

Gas purification process in a geothermal power plant with total reinjection designed for the Larderello area

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ABSTRACT

Many geothermal power plants require systems for steam washing and treatment of non-condensable gases (NCGs). Steam washing is an early-stage unit and the NCG treatment is performed before the reinjection. The paper describes the potential methods for those parts of the process and evaluates the approach of scrubbers and the associated models. The first model is developed for the steam washing scrubber, which eliminates the dissolved solids from the extracted steam. The energy analysis, steam loss, and the efficiency of removal are investigated and potential approaches to the H₂S removal process are discussed. The second model is dedicated to the packed-bed acid-gas scrubber, which efficiently reduces the H₂S content of NCGs before the reinjection into the reservoir. This model is a rate-based approach that considers all the reactions in parallel. Also, a comprehensive model for the sizing of the scrubbers is proposed. The case study is a binary geothermal power plant, designed for the area of Larderello, in which the extracted steam consists of 25 ppm dissolved solids. The power plant design includes the NCG reinjection system, having about 0.3% of H₂S content. The design parameters are found to achieve solid removal efficiency higher than 90%, thus abating the dissolved solids in the steam to less than 3 ppm by the first scrubber. The performance of the selective H₂S removal treatment is optimized by identifying the best operating parameters for the effective removal of the H₂S and keep the CO₂. The selectivity is calculated in various conditions considering recycle-ratio, caustic solution temperature, and caustic solution concentration. The configuration of the second scrubber is optimized with an H₂S removal efficiency of about 99.96 percent, with a selectivity index around 10.

1. Introduction

Geothermal energy is one of the most promising alternative solutions to fossil-fuel-based power generation. The geothermal fluid is extracted from the production wells, which, in vapor dominant geothermal reservoir as occurring at Larderello (Italy) area, is mostly superheated steam with possible impurities including dissolved solids, and non-condensable gases (NCGs). NCGs are present in many geothermal resources with different amounts of acid gas (mainly CO₂ and H₂S) (Manente et al., 2019a). One of the fundamental environmental regulatory requirements for geothermal power plants is to limit the potential CO₂ and H₂S emissions and the reinjection of NCGs is a suitable solution to comply with the regulatory guidelines and potentially achieve the zero-emissions target. The case study of the current research is a designed pilot power plant located in the Larderello area, in

which superheated steam is extracted from two production wells. The geothermal energy of the steam dominated reservoir is exploited to run an organic Rankine cycle (ORC) for power generation while the condensed steam and NCGs are fully reinjected into the reservoir, to achieve the low or zero-emission goal (Manente et al., 2019b; Kaya, 2016a; Kaya, 2016b). The reinjection process includes a compressor train to supply the pressure to the NCG stream. If the configuration of the power plant includes the reinjection system, it often has to deal with the removal of H₂S in the gas recompression section because of constraints imposed by the equipment (compressors and heat exchangers). The acid gas treatment is required to prevent corrosion and failure in time.

The simplified configuration of the power plant is shown in Fig. 1, in which the places of scrubbers are highlighted. The scrubbers are utilized in a wide range of applications for neutralizing gases, acidic

Abbreviations: CS, Caustic Solution; D, Diameter [m]; H, Height [m]; Eff, Efficiency [%]; F, Feed; hr, hour; m, mass flow rate; MHE, Main (condensing) heat exchanger; NCG, Non-Condensable Gases; w,CS, water in Caustic Solution; R, Recycle Ratio; RMSE, Root mean square error; SSE, Error Sum of Squares; SI, Selectivity Index; st, Steam; T, Temperature [°C, unless it is specified]; x, input (Capacity) [Nm³/hr]; w, water; wt., weight

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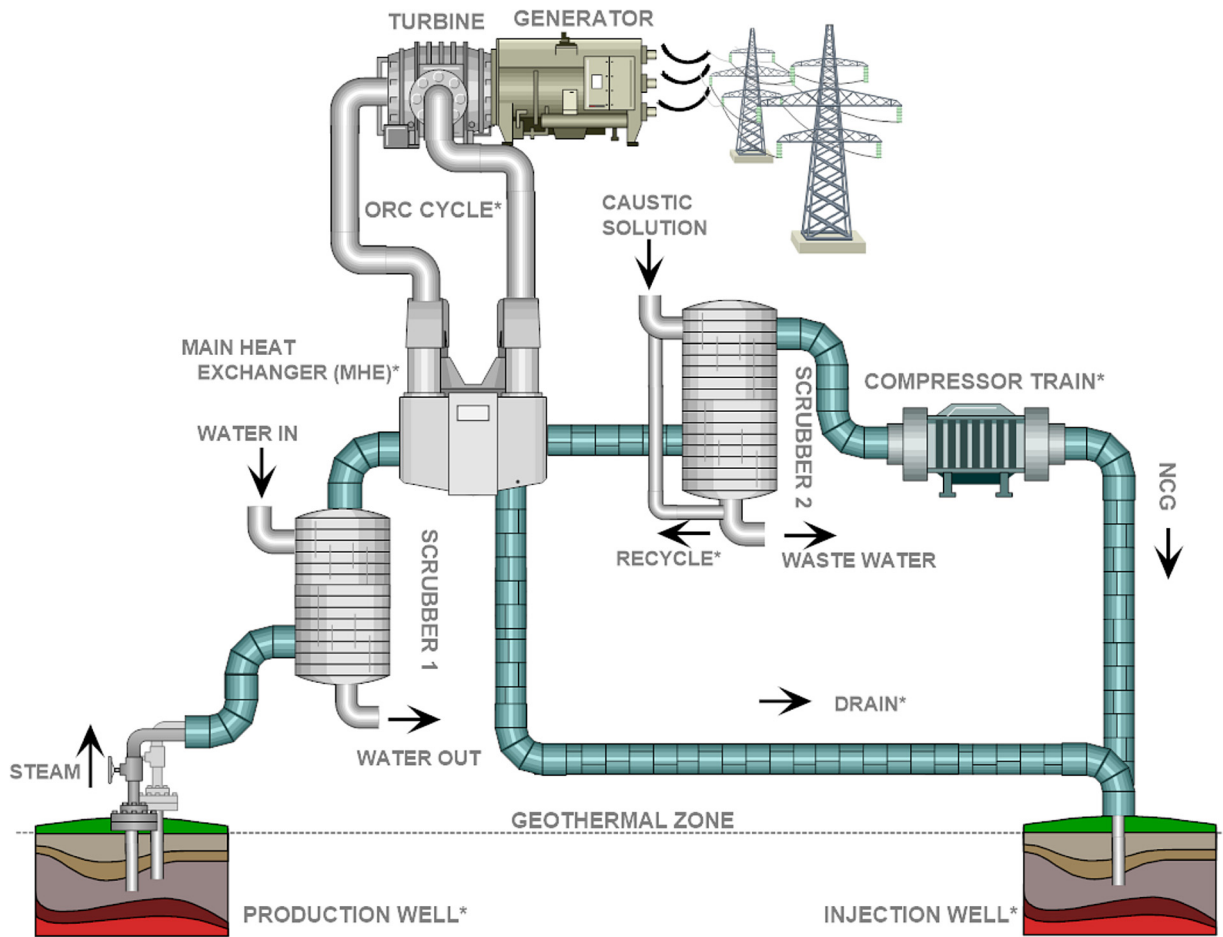


