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A METHOD USING GRANULATED COAL ASH FOR DISPOSAL OF THE SLUDGE CARRIED BY TSUNAMI

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ABSTRACT: Large amounts of sludge and debris accumulated on agricultural and residential areas after the Great East Japan Earthquake. Since the sludge carried by the Tsunami has high contents of unstable-form organic matter "UFOM" (burned at 300℃), this sludge is considered to be the origin of malodorous gas generation that affects human activities. Therefore, disposal of the sludge plays an important role in the reconstruction effort. Previously, it is obvious that granulated coal ash (GCA) comprised of silica (44%), calcium oxide (21%) and aluminum oxide (13%) improves the organic condition of sewage sludge. For example, the generation of malodorous gases, e.g. hydrogen sulfide and ammonia, was greatly reduced after mixing GCA with the sewage sludge. In this study, we aim to propose a method using GCA to disposal the sludge carried by Tsunami. For this purpose, changes in organic conditions and malodorous gas generation of the sludge after mixing GCA are investigated based on laboratory experiments. In the laboratory experiments, the sludge was mixed with GCA, and then was burned at 200℃ to 600℃ (intervals of 100℃) in 4 hours at each temperature step. Furthermore, other experiments were conducted to measure amounts of gas generated from the sludge in the absence and the presence of GCA. It was found that ignition behaviors of the sludge with and without GCA were different, namely, the ignition loss at 300℃ of the sludge mixing with GCA was lower than that of the sludge without mixing GCA. This ensures that organic conditions (e.g. decreases in amounts of UFOM) of the sludge changes after mixing GCA. Moreover, it was also found that malodorous gases did not generate from the sludge mixing with GCA, indicating that GCA affects the digestion process of organic matter. It is expected that our proposed method is also useful for the capitalization of dredged soil and the development of lowland.

Keywords: Debris sludge, granulated coal ash, ignition, gas generation, organic matter.

INTRODUCTION

After the Great East Japan Earthquake, large amounts of sludge have been transported from coastal areas, and accumulated not only on littoral regions but also on agricultural and residential areas (Fig. 1).

Since the sludge comprises large amounts of unstable-form organic matter (UFOM), many serious problems occur. According to previous studies (Tafdrup 1995; Kelleher et al. 2000; Angelidaki and Ellegaaard 2003), organic matter is degraded in anaerobic digestion process by microorganisms, leading to the generation of biogases such as methane gas and hydrogen sulfide gas. Similarly, we found that gases generated from the sludge in in-situ (Fig. 1), which take effect on human activities in the residential areas. Therefore, disposal of the sludge is immediately needed.

Furthermore, the sludge causes some difficulties in the deposal of debris, because large amounts of muddy sand and the sludge present in the debris. After removal of concrete blocks, the debris sludge contains not only soil particles but also woody waste (diameter is several millimeters to several centimeters) which is hard to remove. Since the organic matter that easily adsorbed on

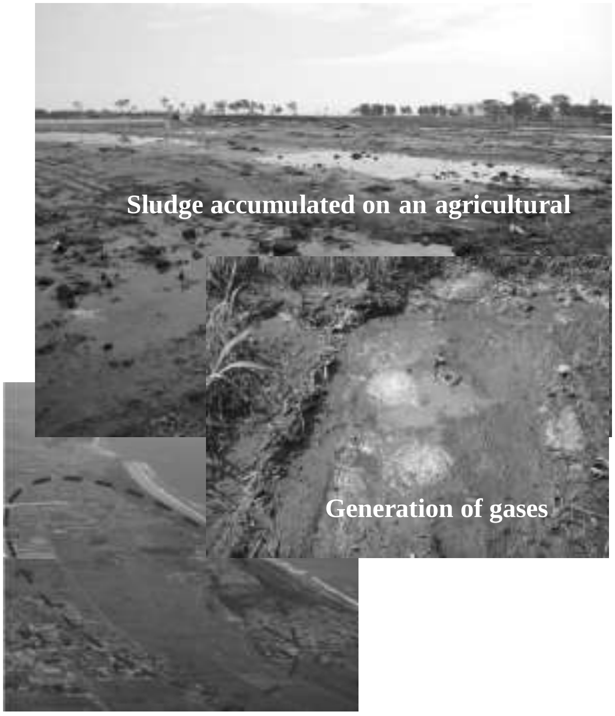

Fig. 1 Accumulated sludge after the Great East Japan Earthquake

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silt and clay particles also presents in the debris sludge, the organic behavior of the debris sludge is expected to be different from that of common sandy mud material. Previously, some methods using solidified materials made from cement compounds were used to disposal soft soil existing organic matter. Unfortunately, there were large variations in the strength of the soft soil that has high organic matter contents, and it was difficult for long-term applications.

