Evaluation and prediction of pollution caused by acid water exuded from mud sediment in urban ground

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Abstract: The pollution of surface and/or ground water caused by the inflow of drainage water from mudstone excavation sites is a serious issue in Japan. It has been recognized that this issue results from the discharge of sulfate generated by the decomposition of pyrite contained in the mudstone. In general, marine mudstone includes the primary framboidal-type pyrite formed during sedimentation and diagenesis. The pyrite in mudstone discharges acid water into the environment by decomposition during the weathering process.

The ground under the big Japanese cities of Tokyo and Osaka contains sand and/or mud sediments formed in the late Pliocene to Pleistocene. When the underground environment in these cities is altered by tunnels and other underground openings pollution by acid water originated from the mud sediments is possible. Therefore, the evaluation and prediction of the possibility of pollution by the acid water from mud sediment is an important theme of environmental geology when tunnels and other underground openings are constructed in these cities.

We examined the geochemical characteristics of the mud distributed underground in the periphery of the cities in Japan to establish an evaluation system for the exudation of acidic water from mud sediment. The ability of exudation of acidic water from the mud sediment can be evaluated by the mole ratio of sulfur content to calcium content in the sediment. We made another attempt to predict the spatial extent of pollution due to the exudation of the acid water and/or the heavy metals from mud sediment by numerical simulation which combines advection/diffusion and geochemical models.

Résumé: La pollution de la surface et/ou les eaux souterraines provoquées par l'apport de l'eau de drainage des emplacements d'excavation de sédiments de boue sont une issue sérieuse au Japon. On l'a identifié que cette issue résulte de la décharge du sulfate produite par la décomposition de la pyrite contenue dans le sédiments de boue. En général, le sédiments de boue marin inclut le framboidal-type primaire pyrite formée pendant la sédimentation et le diagenèse. La pyrite en sédiments de boue décharge l'eau acide dans l'environnement par décomposition pendant le processus de altération.

La terre sous les grandes villes japonaises de Tokyo et d'Osaka contient le sable etou les sédiments de boue ont formé vers la fin de pliocène au pléistocène. Quand l'environnement souterrain dans ces villes est changé par des tunnels et toute autre souterraine d'ouvertures, la pollution par l'eau acide provenue des sédiments de boue est possible. Par conséquent, l'évaluation et la prévision de la possibilité de pollution par l'eau acide du sédiment de boue est un thème important de géologie environnementale quand des tunnels et d'autres ouvertures souterraines sont construits dans ces villes.

Nous avons examiné les caractéristiques géochimiques du souterrain distribué par boue dans la périphérie des villes au Japon pour établir un système d'évaluation pour l'exsudation de l'eau acide du sédiment de boue. Les capacités de l'exsudation de l'eau acide du sédiment de boue peuvent être évaluées par le rapport molaire du contenu de soufre au contenu de calcium dans le sédiment. Nous avons fait une autre tentative de prévoir l'ampleur spatiale de la pollution due à l'exsudation de l'eau acide et/ou les métaux lourds de la boue déposent par la simulation numérique qui combine l'advection, la diffusion et modèles géochimiques.

Keywords: environmental geology, geology of cities, leachate, pollution and sediments

INTRODUCTION

Marine sediments are distributed in the ground under big cities such as Tokyo and Osaka in Japan. The sediments mainly consist of sand and mud, and the marine mud sediments commonly contain pyrite (Figure 1). If the pyrite is allowed to come into contact with groundwater in an oxidized environment, the groundwater becomes acid due to sulfate generated by the decomposition of pyrite (Stumm & Morgan 1996). Around the cities in which the marine mud sediments are distributed severe corrosion of the pipelines have been observed (The Japanese Geotechnical Society & Kansai Geotechnical Consultants Association 1987) and pollution of groundwater both caused by the pyrite oxidation.

At big Japanese cities, infrastructure is often placed deep underground. Associated with opening up of excavation deep underground, the pyrite included in the ground decomposes because of oxidation of peripheral environments. This, it is feared will led to pollution of the groundwater and to corrosion of structural materials, particularly for infrastructure constructed deep underground. Therefore, the evaluation and prediction of the possibility of sulfate and other toxic substance drainage from mud sediments will be an important theme of environmental geology in urban areas.