Fig. 1. Application of the scrubbers in the case study geothermal power plant (* : Details are not shown -the representation is merely schematic).

vapors, and odors in chemical or pharmaceutical industries. They are typically a vertical cylindrical vessel for purification, which is classified on the base of its removal agent. Wet scrubbers remove some gaseous components by dissolving or absorbing them into the liquid solution, while dry scrubbers do not have wastewater or disposals and the removal process is performed by injecting dry sorbent materials. As shown in Fig. 1, the wet scrubber is constituted of a column (Scrubber 1) with two inputs and two outputs, which is used to remove either particulate matter or acid gases from gas streams. The contaminants of the gas phase are transferred from the main feed to the second one by gas absorption, where soluble components of a gas mixture dissolve into a liquid. The liquid absorbing agent can be pure water or other chemical solutions.

As shown in Fig. 1, two types of gas treatment can be found on geothermal power plants. The first one is the wet scrubbing of the steam coming out from the production well and the second one is the acid gas treatment upstream the compressor train.

The first scrubber eliminates dissolved solids in the steam and is based on a simple washing by clean water. The most probable dissolved solids present in the geothermal fluid are silica (SiO_2) and sodium chloride (NaCl), which are dissolved either in the entrained water droplets in saturated steam, or solubilized in superheated steam. These kinds of dissolved solids promote foaming and carryover of water into the steam.

One potential solution to reduce the level of solids in the steam to the acceptable limit is using the wet scrubber, which keeps the subsequent equipment safe by preventing the formation of scales. Many experimental studies investigated the wet scrubbers with water or with chemical solutions including additives (Stefansson, 1997; Gallup and

Barcelon, 2005; Chauhan et al., 2019), aimed at improving the removal efficiency. Also, there are some numerical studies of the process to estimate the efficiency and the hydrodynamic of the column (Chauhan, 2019).

Besides, has a direct effect on exergy loss (power loss) due to the quenching of the superheated steam, the exergy analysis of this type of scrubber was conducted by Hjartarson et al. (2014) (Hjartarson et al., 2014). The second scrubber column, utilized to treat the acid gas, is much more discussed in the literature. The sour gas and the caustic (NaOH) solution are in contact in the scrubber, thereby both H_2S and CO_2 are partially eliminated from the gas. The removal of H_2S is beneficial for preventing corrosion, but the removal of CO_2 is a side reaction that is undesirable and only increases the consumable rates and thus the operational cost. The coexistence of CO_2 and H_2S in caustic soda scrubber was experimentally studied by Üresin et al. (2015) (Üresin et al., 2015). It was found that the gas residence time and related gas superficial velocity are dominant compared to the liquid residence time. Also, the lower residence time decreased both H_2S and CO_2 removal efficiency with a larger effect on the latter. Mamrosh et al. (2014) performed a process simulation of acid gas treatment in different scenarios and proposed a short contact conjugation for a selective H_2S removal in the presence of CO_2 (Mamrosh et al., 2014).

In the first part of the present study, different possible technologies for acid gas removal processes are compared referring to the Larderello pilot power plant and the supporting idea for choosing the steam washing scrubber for solid removal and the caustic scrubber for H_2S removal are discussed. Then, the scrubber sizing and the process simulation are carried out for both selected scrubber-based processes. The main novelty over the currently available literature is the full

Table 1
Correlation equations for the diameter and height of the scrubber.

Function name	polynomial correlation
Diameter estimation (m) [x: Nm ³ /hr]	$D(x) = d_1x^5 + d_2x^4 + d_3x^3 + d_4x^2 + d_5x + d_6$
Height Estimation (m) [x: Nm ³ /hr]	$H(x) = h_1x^7 + h_2x^6 + h_3x^5 + h_4x^4 + h_5x^3 + h_6x^2 + h_7x + h_8$

analysis of the caustic soda absorption, from the scrubber sizing to the optimization of the H₂S removal as a function of the main working parameters like soda concentration, temperature and liquid recirculation ratio. The competitive selectivity of H₂S against CO₂ is also evaluated as a function of the main working parameters.

2. Methods

2.1. Equipment sizing

This part of the study is conducted to assess the scrubber sizing in different capacities. Although there are a lot of stepwise-calculations in literature, this study aims at deriving independent-straight correlations for scrubber column sizing.

As shown in Table 1, two separate polynomial equations were defined for the diameter (*D*) and the height (*H*) of the scrubber with the input of the volumetric flow (*x*). The correlations have a single input of the capacity in the polynomial formulation. The least-square approach is adopted to calculate the coefficients.

The extracted data belong to commercial vertical scrubbers from three well-known scrubber producers (Anon, 2019a, 2019b, 2019c), which are taken as the reference for extracting the correlations. The data include 63 sets of values for the diameter and the height, covering a wide range of scrubber capacity. Table 2 lists the detail of these references. Further, these reference data are shown in Fig. 3 compared with the correlations.

2.2. Steam washing simulation (Solid Removal)

Steam washing systems generally consist of one or more water injection nozzles, where water is sprayed into the steam. The heat transfer between the water and the steam contributes to partial condensation of steam. The washing water and any condensed species are separated from the steam in the scrubber. The simulation of the first wet scrubber is developed in two steps. Firstly, the mass and energy balance of the steam/water system is implemented at different conditions by UniSim® Design Suite software (Honeywell International Inc., 2017). Two inputs of saturated steam and water are fed into a scrubber, which is shown in Fig. 2.