To date, our research group has proposed some methods using granulated coal ash (GCA) for the improvement of the soft soil that has large amounts of organic matter. Fujiwara et al. (2010) reported that the strength of estuarine sludge increased, i.e. become ambulatory (Fig. 2), after mixing GCA (diameter less than 1 cm) with the sludge. According to Saito et al. (2012), the debris sludge could be converted to ground material after mixing with GCA. They reported that mixing GCA increased the strength (e.g., increase of cone index) and decreased malodorous level of the debris sludge.

In this study, we aim to experimentally understand the degradation behavior of unstable-form organic matter (UFOM), which is one of components of the debris sludge. And then, we aim to propose a method to suppress the generation of biogases due to the degradation of UFOM. Particularly, a method to predict the content of UFOM is proposed, and the amount of biogases is determined. Furthermore, we discus on the mixing ratio of GCA to retrain the degradation of organic matter, and mechanisms of GCA to retrain the degradation.

PROPERTIES OF MATERIALS

Granulated Coal Ash (GCA)

Coal ash is granulated by mixing with cement as GCA that basically form in spheres, and GCA's diameter ranges between that of coarse sand and of gravel (less than 40 mm). Component of GCA is given in Table 1.

It has been pointed out that GCA plays an important role in accelerating the purification of deposited sludge, such as the detachment and degradation of organic matter (Asaoka and Yamamoto 2009). According to Asaoka et al. (2009), GCA made it possible to remove hydrogen sulfide which is the origin of hydrogen sulfide gas. Therefore, GCA is widely used to restore the water environment of littoral regions.

Debris Sludge

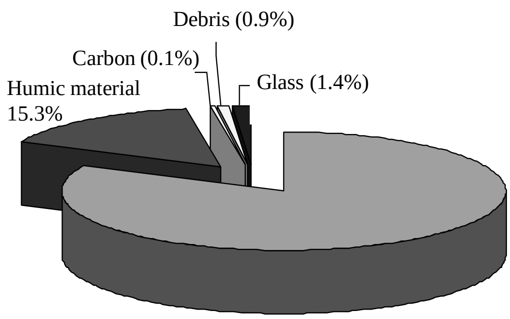
Debris, mixture of sludge and other waste, was collected from Sendai and Natori (Miyagi, Japan). Concrete blocks and woody waste were removed from the debris, and then the debris was filtrated through 10 mm-meshes filed sieve. Only the debris that has diameter less than 10 mm was used as embankment material for sea embankment. This debris is the sludge which is used in this study. Fig. 3 presents (a)

Fig. 2 Improvement of soft soil using granulated coal ash (Fujiwara et al. 2010)

Table 1 Chemical components of GCA

Component	Content [%]
Silicon dioxide (SiO_2)	44
Aluminum oxide (Al_2O_3)	13
Calcium oxide (CaO)	21
Carbon (C)	9
Others	13

(a)



(b)

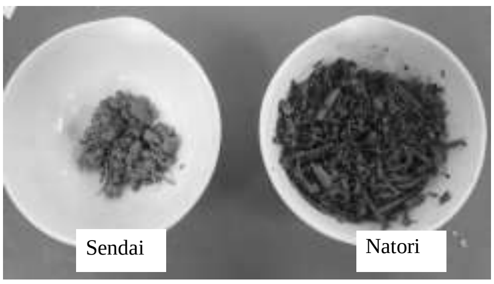


Fig. 3 (a) components of Natori sludge (diameter 1 to 2 mm), and (b) woody waste contained in the debris sludge of 300 g components of Natori sludge (diameter 1 to 2 mm), and (b) woody waste contained in the debris sludge of 300 g. It was found that the debris sludge was mainly comprised of soil particles, woody waste, and other combustible substances that are difficult to define.