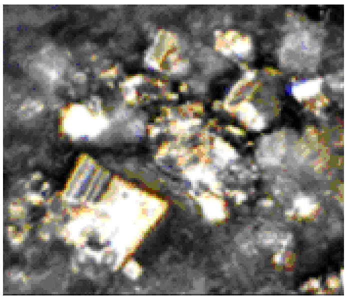

Figure 1. Pyrite in marine mud sediment

In this paper, we will report the results of geochemical analysis and leaching tests on mud sediments, and discuss the exudation mechanism of sulfate and metal elements from mud sediments. In addition, we will discuss the problems associated with predictions of exudation.

EXPERIMENTAL METHOD

Chemical Analysis of Bulk Samples

To understand the petrologic characteristics of mud sediments the major element and metal element contents of all collected samples were analyzed by X-ray fluorescence (XRF, Rigaku ZSX100e). The measured elements are as follows: SiO_2, TiO_2, Al_2O_3, MgO, $Fe_2O_3^t$, MnO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, Cu, Pb, Zn, As, Cr, Ni, Se.

The procedure of analysis is as follows:

1) The samples are dried completely by an electric oven.
2) Powder samples that are under 75 micrometers are created from the dry samples by crushing.
3) Pressing of the powder samples to produce tablet samples for XRF.
4) The tablet samples analyzed by XRF.

Simplified Leaching Test

The simplified leaching test (Hattori, Ohta & Kiya 2003) of mud sediments was performed to recognize the sulfate and metal ion exudation features. The procedure of this test is as follows:

1) The samples are crushed to grain smaller than 10 mm in size after being dried.
2) Portions of 100 g of the crushed samples are mixed with 500 ml-distilled water and the mixture shaken for three minutes.
3) The pH and electric conductivity of the leachate are measured after one hour, 24 hours, 7 days, 28 days and 56 days.
4) The concentrations of metal elements (Cu, Pb, Zn, Fe, As, Cd, Cr, Mn, Se) and cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) in the leachate after 56 days are determined by ICP emission spectrometry (Shimazu ICPS-7500). The SO_4^{2-} and Cl^- concentration in the leachate are determined by the ion chromatography, and the HCO_3^- content is measured by the sulfate titration method.

SAMPLES

The specifications of analysed samples are listed in Table 1.

Table 1. Specification of samples

Location	Geologic Age	Formation	Condition
Minou City, Osaka Prefecture	Pleistocene	Osaka Group (Ma0-4)	Out crop
Bouso Peninsula, Chiba Prefecture	Pliocene - Pleistocene	Kazusa Group	Out crop
Iiyama City, Nagano Prefecture	Pliocene - Pleistocene	Teradomari, Shiiya, Haizume Formations	Tunnel face
All area of Akita Prefecture	Miocene - Pliocene	Nishi-kurosawa, Onnagawa, Funakawa, Kitaura Formations	Out crop
Aomori City	Miocene	Yotuszawa, Wadagawa Formations	Tunnel face
Kochi Prefecture	Cretaceous - Tertiary	Shimanto Group	Out crop

PETROLOGICAL CHARACTERISTICS OF MUD SEDIMENTS

The SiO_2 contents of mud sediments in the Osaka Group range from 58% to 70%. The SiO_2 contents of the Kazusa Group show a narrow range (58 – 62%), and for the mud sediments at Iiyama City ranged from 59 to 66%. The SiO_2 contents of the mud at Akita and Aomori indicated a wide range (55 – 90%). SiO_2 contents of the Simanto Group ranged from 56 to 73%. In the case of the Osaka Group and of the Tertiary sediments at Akita and Aomori, $Fe_2O_3^t$ contents decreased as SiO_2 contents increased. There were no remarkable trends between $Fe_2O_3^t$ content and SiO_2 content in the other mud sediments.

The CaO contents of the mud at Osaka, Akita and Kochi were less than 1.0%. The CaO contents of the mud sediments at Iiyama were about 1.0%, and that of most of the mud sediments at Aomori ranged from 1 to 5%. The contents of CaO in the Kazusa Group were higher than other mud samples, ranging from 5 to 8%.

The majority of the Tertiary mud sediments at Akita and Aomori had high sulfur contents (0.5 - 3.0%). The sulfur contents of the Osaka Group mud sediments were low; some samples were less than 100 ppm. The contents of sulfur in the Kazusa Group samples ranged from 0.1 to 1.0%. The mud sediments st Iiyama contained less than 0.7% of sulfur, and the mud sediments of Simanto Group contained less than 1.0% of sulfur.