The mass distribution coefficient (*k_d*) is used in the estimation of solid matter removal efficiency. It is defined as the ratio of the concentration (*C* [mol/L]) of a specific solid specie in steam to that of the water (Eq. 1).

$$k_d = \frac{C_{i,steam}}{C_{i,water}} \quad (1)$$

The value of this coefficient can be found in the literature for different dissolved solids. For the current simulation, SiO₂ is considered

Table 2
References of dimension database.

Reference	Capacity Range (CFM)	Number of data
Tri-Mer® (Anon, 2019a)	390–100,530	30
Schutte & Koerting® (Anon, 2019b)	400–67,000	16
Met-Pro® Environmental Air Solutions (Anon, 2019c)	1000–25,000	17

and *k_d* value is 0.002 (Seiler, 2010; Richardson et al., 2013).

According to the mass balance, for the *i*th component, Eqn. 2 is considered:

$$m_{i,steam,in} + m_{i,water,in} = m_{i,steam,out} + m_{i,water,out} \quad (2)$$

where the inlet water has no solid matter and thereby is eliminated from the mass balance.

$$m_{st,in}C_{i,st,in} = m_{st,out}C_{i,st,out} + m_{w,out}C_{i,w,out} \quad (3)$$

The concentration of solids in the steam product of the scrubber is derived by Eq. 4:

$$C_{i,st,out} = [m_{st,in}C_{i,st,in}] / [m_{st,in} + \frac{m_{w,out}}{k_d}] \quad (4)$$

Also, the removal efficiency is calculated as Eq. 5.

$$Eff_{removal} = \frac{m_{st,in}C_{i,st,in} - m_{st,out}C_{i,st,out}}{m_{st,in}C_{i,st,in}} * 100 \quad (5)$$

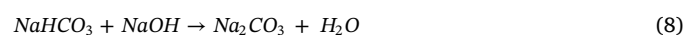
2.3. Process selection for H₂S removal

Many different desulfurization processes may be used for acid gas treatment. The acid gas in the geothermal power plant is the vapor product of the Main Heat Exchanger (MHE). It feeds the compressor train, which increases the average pressure from 10 bar to 60 bar. The H₂S content of this gas stream should be kept within the acceptable range (less than 200 ppm at 60 bar), otherwise, the subsequent equipment would undergo corrosion issues. Five key approaches for acid gas treatment are listed in Table 3, with their specific pros and cons; the basic diagrams are depicted in Fig. 3.

Priority #1: Caustic scrubber. The first-priority approach is the acid gas scrubbing by Soda (NaOH) solution. The soda solution is recommended to be fed into the packed bed wet scrubber and react with the H₂S according to Eq. 6. (Habeeb et al., 2018; Muñoz et al., 2015) a recycle stream is considered to reduce the consumption of fresh caustic solution with minor effect on the removal efficiency.



In addition to H₂S, according to Eq.7 & 8, the CO₂ is partially scrubbed into the caustic solution, which results in increasing the consumption of caustic reactant and precipitation of new salts.



The CO₂ abatement is not desirable for the current project and this side reaction can be limited by reducing the residence time (contact time) of the acid gas in the scrubber column: due to the slower kinetic rate of the CO₂ absorption, a selective absorption should thus be applied.

Priority #2 & 3: Bio-solution or bio-chemical-solution. The biological solution uses the Thiobacillus bacteria to remove H₂S from the sour gas by oxidizing sulfide to elemental sulfur or sulfate (Sulfide is the electron donor for the bacteria) (Fidler et al., 2005; Barbusiński and Kalembe, 2016; Ko et al., 2015; Krayzelova et al., 2015). There are many conditions to satisfy to keep the bacteria activities at a constant rate: a solution is maintaining the temperature, pressure, relative humidity (RH), and the oxygen level of the bioreactor precisely while feeding the acid gas (Priority #3). This solution has no environmental

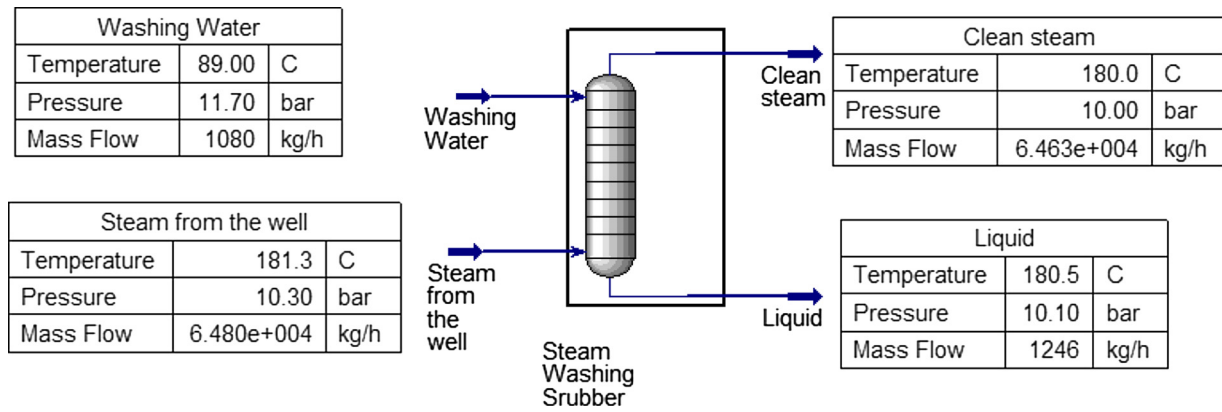
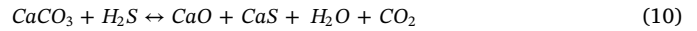


Fig. 2. Energy and Mass analysis of the scrubber by UniSim.

issues and the only wastes are bacteria beds and sulfur elements. This solution needs an advanced conditioning system and a remarkable pressure drop (depending on the type of bacteria) may also be required, which increases the load of the compressor train. The alternative solution is coupling the bioreactor with an efficient chemical method (such as the Caustic scrubber). This approach (Priority #2) derives the advantages from the bacteria solution and the geothermal stream is independent of the bioreactor conditioning and requirement. This method is used in many commercialized biological solutions, which include two units (THIOPAQ, 2019). The first one is a chemical scrubber where the contaminant (sulfide content) of the sour gas is transferred from the gas phase to the liquid phase by sodium hydroxide (NaOH) solution. In the second unit, the spent caustic stream (including the absorbed sulfide) is treated in the bioreactor at atmospheric pressure and temperature.