Fig. 4 depicts a plasticity chat of the debris sludge (diameter < 0.42 mm) of various regions. The plasticity chart is commonly used to decide the fines content of embankment material. For instance, the expansibility of material will increase if liquid limit is less than 50%, leading to a decrease in the strength of the material. From Fig. 4, it is thought that the expansibility of debris sludge (Sendai A and Natori) is high (stability is low).

Fig. 5 shows the relationship between fines content (FC) and ignition loss at 600℃ (IL600) of the debris sludge. In the figure, solid line indicates FC-IL600 of the sludge deposited on places near the sewage outfall, and dot line implies FC-IL600 of tidal flats that have biodiversity. Since organic matter easily adsorbs on fines, amounts of the organic matter can be basically predicted from the relationship between fines content and ignition loss. From this figure, it can be seen that IL600 was high at low FC, which matched the solid line. This indicates that the debris sludge has large amounts of UFOM as well as the sewage sludge.

EXISTENCE FORM OF ORGANIC MATTER IN THE DEBRIS SLUDGE AND ITS EVALUATION METHOD

According to Cuypers et al. (2002), organic matter can be divided into 2 kinds, unstable-form organic matter (UFOM) and stable-form organic matter (SFOM, e.g. humic substances). In digestion processes, the molecule weight of organic matter is decreased due to the degradation of the organic matter. Hydrogen sulfide, ammonia, and other reduced substance are released in the processes, and finally biogases and carbon dioxide are released in the mineralization of the organic matter (Tafdrup 1995). As biogases (e.g. methane, hydrogen sulfide and carbon dioxide) decreases the strength of embankment, it is needed to understand chemical properties (i.e. biogases generation) of UFOM existing in the debris sludge, in order to use the debris sludge as the embankment material.

In the work by Cuypers et al. (2002), UFOM (e.g. fatty acid, peptide, cellulose) was nearly burned at a temperature range of 250－350℃, humic organic matter (e.g. fulvic acid) was burned at 370－390℃, and humic acid was burned at a higher temperature (530-540℃). Hence, organic matter can be also characterized based on the ignition behavior. In this study, the ratio of IL300 (ignition loss at 300℃) to IL600 (i.e. IL300/IL600) was used as an index to represent the amount of UFOM. It is thought that this method is appropriate because it will take low cost for evaluating organic conditions of large amounts of the debris sludge. Note that IL750 can be used instead of IL600 according to different field conditions; however, IL750 may be appropriate for the sediment that has low content of calcium carbonate. We previously found that IL300/IL600 of sewage-derived sludge that had large contents of UFOM was in a range of 0.5-0.6 (UFOM content > 50%). On the other hand, IL300/IL600 of primary production-derived sludge was about 0.3. Since biogases generated from the sludge having IL300/IL600 > 0.5, IL300/IL600 = 0.5 was chosen as a standard for evaluating the organic conditions of the debris sludge in our present work.

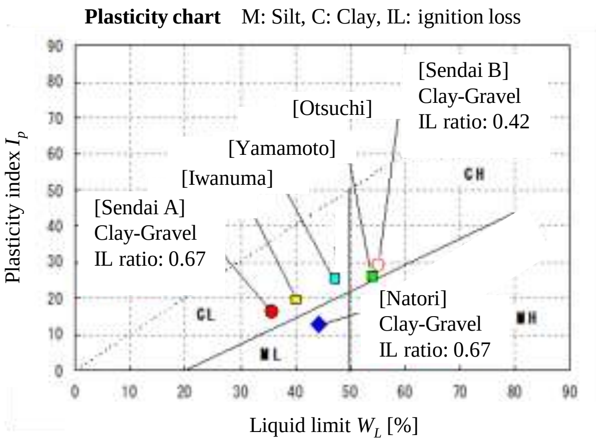


Fig. 4 Plasticity chart of the debris sludge in various regions

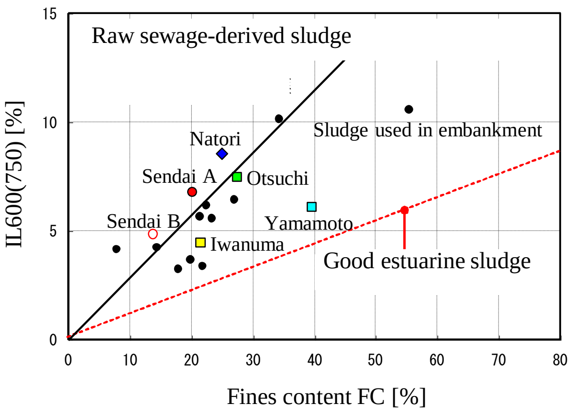


Fig. 5 Relationship between fines content (FC) and ignition loss at 600℃ (IL600).