Arsenic content of the Tertiary mud sediments at Aomori City increased as sulfur content increased, the maximum content being about 2000 ppm. The content of arsenic of other mud sediments ranged from 10 to 30 ppm regardless of sulfur content. Lead content of most of mud sediments ranged from 10 to 40 ppm except the samples from Aomori regardless of sulfur content. The content of lead in the mud sediments of the Wadagawa Formation increased from 20 ppm to 1000 ppm as the sulfur content increased from 1.0 to 2.0%. Most of mud sediments contained zinc about 100 ppm independently of sulfur content.

CHEMICAL FEATURE OF LEACHATE

pH and electric conductivity

Figure 2 shows the relationship between the leachate pH one hour after the leaching test and the pH 56 days after the test. It is an overall trend that the pH 56 days after the test becomes lower than the pH one hour after the test. In the case of the Osaka Group and the Shimanto Group, because the pH decline with time is small, it is consider that the mud sediments of these groups react insignificantly with water. The Tertiary mud sediments at Aomori have a great difference between the pH one hour after the test and the pH 56 days after. Therefore the mud sediments require long time to react with water. The samples of the Osaka Group and the Shimanto Group were collected from surface out crop, while the samples of Tertiary at Aomori were collected at tunnel face in deep underground. Therefore, it suggests that the difference of pH change with time depends on the degree of weathering.

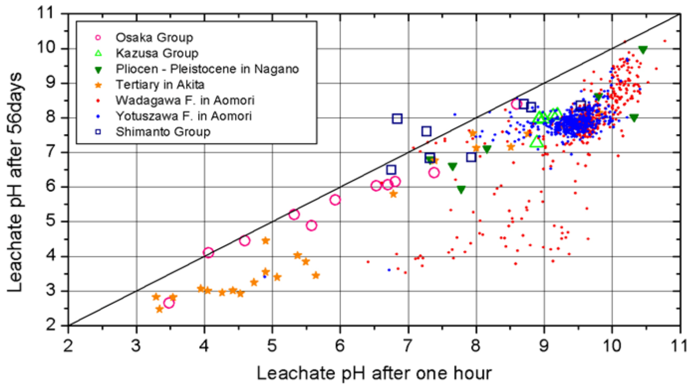

Figure 2. The relationship between the leachate pH after one hour and the pH after 56 days

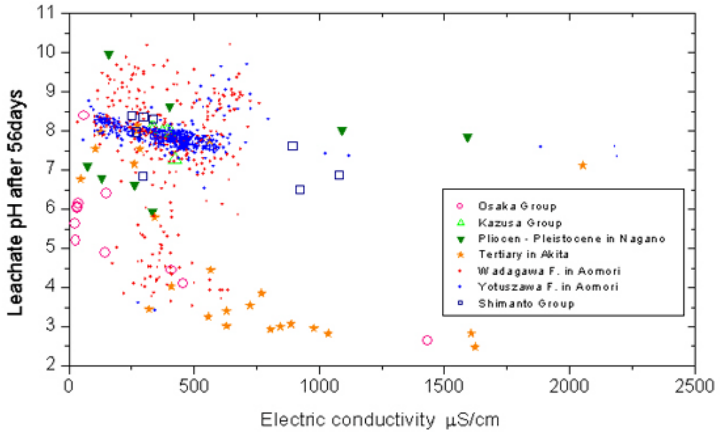

Figure 3. The relationship between pH and electric conductivity after 56 days

The relationship between pH and electric conductivity 56 days after the leaching test is illustrated in Figure 3. It is recognized that pH decreases remarkably with the electric conductivity increases for the mud sediments at Osaka and Akita. However, the Tertiary mud sediments from Aomori did not show any evident trend between pH and electric conductivity.

Cations and anions

Electric conductivity has strong correlation with sulfate concentration and has a slight correlation with bicarbonate ion concentration. Electric conductivity relates to calcium ion concentration better than sodium ion concentration in the case of the mud sediments in the Kazusa Group and in the Tertiary mud sediments at Akita and at Aomori. For the Osaka Group, Tertiary mud sediments at Iiyama and of the Shimanto Group show a good correlation between sodium ion concentration and electric conductivity.

The concentration of sulfur increases as pH decreases (Figure 4). If bicarbonate ion reaches high concentration, the leachate becomes slightly alkaline or alkaline (Figure 4). The trend of calcium ion concentration against pH agrees with the solubility curve of calcium carbonate, with the concentration increases as pH decreases (Figure 5). For the calcium ion concentration there is a close relationship with the salfur concentration. Sodium ion concentration becomes large in the slightly-alkaline to alkaline leachate of the mud sediments from Aomori.

