

Article

A System Analysis of a Bio-Hydrogen Production System Using Granulated Mine Residue as a H₂S Adsorbent

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Abstract: An energy production system that combines biomass and fuel cells produces much energy with minimal environmental impact. However, the hydrogen sulfide (H₂S) contained in gasified biomass degrades fuel cell performance, thus negating the advantages of this combination. In this study, the removal of H₂S by adsorption after biomass gasification was investigated. Metal oxides with high adsorption performance are common H₂S adsorbents. However, they have a significant environmental impact in terms of metal depletion, which is an environmental impact indicator. Therefore, neutralized sediment materials from mine drainage treatments can be used as H₂S adsorbents. A previous study found that the adsorption performance of H₂S adsorbents is equivalent to that of metal oxides, especially in the high-temperature zone (300 °C), and the environmental impact is considerably lower than that of metal oxides. However, because the neutralized sediment is a powder (Φ 4.5 μm on average), there is a possibility that the gas will not flow due to the pressure drop when it is used in a large adsorption column. Therefore, in this study, we propose the use of granulated neutralized sediments for practical plant operations. No studies have investigated the adsorption performance of granulated neutralized sediment through experiments or quantitatively investigated the effect of using waste material as a H₂S adsorbent to reduce the environmental impact of hydrogen production. Based on these data, the sulfur capture capacity of the granulated neutralized sediment was experimentally investigated. The extent to which the environmental impact of the hydrogen production system could be reduced when granulated neutralized sediment was used as the H₂S adsorbent was assessed. Note that the granulated neutralized sediment is formed with about a Φ 0.56–1.25 mm diameter. The granulated neutralized sediment exhibited approximately 76.8% of the adsorption performance of zinc oxide (ZnO) on a conventional adsorbent. In terms of the LCA, the global warming potential (GWP) and the abiotic depletion potential (ADP) were improved by approximately 0.89% (GWP) and 55.3% (ADP) in the entire hydrogen production process. This study demonstrated that the use of waste materials can significantly reduce the environmental impact on the entire system.

Keywords: hydrogen; biomass; desulfurization; neutralized sediment; granulation; life cycle assessment



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1. Introduction

Biomass is a renewable energy with a low environmental impact. However, its calorific value is only approximately 50% lower than that of fossil fuels [1]. Therefore, the use of fuel cells characterized by high energy-conversion efficiency is proposed. The combination of biomass and fuel cells is a promising energy system for increased energy efficiency and low environmental impact because a large amount of energy can be extracted from biomass.

It is necessary to gasify the biomass and convert its main component, methane, into hydrogen to use fuel cells with biomass as a fuel. Biomass gasification methods include

low-temperature gasification via anaerobic digestion and high-temperature gasification via pyrolysis. This study focused on an Advanced Gasification Module (AGM) that could efficiently perform gasification and reform [2]. AGM creates heat energy by burning off gas, air, and char, a waste product of biomass. The heat is transferred to the alumina balls of heat carriers (HCs), which are used as heat sources to gasify the biomass and produce hydrogen through reforming via partial oxidation. This AGM is highly energy-efficient. Our research group has a plant in Minamisunamachi, Tokyo, Japan, that produces hydrogen by gasifying and reforming sewage sludge biomass using an AGM, which was the focus of this study.

When sewage sludge is gasified, hydrogen sulfide (H_2S) is generated as an impurity, which is adsorbed or reacts with fuel cell catalysts and degrades the fuel cell performance. Therefore, in this study, sewage sludge was gasified and reformed in an AGM system, followed by desulfurization. In desulfurization systems, metal oxides are generally used as adsorbents for H_2S . However, metal oxides have a significant environmental impact due to the metal depletion, and an increase in the eco-burden of metal depletion reduces the environmental impact of using biomass. Therefore, in this study, we considered using materials with a low environmental impact as H_2S adsorbents.

Currently, the use of waste materials based on a circular economy is attracting attention, and the reuse of metal waste is increasing remarkably [3]. Based on this concept, in a previous study, we proposed the use of neutralized sediment, a mining waste material, as a H_2S adsorbent [4]. The results of the environmental impact assessment based on the data obtained from the H_2S adsorption experiment showed that the sulfur capture capacity of the H_2S adsorbent was equivalent to that of zinc oxide (ZnO), a typical high-temperature (300 °C) adsorbent, quantitatively indicating that the environmental impact of a desulfurization system using neutralized sediment as a H_2S adsorbent was smaller than that using ZnO [4]. In other words, the neutralized sediment is a promising H_2S adsorbent.

However, one of the challenges in using neutralized sediment as a H_2S adsorbent is the possibility that the gas may not flow, owing to pressure loss because of the nature of the powder (Φ 4.5 μ m on average) of neutralized sediment. Mrosso et al. filled a gas tank with a powder adsorbent; when the gas flowed, the adsorbent clogged the gas and prevented further gas flow [5]. In other words, when the neutralized material is in powder form, it cannot be used as a H_2S adsorbent because the gas cannot flow through it. Therefore, in this study, we propose granulating the neutralized sediment so that the gas can flow to make the neutralized sediment practically available. Granulated neutralized sediment as a H_2S adsorbent is proposed for use in desulfurizing hydrogen production systems.

Previous studies have shown that granulation affects the performance of adsorbents. Narang et al. granulated NaX and CaA zeolite powders using a freeze granulation process and investigated their CO_2 adsorption performance before and after granulation. After investigating the adsorption isotherms for CO_2 of each adsorbent, they found that the CO_2 adsorption capacities of NaX and CaA decreased after granulation [6]. Munusamy et al. prepared granulated MIL-101(Cr) powder mixed with starch and the sodium salt of carboxymethylcellulose, and investigated the adsorption performance of the powder and granulated products on CO_2 , CO, CH_4 , and N_2 . Consequently, the powdered product exhibited a higher adsorption capacity under most conditions. However, at certain temperatures (313 K) and compositions (CO_2/CO), the amount of CO_2 adsorbed by the granulated material was greater than that adsorbed by the powdered material [7]. Thus, granulation affects the adsorption performance; however, changes in the sulfur capture capacity after the granulation of the neutralized sediment have not yet been studied. In addition, the amount of adsorbent used, based on the sulfur capture capacity, is necessary to demonstrate the environmental benefits of granulated neutralized sediment in hydrogen production. In other words, the sulfur capture capacity of neutralized sediment after granulation must be investigated. Therefore, this study investigated the sulfur capture capacity of granulated neutralized sediment and quantitatively revealed how much it differed from that of powdered neutralized sediment.

Next, we referred to the environmental performance based on the life cycle assessment (LCA) methodology. LCA is an internationally standardized method for quantifying the environmental impacts of all inputs and emissions associated with a given process [8]. The LCA evaluates all the stages of resource extraction, production, utilization, recycling, and waste treatment. The ISO 14040 LCA standard is suitable for the environmental impact assessments of hydrogen production [8]. Standard procedures for the LCA of hydrogen technologies have already been determined [8]. Following this methodology, this study evaluates the environmental impact of hydrogen production using LCA [8].

Many publications have focused on the utilization of iron oxide wastes [9–12]. However, these studies focused only on the H₂S adsorption performance and did not conduct a quantitative evaluation of the environment. Therefore, when these waste materials are actually used as H₂S adsorbents, whether they can reduce the environmental impact compared to the case of using a conventional adsorbent has not been investigated. In addition, even when environmental impact assessments have been conducted, previous studies have focused only on impurity adsorption systems and evaluated the environmental impact of replacing adsorbents with waste materials for CO₂ [13] and H₂S adsorbents [4]. However, a quantitative demonstration of the effect of reducing the environmental impact using waste as a H₂S adsorbent in the overall hydrogen production process is required. In a previous study, natural clay was used as a H₂S adsorbent to desulfurize a biomass-derived hydrogen production system using anaerobic digestion, and a process was designed [14]. The LCA was used to calculate the exergy efficiency and environmental impact of the hydrogen production system, and the performance of the system was evaluated in terms of energy and environmental impacts. However, there have been no studies on the process design using mine waste as a H₂S adsorbent for desulfurization in a biomass-derived hydrogen production system using AGM, nor have they been evaluated in terms of energy and environment. Therefore, this study is the first to design a hydrogen production process that includes desulfurization using mine waste as a H₂S adsorbent and to quantitatively demonstrate the effectiveness of waste utilization in the overall hydrogen production process.