Table 2 Conditions of gas generation experiments

Sample	Sludge	Methane fermentation germ	GCA	Wet mass of sludge [g]	Dry mass of sludge [g]	Volume of sludge [mL]	Initial volume of nitrogen gas [mL]
Case 1-1	Sendai	Yes	Yes	85.0	70.3	62	60
Case 1-2	Sendai	Yes	No	85.0	70.3	52	70
Case 1-3	Sendai	No	Yes	85.0	70.3	56	66
Case 1-4	Sendai	No	No	85.0	70.3	46	76
Case 1-5	Natori	Yes	Yes	72.8	55.2	65	57
Case 1-6	Natori	Yes	No	72.8	55.2	54	68
Case 1-7	Natori	No	Yes	72.8	55.2	57	65
Case 1-8	Natori	No	No	72.8	55.2	50	72
Case 2-1	Sendai	Yes	Yes	85.0	70.3	57	65
Case 2-2	Sendai	No	Yes	85.0	70.3	55	67
Case 2-3	Natori	Yes	Yes	72.8	55.2	61	61
Case 2-4	Natori	No	Yes	72.8	55.2	57	65

METHOD FOR EVALUATING ORGANIC PROPERTIES OF THE DEBRIS SLUDGE

Method to Immobilization of UFOM using GCA

To immobile UFOM, the method using GCA proposed by Fujiwara et al. (2010) was used. For evaluating changes in properties of UFOM, the ignition loss test, and the gas generation test were experimentally conducted. In these tests, the debris sludge mixed with GCA was used as test samples. The mixing rate of GCA was decided based on the value of IL300 (the amount of UFOM), as expressed as:

$$W_{GCA} = x \times \frac{FC}{100} \times r \times \alpha \tag{1}$$

where W_{GCA} is the mass of GCA, x indicates the mass of debris sludge, r is IL300/IL600, and α refers to the mixing coefficient of GCA. In the ignition loss test, W_{GCA} was varied to obtain the optimum α.

Experiment Procedures and Conditions

Ignition loss test (determination of W_{GCA})

In the ignition loss test, a sample burned at 110℃ was burned at 300℃ and 600℃ over 4 hours using an electrical muffle furnace. Ignition loss refers to the mass loss at 300℃ or 600℃ comparing to the mass at 110℃. The debris sludge and sewage-derived sludge (sludge accumulated in Fukuyama Inner harbor “Hiroshima, Japan”) were used in the experiments.

Experiments of biogases generation

The debris sludge (Sendai and Naroti) filtrated through 9.5 mm-sieve was used in the experiments. Table 2 lists the experiment conditions, and Table 3 shows the results of the ignition test. Samples were made by mixing GCA with Sendai sludge (wet mass 72.8 g) or Natori sludge (wet mass 85.0 g). The deionized water purged with nitrogen gas was added into the samples. The samples was kept at 35℃ in an incubator over 2 weeks.

Two types of experiments were conducted, one was the deionized water was poured after mixing GCA with the sludge (Table 2, Case 1), and another was the sludge was added after mixing GCA with the deionized water (Table 2, Case 2). Furthermore, experiments of gas generation under addition of methane fermentation germ (5 mL) were also conducted. Gas amount was measured at 2 weeks after starting the experiments. 1 mL of gas in the vial container was sampled, and then concentration of methane gas and carbon dioxide were analyzed using a gas chromatography.

Predictions of Amounts of UFOM Based on the Ignition Loss Test

Ignition behavior of the debris sludge

Two different types (sand content) of Sendai sludge (Sendai A and Sendai B) were used in the ignition loss test. r that was defined as IL300/IL600 were 0.67 and 0.42 for Sendai A and Sendai B, respectively. Based on Fig. 4, a countermeasure is not needed for disposal of Sendai B because the plot (r= 0.42 < 0.5) was in the safety area, whereas a countermeasure is needed for disposal of Sendai A that had high expansibility (r= 0.67 > 0.5). Noted that, since Natori sludge had large amounts of woody waste, r was extremely varied.