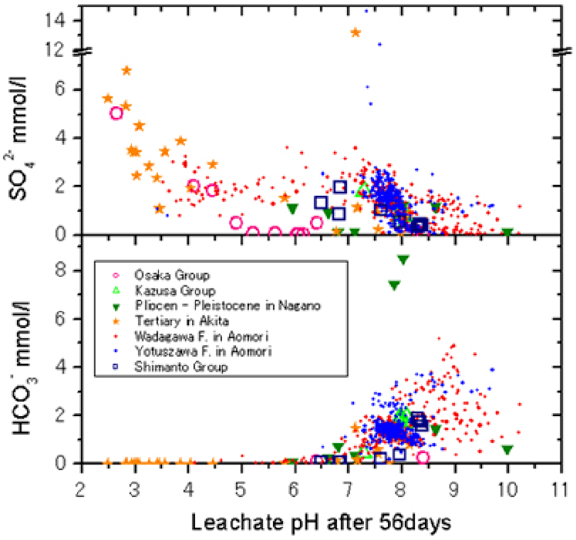

Figure 4. The anion concentration against pH in leachate

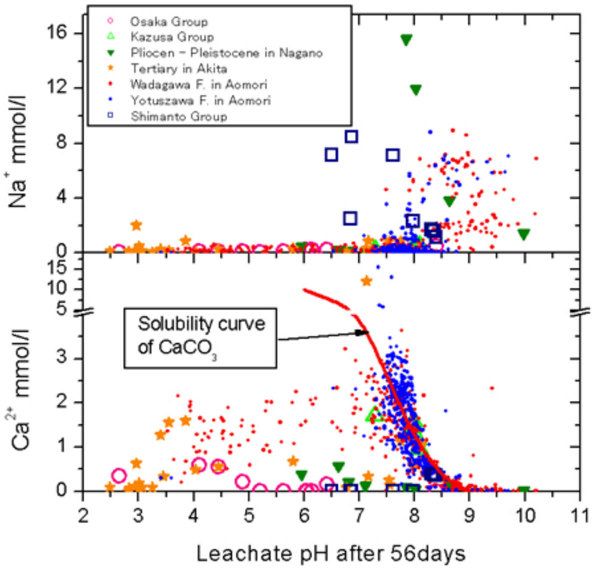

Figure 5. The cation concentration against pH in leachate

Metal elements

Arsenic is leached from the mud sediments of the Kazusa Group, the Tertiary mud sediments at Iiyama, from the sediments at Aomori and from the Shimanto Group. Most of the arsenic leaching is observed in the slightly-alkaline to alkaline leachate (Figure 6).

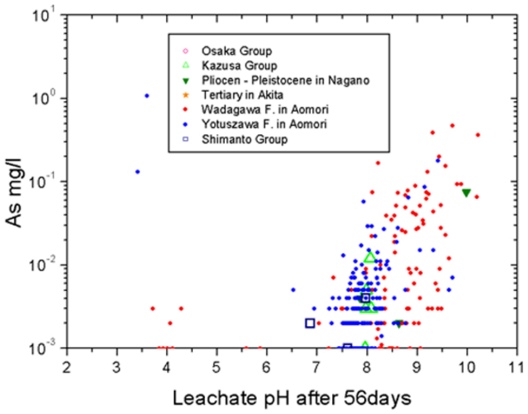

Figure 6. The arsenic concentration against pH in leachate

As the pH of the leachate decreases, so the concentration of other metal elements such as iron and copper increases. The trend of iron concentration against pH agrees with the solubility curve of ferric hydroxide (Figure 7).

