

Sulfate and organic matter concentration in relation to hydrogen sulfide generation at inert solid waste landfill site -
limit value for gypsum -

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Abstract: In order to suggest a limit value for gypsum (CaSO_4) for the suppression of hydrogen sulfide (H_2S) generation at an inert solid waste landfill site, the relationship between raw material (SO_4 and organic matter) for H_2S generation and generated H_2S concentration, and the balance of raw material (SO_4) and product (H_2S) considering generation and outflow were investigated. SO_4 concentration should be less than approximately 100 mg- SO_4/L in order to suppress H_2S generation to below 2000 ppm. Total organic carbon (TOC) concentration should be less than approximately 200 mg-C/L assuming a high SO_4 concentration. The limit value for SO_4 in the ground is 60 mg- SO_4/kg with 0.011 w% as gypsum dihydrate, i.e., approximately 1/10 of the limit value in inert waste as defined by the EU Council Decision (560 mg- SO_4/kg -waste). The limit value for SO_4 in inert waste as defined by the EU Council Decision is high and TOC is strictly excluded. The cumulative amount of SO_4 outflow through the liquid phase is much larger than that through the gas phase. SO_4 concentration in pore water decreases with time, reaching half the initial concentration around day 100. SO_4 reduction by rainfall can be expected in the long term.

Key Words: landfill site, waste gypsum board, hydrogen sulfide, sulfate, organic matter, limit value for gypsum

1. Introduction

Hydrogen sulfide (H_2S) gas at 20–30 ppm produces a strong offensive odor likened to rotten egg (Reiffenstein et al., 1992), and its inhalation at 750–1000 ppm leads to abrupt physical collapse (Milby and Baselt, 1999) (Hereafter, H_2S concentration exceeding 1000 ppm is called high concentration.). H_2S is generated at landfill sites globally (Lee et al., 2006; Eun et al., 2007; Xu et al., 2010; Fang et al., 2012; López and Lobo, 2014; Yue et al., 2014). In 1999, three workers at an inert solid waste landfill site in Japan died after exposure to H_2S at 15000 ppm. In Japan, as inert solid waste landfill sites accept waste plastic, rubber, metal, glass, ceramic, and construction and demolition debris (stones, bricks, and blocks), it is not necessary to install gas bent pipes, liners for leachate, or water treatment facilities. Around the time of the accident, waste gypsum board without protective paper sheet was also accepted. H_2S gas is produced at landfills when sulfate-reducing bacteria (SRB) consume and convert sulfate (SO_4) under anaerobic conditions (Lee et al., 2006; Townsend et al., 2004, 2005). The source of SO_4 in construction and demolition debris is predominantly gypsum (CaSO_4) (Jang and Townsend, 2001). SRB also consume organic matter. At inert solid waste landfill sites in Japan, not biodegradable organic matter but waste gypsum board from which protective paper sheet had been removed had been accepted. However, because organic matter in the base material of waste gypsum board (gypsum part) could be a source of H_2S (Inoue, 2005), the Ministry of the Environment in Japan prohibited the disposal of waste gypsum board at inert solid waste landfill sites in 2006 (Notice: Treatment of waste gypsum board from which protective paper sheet had been removed). Measures to prevent H_2S generation or diffusion at landfill sites include suppressing the creation of anaerobic conditions (by draining water and/or introducing oxygen) (Masamoto et al., 2012) and trapping generated H_2S (by conversion into iron sulfide using iron-containing material (Naruoka and Ono, 2004; Bergersen and Haarstad, 2014) and adsorption by activated carbon (Adib et al., 1999) or zeolite (Karge and Raskó, 1978)). The Ministry of the Environment in Japan recommended the appropriate installation of cover soil (to prevent rainwater percolation and trap H_2S by iron contained in cover soil) and gas bent pipes (to supply oxygen). If waste gypsum board was properly presorted at construction and/or demolition sites, it would be possible to dispose gypsum-free construction and demolition waste (CDW) at inert

solid waste landfill sites. However, in regard to CDW contaminated with waste gypsum board due to poor presorting at the site, the disposal at inert solid waste landfill sites would be allowed only after the removal of waste gypsum board by sorting at an intermediate waste treatment facility. Although waste gypsum board removal may be difficult because gypsum board is fragile and easily disintegrates into fine particles, no directive, such as a limit value for gypsum, has been enforced in Japan. In order to suppress H₂S generation at inert solid waste landfill sites, a directive for sorting at construction, demolition and/or sorting sites, i.e., a limit value, should be set. Ono and Tanaka (2003) investigated the relationship between eluted substances and generated H₂S by immersing ten actual waste samples (CDWs and waste gypsum board) in water, and suggested that total organic carbon (TOC) concentration should be below 30 mg-C/L to suppress H₂S generation at a high concentration. However, as only ten samples were used, the relationships of SO₄ concentration with generated H₂S and H₂S generation potential when both SO₄ and TOC concentrations were varied widely were unknown.

In EU, pursuant to Council Directive (EC, 1999), landfills were classified into three types: landfill for hazardous waste, that for non-hazardous waste, and that for inert waste, according to the environmental pollution risk posed by the accepted waste. The EU Council Decision (EC, 2002) states: “2.2.3. Gypsum waste; Non-hazardous gypsum-based materials should be disposed of only in landfills for non-hazardous waste in cells where no biodegradable waste is accepted.” Therefore, no waste gypsum board is accepted at the landfills for inert waste. As only selected CDWs, such as concrete, brick, tile, ceramic, and their mixtures, are accepted at the landfills for inert waste, waste gypsum board should be removed. Furthermore, the limit values for SO₄ and dissolved organic carbon are applied to waste acceptable at the landfills. However, the H₂S generation potential of waste having SO₄ at the limit value is unknown.

At first, the SO₄ concentration that generates H₂S at a high concentration should be investigated experimentally. However, if SO₄ outflow by diffusion or rainfall was rapid, the limit value for SO₄ would be high. In this regard, not only SO₄ concentration but also SO₄ balance is important.