Table 3 Result of the ignition loss test

Sludge	IL300 [%]	IL600 [%]	IL300/IL600
Natori	7.00	12.25	0.57
Sendai	1.86	3.51	0.53

Fig. 6 presents the ignition loss of various components existing in Natori sludge. In the component passed through 75 µm-sieve, IL300 was larger than 10% (r= 0.66), indicating that 60% of UFOM presented in this component. Since r and IL600 of the component passed through 2 mm-sieve decreased, it is thought that large amounts of inorganic material contain in the component that had a diameter range of 0.075-2 mm.

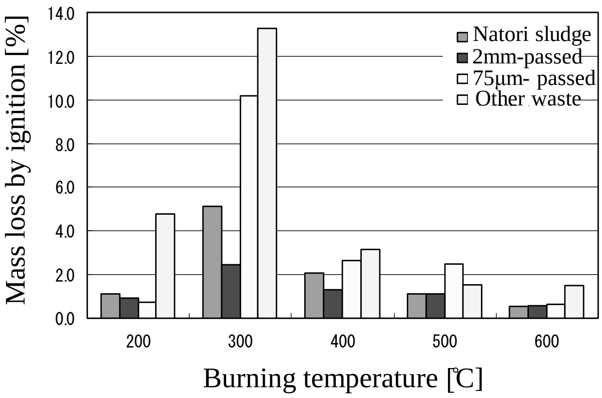


Fig. 6 Ignition loss of various components existing in Natori sludge

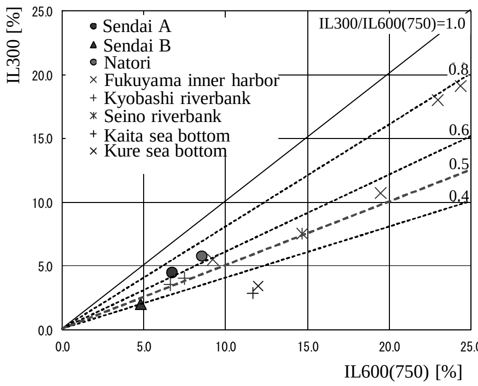


Fig. 7 Relationship between ignition loss at 600℃ (IL600) and IL300

Fig. 7 shows the relationship between IL600 and IL300 of the sampling debris sludge. It can be seen that r was higher than the standard value (r= 0.5).

Determination of the mixing amount of GCA

Fig. 8 presents the relationship between the mixing coefficient (α') of GCA and IL300/IL600 (r) of Natori sludge, Fukuyama sludge, and Kyobashi sludge (sewage-derived sludge). α' is the mixing coefficient of each sludge, thus it is varied due to the sludge condition. Since Natori sludge contained woody waste, there was large variances in r, leading to the difficulty in determination of α'. Therefore, we firstly determined α' of Fukuyama and Kyobashi sludge, and then we applied α' to the debris sludge.

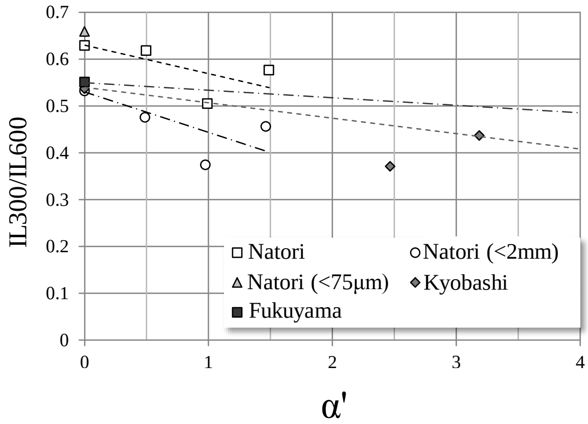


Fig. 8 Decreases in IL300 due to addition of GCA

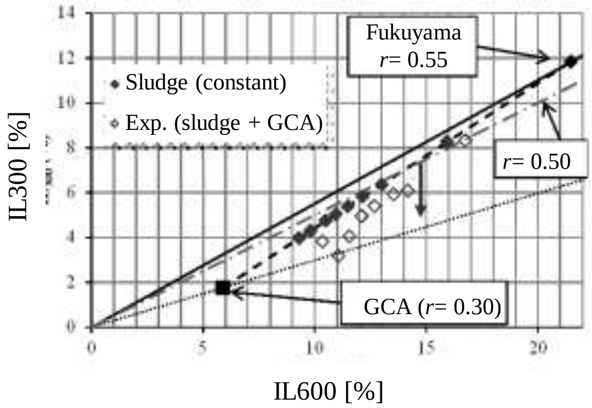


Fig. 9 Relationship between IL600 and IL300 of Fukuyama sludge in cases that α'= 1 to 6.48