This study focused on the use of a granulated H₂S adsorbent to desulfurize a biomass-based hydrogen production system using an AGM. The granulation of neutralized sediments has been proposed for practical use. Because the sulfur capture capacity of the granulated neutralized sediment remains unknown, H₂S adsorption tests were conducted to quantitatively demonstrate this capacity. In addition, a process design for a biomass-derived hydrogen production AGM system, including desulfurization using granulated neutralized sediment as a H₂S adsorbent, was developed to obtain inventory data for the LCA. The performance of the hydrogen production system was evaluated in terms of exergy efficiency to confirm the performance of the proposed system. Based on the process design results, an environmental impact assessment using the LCA was conducted to quantitatively demonstrate the environmental benefits of replacing conventional H₂S adsorbents with granulated neutralized sediment. SimaPro version 9.2.0.1 was used to assess the environmental impact of the system using the LCA.

2. Methods

2.1. Dynamic Adsorption Experiment

Figure 1 shows the fixed-bed distribution reactor used in the dynamic desulfurization system. This apparatus featured a stainless-steel tube reactor with an inner diameter of 15.8 mm and a length of 82 mm, filled with an adsorbent with an inner diameter of 10 mm and a height of 5 mm, and covered with a sintered filter. The particle size of the adsorbent was standardized to Φ 0.56–1.25 mm by using a sieve. When the adsorbent was filled, the top and bottom were clipped with glass wool to prevent movement. The gas flow rate at the reactor inlet was adjusted using a mass flowmeter to ensure a constant flow rate. The gas was maintained at a constant composition using an already adjusted cylinder. The pressure was measured using a digital pressure gauge installed at the rear of the reactor. An annular electric furnace was installed around the reaction tube to control the furnace temperature.

Thermocouples were inserted at the bottom of the reaction tube to measure the temperature inside the furnace. A suction pump was installed at the rear of the reactor to create a vacuum inside the reactor. DOWA Holdings Co., Ltd. (Tokyo, Japan) provided adsorbent samples of the granulated neutralized sediment. However, the granulation method could not be disclosed owing to patent information [15].

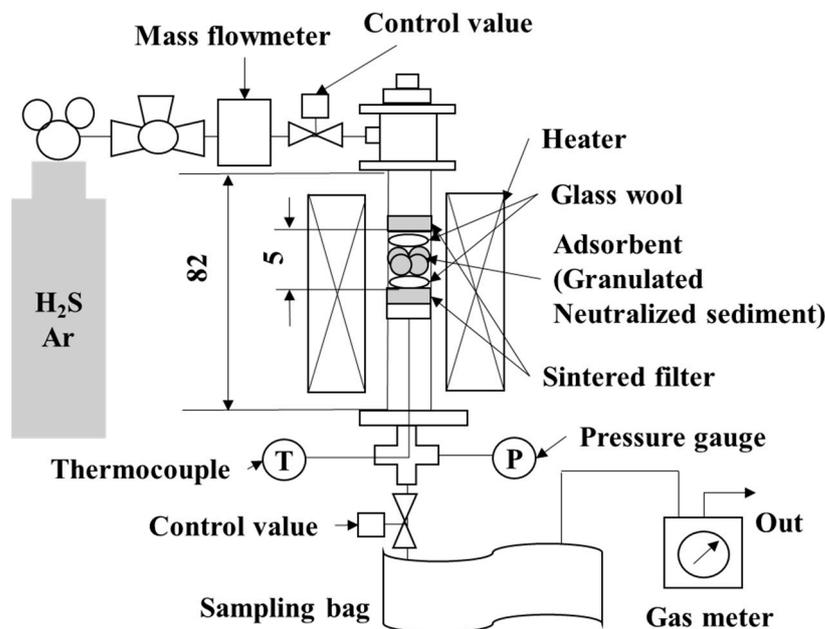


Figure 1. Schematic of dynamic H₂S adsorption experiment.

The experimental procedure was performed by increasing the adsorption temperature and distributing Ar at a rate of 50 mL/min. The sample gas was supplied from the front stage at a rate of 20 mL/min and collected in a gas bag at the rear of the reactor. At this time, the pressure in the reactor was 0.1 MPa (normal pressure). The H₂S concentration in the collected gas was analyzed using a gas chromatograph (GC-8A, Shimadzu Corporation, Kyoto, Japan), and the detection limit of the H₂S concentration at the reactor outlet was set at 10 ppmv. In this experiment, the adsorption temperature was varied to 200 °C, 250 °C, and 300 °C, assuming the adsorption temperature during high-temperature gasification [16]. The gas was H₂S-Ar (170 ppm balance), based on the hydrogen sulfide concentration in biogas from sewage sludge [17]. The amount of sulfur adsorbed was determined from the sulfur capture capacity (S_{cap}) as follows:

$$S_{cap} = \frac{\int_0^{t_{st}} FR(C_{inlet} - C_{outlet}(t)) dt \times M_S \times 10^3}{22.4 \times W_{sorberent}} \tag{1}$$

where S_{cap} [g-S/kg-adsorbent] is the saturated adsorption volume, t_{st} [s] is the breakthrough time, FR [Nm³/s] is the flow rate, C_{inlet} [-] is the inlet H₂S concentration, $C_{outlet}(t)$ [-] is the outlet H₂S concentration, M_S is the molar mass of sulfur, and $W_{sorberent}$ [kg] is the amount of adsorbent used.

In addition, it was assumed that Ar was not adsorbed. The sulfur capture capacity of the granulated neutralized sediment was calculated using Equation (1) and compared with that of ZnO, a conventional high-temperature adsorbent, to analyze the availability of the granulated neutralized sediment. ZnO, the subject of comparison in this study, was fabricated by synthesizing graphite oxide on powdered ZnO. For the synthesis, a mixture of ZnO, sulfuric acid, phosphoric acid, and graphite powder was placed in an ice bath, and KMnO₄ was added dropwise and stirred for 1 h, followed by oxidation for 18 h. The mixture was again placed in an ice bath, and deionized water was added, stirred for 1 h, and centrifuged. The remaining solid paste was washed twice with deionized water

and HCl, washed twice with deionized water, and freeze-dried overnight. The detailed conditions are described in [18]. Two coefficients of variation were defined to ensure the reliability of the sulfur capture capacity at each adsorption temperature. The outlet H₂S concentration at each time point was defined as CV1, and the sulfur capture capacity at the same adsorption temperature was defined as CV2. The experiments were repeated three times at each adsorption temperature.

2.2. Simulation Method

2.2.1. Simulation Conditions

Based on the results of the adsorption experiments, a hydrogen production plant using sewage sludge as fuel was designed. First, the system was designed under steady-state conditions using a process simulator to evaluate its performance. A schematic of the hydrogen production system is shown in Figure 2, and the plant conditions are listed in Table 1. The fuel utilization (U_f) of H₂ was set to 75%. The plant-scale data and the input steam to carbon feedstock molar ratio (S/C) were obtained from a demonstration plant in Minamisunamachi, Tokyo, Japan.

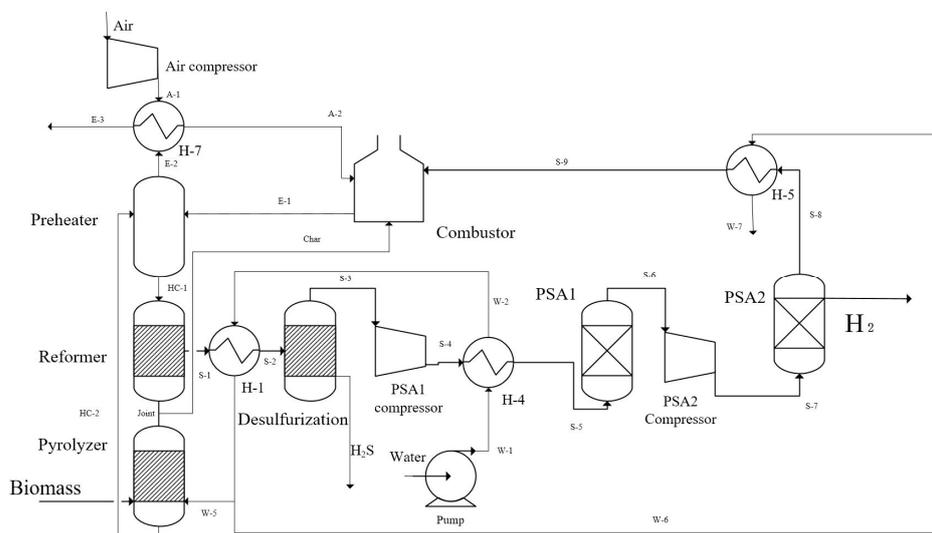


Figure 2. Process diagram of the hydrogen production system.

