

H₂S in Geothermal Power Plants: from Waste to Additional Resource for Energy and Environment

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Geothermal energy is a sustainable and clean energy source. Unfortunately, utilization of high-enthalpy geothermal systems is generally associated with emissions of gases like carbon dioxide (CO₂), hydrogen sulfide (H₂S), hydrogen (H₂), nitrogen (N₂), methane (CH₄), and argon (Ar). The emission of some of these gases, particularly CO₂, H₂S and H₂, is one of the main environmental concerns associated with the use of geothermal energy. The sequestration of these gases and their geological storage is the most diffuse viable option for reducing emissions. However, there is interesting technology, called AG2STM, that allows to convert H₂S and CO₂ into syngas. In this work, the match of this technology with geothermal power plant is analyzed as a new potential industrial route. The study is based on two different geothermal power plants located in Hellisheiði and Nesjavellir (Iceland) that globally emit 61,800 t of CO₂ and 28,200 t/y of H₂S. The simulations provide some interesting results: (I) the total conversion of H₂S that avoids its underground re-injection with the related environmental problem, (II) the reduction of CO₂ emissions (about 8 %) and (III) the increasing of the global thermal energy produced with the same amount initial geothermal energy. The latter is due to the possibility to burn extra hydrogen coming from the AG2STM process. Finally, other advantages of this match are the production of an extra medium pressure steam and the possible reuse of the amount of H₂ related to the geothermal plants emissions.

1. Introduction

Nowadays, geothermal power is considered to be a sustainable, renewable source of energy because the heat extraction is smaller compared with the Earth's heat content. The greenhouse gas emissions of geothermal electric stations are on average 45 grams of carbon dioxide per kilowatt-hour of electricity (Tomasini-Montenegro et al., 2017). For these reasons, geothermal electricity generation is currently used in 24 countries (Holm et al., 2010), while geothermal heating is in use in 70 countries (Fridleifsson et al., 2008). In 2015, the worldwide geothermal power capacity amounts to 12.8 GW, of which 28 % or 3,548 MW are installed in the United States. International markets grew at an average annual rate of 5 percent over the three years to 2015, and global geothermal power capacity is expected to reach 14.5 – 17.6 GW by 2020 (Ruggero, 2017). Geothermal power stations are similar to other steam turbine thermal power stations in that heat from a fuel source is used to heat water or another working fluid (Kehlhofer et al., 2009). The working fluid is then used to turn a turbine of a generator, thereby producing electricity. The fluid is then cooled and returned to the heat source. Said this, the geothermal technologies, that are currently used, are dry steam power stations, flash steam power stations and binary cycle power stations (DiPippo, 2012), as reported in Figure 1. However, one of the main disadvantage of these technologies is the atmospheric disposal of geothermal gases. The emitted gases have both local and global environmental effects, making lowering the gas emissions from geothermal power plants one of the important challenges of the geothermal industry (Aradóttir et al., 2015). Geothermal gases can be divided into two categories depending on their solubility in water. The sour gases CO₂ and H₂S

are soluble in water but other geothermal gases H_2 , N_2 , CH_4 and Ar are much less soluble in water and need to be separated from the soluble gases. Indeed, injection of insoluble gases, even in small quantities will lead to a build-up of gas pressure in the aquifer receiving the water and inhibit the solubility of the sour gases in the aqueous phase or call upon unpractical amounts of water needed for complete dissolution of the geothermal gas.