In this study, in order to suggest the limit value for gypsum (CaSO₄) for the suppression of H₂S generation at inert solid waste landfill sites in Japan and other countries, the following two points were investigated:

- Relationship between raw material (SO_4 and organic matter) for H_2S generation and generated H_2S concentration
- Balance of raw material (SO_4) and product (H_2S) considering generation and outflow

2. Materials and methods

SRB, which are mesophilic bacteria, were cultured with various concentrations of raw material (SO_4 and organic matter) for H_2S generation at $36\text{ }^\circ\text{C}$ in an incubator, and the concentration of generated H_2S was measured. Specifically, first, the required time for H_2S generation was investigated in order to determine the incubation period. Then, after preparing various concentrations of raw material, the concentration of generated H_2S was measured at the required time.

2.1. Materials

As basic experiments were conducted in this study, the actual sample, i.e., leachate from landfill site, was not used. Calcium sulfate (gypsum dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Japanese Food Additives, Wako Pure Chemical Industries) was used as SO_4 . Dried yeast (Dried Yeast Extract D-3, Wako Pure Chemical Industries) and lactose (Lactose Broth DAIGO, Wako Pure Chemical Industries) were equivalently mixed and used as organic matter. As nutrient for microorganisms, BOD Nutrient Buffer (Pillows for 6 L sample, APHA Formulation, Hach Co.) was used. One pillow was mixed with pure water to make 40 mL (high-concentration nutrient). Silica sand (Toyoura Keiseiki Kogyo) was used as microorganism carrier and black sediment in an ornamental pond was used for seeding. Five grams of black sediment and 1000 mL of pure water were mixed and shaken for five minutes, and nitrogen gas (N_2) was bubbled for five minutes. The supernatant was used as seeding liquid.

The required amounts of SO_4 and organic matter were set based on the experimental conditions. Two milliliters of high-concentration nutrient and 25 mL of seeding liquid were introduced into a plastic bottle and pure water was added to make 500 mL. The mixture was shaken for five minutes and N_2 gas was bubbled for five minutes, and this is called H_2S generation solution hereafter.

2.2. Experimental methods

2.2.1. H₂S generation system

Two spoonsful of silica sand, 80 mL of H₂S generation solution, and 10 mL of N₂ gas were introduced into a 100 mL plastic syringe. A silicone tube with a silicone inlet plug for gas chromatography was attached to the tip of the plastic syringe, and this is called the H₂S generation system hereafter. The schematic diagram of the H₂S generation system is shown in Fig. 1.

Fig. 1 Schematic diagram of H₂S generation system

2.2.2. Required time for H₂S generation

The required times for H₂S generation were investigated. The H₂S generation system was set in an incubator at 36 °C, all gases in the plastic syringe were collected by a syringe with a needle, and H₂S concentration was measured every day. The plastic syringe was refilled with 10 mL of N₂ gas.

Three prepared concentrations each of SO₄ and TOC in the H₂S generation system were used (SO₄: 30, 500, and 1200 mg-SO₄/L, and TOC: 10, 200, and 450 mg-C/L), and three repetitions were conducted, i.e., 3*3*3 = 27 experiments. The maximum concentration of SO₄ (1200 mg-SO₄/L) corresponds to approximately 70% solubility of gypsum dihydrate in water (approximately 1700 mg-SO₄/L (American Chemical Society, 2006)). The maximum TOC (450 mg-C/L) corresponds to approximately three times the limit value for the percolation test (160 mg-C/L) for inert waste defined by the EU Council Decision (EC, 2002).

2.2.3. Relationship between raw material (SO₄ and organic matter) for H₂S generation and generated H₂S concentration

Using various prepared concentrations of raw material (SO₄ and TOC) for H₂S generation, the concentrations of generated H₂S were measured. Eight prepared concentrations each of SO₄ and TOC in the H₂S generation system were used (SO₄: approximately 10, 30, 50, 100, 200, 500, 800, and 1200 mg-SO₄/L, and TOC: approximately 0, 10, 20, 50, 100, 200, 320, and 450 mg-C/L), and three repetitions were conducted, i.e., 8*8*3 = 192 experiments. Measurements of gas and liquid phases were conducted on days 0 and 7 as described in section 2.2.4.

2.2.4. Analytical procedure

Gas and liquid phases in the H₂S generation system were measured. In regard to the gas phase, H₂S was measured with a portable gas detector for worker safety confirmation (XS-2200, controlled potential electrolysis, New Cosmos Electric Co., Ltd.). The gas detector was placed inside a plastic bag to which collected gas was introduced, and the indicated value of H₂S concentration was read. As the indicated value was different from the concentration of standard H₂S gas, a calibration curve was prepared (Fig. 2).

Measurement items for the liquid phase were pH (HORIBA B-212), oxidation-reduction potential (ORP, HORIBA-D-55 and 9300-10D), dissolved oxygen (DO, HORIBA-D-55, 9520-10D), TOC (Shimadzu TOC-V_{WS}), and SO₄ (Thermo Fisher Scientific, ICS-1100).

Fig. 2 Calibration curve for H₂S

3. Results

3.1. Required times for H₂S generation

The relationship between elapsed time and concentration of generated H₂S is shown in Fig. 3. H₂S concentrations were high from days 4 to 8 except for TOC 0 mg-C/L (H₂S was below detection limit: < 0.1 ppm). Although the concentration varied every day, the required time for H₂S generation was estimated to be approximately 7 days in the H₂S generation system.

Fig. 3 Relationship between elapsed time and generated H₂S concentration

3.2. Relationship between raw material (SO₄ and organic matter) for H₂S generation and generated H₂S concentration

The generated H₂S concentrations for each prepared concentration of raw material are shown in Fig. 4 by circles (median, n = 3). Measurement day was day 7 according to the results in section 3.1. Only the generated H₂S concentrations obtained when SO₄ concentration was 1200 mg-SO₄/L are indicated in Fig. 4. H₂S was < 10 ppm when TOC concentration was < 50 mg-C/L. H₂S exceeded 1000 ppm when TOC concentration was > 300 mg-C/L.

Measured pH values were 6.2/6.8/7.5 (minimum/average/maximum, hereafter) on day 0 and 5.6/6.5/6.8 on day

7 (Table 1). ORPs were 209/279/395 on day 0 and -111/131/448 mV (Eh) on day 7 (Table 2). DOs were 0.0/0.4/1.9 on day 0 and 0.0/0.3/2.8 mg-O₂/L on day 7. Measured values of pH and ORP on day 7 were low when TOC concentration was high.