Table 1. The parameters used in the Pt degradation model.

Plant scale	828 kg/d
Steam/Carbon	1.4
U _f	75%
Lifetime	10 years

The proposed gasification process using sewage sludge by AGM was assumed as follows: (1) the AGM process gasified biomass at 600 °C by the heat of HCs, and (2) the gasified biomass (bio-syngas) was synthesized through the reforming process at 900 °C. Notably, this reaction is based on partial oxidation. The compositions of the sewage sludge and gasified biomass are shown in Tables 2 and 3, respectively [2]. In addition to H₂S, other impurities, such as NH₃ and HCl, existed in the fuel gas before refinement. Because the effects of these impurities on the fuel cell unit were less significant than those of H₂S, they were not considered in this study. In addition, the HC should not be replaced for ten years.

Table 2. Chemical properties of sewage sludge.

Carbon [wt.%]	39.14
Hydrogen [wt.%]	6.22
Nitrogen [wt.%]	4.72
Sulfur [wt.%]	0.65
Chlorine [wt.%]	0.21
Oxygen [wt.%]	31.06
Ash [wt.%]	18.00
Volatiles [wt.%]	81.50
Higher Heating value [kJ/kg]	17,299

Table 3. Molar fraction of pyrolyzed gas.

H ₂	9.8	mol%
CO	8.7	mol%
CH ₄	12.3	mol%
CO ₂	25.0	mol%
N ₂	35.2	mol%
H ₂ S	0.020	mol%
C ₂ H ₄	0.5	mol%
C ₂ H ₆	8.5	mol%

After gasification and reforming, the desulfurization system removed H₂S from the bio-syngas using a H₂S adsorbent. The desulfurization temperature was set at 300 °C, and two patterns were considered: using ZnO as the H₂S adsorbent (conventional case) and using granulated neutralized sediment (proposed case). The sulfur capture capacity of ZnO at 300 °C was based on the literature [18], and that of granulated neutralized sediment at 300 °C was taken from the experimental results of this study. The size of the adsorption column using the granulated neutralized sediment was assumed to be the same as that of ZnO. In addition, to quantitatively demonstrate the advantage of using granulated neutralized sediment, the reduced pressure drop was calculated when powder-neutralized sediment and granulated neutralized sediment were used as H₂S adsorbents in the desulfurization system. Ergun's equation was used to calculate the pressure loss [19].

$$-\frac{\Delta P}{L} = 150\mu \frac{(1-\varepsilon)^2}{d^2\varepsilon^3} U + \frac{1.75\rho(1-\varepsilon)}{d\varepsilon^3} U^2 \quad (2)$$

where P is the pressure [Pa], L is the length of the adsorption column [m], μ is the viscosity [Pa·s], d is the particle diameter [m], ε is the void fraction, ρ is the bulk density [kg/m³], and U is the velocity [m/s]. The viscosity was calculated from the biogas composition, and the experimental values were used to determine the porosity, particle size, and bulk density. The length of the adsorption column and the flow velocity were obtained from a hydrogen production plant in Minamisunamachi.

Desulfurized biogas is separated from hydrogen and other substances using pressure swing adsorption (PSA). In this study, 2-step PSA was used instead of the common 1-step PSA. Because of the same separation performance and smaller operating pressure compared to 1-step PSA, 2-step PSA is known to have a smaller environmental impact than 1-step PSA [20].

In this study, HAS-Clay and Zeolite were used as adsorbents in the first and second stages, respectively, because they have been used in previous studies. Both operating pressures and filling volumes of the adsorbent were set at 0.4 MPa and 5 kg, respectively. The sulfur capture capacity of HAS-Clay was obtained from Kuroda et al. [21] and that of Zeolite 5 A was obtained from Yang et al. [22,23]. Other design considerations included a 5% loss of sensible heat from the inlet gas owing to the heat dissipation at the heat exchanger.

2.2.2. Energy and Exergy Analysis

Exergy analysis was used to evaluate the performance. Recently, exergy analysis has been increasingly applied to the thermodynamic analysis of thermal processes and plant systems. This concept is beneficial because the first-law analysis is insufficient for evaluating the energy performance [24]. Exergy analysis aims to identify the magnitude and location of exergy losses, improve existing systems, and develop new processes or systems [25].

Exergy can be defined as the sum of the chemical exergy (Ex_{ch}) and physical exergy (Ex_{ph}) [25]:

$$Ex = Ex_{ch} + Ex_{ph} \quad (3)$$

where the chemical and physical exergies may be defined as:

$$Ex_{ch} = \sum_i n_i \left(e_{0_i} + RT_0 \ln \frac{n_i}{\sum n_i} \right) \quad (4)$$

$$Ex_{ph} = \sum_i n_i \{ (h_i - h_0) - T_0 (s_i - s_0) \} \quad (5)$$

where n_i is the molar yield of the gas component i [mol/kg], R is the gas constant [J/mol K], e_{0_i} is the standard chemical exergy of a pure chemical compound i [kJ/mol], h and s are the enthalpy [kJ/mol] and entropy [J/mol K] at the designed temperature and pressure, respectively, and h_0 and s_0 are the enthalpy and entropy, respectively, under standard conditions.

The correlation developed by Szargut and Styrylska was used to calculate the exergy of the biomass with less complexity [26]:

$$Ex_{biomass} = \dot{m} \beta LHV_{biomass} \quad (6)$$

The equation for the correlation factor, β , is:

$$\beta = \left[1.0412 + 0.2160 \left(\frac{H}{C} \right) - 0.2499 \left(\frac{O}{C} \right) \left\{ 1 + 0.7884 \left(\frac{H}{C} \right) \right\} + 0.450 \left(\frac{N}{C} \right) \right] \times \frac{1}{1 - 0.3035 \left(\frac{O}{C} \right)} \quad (7)$$

where O , C , H , and N are the weight fractions of oxygen, carbon, hydrogen, and nitrogen in the biomass, respectively. The exergy efficiency, ε , expresses all exergy inputs as used exergy and all exergy outputs as utilized exergy [27]:

$$\varepsilon = \frac{E_{out}}{E_{in}} = \frac{E_{H_2}}{E_{biomass} + E_{water} + E_{air} + E_{electricity}} \quad (8)$$

where E_{in} and E_{out} are the total input and output exergies [kJ], respectively, E_{H_2} is the exergy of hydrogen, $E_{biomass}$ is the exergy of the biomass feedstock [kJ], E_{water} is the exergy of the input water (kJ), E_{air} is the exergy of the input air [kJ], and $E_{electricity}$ is the exergy of the input electricity [kJ].

2.3. Life Cycle Assessment

2.3.1. Goal and Scope Definition

The LCA accounts for the environmental performance of a product throughout its life, from raw material extraction to disposal, and includes manufacturing and transportation [28]. In this study, we compared the environmental impacts of using ZnO and granulated neutralized sediments as H₂S adsorbents. Figures 3 and 4 illustrate the system boundaries for hydrogen and granulated neutralized sediment production, respectively. The scope of the environmental impact assessment was the manufacturing and utilization stages. Specifically, the system boundary of hydrogen production included the process from biomass gasification to pure hydrogen production (concentration 99.99 mol%), and that of granulated neutralized sediment production included granulation and transportation of the neutralized sediment. Based on the function of the hydrogen production system, the functional unit was defined as 1 kg of hydrogen. It was assumed that the granulation of

the neutralized sediment would occur in Misaki-cho, Okayama Prefecture, based on the production area of the neutralized sediment. In addition, it was assumed that hydrogen production from biomass occurred in Minamisunamachi, Tokyo, where the plant owned by our research group is located. In other words, granulated neutralized sediment was transported from Misaki-cho to Minamisunamachi. The service life of the hydrogen production plant is assumed to be 10 years.