Fig. 9 show the relationship between IL600 and IL300 of Fukuyama sludge (water content based on the mass basis was 500%) in cases that α' was varied in a range of 1−6.48. As the water content of each sludge was different, variations due to different water contents could be adjusted as Eq. 2 based on Fig. 8.

$$k = 0.3\frac{w}{100} + 0.9 \qquad (2)$$

where k is the correction coefficient, and w indicates the water content of debris sludge.

In Fig. 9, dashed line and ◆ implies a sum of ignition losses of the sludge and GCA, and ◇ implies the experimental value of the ignition loss. It can be seen that the experimental value was lower than the dashed line, indicating that IL300 decreased after mixing GCA. Based on this result, decrease in IL300/IL600 can be expressed as:

$$\varDelta\frac{IL300}{IL600} = 0.07\alpha'/k = 0.07\alpha \qquad (3)$$

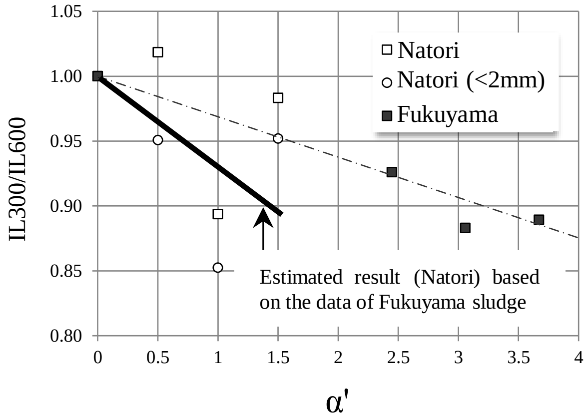


Fig. 10 Comparison of the decrease in ignition loss predicted from Eq. (3) with the experimental value

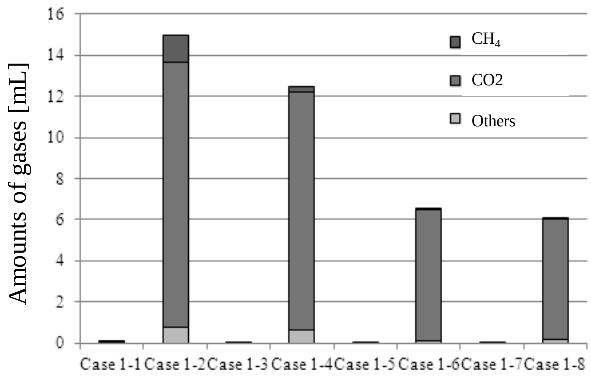


Fig. 11 Amounts of gases generated from Sendai sludge (dry mass 70.3 g), and Natori sludge (dry mass 55.2 g)

Fig. 10 shows the comparison of the decrease in ignition loss predicted from Eq. (3) with the experimental value of Fukuyama sludge (Fig. 9) and Natori sludge. To decrease 10% of ⊿IL300 of Fukuyama sludge, α' should be equaled to 3.1 (Fig. 10). Therefore, α is equaled to 1.45 (bold line in Fig. 10) for Natori sludge (w= 25%). It was found that the experimental value of Natori sludge (passed through 2 mm-sieve) was roughly represented by Eq. (3), indicating that Eq. (3) can be used to predicted the decrease in IL300 of the debris sludge.

Amounts of Biogases Generated from the Debris Sludge

To decrease 0.07 of IL300/IL600 of Natori sludge (FC= 21%, IL300/IL600= 0.057), the mixing coefficient of GCA (α) must be equaled to 1.0. Based on Eq. (1), the mass of GCA was equaled to 12% of the sludge mass.