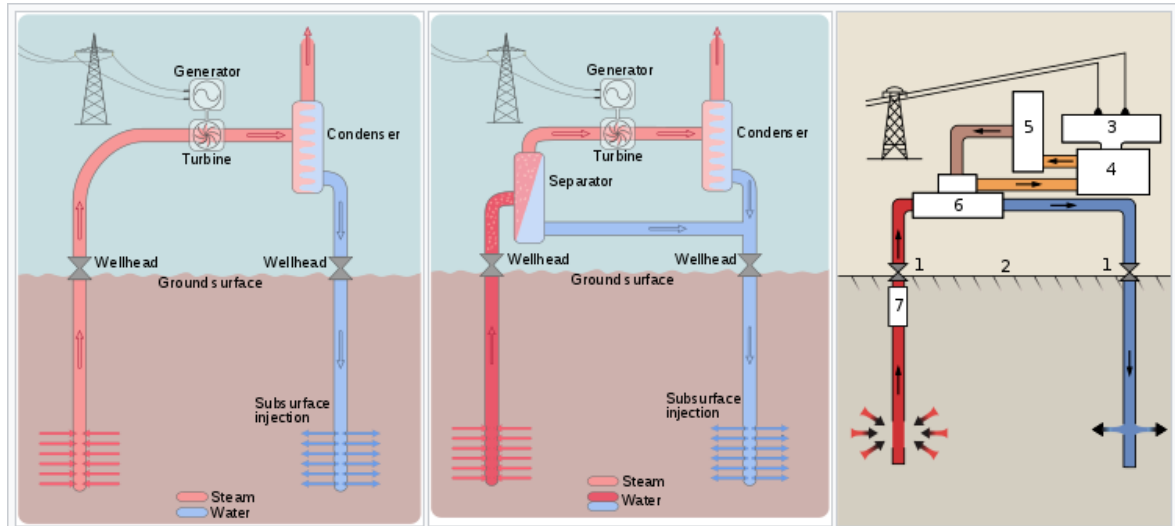


Figure 1: Dry steam (left), flash steam (centre), and binary cycle (right) power stations (Duffield and Sass, 2003)

In this work, the industrial power plants of Nesjavellir and Hellisheiði were taken in consideration as a base case study. Indeed, Gunnarsson et al. (2013) provided some useful data for our simulation, analysing in-deep the emissions of these two plants. The latter are located to the north and south of the Hengill central volcano which is located in the western volcanic zone SW-Iceland, approximately 20-25 km southeast of Reykjavík. Currently Nesjavellir power station is producing 290 MW_{th} and 120 MWe. Total installed capacity in Hellisheiði power plant is 303 MWe and 133MW_{th}. Composition of gases is shown in Table 1. Both gases are characterized by low CO_2 and high H_2S and H_2 concentration. Higher concentration of H_2 and H_2S from Nesjavellir power plant compared to the gas from Hellisheiði Power Plant is mainly due to the higher initial steam fraction in the geothermal reservoir.

Table 1: Composition of geothermal gas emitted from Hellisheiði and Nesjavellir power plants

	CO_2	H_2S	H_2	CH_4
Nesjavellir	43.0%	33.9%	23.0%	0.2%
Hellisheiði	58.1%	29.4%	12.3%	0.2%

In order to abate and reduce the emissions of these sour gases, a gas separation station was built next to Hellisheiði power plant to treat the geothermal gas prior to dissolution in water. Figure 2 shows a simplified schematic diagram of the gas separation process. Three kinds of technologies were initially under scrutiny in the station: a membrane system for H_2 and N_2 removal, a system comprised of absorption and desorption towers which separates the soluble gases CO_2 and H_2S from the rest of the geothermal gases and a distillation column to separate CO_2 from H_2S . The operation of the adsorption and desorption unit has been a success and it effectively separated the soluble and non-soluble gases. Membrane system has not been tested to date, but it is design to also separate the non-soluble gases from the soluble gases. In the distillation column the difference in volatility of CO_2 and H_2S are used to separate the two gases. Liquid H_2S and water mixture that concentrated on the bottom of the distillation column is highly corrosive and operation had to be stopped because of severe corrosion in the cooling element at the bottom of the column. For these reasons, novel pilot injection projects, called CarbFix and SulFix, were investigated. This technology allows to sequestering CO_2 and H_2S into minerals within the subsurface (Aradóttir et al., 2015). Briefly, CarbFix is a developed technology to dissolve the gases into formation fluids and well water during injection. Once dissolved, the gases are no longer buoyant compared to pore fluids, improving considerably security due to decreased leakage risks. This approach of solubility trapping also promotes carbonation of the host rock and thus facilitates the safe long-term sequestration of CO_2

and H₂S in the subsurface. On the other hand, The SulFix aims at assessing the feasibility of in situ H₂S mineral sequestration in basaltic rocks by applying similar methods and technology as CarbFix. The main difference between the projects is, however, that in SulFix, dissolved gases are injected back into the high-temperature geothermal reservoir (below 800 m depth), whereas being injected above it in CarbFix. 90 °C hot geothermal water is furthermore used for dissolving gases in SulFix, while relatively fresh, 30° C warm groundwater is used in CarbFix. Despite this, these new technologies have some disadvantages including the need to compress acid gases, with the related costs, and the injection of a pollutants (i.e. H₂S and CO₂) in the subsoil is a temporary solution that can lead to significant environmental impacts in the future.