Fig. 4 Relationship between raw material (SO₄ and organic matter) for H₂S generation and generated H₂S concentration

Table 1 pH change

Table 2 ORP change

4. Discussion

4.1. Limit values for SO₄ and organic matter to suppress H₂S generation at a high concentration

The contour lines of generated H₂S concentrations after day 7, which were drawn based on Fig. 4 data, are shown in Fig. 5. Generated H₂S concentrations of 1000 and 2000 ppm are shown by a bold broken line and a bold solid line, respectively. In the area with less than 100 mg-SO₄/L, the higher SO₄ concentration was, the higher H₂S concentration was. The contour lines of 1000 and 2000 ppm H₂S were linear in the direction of the TOC axis. H₂S was generated at 1000 and 2000 ppm when SO₄ concentration was approximately 50 and 100 mg-SO₄/L, respectively. In the area with more than 100 mg-SO₄/L, the higher TOC concentration was, the higher H₂S concentration was, regardless of SO₄ concentration. The contour lines of 1000 and 2000 ppm H₂S were linear in the direction of the SO₄ axis. H₂S was generated at 1000 and 2000 ppm when TOC concentration was approximately 200 and 250 mg-C/L, respectively.

The contour lines of ORP after day 7 are shown in Fig. 6. Generated H₂S concentrations of 1000 and 2000 ppm are shown by a bold broken line and a bold solid line, similarly to Fig. 5. A distinct vertical line in the direction of the SO₄ axis appeared at approximately 100 mg-C/L TOC. ORP was < -20 mV in the area of approximately > 100 mg-C/L TOC. The contour lines of ORP did not agree with the H₂S emphasized line. The area with > 1000 ppm H₂S was located at < -40 mV ORP. Ono and Tanaka (2003) reported that H₂S exceeded 1000 ppm when ORP was < -30 mV in the experiment using CDW, and their result agreed with ours.

Although it is understood that one of the necessary conditions for suppressing H₂S generation is the decrease of TOC concentration, the main theme of this study is gypsum content, as mentioned above. Then, the relationship between SO₄ concentration and generated H₂S in the area of high H₂S concentration, i.e., 300 mg-C/L TOC, is shown in Fig. 7.

The limit values for SO₄ and dissolved organic carbon (TOC in eluate, i.e., TOC hereafter) in acceptable waste at the landfill for inert waste as defined in the EU Council Decision (EC, 2002) are shown in Fig. 5. The limit values were obtained from the following tests: the leaching test by mixing water and waste at the liquid/solid ratios of 2 and 10 L-water/kg-waste, and the percolation test. The limit values for SO₄ are 560 and 1000 mg-SO₄/kg-waste (corresponding to 0.10 and 0.18 w% of gypsum dihydrate) at the liquid/solid ratios of 2 and 10 L/kg in the leaching test, respectively. The limit values for TOC are 240 and 500 mg-C/kg-waste at the liquid/solid ratios of 2 and 10 L/kg in the leaching test, respectively. If those values were simply converted into concentration in eluate, the limit values for SO₄ would be 280 and 100 mg-SO₄/L, and those for TOC would be 120 and 50 mg-C/L. On the other hand, the limit values for SO₄ and TOC are 1500 mg-SO₄/L and 160 mg-C/L in the percolation test, respectively. The limit value for SO₄ of 100 mg-SO₄/L at the liquid/solid ratio of 10 L/kg would suppress the generation of 2000 ppm H₂S according to Fig. 5. However, more than 2000 ppm H₂S would be generated at the limit value for SO₄ of 280 mg-SO₄/L at the liquid/solid ratio of 2 L/kg. On the other hand, the limit value for TOC in the leaching test is lower than 200 mg-C/L, i.e., the bold broken line of 1000 ppm H₂S in Fig. 5.

From the above, SO₄ concentration should be less than approximately 50 mg-SO₄/L in order to suppress H₂S generation to less than 1000 ppm (less than approximately 100 mg-SO₄/L for 2000 ppm H₂S) according to the results of this study. Otherwise, TOC concentration should be less than approximately 200 mg-C/L assuming a high SO₄ concentration.

The SO₄ concentration that can generate 2000 ppm H₂S, i.e., 100 mg-SO₄/L, is converted into content in solid waste as follows. Dumped and compacted solid waste at a landfill forms the waste ground. Assuming a 1 m³ ground made of inert waste, a particle density of 2.5 t/m³, a bulk density of 1.0 t/m³, and a porosity of 0.6, saturated pore water (= *V*) is 0.6 m³ (Asakura et al., 2009), i.e., liquid/solid ratio is 0.6 L/kg (called ground condition A, hereafter).

SO₄ content in the ground is 100 mg-SO₄/L * 600 L/1000 kg = 60 mg-SO₄/kg, i.e., the total amount of SO₄ is 60 g and 0.011 w% is gypsum dihydrate. Therefore, the limit value for SO₄ in the ground in order to suppress the generation of 2000 ppm H₂S is 60 mg-SO₄/kg with 0.011 w% as gypsum dihydrate.

The limit value for SO₄ of 60 mg-SO₄/kg is approximately 1/10 of the limit value defined by the EU Council Decision (560 mg-SO₄/kg-waste) (EC, 2002). Therefore, the limit value for SO₄ defined by the EU Council Decision (EC, 2002) is high. On the other hand, TOC is strictly excluded from the point of view of H₂S generation suppression.

The relationship between raw material and generated H₂S concentration obtained in this study should be compared with monitoring results at actual landfill sites. However, there are few reports that have data for both SO₄ and generated H₂S. López and Lobo (2014) reported SO₄ concentrations of 100–800 mg-SO₄/L and > 500 ppm H₂S as the monitoring results at an actual landfill site.

Fig. 5 Contour lines of generated H₂S concentration after experiment

Fig. 6 Contour lines of ORP after experiment

Fig. 7 Relationship between SO₄ concentration and generated H₂S

4.2. Sulfur balance

H₂S concentration changes were simulated when a sufficient amount of SO₄ existed to generate a high concentration of H₂S. Even if 1000 ppm H₂S were generated in the ground and H₂S in the air were increased, the concentration would not reach 1000 ppm. Therefore, the generation of 2000 ppm H₂S in the ground, i.e., twice the amount, was assumed in this simulation. The ground was saturated with pore water, SO₄ was leached from the ground and existed in the pore water, and 2000 ppm H₂S was generated and existed on the ground surface. SO₄ in the pore water was converted into H₂S that would diffuse into the air, and SO₄ was washed out by rainfall. SO₄ in the ground was decreased by those two processes. H₂S washout by rainfall as ignored. The assumed phenomena of H₂S generation and sulfur outflow are shown in Fig. 8.

