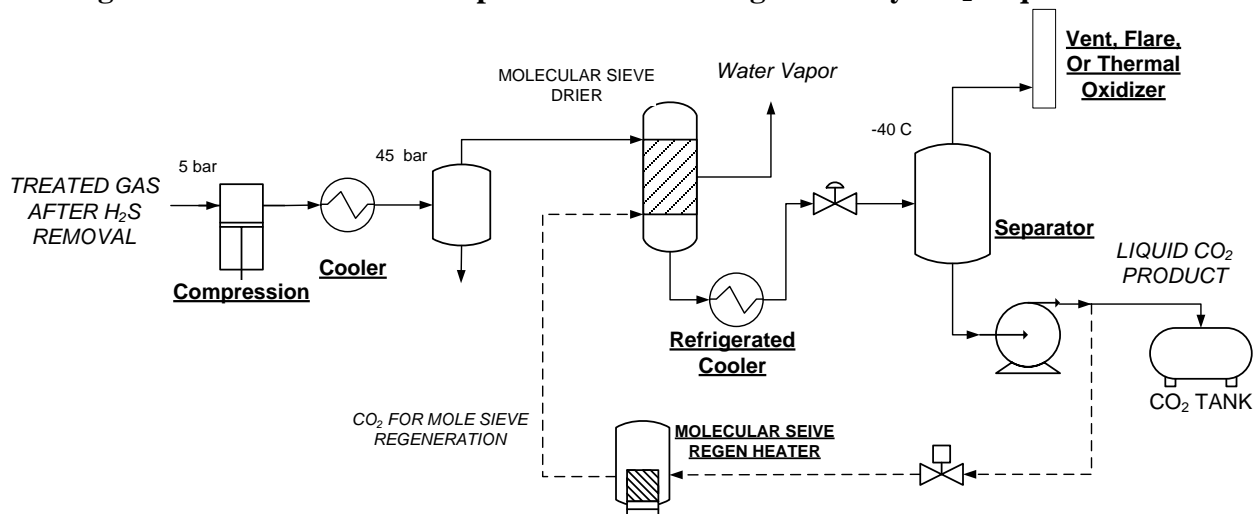## 3.2 Liquefied, Industrial-grade CO_2 Product

Apart from some residual water vapor, CO_2 is often the highest boiling-point constituent of significant concentration in the NCG once the H_2S has been removed, and it may be possible to separate a liquefied CO_2 product stream by a relatively simple chilling and dehydration process. For all of the Icelandic cases considered, it is estimated that it would be possible to make an industrial-grade CO_2 product with a purity in the 98-99 mole percent range, assuming that there is no requirement to recover as a product a high percentage of the CO_2 in the NCG. A schematic of such a conceptual process is shown in Figure 4.

In this process, the NCG is compressed to 27-43 bar (depending on the composition), dried to less than 1 ppm water with a molecular sieve adsorbent system, chilled with a refrigeration loop to condense the CO_2 to liquid, then flashed to separate most of the remaining NCG from the liquid CO_2. The resulting CO_2 purity is in the 98-99 mole percent range. A fraction of the product CO_2 is recycled and heated to regenerate the molecular sieve bed. Depending upon the composition of the NCG, the residual gas could contain a significant concentration of methane or H_2 that could be burned to generate heat for use in other processes or to generate steam for additional power generation.

For the NCG gas composition given in Section 3.1, this process is estimated to be capable of producing a 99% pure CO_2 liquid product (impurities mostly N_2 and O_2) while recovering about 80% of the CO_2 in the NCG feed in the liquid product.

If a higher purity liquefied CO_2 product is desired, then a low-temperature distillation process would be required in place of the flash. This option would probably substantially increase the capital cost of the process. Very high quality CO_2 products, such as food grade, may require additional treatment, such as a carbon bed, in addition to the low temperature distillation.

Figure 4. Schematic of Conceptual Process for Higher Purity CO_2 Liquid Product

4 Conclusion

The selective removal of H_2S from NCG can be done using once-through water scrubbing in a column equipped with either a low pressure bottoms liquid flash or a bottoms liquid reboiler. The selective removal of H_2S from the NCG may be desired in order to allow for minimization of water usage, the capability to inject CO_2-containing and H_2S-containing water streams into separate wells, and the capability of recovering a CO_2 product. Two types of CO_2 products were envisioned – a lower purity, low pressure gas and a higher purity liquid – and these products can likely be recovered from the NCG, after it has been reduced in H_2S concentration.

The situation in Icelandic geothermal power plants is particularly well-suited to this process, because there is plentiful cold ground water available, there is waste heat available from brine, and injection of the sour water appears to be feasible. Further study of this concept is being pursued by the SulFix team, including pilot testing of parts of the process.

5 References

1. Júlíusson, B.M.; *Reducing H₂S Emissions from Geothermal Power Plants*. Collaboration of Icelandic Energy Companies; GEORG (Geothermal Research Group), From Waste to Value Seminars; April 2013; Reykjavík, Iceland.

2. Mamrosh, D.L., McIntush, K.E., Beitler, C., Markússon, S.H., Einarsson, K.; *Screening of H₂S Abatement Options for Geothermal power Noncondensable Gas at Bjarnarflag*; paper presented at the GRC Annual Meeting; October 2012; Reno, NV.

3. Fisher, K.S., Lundeen, J.E., Leppin, D.; *Fundamentals of H2S Scavenging for Treatment of Natural Gas*; paper presented at The Ninth GRI Sulfur Recovery Conference, October 1999, San Antonio, TX.

4. Dunstall, M.G., Graeber, G.; *Geothermal Carbon Dioxide for Use in Greenhouses*; GHC Bulletin, January 1997.