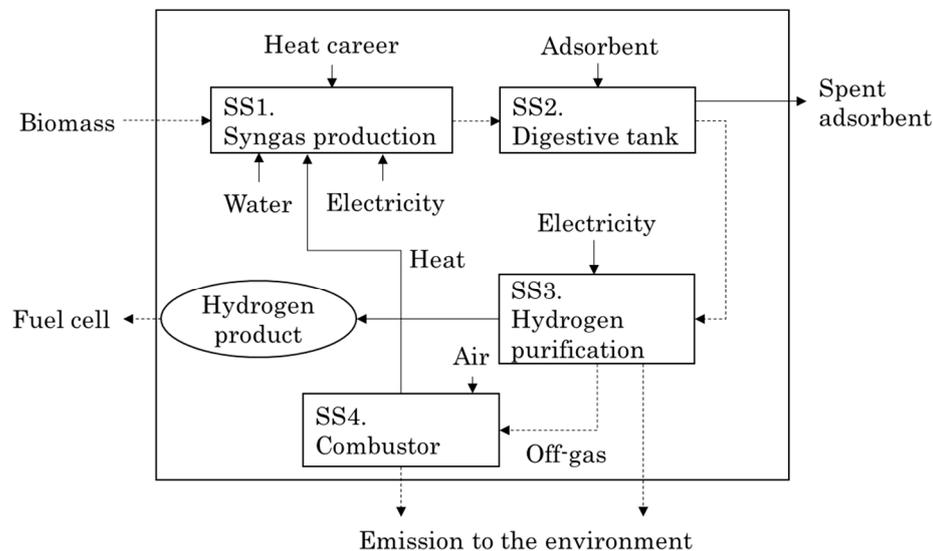


Figure 3. System boundary of hydrogen production.

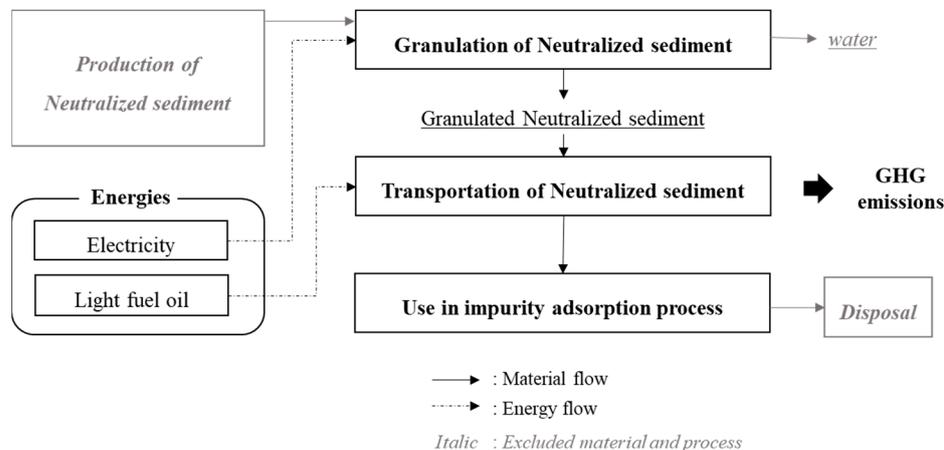


Figure 4. System boundary of granulated neutralized sediment production.

Four subsystems were defined for syngas production: pyrolyzer and reformer (SS1), desulfurization (SS2), hydrogen purification including 2-step PSA (SS3), and combustor (SS4). As shown in Figure 3, the disposal phase of the adsorbent was excluded from the system boundary because the adsorbent after H₂S adsorption can be used in agriculture. Previous studies have shown that crop yields increase when H₂S is dissolved in water and is taken up by seeds and roots [29]. Our research group is also studying the use of adsorbents after the adsorption of impurities in agricultural soil to grow komatsuna [30]. Therefore, the environmental impact of the adsorbent after H₂S adsorption at the disposal stage was ignored because there was a destination for its use.

The databases of background processes (production of water, electricity, light fuel oil, HC (alumina), and ZnO) were obtained from Ecoinvent 3.2 and CML databases using SimaPro Version 9.2.0.1. Among 11 impact indicators, the hydrogen production system in this study is known to have almost no emissions of CFCs (related to ozone layer depletion),

dichlorobenzene (related to human toxicity, marine aquatic ecotoxicity, freshwater aquatic ecotoxicity, and terrestrial ecotoxicity), C₂H₄ (related to photochemical oxidation), SO_x and NO_x (related to acidification), and PO₄ (related to eutrophication). On the other hand, CO₂ emissions from the exhaust gas, electricity consumption, and the use of metal oxides as H₂S adsorbents are cited; CO₂ emissions and electricity consumption have a significant impact on the global warming potential (GWP100), while the use of metal oxides has a significant impact on the abiotic depletion potential (ADP). In addition, since fossil fuel use in this study is primarily due to electricity use, the abiotic depletion potential of fossil fuels was expected to increase or decrease similarly to the GWP. Based on the above, the GWP100 and ADP were selected as impact areas for this study.

In Figure 4, the power required for granulation was obtained by referring to data from a previous study by Michiura et al. [31]. The inventory data for 1 kg of granulated neutralized sediment were prepared based on the system boundary shown in Figure 4. The production of powdered neutralized sediment was disregarded based on the concept of determining the correct environmental impact of waste utilization from a previous study.

Another solution for metal depletion based on a circular economy is to reduce the use of metal oxides through regeneration. In a previous study, ZnO was regenerated, and its H₂S adsorption performance was equivalent to that before the regeneration [32]. However, the environmental impact of regeneration on the overall hydrogen production system has not yet been quantified because regeneration requires high temperatures (700–800 °C), which is expected to increase the GWP due to energy use. Therefore, this study quantified the environmental impact of metal oxide regeneration on the overall hydrogen production system and compared it to the case of waste-granulated neutralized sediment. The regeneration method for ZnO was based on the literature. According to the literature, ZnO can be regenerated up to four times because up to four times the amount of adsorption remains the same [25]. In this study, the regenerated ZnO was denoted as ZnO_re.

In this study, an LCA was performed based on the H₂S adsorption by ZnO and granulated neutralized sediment without water vapor. However, previous studies have shown that water significantly affects the H₂S adsorption performance of adsorbents. Specifically, it was found that a certain amount of water promotes the dissociation of H₂S and increases the sulfur capture capacity, whereas a large amount of water causes the internal pores to become clogged, reducing the sulfur capture capacity [33,34]. Therefore, it is essential to consider the effect of water vapor when performing an LCA that considers realistic conditions. Therefore, in this study, a sensitivity analysis was conducted using data on the relationship between relative humidity (RH) and H₂S adsorption performance in previous studies. From this sensitivity analysis, we quantitatively investigated whether the use of granulated neutralized sediment had a smaller environmental impact than the use of conventional adsorbents, even after considering the RH. The relationship between the adsorption performance of ZnO and RH was taken from Zhao et al., and the relationship between the adsorption performance of Fe₂O₃, which is considered to be the main component of the neutralized sediment, and RH was taken from Huang et al. [34,35]. When creating the approximate equation, the data for which no specific values were given were approximated. From each dataset, the approximate equations for the RH and the sulfur capture capacities were created and based on those equations, the sulfur capture capacities were calculated at 0%, 25%, 50%, and 75% RH. However, because the sulfur capture capacity hardly changed when the RH exceeded 80% (ZnO) and 55.39% (Fe₂O₃), the approximate equations were set to 0% < *x* < 80% (ZnO) and 0% < *x* < 55.39% (Fe₂O₃), respectively, where *x* is the RH. Consequently, the approximate equations for ZnO and granulated neutralized sediment were given by Equations (9) and (10), respectively.

$$q_{ZnO,x} = -78.498x^2 + 80.56 + 4.3105(R^2 = 0.998) \quad (9)$$

$$q_{GNS,x} = -0.4526x^2 + 0.1413 + 0.1118(R^2 = 0.8651) \quad (10)$$

where $q_{ZnO,x}$ and $q_{GNS,x}$ are the provisional sulfur capture capacities of ZnO and the granulated neutralized sediment at RH x , respectively.