H₂S concentration in the air at 1 m height when 2000 ppm H₂S exists on the ground surface is calculated by

using equation 1 (Sagara, 2009).

$$C(z,t) = C_A[1 - \text{erf}\{z/(\sqrt{4Dt})\}] \quad (1)$$

where $C(z,t)$: concentration at z and t , C_A : concentration at generation surface, z : height, D : diffusion coefficient in air ($0.15 \text{ cm}^2/\text{s}$ (Moulin et al., 2002)), and t : elapsed time.

In regard to SO_4 decrease by H_2S diffusion, the outflow flux of H_2S that is converted from SO_4 is calculated by using equation 2 (Sagara, 2009).

$$N_A = (CD/z)\ln\{(1-X_{A1})/(1-X_{A2})\} \quad (2)$$

where N_A : flux, X_{A1} : H_2S mole fraction on the ground surface, and X_{A2} : H_2S mole fraction in air at height z .

Next, SO_4 outflow by rainfall is calculated as follows. According to Fig. 7, the SO_4 concentration that generates 2000 ppm H_2S is approximately $100 \text{ mg-SO}_4/\text{L}$ ($= C_0$). Assuming ground condition A and 1.7 m/y of precipitation Q , which is the average in Japan, 4.7 L/d of rainwater is supplied to an area measuring 1 m^2 . It is assumed that the rainwater is introduced into the pore water, the two waters are completely mixed in the ground, and SO_4 flows out of the ground with the outflow of water. Thus, SO_4 concentration in the pore water is calculated by using equation 3 (Sagara, 2009).

$$C(t) = C_0 e^{-Qt/V} \quad (3)$$

where $C(t)$: concentration at t , and V : volume of pore water.

The concentration changes of H_2S in the air at 1 m height and SO_4 in the pore water, and SO_4 outflow (conversion into H_2S and diffusion into the air ($\text{outflow}_{\text{gas}}$), and washout by rainfall ($\text{outflow}_{\text{liquid}}$)) are shown in Fig. 9. H_2S exceeds 1000 ppm in one day. The cumulative amount of SO_4 outflow by rainfall almost corresponds to the total outflow, i.e., outflow through the liquid phase is much greater than that through the gas phase. SO_4 concentration in the pore water decreases with time to half the initial concentration around day 100. However, the simulation model does not consider the decrease of H_2S generation potential by subsequent SO_4 reduction. SO_4 reduction by rainfall can be expected in the long term. However, an exceedingly low content of waste gypsum board corresponding to 0.011 w\% gypsum dihydrate is assumed in this simulation. SO_4 in the pore water is saturated (approximately $1700 \text{ mg-SO}_4/\text{L}$ (American Chemical Society, 2006)) with 0.2 w\% gypsum dihydrate. Therefore, if

more gypsum dihydrate exists, SO_4 reduction by rainfall may take an even longer time as SO_4 will be supplied by gypsum dihydrate subsequent to SO_4 outflow.

Fig. 8 Assumed phenomena of H_2S generation and sulfur outflow

Fig. 9 Concentration changes of H_2S and SO_4 , and SO_4 outflow

4.3. Limitations of this study and application of results

In this study, the medium for microbial culture was used as organic matter because it is easily degraded and utilized by microorganisms. The amount of organic matter was indicated by TOC in this study. In regard to TOC measurement, both easily degradable organic matter and hardly degradable ones (organic matter that could not be utilized by microorganisms, such as humic substances or plastic, or organic matter that takes time to decompose, such as cellulose) are regarded as organic carbon. As it is predicted that leachate in actual landfill sites contains many types of organic matter, only a part of TOC in the actual landfill sites corresponds to TOC in this study. Therefore, the limit value for TOC suggested in this study is underestimated. Further investigations using an index that indicates organic matter available to microorganisms, such as biochemical oxygen demand, and using another organic matter, such as eluate from wood, are needed. As the actual landfill site is a heterogeneous system, the results obtained in this study that assumed a homogeneous system would explain only a part of all phenomena occurring in the actual site. In order to apply the limit value to an actual landfill site, the acceleration or suppression of H_2S generation in a heterogeneous system should be investigated in the future.

In this study, the relationship between raw material (SO_4 and TOC) for H_2S generation and generated H_2S concentration was investigated. The results may be used as basic data for deciding the limit value for gypsum in inert solid waste to be disposed of in landfill sites.

5. Conclusion

In this study, in order to determine the limit value for gypsum (CaSO_4) for the suppression of H_2S generation at inert solid waste landfill sites in Japan and other countries, the relationship between raw material

(SO₄ and organic matter) for H₂S generation and generated H₂S concentration, and the balance of raw material (SO₄) and product (H₂S) considering generation and outflow were investigated.

SO₄ concentration should be less than approximately 50 mg-SO₄/L in order to suppress H₂S generation to less than 1000 ppm (less than approximately 100 mg-SO₄/L for 2000 ppm H₂S). Otherwise, TOC concentration should be less than approximately 200 mg-C/L assuming a high SO₄ concentration. The limit value for SO₄ in the ground in order to suppress the generation of 2000 ppm H₂S is 60 mg-SO₄/kg with 0.011 w% as gypsum dihydrate.

The limit value for SO₄ of 60 mg-SO₄/kg is approximately 1/10 of the limit value defined by the EU Council Decision (560 mg-SO₄/kg-waste). Therefore, the limit value for SO₄ as defined by the EU Council Decision is high and TOC is strictly excluded from the point of view of H₂S generation suppression.

H₂S concentration changes were simulated when a sufficient amount of SO₄ existed to generate 2000 ppm H₂S. The cumulative amount of SO₄ outflow through the liquid phase was much larger than that through the gas phase. SO₄ concentration in the pore water decreased with time, reaching half the initial concentration around day 100. SO₄ reduction by rainfall could be expected in the long term.