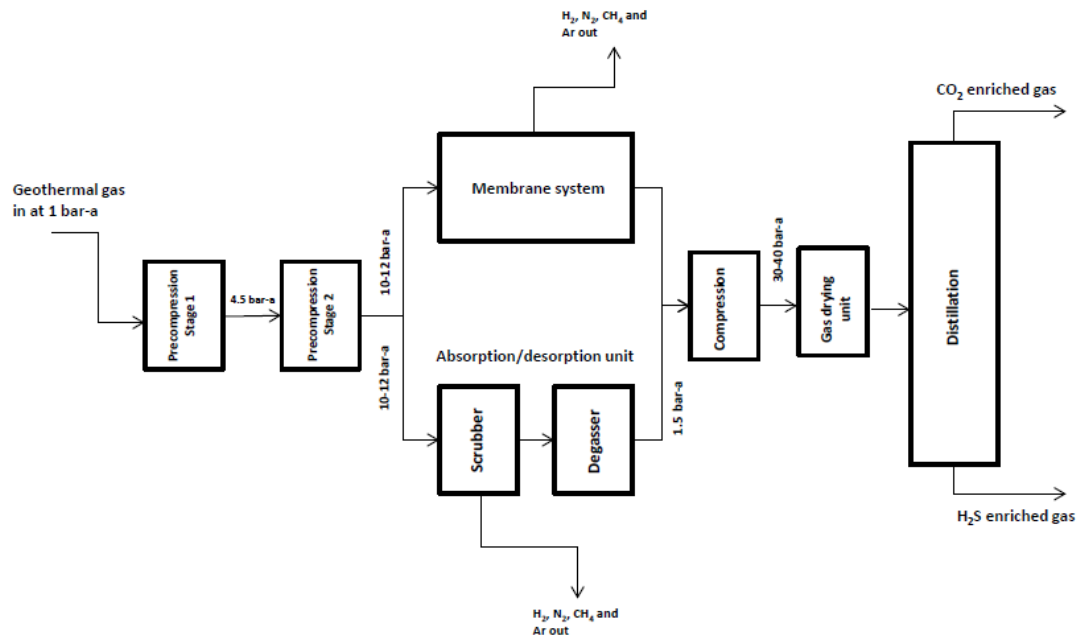


Figure 2: Simplified schematic overview of the gas separation station operated with Hellisheiði power plant, Iceland (Gunnarsson et al., 2013).

However, based on recent advances (Bassani et al. 2016) and patented technology (Manenti et al., 2017), there is an industrial promising way to convert H₂S and CO₂ into valuable products and specifically into syngas according with the oxy-reduction reaction that takes place into a regenerative thermal reactor (RTR):



The AG2S (Acid Gas to Syngas) technology exploits the hydrogen content of H₂S as reducing agent for CO₂ (El-Melih et al., 2016) and, at the same time, allows to use energy sources currently still unexploited due to their relevant sulphur content (Bassani et al., 2015). The target of this work is to evaluate the potential application of this novel technology to geothermal power plant in order to reduce the emissions of sour gases with the contemporary productions of syngas that is a valuable product that could be sell or burn in order to increase the production of thermal energy.

2. Novel process and simulations

In this section, AG2STM technology will be briefly presented with the related tools used for the simulations. As already mention before, this is a novel process that allows to treat acid gases (i.e. H₂S and CO₂). The core of the plant is the regenerative thermal reactor (RTR), which has a different configuration compared with the typical Claus furnace. RTR is mainly composed by a furnace, a waste heat boiler (WHB) and a heat exchanger. This design allows to produce a greater amount of H₂. The key idea is to feed an optimal ratio of H₂S and CO₂ and to preheat the inlet acid gas before the combustion. In this way, H₂S pyrolysis produces hydrogen selectively. Indeed, it is convenient to feed the acid gases to the RTR at high temperatures (e.g. 700°C) in order to reduce the oxygen flow rate required to reach the furnace temperatures (1,100 – 1,350°C). So, the oxygen stream is much lower than the typical oxygen provided to the Claus processes and the H₂S potential for pyrolysis is completely exploited. It is important to emphasize that the reactor is simulated using DSMOKE software with a

detailed kinetic scheme (Ranzi et al., 2013). The latter is coupled within Aspen HYSYS with the use of MATLAB. This allows to include the detailed kinetics, within non-ideal reactor models and in turn into commercial environments for the simulation of chemical plants. The detailed kinetic scheme selected is the one developed in this work. The catalytic reactor configuration is the typical one of the Claus process (Manenti et al., 2013), but the reactions involved are mainly the hydrolysis of carbon disulphide (CS_2) and carbon sulphide (COS). The simulation of the catalytic reactor is carried out using conversion reactor in Aspen HYSYS. The typical conversion of hydrolysis reaction is about 75 % on alumina catalyst and of about 100 % for Claus reaction (Rhodes et al., 2000). The full and in-deep discussion about the methodology used is reported by Bassani et al. (2018).