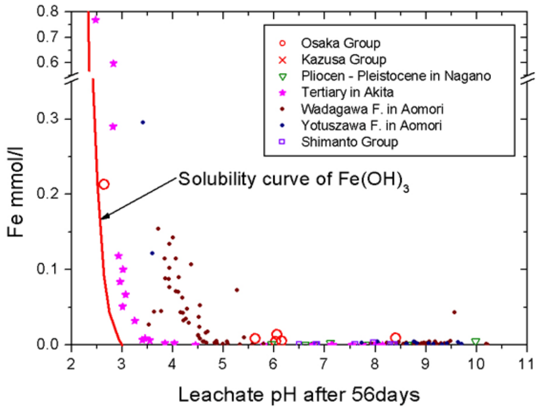

Figure 7. The iron concentration against pH in leachate

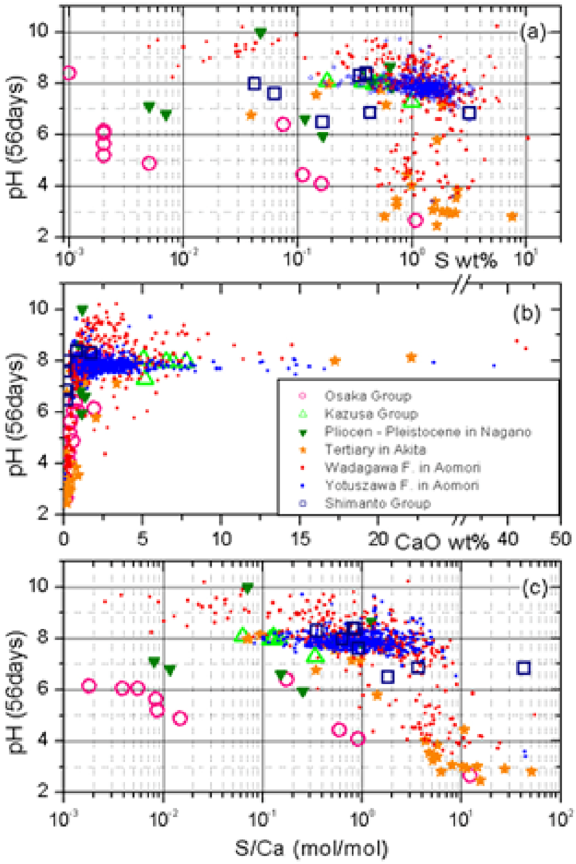

Figure 8. The petrologic characteristics against leachate pH

Elements content in sediments and water quality of leachate

It is expected that pH of leachate is related to sulfate content in sediment because acid water drainage is caused by decomposition of pyrite in sediment. However, the relationship between the pH and the sulfur content is not significant (Figure 8a).

For the decomposition of calcium bearing minerals, such as calcite, the sulfuric acid water is neutralized. Therefore, it seems that the sediment samples that drain acid water include low content of calcium. As shown in Figure 8b, if the pH of leachate is lower than 5.0 the sediment shows very little CaO content.

At the excavation work in the Hakkouda Tunnel, the possibility of acid water drainage from mudstone was evaluated by the S/Ca mole ratio (Hattori *et al.* 2003). In the case of the Tertiary mud sediments, pH of the leachate become lower than 5.5 if the S/Ca mole ratio is over 1.0. The leachate pH of mud sediment of the Osaka Group is lower than 4.5 when the sediment had a S/Ca mole ratio more than 0.5 (Figure 8c).

Sulfur concentration in leachate has positive correlation with sulfur content of sediment (Figure 9). However, there is no relationship between cation concentrations of leachate and the element content of sediment (Figure 10). In the same way metal concentration in leachate has no correlation with the metal content of sediment.

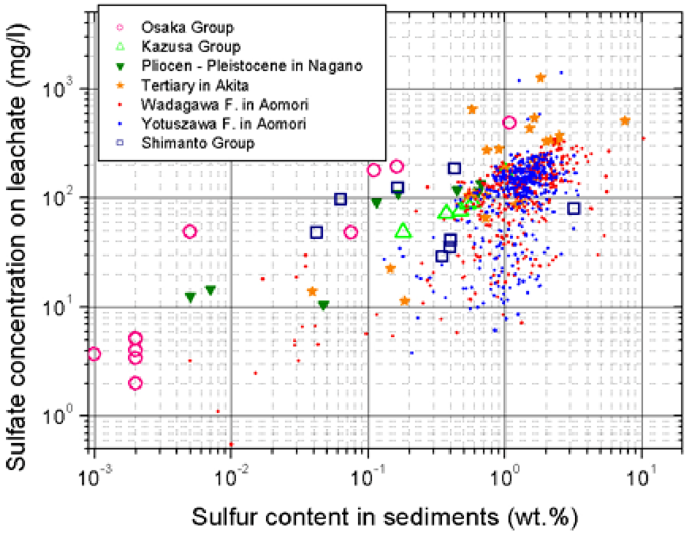

Figure 9. The relationship between sulfur content in sediment and sulfate concentration in leachate