Fig. 11 shows amounts of gases generated from Sendai sludge (dry mass 70.3 g), Natori sludge (dry mass 55.2 g), and Fig. 12 shows amounts of gases per unit dry mass of the sludges. It can be seen from Fig. 11 that gases generated from the debris sludges, and mounts of the gases were higher either in the case of fermentation germ addition and long period of the experiment. Conversely, there was no gas generation in the case of addition GCA, revealing that GCA inhibits the gas generation.

From Fig. 12(a), the amount of gases from Sendai sludge (0.2 mL) was higher than that of Natori sludge (0.1 mL). It is thought that woody waste existing in Natori sludge is one of factors associated with the difference in the gas amount. Therefore, gas generation after removal woody waste was investigated. From the experiment result, it was found that the amount of gases from Sendai sludge was 0.23 mL, and from Natori sludge was 0.15 mL after removing the woody waste (Fig. 12(b)).

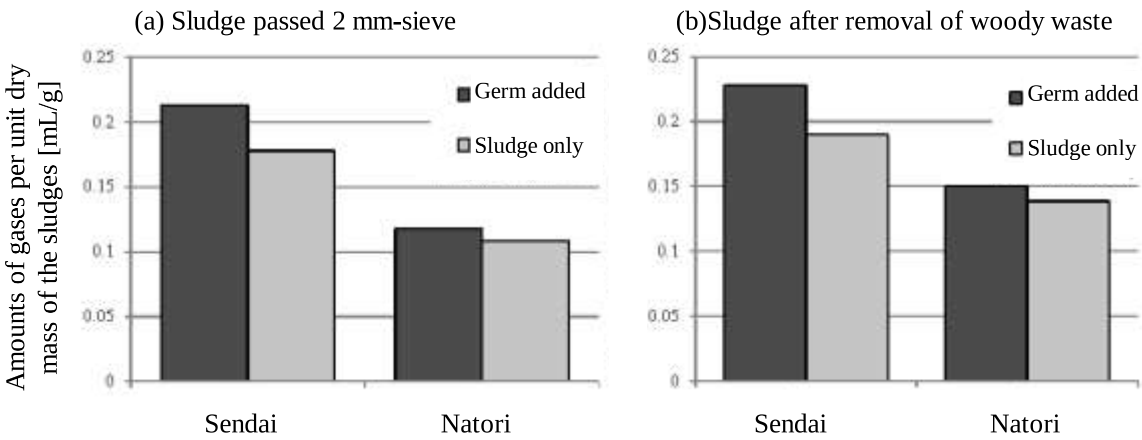


Fig. 12 Amounts of gases per unit dry mass of the sludges

IMMOBILIZATION OF UFOM USING GRANULATED COAL ASH (GCA)

Redox Potential under GCA-Mixed Condition

Fig. 13 presents the redox potential of the sludge after gas generation, as a function of pH. In the figure, dashed line indicates the relation of redox couple (H^+/H_2) based on the Nernst equation. It was found that pH of the sludge increased to 9-10 after mixing GCA. ORP was also increased in the case that GCA mixed sludge, whereas ORP decreased in both cases that fermentation germ was added and the debris sludge was added after pouring water in GCA.

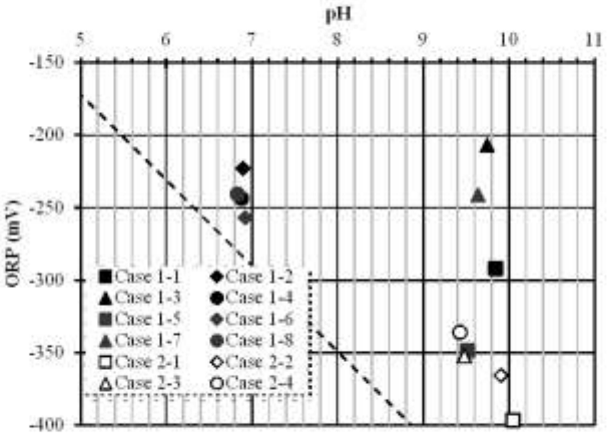


Fig. 13 Relationship between pH and ORP of the debris sludge after gas generation