Priority #4: Lime scrubbing is a cheap and easy-handling process for removing the H_2S content from the acid gas like the geothermal gas stream. In this process, according to Eq. 9, CaO reacts with H_2S , which is converted into CaS . Also, in an alternative reaction, the limestone can be utilized to react with H_2S according to Eqn. 10. The process has low cost and is easy to control but a high temperature is required for the equilibrium to reach the desired result (Jafarnejad, 2016; Kulkarni and Ghanegaonkar, 2019; Husmann et al., 2016; Poullikkas, 2015).



Also, the result of this approach will not be better than 500 ppm, which is not enough for the presently investigated case study of the Larderello area.

Priority #5: Water scrubbing, in which the concept is that the sour

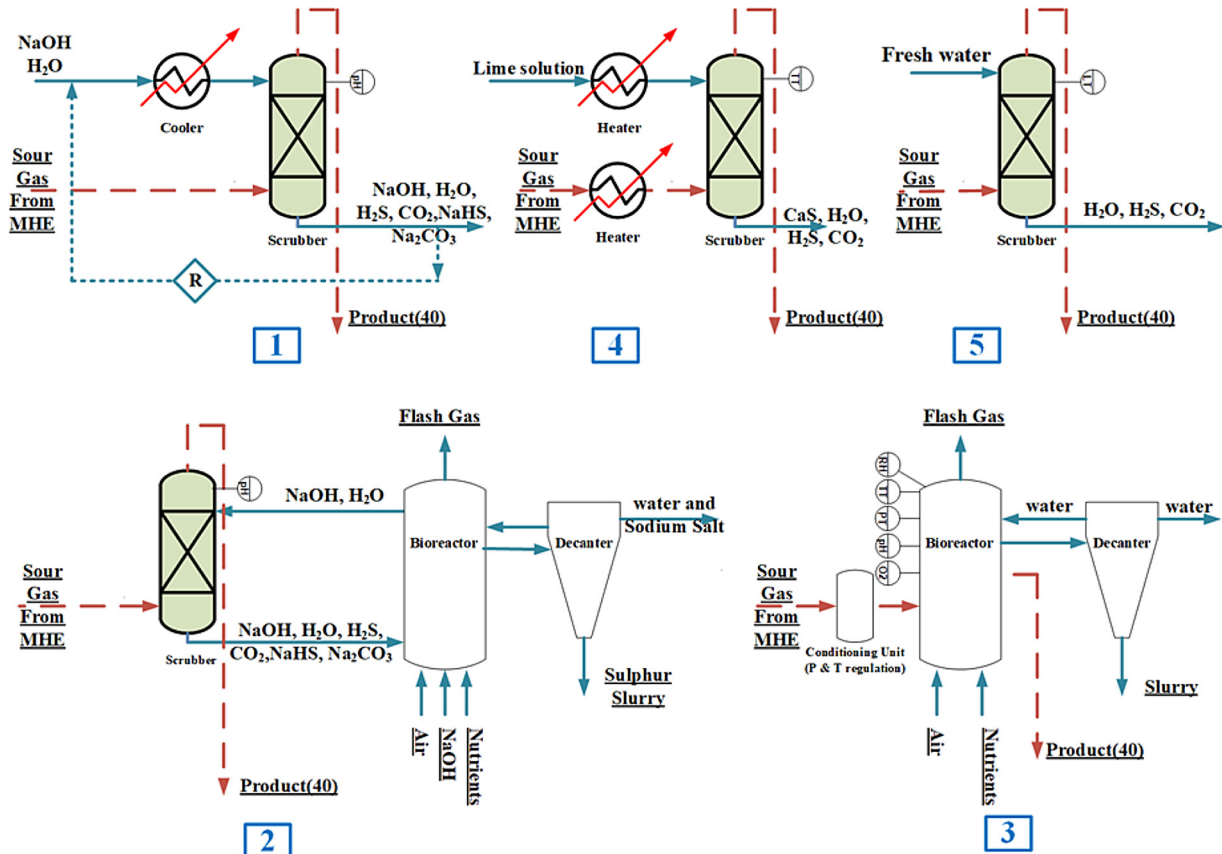


Fig. 3. Simplified schematics of available solutions (numbers are corresponding to the priority in Table 1).

Table 3
Pros and cons of the selected approaches for geothermal gas treatment.

Priority	method	Concept	Advantages	Disadvantages
1	Chemical Scrubbers (Habeb et al., 2018; Muñoz et al., 2015)	Method: Oxidizing sulfide to elemental sulfur or sulfate Consumables: 1 Sodium hydroxide 2 Water	-Partial Selectivity between CO ₂ and H ₂ S -Average CAPEX -Removal efficiency up to 99%	-High OPEX (Cost of fresh Soda solution) -pH control is required -Useless Sour water
2	Bio-Chemical scrubber (Fidler et al., 2005; THIOPAQ, 2019)	Method: 1 Absorption of Sulfide 2 Oxidizing sulfide to elemental sulfur or sulfate by bacteria Consumables: 1 Sodium hydroxide 2 Thiobacillus bacteria 3 Nutrients 4 Water 5 Air	-Full Selectivity between CO ₂ and H ₂ S -Low OPEX -Removal efficiency up to 99% -No useless product -Environmentally friendly process	-High CAPEX (Cost of bioreactor and control systems) -High residence time (up to 8 minutes) -Sensitive to operating conditions/contamination -pH control, high pressure and temperature are required -Limit of 200 ppm -Satisfactory performance at ambient temperature and pressure, natural pH
3	Bioreactor (Fidler et al., 2005; Barbusiński and Kalemba, 2016; Ko et al., 2015; Krayzelova et al., 2015)	Method: oxidizing sulfide to elemental sulfur or sulfate Consumables: 1 Thiobacillus bacteria 2 Nutrients 3 Water 4 Air	-Full Selectivity between CO ₂ and H ₂ S -Average CAPEX -Low OPEX -Removal efficiency up to 99% -No useless product	(Cost of bioreactor and control systems) -High residence time (up to 8 minutes) -Sensitive to operating conditions/contamination -pH control, high pressure and temperature are required -Limit of 200 ppm -Approved performance at ambient temperature and pressure, natural pH
4	Lime Scrubbing (Jafarinejad, 2016; Kulkarni and Ghanegaonkar, 2019; Husmann et al., 2016; Poullikkas, 2015)	Consumables: 1 Lime (CaO) /Limestone (CaCO ₃) 2 Water	-Low CAPEX -Low OPEX	-Maximum efficiency 90 - 95% -Residual H ₂ S of 500 ppm -High temperature is required (600 - 900°C) -High residence time (up to hours)
5	Water Washing (Lien et al., 2014)	Consumables: 1 Water	-Low CAPEX -Low OPEX	-High water consumption -High Sour water product (Environmental issues) -No Selectivity between CO ₂ and H ₂ S -Efficiency around 30 - 60% -Clogging due to bacterial growth -Possible foaming -Low flexibility toward alteration of feed gas

gases such as CO₂ and H₂S are soluble in water. Therefore, the water is used as an absorbent to remove H₂S in the washing column, where the gas is continuously fed from the bottom through the diffuser producing bubbles and adsorbing the H₂S content of the sour gas. The process is simple and low-cost, but the efficiency is low and it consumes a high flow rate of feed water, which is usually not abundant in geothermal sites. Considering all these disadvantages, this is not an efficient approach unless the cost is limited and the low efficiency (< 60%) admissible (Lien et al., 2014).