Equation (11) was calculated for the sulfur capture capacity at each RH from 0% to 75% to match the sulfur capture capacity at RH 0% to the data of this study.

$$q'_{i,x} = \frac{q_{i,x}}{q_{i,0\%}} \times q_{ex,i} (i = ZnO, GND; x = 0\%, 25\%, 50\%, 75\%) \quad (11)$$

where $q'_{i,x}$, $q_{i,x}$, and $q_{ex,i}$ are the sulfur capture capacity of i in RH x [g-S/100 g-sorbent], provisional sulfur capture capacity of i in RH x , and sulfur capture capacity of i in the experiment [g-S/100 g-sorbent], respectively.

Based on these equations, the sulfur capture capacities of ZnO and granulated neutralized sediment at each RH level were calculated, and a sensitivity analysis was performed.

2.3.2. Inventory Analysis

The inventory data for the hydrogen production system and granulated neutralized sediments are listed in Tables 4 and 5, respectively. The inventory data for hydrogen production were calculated based on the data for the hydrogen production system in Section 3.2. Thus, the adsorption temperature for desulfurization was set to 300 °C. An environmental impact assessment was conducted based on the inventory results.

Table 4. Inventory data of hydrogen, 1 kg production.

Parameters	Value	Unit
Input		
SS1 Syngas production		
Biomass feedstock	2.97×10^1	kg
HC	4.46×10^{-2}	kg
Water	2.62×10^1	kg
Electricity	1.94×10^{-2}	kWh
SS2 Desulfurization		
ZnO (Conventional)	7.67×10^{-1}	kg
Granulated neutralized sediment (proposal)	1.15	kg
SS3 Hydrogen purification		
HAS-Clay	9.81×10^{-4}	kg
Zeolite 5A	9.81×10^{-4}	kg
Electricity	1.18×10^1	kWh
SS4 Combustor		
Air	1.33×10^2	kg
Electricity	3.51×10^{-1}	kWh
Output		
Wastewater	3.10×10^1	kg
Hydrogen	1.00	kg
Carbon dioxide	3.27×10^1	kg
Oxygen	3.41×10^1	kg
Nitrogen	9.01×10^1	kg

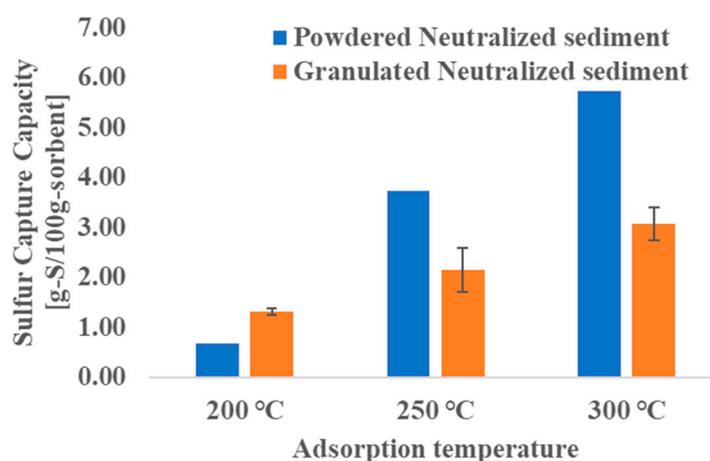
Table 5. Inventory data of granulated neutralized sediment, 1 kg.

Parameters	Value	Unit
Input		
Granulation		
Powdered neutralized sediment	1.00	kg
Electricity	3.09×10^2	MJ
Transportation		
Light fuel oil	9.05×10^{-2}	kg
Output		
Granulated neutralized sediment	1.00	kg

3. Results and Discussion

3.1. Results of Dynamic Adsorption

Figure 5 shows the sulfur capture capacity of the granulated neutralized sediment at 200, 250, and 300 °C. The duration of the experiments was 5 (200 °C), 10 (250 °C), and 11 h (300 °C), and the adsorption amounts were 1.31 (200 °C), 2.15 (250 °C), and 3.08 (300 °C) g-S/100 g-sorbent (CV1 < 1.40%, CV2 < 34.7%). As shown in Figure 5, the highest sulfur capture capacity was observed at 300 °C, whereas the lowest sulfur capture capacity was observed at 200 °C. The increase in the adsorption capacity at higher temperatures could be attributed to the chemisorption of the granulated neutralized sediment. Because chemisorption is adsorption due to a chemical reaction between the adsorbent and the target substance, the sulfur capture capacity improves at high temperatures, where reactions are more likely to occur [36]. Fe can adsorb H₂S via a chemical reaction at approximately 200 °C [37]. Thus, it can be assumed that the adsorption method for neutralized sediments varies with temperature.

**Figure 5.** Results of dynamic adsorption test.

According to the literature, the sulfur capture capacities of powdered neutralized sediment are 6.71×10^{-1} (200 °C), 3.73 (250 °C), and 5.73 (300 °C) g-S/100 g-sorbent [4]. Therefore, the sulfur capture capacity of granulated neutralized sediment was 95.1% greater (200 °C), 42.4% (250 °C), and 46.2% (300 °C) lower than that of powdered sediment. While the adsorption performance of the granulated neutralized sediment improved at 200 °C compared to that of the powdered sediment, it decreased at 250, and 300 °C. Previous studies have indicated that a reason for the decrease in the adsorption after granulation is the decrease in the surface area. Costa et al. confirmed that the surface area of granulated iron oxide is smaller than that of a powdered adsorbent and that the sulfur capture capacity is also reduced [38]. The specific surface area of the powdered

neutralized sediment is expected to be larger than that of the granulated neutralized sediment because the neutralized sediment contains more iron and is likely to undergo the same surface area changes as the adsorbent of Costa et al. [38]. However, at an adsorption temperature of 200 °C, the sulfur capture capacity of the neutralized sediment was higher after granulation. Long and Loc showed that the granulation of powdered Fe₂O₃-based adsorbents increased their sulfur capture capacity [39]. They cited an increase in the specific surface area as the cause of the increase in the sulfur capture capacity after granulation [39]. However, the results of the adsorption tests at 250 °C and 300 °C suggest that the specific surface area of the granulated neutralized sediment was lower than that of the powdered sediment. Therefore, further investigation into the structural changes in materials fed into the granulation process in response to temperature changes will help clarify the cause of this phenomenon.

Figure 6 compares the sulfur capture capacities of the granulated neutralized sediment and ZnO, a conventional adsorbent. The sulfur capture capacity of the granulated neutralized sediment (g-S/100 g-sorbent) was evaluated based on its weight, including the material added during granulation. Therefore, the sulfur capture capacity of ZnO was not assessed at 7.22 g-S/100g-ZnO, as shown by Song et al., but was evaluated by weight, including the rGO that was fed into the ZnO during granulation [18]. The calculations were performed using a ZnO-to-ZnO/rGO weight ratio of 63.7 wt.%. It was found to be 4.60 g-S/100 g-sorbent (shown in Figure 6). Consequently, at an adsorption temperature of 300 °C, the sulfur capture capacity of granulated neutralized sediment was approximately 23.2% lower than that of ZnO. In a previous study, at certain adsorption temperatures, the sulfur capture capacity of neutralized sediment was approximately 90% lower than that of metal oxides. Thus, the sulfur capture capacity of the granulated neutralized sediment can be regarded as almost the same as that of ZnO.

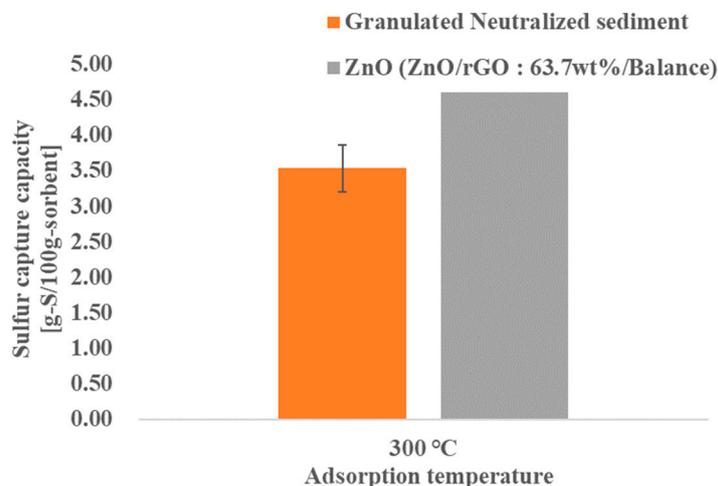


Figure 6. Comparison of performance between conventional and proposed adsorbents.