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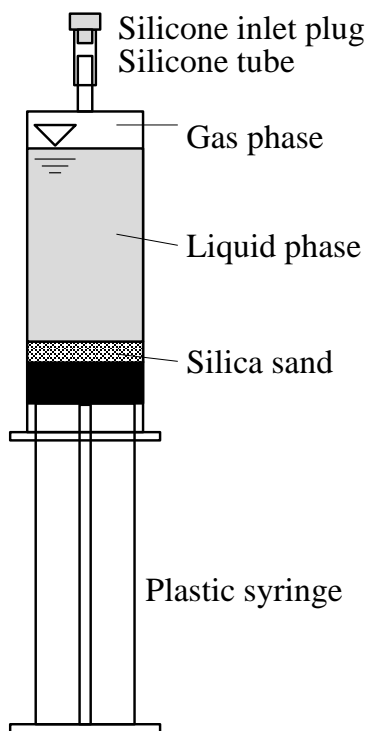


Fig. 1 Schematic diagram of H₂S generation system

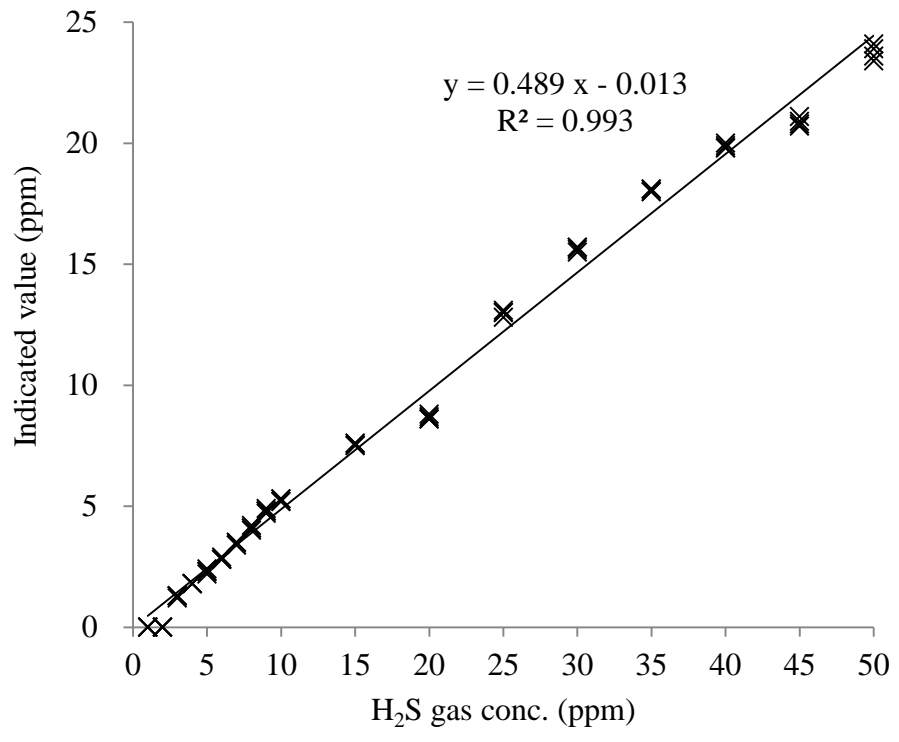


Fig. 2 Calibration curve for H₂S

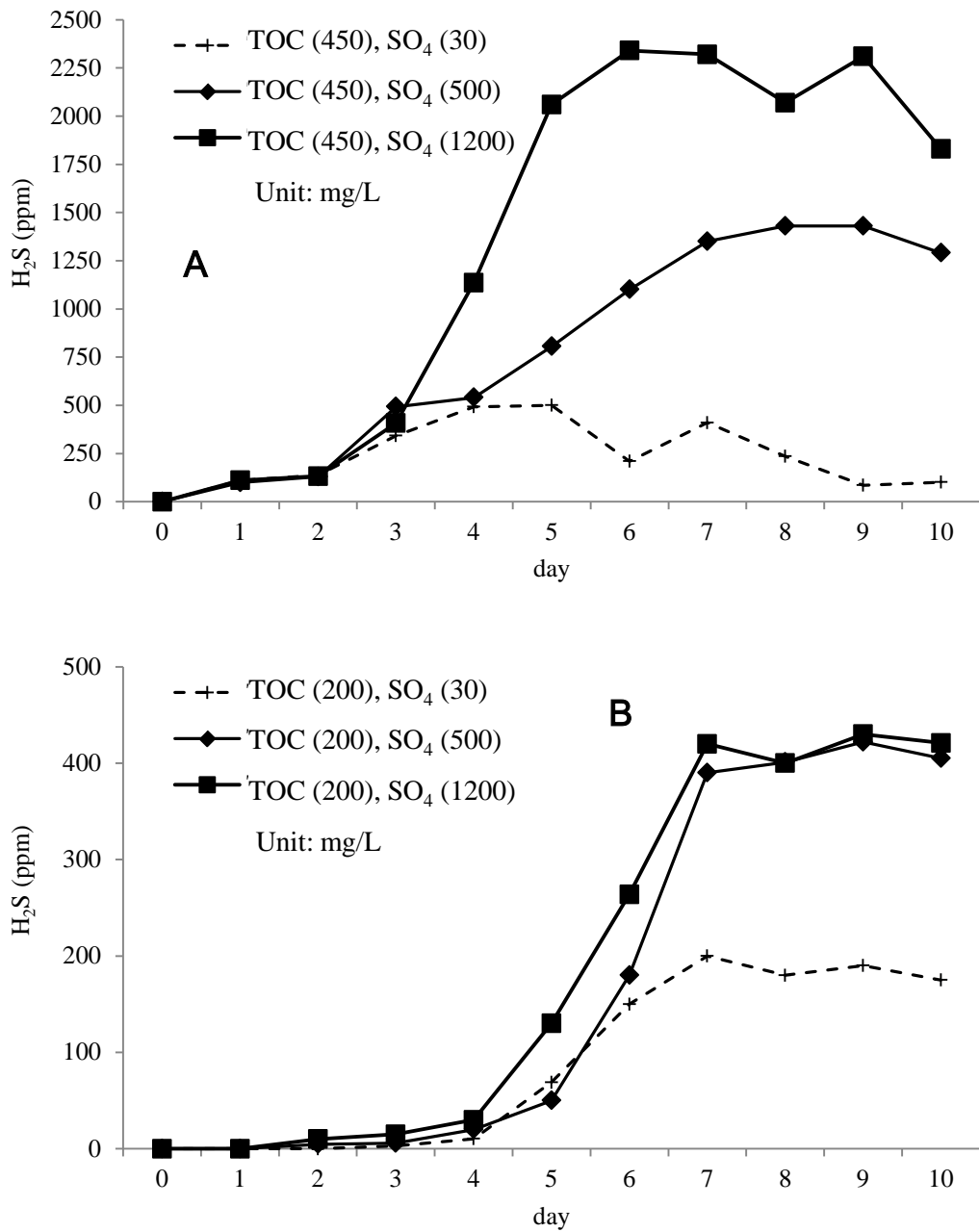


Fig. 3 Relationship between elapsed time and generated H₂S concentration (A: TOC 450 mg-C/L, B: TOC 200 mg-C/L)