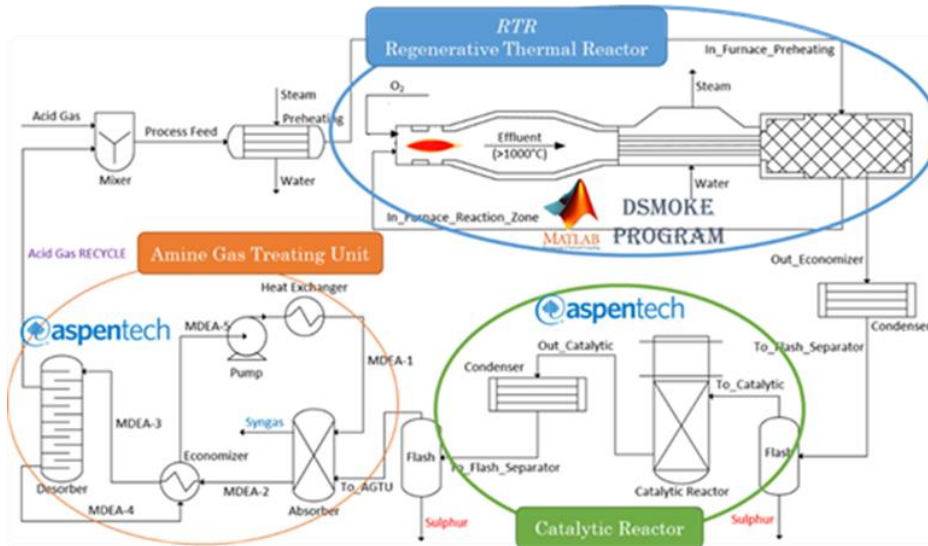


Figure 3: PFD of AG2S™ process

Figure 3 schematically summarizes the process flow diagram of the AG2S™ technology and also indicates the simulation tools used for each unit. This process configuration takes advantage by the unreacted acid gases recycle. The key idea of this work is the direct application of this process to a geothermal power plant (with particular reference to Nesjavellir and Hellisheiði plants) in order to reduce the sour gases emissions, with the contemporary productions of valuable product.

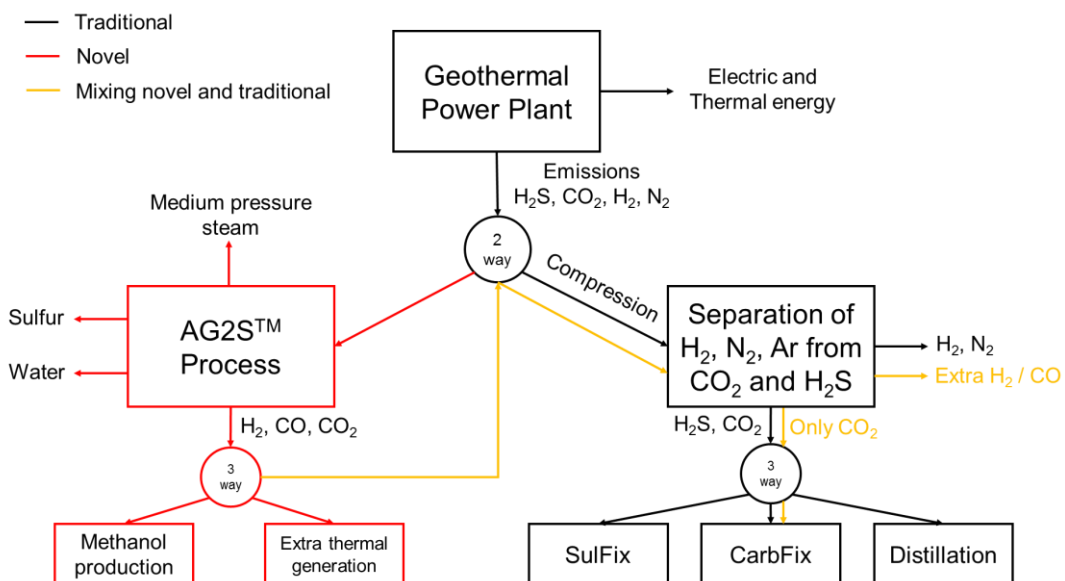


Figure 4: Block flow diagram of the traditional and of the novel solution of the geothermal power plant.