In the power plant of the Larderello case study, in addition to the main plant, a reduced-scale test unit is designed for the evaluation of the main proposed configuration and the H₂S removal unit is dedicated only to that temporary test unit. The test unit is expected to be fast-response and to operate efficiently while minimizing the environmental impact during the demonstration tests. The most important features of this unit are the efficiency, cost, and ease of control. The expected efficiency can be achieved both by chemical scrubbers and Bio-solutions. Regarding the cost of the unit, capital expenditure (CAPEX) is much more relevant than the operating expenses (OPEX) because the latter would be negligible compared to CAPEX for any of the proposed solutions for a one-week run. However, considering the CAPEX, the chemical scrubber using the caustic solution will stand on the first order of priority.

2.4. Simulation of H₂S removal (Caustic Scrubbing)

The simulation of the H₂S removal unit is performed by using Honeywell's UniSim® Design Suite (Honeywell International Inc.,

2017), according to the schematic of the number 1 in Fig. 3. The equipment mainly includes a scrubber column and a heat exchanger (cooler). It adjusts the temperature of the caustic input of the scrubber and improves the kinetics of the reaction between the caustic solution and the CO₂/H₂S content of the sour gas. The configuration with the recycle (R) stream is considered to back mix a part of the scrubber liquid output with an upstream fresh caustic stream, therefore reducing the fresh feed requirement. The recycle ratio, given by Eq. 11, is defined as the ratio of the returned mass flow (m_R) to the mass flow which is leaving the system (m_{out}).

$$R = m_R / m_{out} \quad (11)$$

The effects of adjusted temperature for caustic feed, the recycle ratio and the caustic solution concentration are investigated by the implemented simulation tool and the results are analyzed in order to find the most efficient operating conditions of the gas treatment, with special emphasis on selective H₂S removal. The simulation is based on the reaction rates concept, which is a reliable way to model the absorber column when there is a lack of data on tray efficiencies and geometries. It examines the heat and mass-transfer processes without equilibrium assumptions between the phases.

The reactions and chemistry of the process are listed in Table 4, which are all associated with the simulation and underlay the absorption of CO₂/H₂S components. It provides more insight by indicating concentration and temperature-dependent equilibrium data (Lee, 2008) to evaluate how each reaction involves the overall process. The absorber bottom pressure is the pressure of the feed gas stream entering at the bottom of the column and the top pressure reflects a small pressure

Table 4

List of reactions involving caustic scrubbing process.

No	Reaction Stoichiometry	Reaction Heat [kJ.kmol ⁻¹] (at 25 °C)	Reaction Rate $k = A \exp(-E/RT)^b$ [kmol.m ⁻³ s ⁻¹] [T: K]		
			A	E	b
1	$2H_2O \leftrightarrow H_3O^+ + OH^-$	+1.701×10 ⁵	Gibbs Free Energy $k_{eq} = -\Delta G_{reaction}/RT$		
2	$H_2O + HCO_3^- \leftrightarrow H_3O^+ + CO_3^{2-}$	+2.418×10 ⁵			
3	$2H_2O + CO_2 \leftrightarrow H_3O^+ + HCO_3^-$	+8.761×10 ⁴			
4	$H_2O + H_2S \leftrightarrow H_3O^+ + HS^-$	+2.6246×10 ⁵			
5	$H_2O + HS^- \leftrightarrow H_3O^+ + S^{2-}$	+2.418×10 ⁵			
6	$CH_3SH + H_2O \leftrightarrow H_3O^+ + CH_3S^-$	+2.647×10 ⁵			
7	$C_2H_5SH + H_2O \leftrightarrow H_3O^+ + C_2H_5S^-$	+2.882×10 ⁵			
8	$COS + OH^- \leftrightarrow CO_2SH^-$	+2.855×10 ⁵			
9	$NaOH \leftrightarrow Na^+ + OH^-$	+6.640×10 ⁴			
10	$CO_2 + OH^- \rightarrow HCO_3^-$	+5.368×10 ⁵	1.33×10 ¹⁷	1.32579×10 ⁴	0
11	$HCO_3^- \rightarrow CO_2 + OH^-$	-5.368×10 ⁵	6.63×10 ¹⁶	2.56740×10 ⁴	0
12	$CO_2SH^- \rightarrow CO_2 + HS^-$	-3.9351×10 ⁵	5.00×10 ⁶	9.14054×10 ³	0
13	$CS_2 + OH^- \rightarrow CS_2OH^-$	+2.661×10 ⁴	1.53×10 ⁶	1.20086×10 ⁴	0
14	$CS_2OH^- + OH^- \rightarrow CO_2SH^- + HS^-$	+1.435×10 ⁵	2.97×10 ¹²	1.23088×10 ⁴	0

difference of about 20–35 kPa.

The selectivity index (SI) is defined as Eq. 12 and equals to the ratio of relative amount H₂S which is removed (nominator) to that of the CO₂ (denominator) to show how the scrubber is capable of removing H₂S and not the CO₂.

$$SI = \frac{(m_{H_2S,in} - m_{H_2S,out})/m_{H_2S,in}}{(m_{CO_2,in} - m_{CO_2,out})/m_{CO_2,in}} \quad (12)$$

which can be rewritten as Eq. 13:

$$SI = K_0 \cdot \frac{\Delta m_{H_2S}}{\Delta m_{CO_2}} \times \frac{m_{CO_2,in}}{m_{H_2S,in}} \quad (13)$$

3. Results and discussion

3.1. Equipment sizing

All data are considered for final regression and correlated in the form of Eq. $D(x)$ and $H(x)$ (Table 1). The coefficients are found as shown in Table 5 and both correlations are fitted with more than 97.8% accuracy. The statistical analysis results are listed in Table 6, which provides more insight into the accuracy and reliability of the proposed correlations. Both the reference data and the correlations are shown in Fig. 4, standing for a reasonable agreement. These two equations are a rule of thumb calculation that allow to roughly, but reliably, calculate the diameter and height of the scrubber.