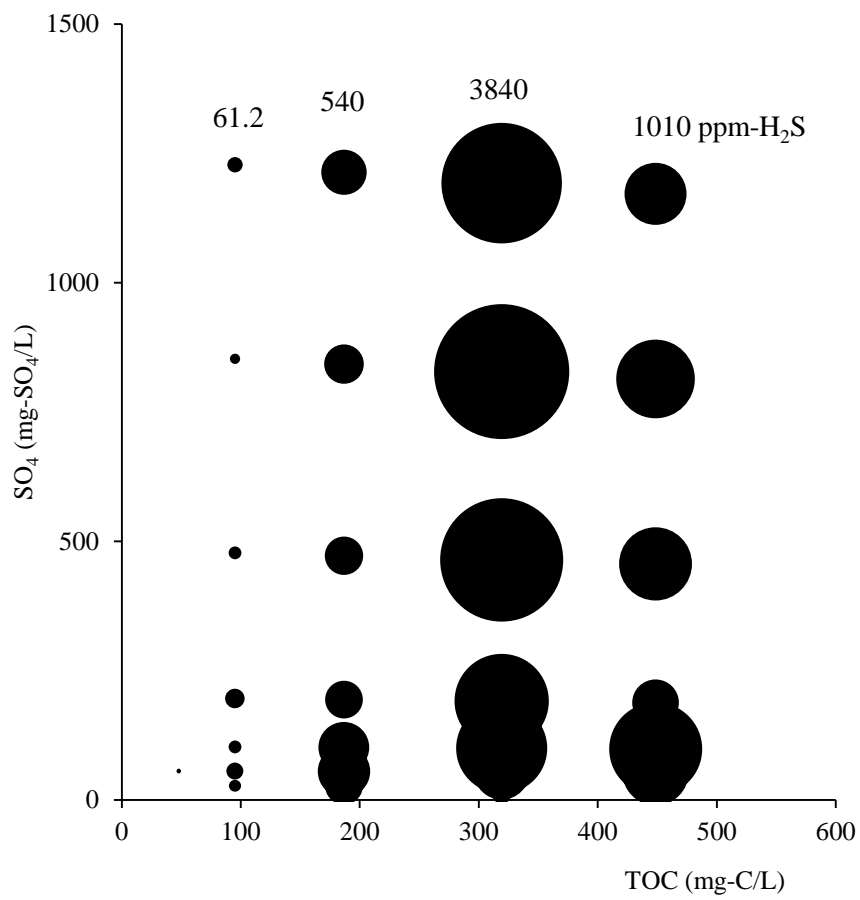


Fig. 4 Relationship between raw material (SO₄ and organic matter) for H₂S generation and generated H₂S concentration

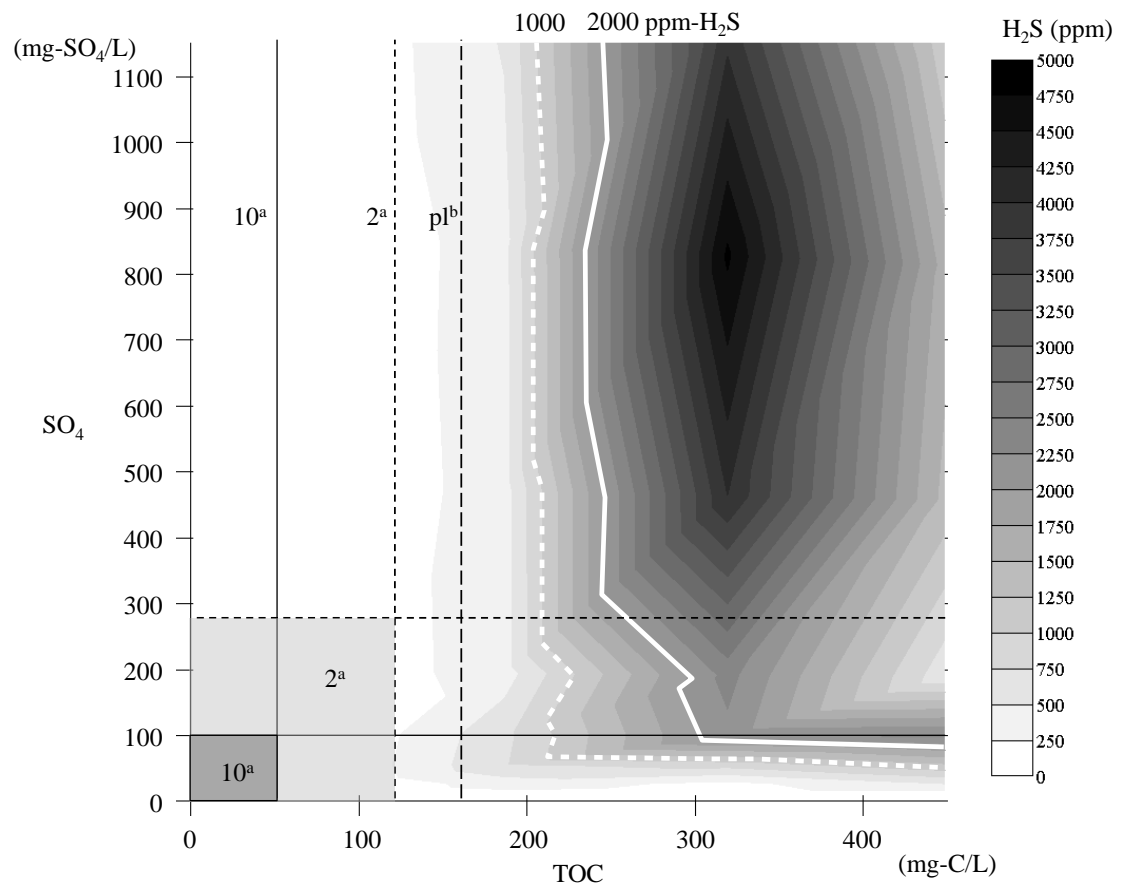


Fig. 5 Contour lines of generated H₂S concentration after experiment

^a liquid/solid ratio of leaching test and ^b percolation test defined in EU Council Decision (EC, 2002)