Next, the sulfur capture capacity of the granulated neutralized sediment was compared with that of other adsorbents made from waste materials to determine whether the granulated neutralized sediment had a higher or lower adsorption performance. Sakabe et al. proposed activated coke made from ligneous biomass as a high-temperature H₂S adsorbent and showed that its sulfur capture capacity at 200 °C was 0.36 g-S/100 g-sorbent [40]. The sulfur capture capacity of granulated neutralized sediment at 200 °C was 1.31 g-S/100 g-sorbent, which was 3.64 times higher than that of waste material in a previous study. Therefore, the adsorption performance of granulated neutralized sediment is very high compared with that of other adsorbents using waste materials.

3.2. Results of Exergy Analysis

The exergy efficiency of the sewage-sludge-derived hydrogen production system is shown in Figure 7. The figures in parentheses represent the percentages of total input; the exergy efficiency was 26.1%.

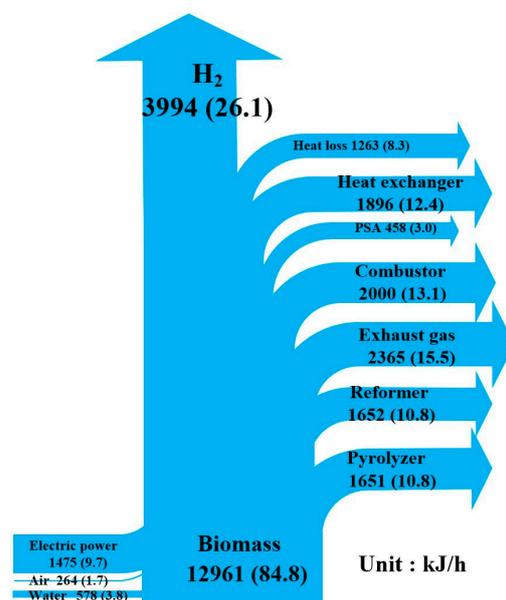


Figure 7. Hydrogen production system exergy diagram (percentage of total exergy, %).

The exergy efficiency of the system proposed in this study was compared with that of the biomass-derived hydrogen production in previous studies to determine whether the exergy efficiency in this study was higher or lower. Zhang et al. showed that the exergy efficiency for hydrogen production from sewage sludge is 5.37–19.6%, which is lower than the exergy efficiency in this study of 26.1% [41]. The higher exergy efficiency observed in this study occurred because steam reforming was the gasification method used in the previous study. In contrast, this study used partial oxidation, which requires less energy because it is exothermic. Cohce et al. partially oxidized palm oil waste to produce hydrogen [42]. However, the exergy efficiency of the entire system was 19–22%, which was slightly lower than that in this study [42]. This may be because the highly efficient AGM system with HC minimized the heat loss during pyrolysis. In other words, the hydrogen production system proposed in this study, which is based on a hydrogen production plant using sewage sludge in Minamisunamachi, Tokyo, has very high exergy efficiency.

The pressure drops across the adsorption column for the powdered and granulated neutralized sediment were 2.43 MPa and 2.89×10^{-4} MPa, respectively. When the biogas was pressurized in front of the desulfurization system, considering the pressure loss, 4.01×10^3 kJ/h and 2.15 kJ/h of electricity were required for the powder-neutralized and granulated neutralized sediments, respectively. In other words, approximately 1800 times more power was necessary for the powder-neutralized sediment than for granulated-neutralized sediment. An increase in power consumption decreases the overall exergy efficiency of hydrogen production and increases the environmental impact, particularly in terms of the GWP. These results indicate that using granulated neutralized sediment instead of powder is practical in terms of the exergy efficiency and environmental impact.

3.3. LCA Results

3.3.1. Comparison between ZnO and Granulated Neutralized Sediment

The LCA results for the GWP and ADP are shown in Figures 8 and 9, respectively. In terms of the GWP, the environmental impact of the conventional case was 4.66×10^1 kgCO₂eq, and those of SS1, SS2, SS3, SS4, and Output were 2.78×10^{-2} kgCO₂eq (0.06%),

5.63×10^{-1} kgCO₂eq (1.2%), 1.19×10^1 kgCO₂eq (25.8%), 1.43 kgCO₂eq (3.1%), and 3.27×10^1 (70.1%), respectively (Figure 8). From SS1 to SS4, the GWP of SS3 was the largest among the conventional cases. The reason for the largest GWP of SS3 is that the power consumption of the PSA was high because of its significant power consumption. This result indicates that, even if the PSA was changed from 1- to 2-step PSA, 2-step PSA still accounted for a large portion of the overall environmental impact of hydrogen production. In addition, the GWP of SS4 was the second highest among the conventional cases. This was due to the use of a large amount of air, which increased the air pressurization power and electricity consumption. In addition, the overall hydrogen production system had the highest environmental impact in the Output. This is due to the CO₂ in the exhaust gas. From this result, it can be considered that it is important to reuse or immobilize the CO₂ in the exhaust gas instead of releasing it into the atmosphere.

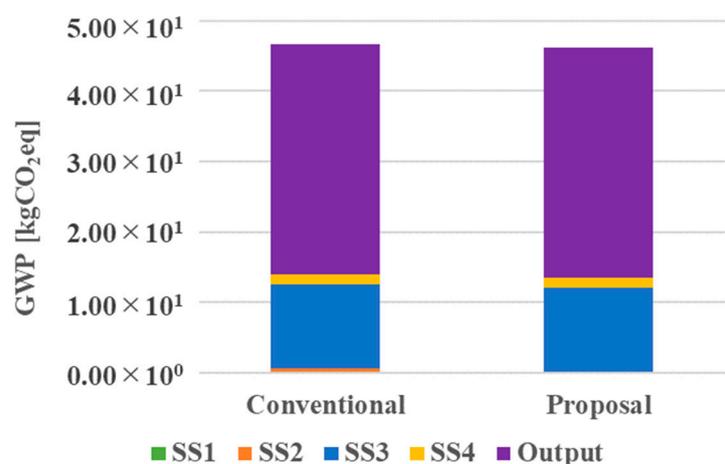


Figure 8. Results of GWP in conventional and proposed cases.

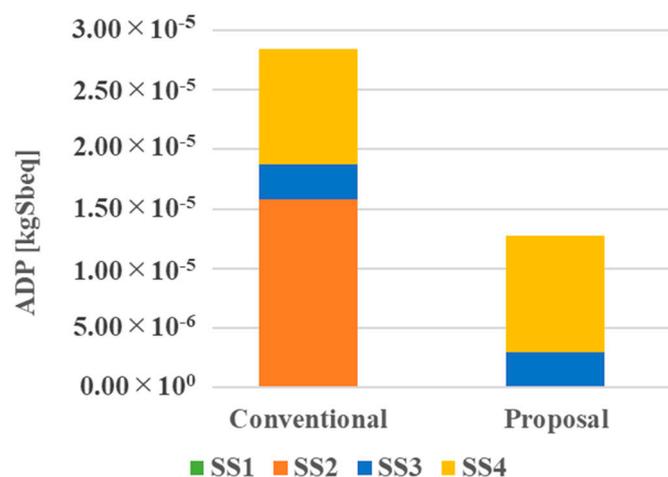


Figure 9. Results of ADP of the conventional and proposed cases.

In the proposed case, the GWP of the hydrogen production system was 4.62×10^1 kgCO₂eq, and those of SS1, SS2, SS3, SS4, and Output were 2.78×10^{-2} kgCO₂eq (0.06%), 1.49×10^{-1} kgCO₂eq (0.3%), 1.19×10^1 kgCO₂eq (25.8%), 1.43 kgCO₂eq (3.1%), and 3.27×10^1 (70.8%), respectively. When comparing the GWP of desulfurization (SS2) between the conventional and proposed cases, it can be seen that the environmental impact of SS2 in the proposed case is 73.5% smaller than that in the conventional case. As shown in Table 4, the amount of granulated neutralized sediment used was greater than that of ZnO. This implies that the GWP in 1 kg of granulated neutralized sediment was more negligible than that in 1 kg of ZnO, which was greater than the difference in the amount

used. The GWP of 1 kg of granulated neutralized sediment was 81.7% lower than that of 1 kg of ZnO. In addition, a comparison between the overall environmental impacts on the GWP of hydrogen production in the conventional and proposed cases showed that the environmental impact of the proposed case was 0.89% smaller than that of the conventional case. This indicates that the GWP of the entire hydrogen production could be reduced by 0.89% by using granulated H₂S adsorbent instead of ZnO. In other words, using granulated neutralized sediment in the desulfurization system reduces the environmental impact in terms of the GWP.