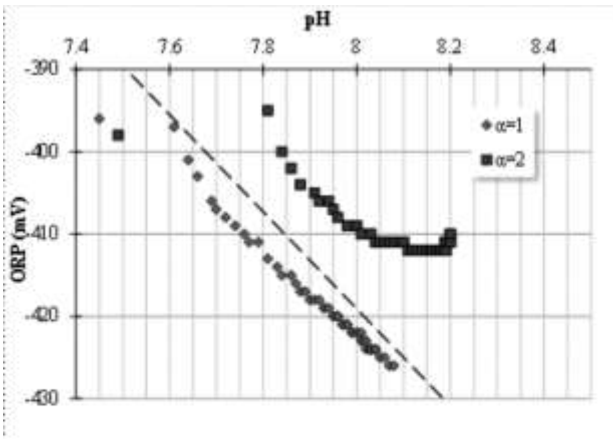


Fig. 14 Relationship between pH and ORP of Fukuyama sludge after mixing GCA

Table 4 Reactions that may occur by GCA added

Reaction	Chemical equation
RT1	$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$ $CH_3COO^- + SO_4^{2-} + 3H^+ \rightarrow 2CO_2 + H_2S + 2H_2O$
RT2	$Mn_2O_3 + H_2S + 4H^+ \rightarrow 2Mn^{2+} + S^o + 3H_2O$
RT3	$Fe^{2+} + HS^- \rightarrow FeS\downarrow + H^+$ $2FeS + 2H^+ \rightarrow FeS_2\downarrow + Fe^{2+} + H_2(gas)$

Fig. 14 presents variations of pH and ORP of Fukuyama sludge after mixing GCA (α= 1 and 2) in one hour. Similar to Fig. 13, pH of the sludge increased after mixing GCA. The increase of pH may be caused by the elution of OH^- and cations from the GCA components (for example, hydrolysis of CaO). ORP was also decreased in both cases. In the case of α= 1, the decrease gradient of ORP was parallel to the gradient of the Nernst equation, indicating that the decrease of ORP was not due to the mixture of GCA, but the increase of pH.

On the other hand, in the case of α= 2, there was a small reduction in ORP, and no more reduction in ORP at 10 min after addition of GCA, revealing that reduction reactions were habited by GCA.

Effects of GCA on Anaerobic Digestion Process

In anaerobic digestion processes, carbon dioxide (CO_2), hydrogen sulfide gas (H_2S), and methane gas (CH_4) are generated in the mineralization of organic matter. From the gas generation experiment, 90% of gases was carbon dioxide (CO_2), and there was no generation of H_2S.

Table 4 lists some reactions that may occur in the case of GCA added. In anaerobic digestion processes, reduced substances are released, and then biogases are generated by bacteria, e.g. sulfate-reducing bacterium (RT1). It is commonly known that activities of sulfate-reducing bacterium are retarded in alkaline conditions. This ensures that the activities of sulfate-reducing bacterium is retarded due to increases in alkalinity of the sludge after adding of GCA. As a result, the degradation of organic matter (release of reduced substances) is retarded, leading to the decrease of ORP reduction. Noted that, this did not mean that the activities of sulfate-reducing bacterium are stopped by GCA. Furthermore, oxidants eluted from GCA play a role as electron acceptor, resulting in the increase of ORP (RT2 and RT3).

CONCLUSIONS

In this study, laboratory experiments were conducted to propose a method using granulated coal ash for disposal of the debris sludge carried by the Great East Japan Earthquake. Specific findings were summarized as below:

- In spite of low ignition loss, the debris sludge contained large amounts of organic matter. This organic matter had similar characteristics to the unstable-form organic matter existing in the sludge derived from raw sewage.

- An equation was proposed to determine the amount of GCA for improving organic conditions of the debris sludge. For example, to decrease a unit of IL300/IL600 of Natori sludge, the required mass of GCA was 10% of Natori sludge mass.
- Large amounts of organic matter that is the origin of biogases presented in the debris sludge. It was found that the amount of gases per unit mass of Sendai sludge was larger than 0.2 mL, and of Natori sludge was larger than 0.1 mL. However, the gas generation was habited by GCA addition.
- GCA changed the degradation behavior of organic matter by its water absorbability. Synchronously, oxidants eluted from GCA improved redox condition of the debris sludge, leading to the degradation restriction of organic matter.
- Gas generation from the debris sludge could be habited by increases of pH due to addition of GCA. Moreover, this effect increased according to the water absorbability of GCA.

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