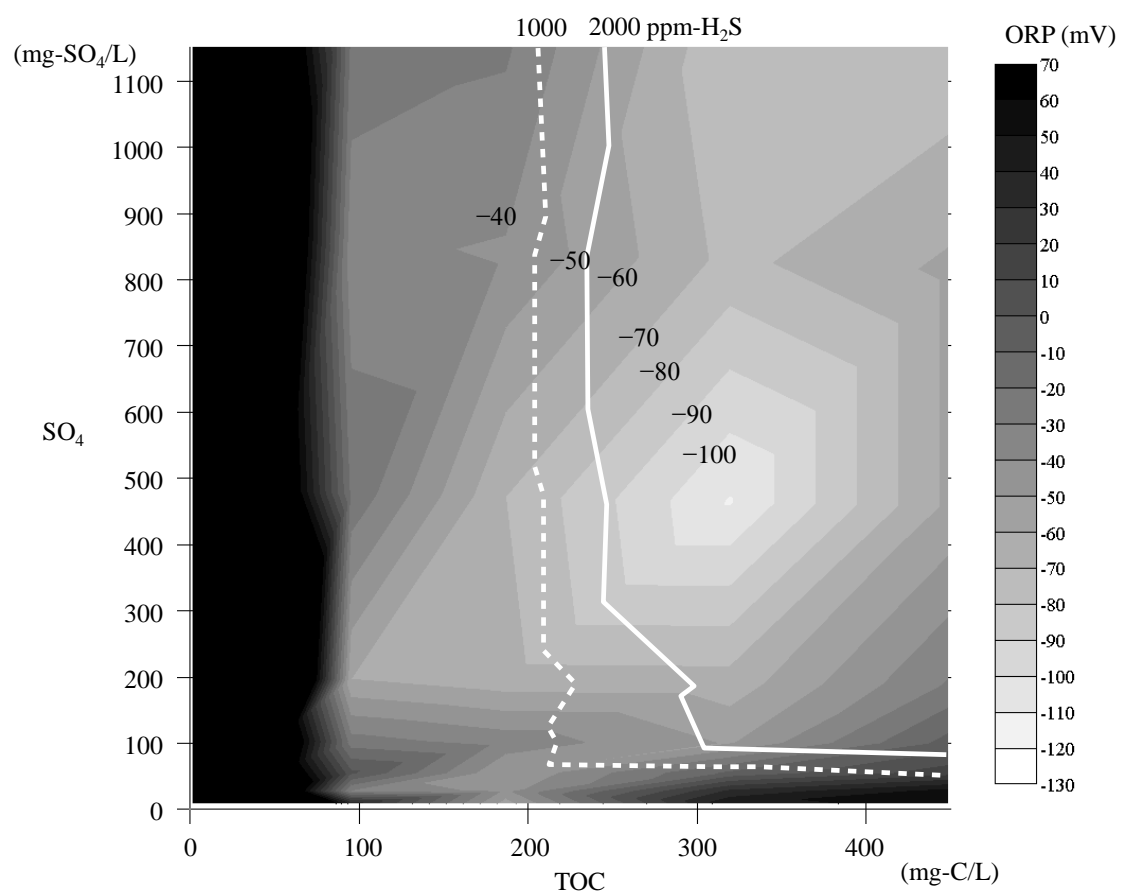


Fig. 6 Contour lines of ORP after experiment

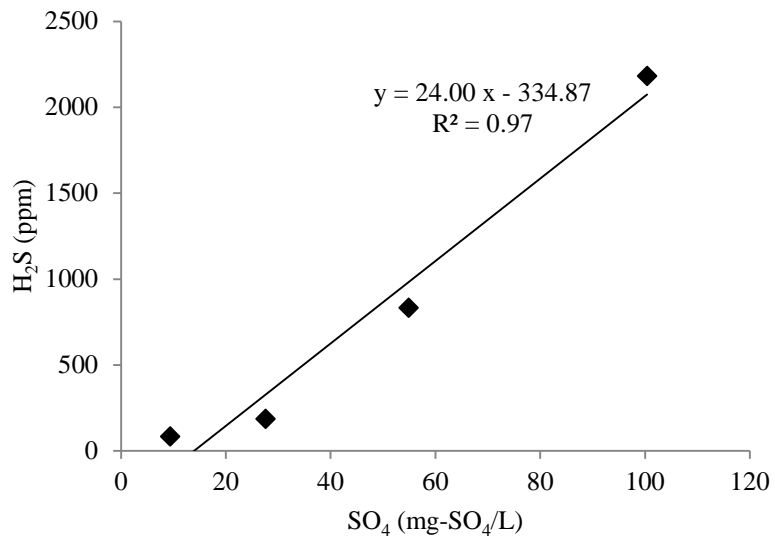


Fig. 7 Relationship between SO₄ concentration and generated H₂S

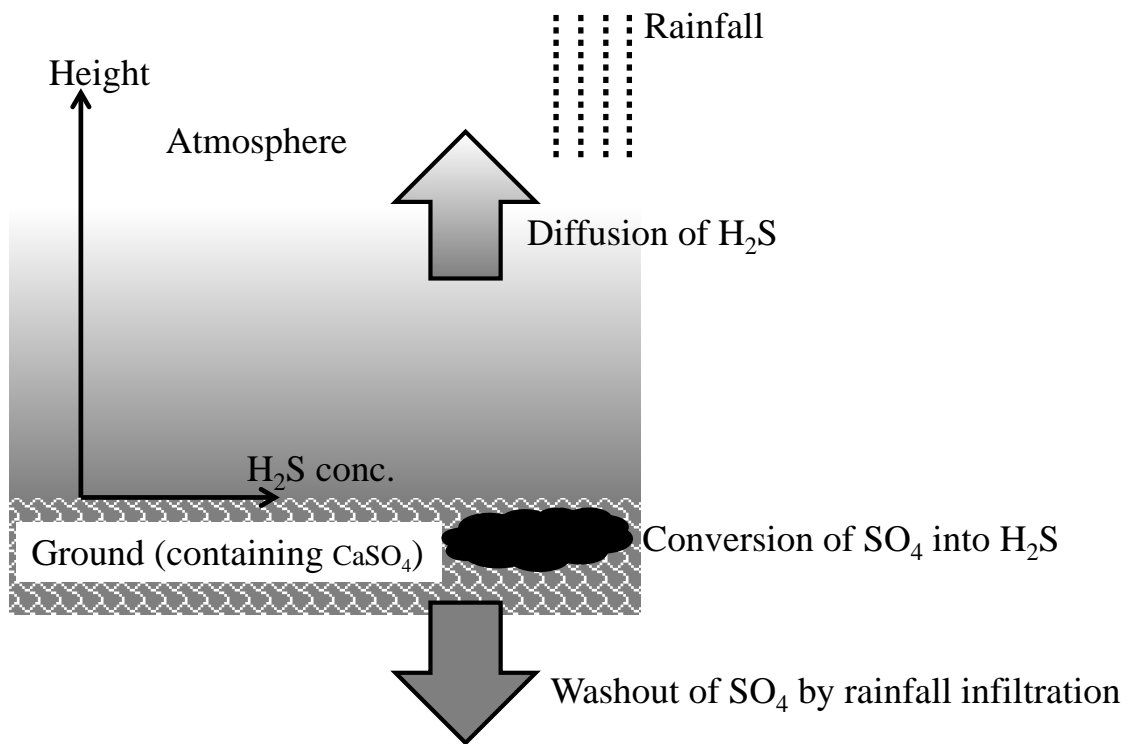


Fig. 8 Assumed phenomena of H₂S generation and sulfur outflow

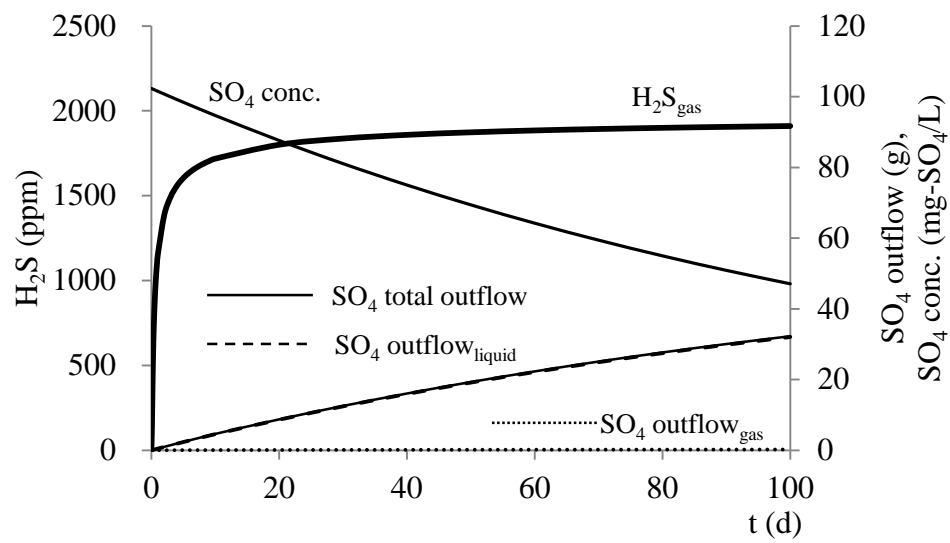


Fig. 9 Concentration changes of H₂S and SO₄, and SO₄ outflow

1

Table 1 pH changes

TOC ^a SO ₄ ^b	0	10	20	50	100	200	320	450
10	7.0/6.6 ^c	7.3/6.8	7.5/6.6	7.2/6.8	7.0/6.8	7.0/6.3	6.6/6.0	6.4/5.6
30	6.7/6.6	7.2/6.8	7.3/6.7	7.0/6.8	7.0/6.8	6.8/6.5	6.6/6.0	6.6/5.6
50	6.7/6.6	7.2/6.8	7.3/6.7	7.0/6.8	6.9/6.8	6.8/6.4	6.5/6.4	6.4/5.6
100	7.2/6.6	7.0/6.8	7.3/6.7	7.0/6.8	7.0/6.8	6.8/6.5	6.6/6.6	6.6/5.8
200	7.1/6.6	7.0/6.7	7.1/6.6	6.9/6.6	6.8/6.6	6.9/6.5	6.4/6.4	6.5/5.7
500	7.1/6.6	7.0/6.8	6.9/6.6	6.9/6.6	6.9/6.6	6.9/6.3	6.4/6.8	6.6/6.2