The novel process flowsheet is provided in the Figure 4. The black line represents the traditional process while the red line the application of AG2S™ process with the related surplus production of syngas. Moreover, a third scenario could be considered (orange line) and is the possibility of mixing the old and the novel process in order to obtain extra pure syngas (i.e. without CO₂).

3. Results and discussions

In this section are presented and discussed the principal results of the simulation of AG2S™ applied to Nesjavellir and Hellisheiði geothermal power plants. The detail operating conditions of the simulation have been already reported and analysed in-deep in the previous work of Bassani et al. (2018). For this reason in Table 1 are reported the principal results of the simulations in terms of some key parameters.

Table 2 Results of simulations in terms of key parameters: Hellshedi and Nejavelli cases

	Hellsheidi	Nesjavellir
Inlet H ₂ S/CO ₂ Ratio	4.0	4.0
Oxygen [kg/h]	704.0	471.0
CO ₂ Reuse [kg/h]	406.1	270.4
H ₂ S Abated [kg/h]	2,112.5	2,318.6
H ₂ Produced [kg/h]	17.5	11.8
CO Produced [kg/h]	267.7	179.6
Steam Produced [kg/h]	1,672.0	1,112.3
Sulfur Produced [kg/h]	1,988.2	1,329.4
CO ₂ Reuse [%]	7.5	11.7
H ₂ S Converted [%]	100.00	100.00

As already mentioned, an important for this process is the inlet ratio between H₂S/CO₂ to the regenerative thermal reactor. For both cases, this value is equal to 4 and it is higher than the stoichiometric one (see equation (1)). It is a suitable starting point, but, on the other hand, is not the optimal one because there is unconverted CO₂ in the outlet stream. This lead to an outlet ratio between H₂ and CO that is equal to about 0.9 for both cases instead of 1 derived by reaction (1). For sure, a future study on the inlet optimal ratio will be conducted in order to increase the yield of this process. The main goal of this new process, as mentioned above, is the reduction of H₂S and CO₂ emissions. The latter was completely achieved with regard to H₂S emissions which was converted to 100 %, while for CO₂, a conversion of around 9 % (i.e. the average of the two cases) was achieved. This result is very important from the point of view of downstream separations. Indeed, if the already existing separation pilot plant was used, a lower volume of gas has to be compressed. It would be possible to exploit other methods for the separation of CO₂ from the syngas (e.g. carbon capture (Pettinau et al., 2013)) due to the fact that there is not H₂S which is generally a poison. Another advantage is the possibility to use that stream for methanol production plants starting from a syngas composition rich in CO₂ (Bozzano and Manenti, 2016). In addition to this important advantage and the consequent energy savings, there is the production of an additional quantity of H₂ (about 14 %) and CO, which mixture is called syngas. The latter can have different uses: (i) it can be directly used for the production of additional thermal power, or from the same point of view, decreasing the use of the raw material to obtain the same thermal energy required with the consequent reduction of emissions. Alternatively, syngas can be either directly sell or used, for instance, in a methanol production process. Moreover, there is the production of about 1,800 kg/h of medium pressure steam (i.e. 40 bar) in the waste heat boiler of the regenerative thermal reactor. This steam can be used for example in order to increase the electric power produced. Finally, there is the production of elemental sulphur that could be also sell despite its low market value. The only drawback is the use of oxygen which is an additional cost to the plant that can be easily covered by the sale of hydrogen or from the saving of raw material for the production of the same amount of energy. In this way, the re-injection of sulphur compounds in the ground is avoided.

4. Conclusions

The aim of this work was to demonstrate the potentiality of AG2S™ technology application on the geothermal power plant in order to sour gases emissions and, at the same time, to increase the production of hydrogen. The study was based on two different plant cases located in Hellisheiði and Nesjavellir (Iceland) that globally emit 61,800 t of CO₂ and 28,200 t/y of H₂S. The simulations showed some interesting results. As first, the total conversion of H₂S is reached avoiding its underground injection with the related environmental problem. As second, the reduction of CO₂ emissions and the contemporary possibility to decrease the emissions using less raw material for producing the same amount of energy. Indeed, the extra amount of hydrogen produced by

AG2S™ process could be burned generating energy surplus. Finally, other advantages of this match are the production of an extra medium pressure steam and the possible reuse of the amount of H₂ related to the geothermal plants emissions. Possible future developments could be the optimisation of AG2S™ process and the design of a pilot scale plant.

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