Two configurations are assumed for the Larderello case study power plant. The first one is the full-capacity plant including the steam washing scrubber and the second one is designed based on a reduced-scale capacity, having a caustic scrubber. The scrubbers' capacities are about 80,000 and 500 Nm³/hr, respectively. The former is for the steam

Table 5Coefficient of proposed correlations (d for the diameter and h for the height function).

Index (i)	d_i	h_i
1	1.482×10^{-25}	5.747×10^{-35}
2	-7.708×10^{-20}	-4.379×10^{-29}
3	1.519×10^{-14}	1.343×10^{-23}
4	-1.438×10^{-9}	-2.125×10^{-18}
5	8.714×10^{-5}	1.846×10^{-13}
6	3.467×10^{-1}	-8.643×10^{-9}
7	0	2.158×10^{-4}
8	0	3.12

Table 6

Statistical analysis results for the correlations.

Criterion	Parameter	
	D(x)	H(x)
SSE	0.4176	1.868
R-square	0.995	0.9775
Adjusted R-square	0.9943	0.9735
RMSE	0.1009	0.2188

washing scrubber with the feed of superheated steam in the full-scale plant, while the latter is the vapour-phase product of the MHE (feed of H₂S removal scrubber) in the reduced-scale plant. The diameter and height estimations are 3.2 m and 6.3 m respectively for the former, while they are estimated 0.4 m and 3.2 m respectively for the latter.

3.2. Steam washing simulation

The result of the simulation of the steam washing scrubber is shown in Fig. 5, where both the efficiency of the solid removal and mass and energy loss of steam are shown versus the relative mass flow of the water. The assumed case study is for SiO₂, which is one of the key dissolved solids of geothermal fluid. The desirable effect of a higher flow rate of feed water is the higher removal efficiency, while the undesirable effects are the loss of steam and the related energy, which are critical for power plant design. According to the results, 0.02 water ratio is required to achieve 90% SiO₂ removal efficiency. This amount of water also contributes to about 1.7% of the steam loss, which directly affects the power plant energy output. The extracted steam from the well in the geothermal site for the pilot power plant contains about 25 ppm of SiO₂, thereby the steam washing scrubber reduces Silica content to less than 3 ppm with 90% removal efficiency.

3.3. Model simulation of the H₂S removal

After the sizing of the scrubbers, the process simulation is employed to investigate the effect of parameters on the efficiency of the packed column in gas treatment. The results are shown in Fig. 6a for the recycling ratio, Fig. 6b for the temperature of the caustic solution, and Fig. 6c for the relative mass flow of water (m_w/m_F) and the relative mass flow of soda in the caustic solution ($m_{NaOH,CS}/m_F$). In Fig. 6c, the non-dimensional relative mass flow, defined as the ratio of NaOH mass in the caustic solution (CS) to the mass flow of the sour gas feed (m_F), is chosen to consider the effects of both the feed flowrate and

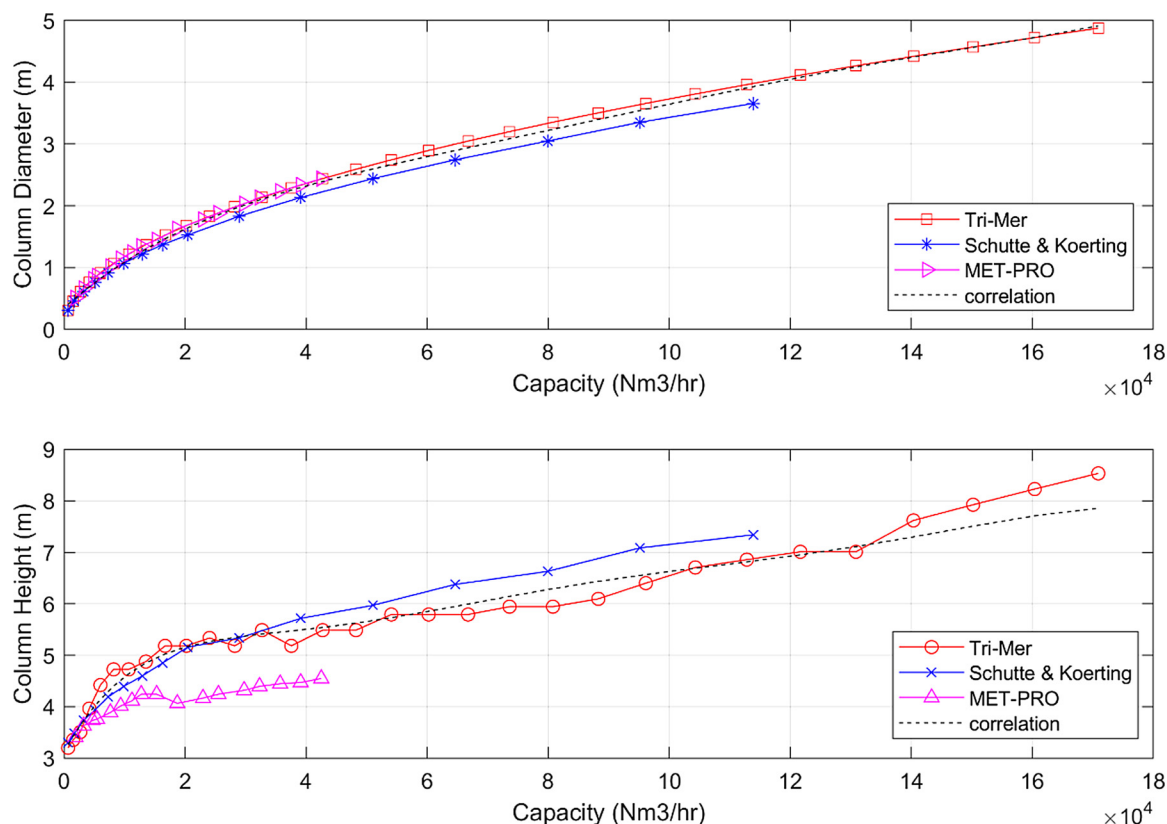


Fig. 4. Reference size data and the resulting correlations.

concentration of the fresh caustic solution. Thereby, by using the nondimensional ratio, the results and the efficiency estimations will be valid for a wide range of feed flow, caustic solution flow, and concentration value.