800	6.8/6.3	7.0/6.6	6.9/6.4	6.9/6.6	6.8/6.7	6.7/6.5	6.2/6.8	6.4/6.2
1200	6.6/6.6	7.0/6.6	6.9/6.4	6.7/6.6	6.8/6.6	6.6/6.7	6.2/6.6	6.4/6.4

2 ^amg-C/L, ^bmg-SO₄/L, ^cpH value on day 0/7 (n = 3, median)

3

1

Table 2 ORP changes

TOC ^a SO ₄ ^b	0	10	20	50	100	200	320	450
10	329/448 ^c	254/322	222/224	215/165	310/36	219/-55	279/48	232/52
30	355/417	296/342	224/231	218/125	299/-32	220/-43	289/32	219/54
50	361/439	272/345	239/245	230/105	312/2	219/-50	280/-8	209/16
100	363/437	289/347	243/256	236/120	304/-26	225/-34	283/-51	214/-6
200	338/321	300/370	250/354	237/219	395/-60	257/-66	255/-66	329/-29
500	356/336	304/387	262/322	241/109	387/-22	262/-70	247/-111	313/-58
800	362/341	324/373	251/329	234/145	371/-38	254/-41	255/-73	311/-58
1200	358/358	290/370	257/331	232/104	358/-19	250/-26	253/-78	311/-79

2 ^amg-C/L, ^bmg-SO₄/L, ^cORP (mV (Eh)) value on day 0/7 (n = 3, median)

3