Regarding the ADP, the environmental impact of the conventional case was 2.84×10^{-5} kgSbeq, and those of SS1, SS2, SS3, and SS4 were 1.92×10^{-8} kgSbeq (0.07%), 1.58×10^{-5} kgSbeq (55.5%), 2.90×10^{-6} kgSbeq (10.2%), and 9.73×10^{-6} kgSbeq (34.2%), respectively (Figure 9). The ADP of SS2 was the greatest among the conventional cases. The reason for the high ADP of SS2 is the large ADP of the ZnO used in the desulfurization system. Thus, the use of ZnO in the desulfurization system significantly affected the ADP. In addition, the ADP of SS4 was the second greatest among the conventional cases. This was attributed to the large amounts of air and electricity consumed by the compressor. In the proposed case, the ADP of the hydrogen production system was 1.27×10^{-5} kgSbeq, and those of SS1, SS2, SS3, and SS4 were 1.92×10^{-8} kgSbeq (0.15%), 6.70×10^{-8} kgSbeq (0.53%), 2.90×10^{-6} kgSbeq (22.8%), and 9.73×10^{-6} kgSbeq (76.5%), respectively. When comparing the ADP of desulfurization (SS2) in the conventional and proposed cases, the environmental impact of SS2 in the proposed case was 99.6% smaller than that in the conventional case. This means that the ADP in 1 kg of granulated neutralized sediment was considerably lower than that in 1 kg of ZnO. The ADP of 1 kg of granulated neutralized sediment was 99.6% lower than that of 1 kg of ZnO. In addition, a comparison between the overall environmental impact of the ADP on hydrogen production in the conventional and proposed cases showed that the environmental impact of the proposed case was 55.3% smaller than that of the conventional case. This indicates that the ADP of the entire hydrogen production could be reduced by 55.3% by using granulated H₂S adsorbent instead of ZnO. In other words, using granulated neutralized sediment instead of ZnO in a desulfurization system drastically reduces the environmental impact of ADP.

3.3.2. Comparison between ZnO_re and Granulated Neutralized Sediment

The LCA results for the GWP and ADP are shown in Figures 10 and 11, respectively. In terms of the GWP, the environmental impact of the conventional case (regeneration) was 4.63×10^1 kgCO₂eq, and those of SS1, SS2, SS3, SS4, and Output were 2.78×10^{-2} kgCO₂eq (0.06%), 3.02×10^{-1} kgCO₂eq (0.65%), 1.19×10^1 kgCO₂eq (25.7%), 1.43 kgCO₂eq (3.1%), and 3.27×10^1 (70.5%), respectively (Figure 10). When comparing the GWP of desulfurization (SS2) in the conventional (regeneration) and proposed cases, the environmental impact of SS2 in the proposed case was 50.6% smaller than that in the conventional case (regeneration). In addition, a comparison between the overall environmental impact on the GWP of hydrogen production in the conventional (regeneration) and proposed cases showed that the environmental impact of the proposed case was 0.33% smaller than that of the conventional case (regeneration). This indicated that the GWP of the entire hydrogen production process using granulated neutralized sediment was slightly lower than that using ZnO_re.

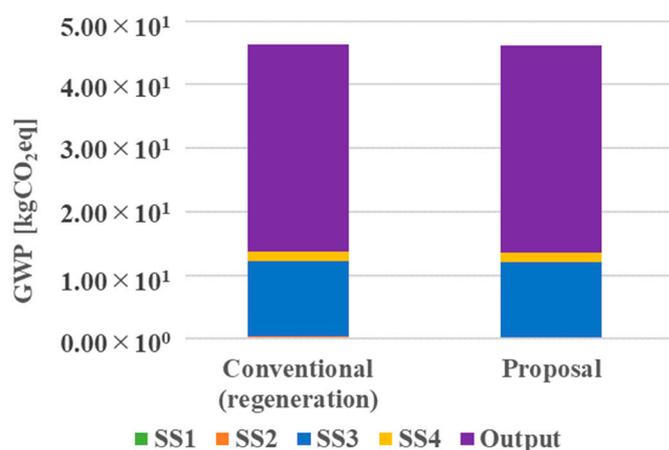


Figure 10. GWP results in the conventional (regeneration) and proposed cases.

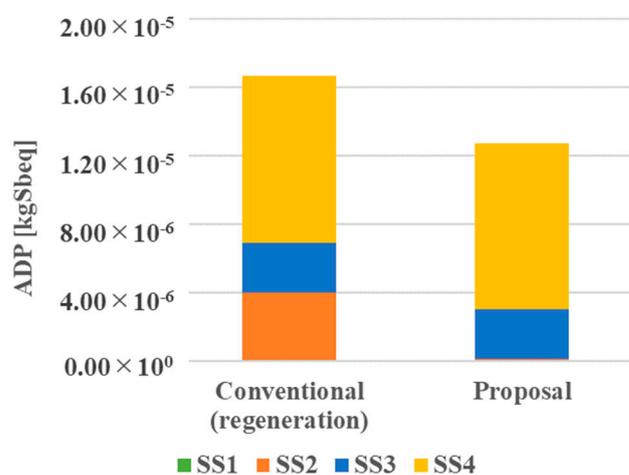


Figure 11. ADP results of the conventional (regeneration) and proposed cases.

In terms of the ADP, the environmental impact of the conventional case (regeneration) was 1.66×10^{-5} kgSbeq. Those of SS1, SS2, SS3, and SS4 were 1.92×10^{-8} kgSbeq (0.12%), 3.98×10^{-6} kgSbeq (23.9%), 2.90×10^{-6} kgSbeq (17.5%), and 9.73×10^{-6} kgSbeq (58.5%), respectively (Figure 11). When comparing the ADP of desulfurization (SS2) in the conventional (regeneration) and proposed cases, the environmental impact of SS2 in the proposed case was 98.3% smaller than that in the conventional case (regeneration). In addition, a comparison between the overall environmental impact of ADP on hydrogen production in the conventional (regeneration) and proposed cases showed that the environmental impact of the proposed case was 23.5% smaller than that of the conventional case (regeneration). This indicated that the ADP of the entire hydrogen production process using granulated neutralized sediment was smaller than that using ZnO_re. In other words, the environmental benefits in the GWP and ADP from using waste materials such as granulated neutralized sediment as H₂S adsorbents are more significant than those of metal oxide regeneration.

3.3.3. Sensitivity Analysis

The LCA results for the GWP and ADP are shown in Figures 12 and 13, respectively. For clarity, the conventional and proposed cases are abbreviated as Con and Pro, respectively. In terms of the GWP, the environmental impacts of SS2 in the conventional case were 5.64×10^{-1} kgCO₂eq (RH 0%), 1.25×10^{-1} kgCO₂eq (RH 25%), 1.00×10^{-1} kgCO₂eq (RH 50%), and 1.19×10^{-1} kgCO₂eq (RH 75%), while those in the proposed case were 1.49×10^{-1} kgCO₂eq (RH 0%), 1.41×10^{-1} kgCO₂eq (RH 25%), 2.41×10^{-1} kgCO₂eq (RH 50%), and 2.41×10^{-1} kgCO₂eq (RH 75%). Therefore, the GWP in SS2 of the proposed case

was 73.5% smaller (RH0%) and 12.3% (RH 25%), 141% (RH 50%), 103% (RH 75%) larger than those of the conventional case. These results show that at a higher RH, the GWP in the SS2 in the proposed method was larger than that in the conventional case. This is thought to be because the increase in RH increased the sulfur capture capacity of ZnO by approximately five times, reducing the amount of adsorbent used, whereas the increase in humidity decreased the sulfur capture capacity of the granulated neutralized sediment by approximately 40% compared to the RH 0% case, increasing the amount of adsorbent used. In terms of the GWP, the total environmental impacts in the conventional case were 4.66×10^1 kgCO₂eq (RH 0%), 4.62×10^1 kgCO₂eq (RH 25%), 4.61×10^1 kgCO₂eq (RH 50%), and 4.62×10^1 kgCO₂eq (RH 75%), while those in the proposed case were 4.62×10^1 kgCO₂eq (RH 0%), 4.62×10^1 kgCO₂eq (RH 25%), 4.63×10^1 kgCO₂eq (RH 50%), and 4.63×10^1 kgCO₂eq (RH 75%). Therefore, the total GWP of the proposed case was 0.89% smaller (RH0%) and 0.03% (RH 25%), 0.31% (RH 50%), and 0.26% (RH 75%) larger than those of the conventional case. These results show that the total GWP of the proposed case was slightly larger than that of the conventional case for a larger RH; however, this difference is not significant. This is thought to be because the GWP of SS2 accounted for only a small percentage (1–4%) of the total GWP, and changes in SS2 did not have a significant impact on the overall environmental impact. Therefore, the changes in RH had a very small impact on the overall GWP of hydrogen production.