The kinetics of CO_2 and H_2S absorption are different, which underlies the selective absorption of H_2S . The kinetic rate of CO_2 absorption is slower than the H_2S one and, therefore, limiting the contact-time inside the scrubber improves the selectivity of H_2S vs CO_2 . Increasing the liquid recycle ratio contributes the column to be filled

more with liquid rather than the gas, therefore, this fact reduces both the superficial flow and the residence time of the gas, which has a noticeable effect on the CO_2 absorption, having a relatively weak reactivity with NaOH . Thereby, a higher amount of unreacted NaOH becomes available to be involved in the faster reaction of H_2S absorption. As shown in Fig. 6a, the efficiency of H_2S removal is improved while the CO_2 removal is decreased. The other consequence of considering a higher recycle ratio means having a longer residence time of the liquid, which enhances the absorption of both acid components, but

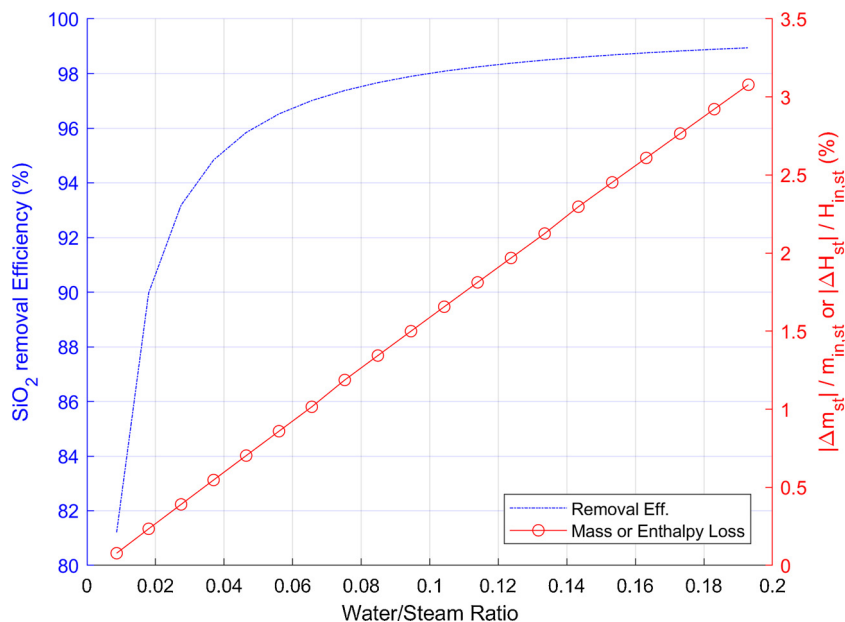


Fig. 5. the performance of the steam washing scrubber in different water/steam ratios.

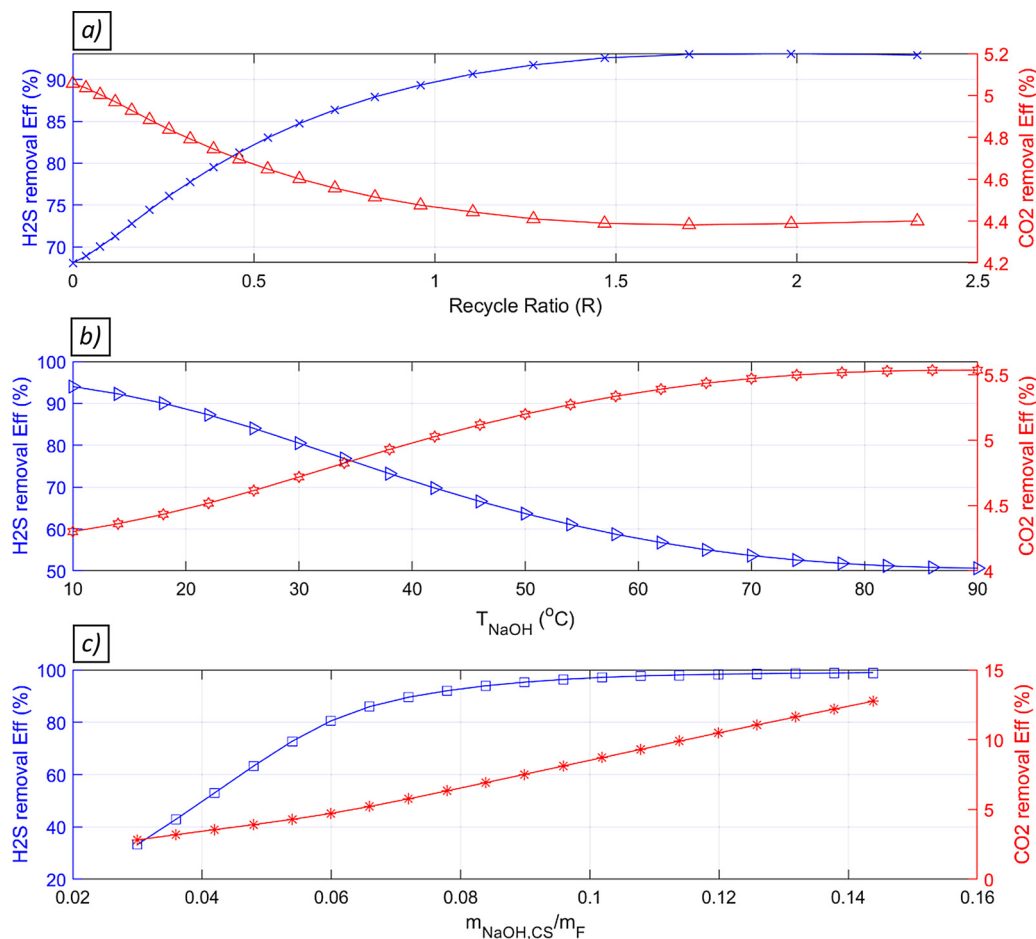


Fig. 6. The effect of different parameters on the removal efficiency.

the relevance of the effect is less than the gas residence time (Turpin et al., 2008). Moreover, it is found that the recycle ratio higher than 1.5 does not change the efficiency.

It is found that, in the present case, the temperature has two different effects regarding the major component (CO_2 , 95%) and the minor component (H_2S , 2%). The result of these two parallel reactions at different temperatures is shown in Fig. 6b, where higher temperature yields higher CO_2 removal efficiency, which is also reported in the literature (Yincheng et al., 2011; Tavan and Hosseini, 2017), and lower H_2S removal efficiency, in agreement with previous studies (Bashipour et al., 2017; Mamrosh et al., 2020). Therefore, the H_2S removal efficiency increases at lower temperatures, while it brings lower corrosivity. The rationale behind this behavior is that the CO_2 absorption is liquid mass transfer controlled, while the H_2S adsorption is dominantly a gas-film mass transfer process (Siu-Ming and Chi-Chun, 1987; Sheng et al., 2019).

The main absorption agent is the NaOH content and higher concentrations increase the removal efficiency, but the increasing profile is different for H_2S and CO_2 . As shown in Fig. 6c, the slope of the increase for H_2S in low concentration value is significantly higher than CO_2 . On the other hand, the H_2S removal efficiency increment when non-dimensional NaOH concentration is higher than 0.1 is marginal.

Another important parameter influencing the process is the water content in the caustic solution, which has a co-effect on the system. A higher value of water content means having a leaner NaOH solution leading to a lower mass transfer coefficient. On the contrary, the water is an adsorption agent itself and positively takes part in the absorption process. These opposite effects are investigated in detail to determine the overall behavior of the system with a different water content of the

caustic solution.

The positive effect of NaOH relative mass flow as the main absorption agent is clear: therefore, a fixed value of 1.6 is considered to assess the mutual effect of the other three parameters. The H_2S removal efficiency of the system is shown in Fig. 7a. The trend of efficiency for different temperatures is not the same, but the maximum efficiency is achievable at a high recycle ratio and a low relative mass flow rate in the caustic solution. In parallel, the selectivity index is calculated, which already considered the undesirable efficiency of CO_2 . As shown in Fig. 7b, the previous conclusion is confirmed and the most efficient cases are those with high recycle ratio and low water composition in Caustic solution (higher NaOH concentration). Under these conditions, the selectivity index of about 10 may be achieved.

Considering the effects of all the investigated parameters, the outcomes are summarised in the following:

- The approximate optimizing values for the recycle ratio is higher than 2;
- The temperature of the caustic soda is less than 20 °C (the setpoint also depends on economic analysis, considering the seasonal variation and average ambient temperature);
- The relative mass flow of NaOH is higher than 0.1 and the H_2O relative mass flow is about 0.5. By using the last two values, the concentration of the caustic solution is found to be 25...30 wt.%.
- The resulting efficiency of the system under these conditions is calculated at about 99.96%.

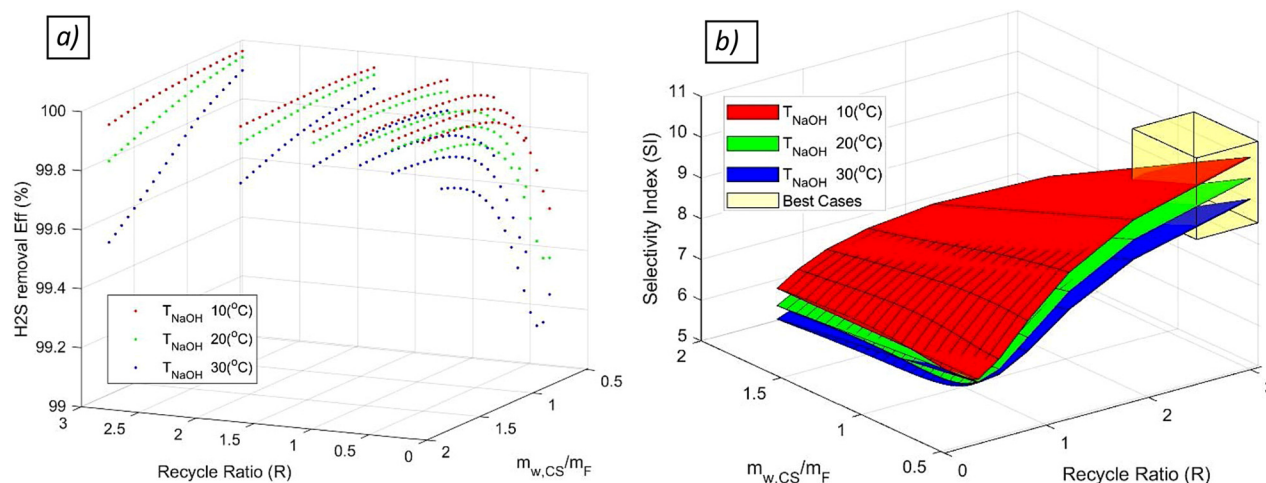


Fig. 7. Sensitivity analysis of the system: H₂S removal efficiency (a) and H₂S selectivity index (b) in different recycle ratio of relative water flow rate.

4. Conclusions

Two key parts of the process in geothermal power plants are steam washing and gas treatment. The former is performed to eliminate the dissolved solids (e.g. SiO₂) and the latter is required for the reinjection of NCGs in order to limit the emissions to the atmosphere. The current study is conducted to review the related approaches for the case study of a pilot power plant located in the vapor dominant Larderello area. The scrubber method is chosen for both objectives of dissolved solid removal from the steam and H₂S removal from the NCGs. The removal process is modeled by means of UniSim Design Suite, which calculates the amount of steam and energy loss as the result of the condensation and then estimates the removal efficiency of solids up to 99%. It is found that a higher amount of washing water increases the efficiency but contribute to larger energy loss, therefore the feed flow should be chosen wisely. For example, 90% removal efficiency and 1.7% steam loss results in 0.02 water/Steam ratio. The second part of the study represents a reaction-based model, which is developed to predict the H₂S removal efficiency and to study the effect of the side reaction of CO₂ abatement. The optimal operating condition to have a satisfactory selective H₂S abatement by using the caustic scrubber is found. The Maximum selectivity and the highest H₂S removal efficiency are found to be corresponding to the caustic feed condition and lower temperatures, higher concentrations and higher recycling ratios are desirable. The relative impact of NaOH and water contents in the caustic solution, are well assessed. The scrubber-based gas treatment with the recycle configuration is found to reach 99.96% efficiency under optimized operating conditions. A parametric analysis of scrubber design and performance is conducted. Also, two correlations to determine the size of industrial-scaled scrubbers covering a wide range of capacities, which are capable of achieving reasonable predictions.

CRedit authorship contribution statement

Pouriya H. Niknam: Methodology, Software, Investigation, Validation, Writing - original draft. **Lorenzo Talluri:** Formal analysis, Methodology, Investigation, Resources. **Daniele Fiaschi:** Conceptualization, Writing - review & editing, Supervision, Funding acquisition. **Giampaolo Manfrida:** Conceptualization, Writing - review & editing, Project administration, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to

influence the work reported in this paper.

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