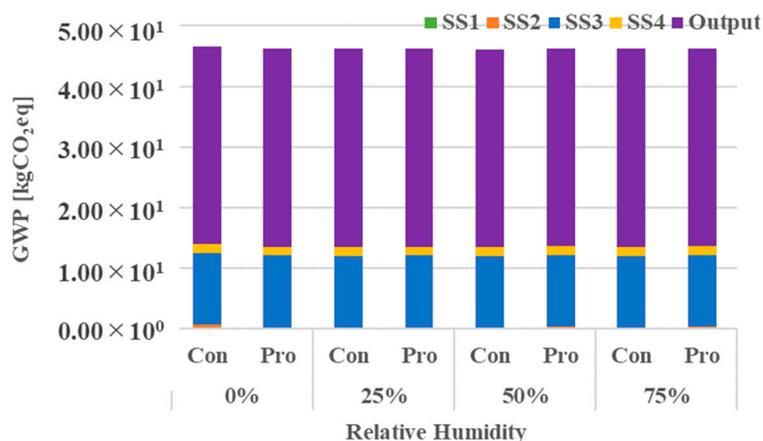


Figure 12. Result of GWP in the sensitivity analysis.

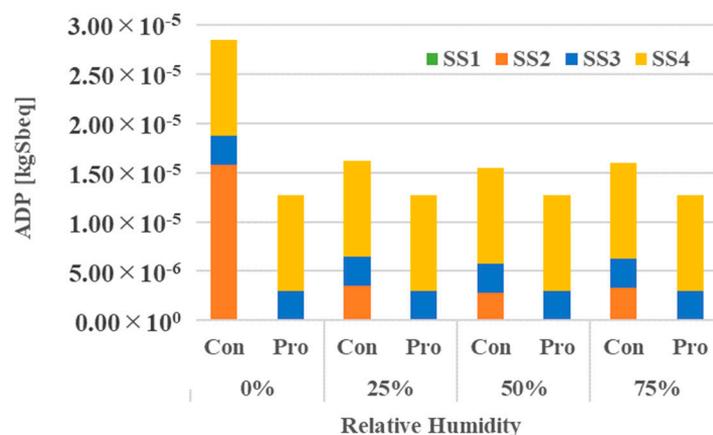


Figure 13. ADP results in the sensitivity analysis.

Next, in terms of the ADP, the environmental impacts of SS2 in the conventional case were 1.58×10^{-5} kgSbeq (RH 0%), 3.51×10^{-6} kgSbeq (RH 25%), 2.80×10^{-6} kgSbeq (RH 50%), and 3.33×10^{-6} kgSbeq (RH 75%), while those in the proposed case were

6.70×10^{-8} kgSbeq (RH 0%), 6.31×10^{-8} kgSbeq (RH 25%), 1.08×10^{-7} kgSbeq (RH 50%), and 1.08×10^{-7} kgSbeq (RH 75%). Therefore, the ADPs of SS2 in the proposed case were 99.6% (RH0%), 98.2% (RH 25%), 96.1% (RH 50%), and 96.8% (RH 75%) smaller than those of the conventional case. These results showed that, regardless of the change in RH, the ADP in SS2 of the proposed case was minimal compared to that of the conventional case. This is thought to be because the ADP per kg of ZnO is very large compared to that of the granulated neutralized sediment, and the change in the sulfur capture capacity due to RH has almost no effect. In terms of the ADP, the total environmental impacts in the conventional case were 2.84×10^{-5} kgSbeq (RH 0%), 1.62×10^{-5} kgSbeq (RH 25%), 1.55×10^{-5} kgSbeq (RH 50%), and 1.60×10^{-5} kgSbeq (RH 75%), while those in the proposed case were 1.27×10^{-5} kgSbeq (RH 0%), 1.27×10^{-5} kgSbeq (RH 25%), 1.28×10^{-5} kgSbeq (RH 50%), and 1.28×10^{-5} kgSbeq (RH 75%). Therefore, the total ADPs in the proposed case were 55.3% (RH0%), 21.3% (RH 25%), 17.5% (RH 50%), and 20.2% (RH 75%) smaller than those in the conventional case. These results show that the overall ADP of the proposed case was smaller than that of the conventional case at any RH, although the effect decreased as the RH increased. The reason for the decrease in the overall ADP in the conventional case is thought to be that ADP in SS2 accounts for a large percentage (55.3%) of the total GWP, and the increase in the sulfur capture capacity of ZnO and the decrease in the amount of ZnO used because of the increase in RH had a significant effect. In addition, the reason why the overall ADP of the proposed case was smaller than that of the conventional case, regardless of the increase in RH, is considered to be that, as in the case of SS2, the environmental load per kg of the granulated neutralizing agent was minimal compared to that of ZnO; therefore, the changes in adsorbent use due to RH have little effect.

The results of the sensitivity analysis indicated that the use of granulated neutralized sediment as a H₂S adsorbent has a significant effect on reducing the environmental impact of the hydrogen production system, even when changes in the RH are considered.

4. Conclusions

This study focused on the great environmental impact of metal oxides used in desulfurization systems for biohydrogen production. Using neutralized sediment, a waste product of mineral water treatment was proposed as an alternative H₂S adsorbent from the perspective of the circular economy. The focus was on using granulated neutralized sediment because it is a powder, and when used in large adsorption towers, the gas may not flow owing to a pressure loss. However, the sulfur capture capacity of granulated neutralized sediment, and the effect of waste utilization on the overall environmental impact of hydrogen production, have not yet been investigated. Therefore, in this study, the sulfur capture capacity of granulated neutralized sediment was measured. The extent to which the environmental impact of the entire hydrogen production process could be reduced was examined by substituting the granulated neutralized sediment with ZnO, a conventional adsorbent. The results are as follows:

- The sulfur capture capacity of the granulated neutralized sediment was the largest at 300 °C. The sulfur capture capacity of the granulated neutralized sediment at 300 °C was approximately 46.2% and 23.2% lower than that of the powdered sediment and ZnO, respectively.
- The exergy efficiency of the hydrogen production system was 26.1%.
- The GWP and ADP of the hydrogen production system using granulated neutralized sediment were approximately 0.89 and 55.3% smaller, respectively, than those using ZnO.
- The GWP and ADP of the hydrogen production system using granulated neutralized sediment were approximately 0.33 and 23.5% smaller, respectively, than those using ZnO_{re}.
- The results of the sensitivity analysis showed that the use of the granulated neutralized sediment as a H₂S adsorbent had a significant effect on reducing the ADP of the

hydrogen production system by more than 17.5%, even when changes in the RH were considered.

In other words, from the perspective of a circular economy, it was quantitatively demonstrated that using waste as a H₂S adsorbent could significantly reduce the environmental impact of the entire hydrogen production system. This is an example of how waste materials can substantially reduce the environmental impact of the entire system. This study will help promote the use of waste materials in the future. In this study, the process design and LCA were conducted assuming high-temperature adsorption; however, neutralized sediment can also adsorb H₂S in low-temperature zones. Therefore, in future studies, a low-temperature desulfurization system using neutralized sediment should be considered, and the overall design of the hydrogen production system and its energy and environmental impacts should be assessed.

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