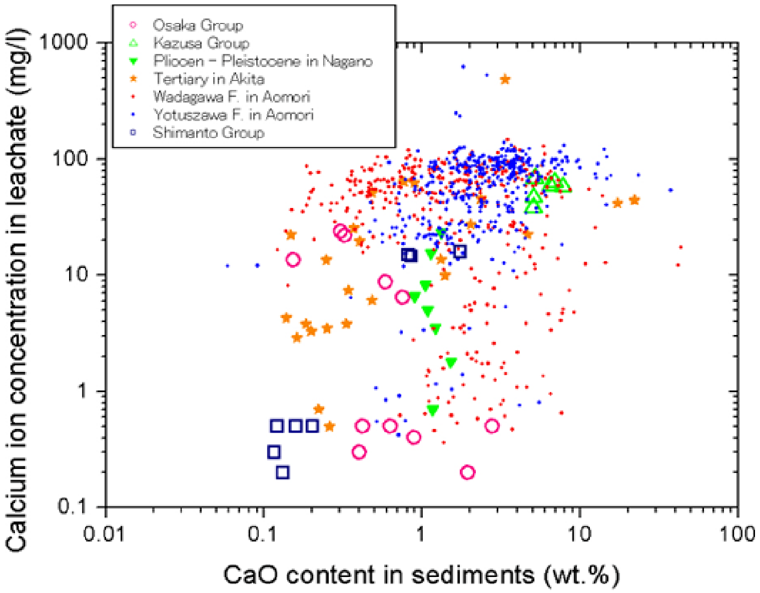

Figure 10. The relationship between CaO content in sediment and calcium ion concentration in leachate

ACID WATER DRAINAGE MECHANISM OF MUD SEDIMENTS

Mud sediment and water reaction system

It is considered that the amount of drained salfate is appropriate for the volume of pyrite in the sediment because of the relationship between the sulfate concentration in leachate and the sulfur content in sediment (Figure 9). The calcium ion concentration in leachate is controlled by the solubility of calcium carbonate (Figure 5). Therefore, the authors contend that decomposition of calcite influences the water quality of leachate considerably, although mineralogical data that obtained by XRD did not always support this through the relationship between calcite volume and leachate pH.

The calcium ion mole concentration is nearly equal to the sulfate mole concentration in leachate except for strong acid leachate (Figure 11). Therefore, it is assumed that each ion is drained to leachate by reaction of pyrite and calcite in water, which modelled in equation 1, 2 and 3.

$$FeS_2 + 7/2O_2 + H2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad (2)$$

$$FeS_2 + 2CaCO_3 + 7/2O_2 + 2H_2O = Fe^{2+} + 2Ca^{2+} + 2SO_4^{2-} + 2HCO_3^- \qquad (3)$$

If the sediment and water react according to equation 3, ferric mole concentration becomes a half of sulfate mole concentration. However, the leachate contains a little amount of iron compared to sulfate (Figure 12). As the iron concentration is controlled by the solubility of ferric hydroxide the ferrous component of the right side of the equation 3 is oxidized and ferric hydroxide is precipitated (shown by equation 4 and 5).

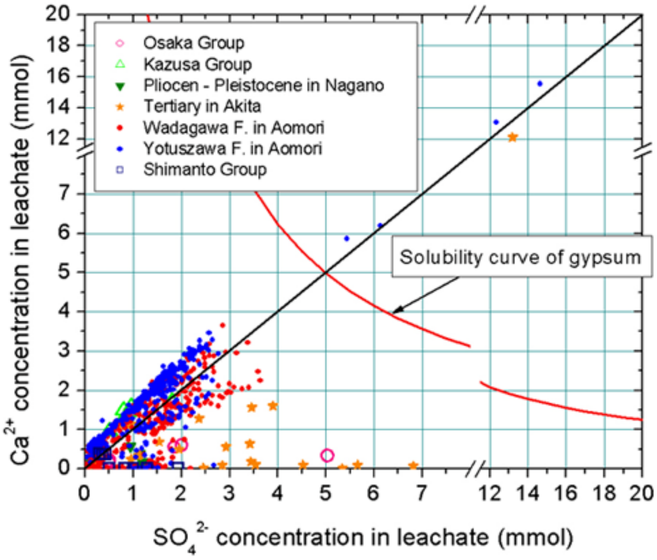

Figure 11. The calcium ion concentration against the sulfate concentration in leachate

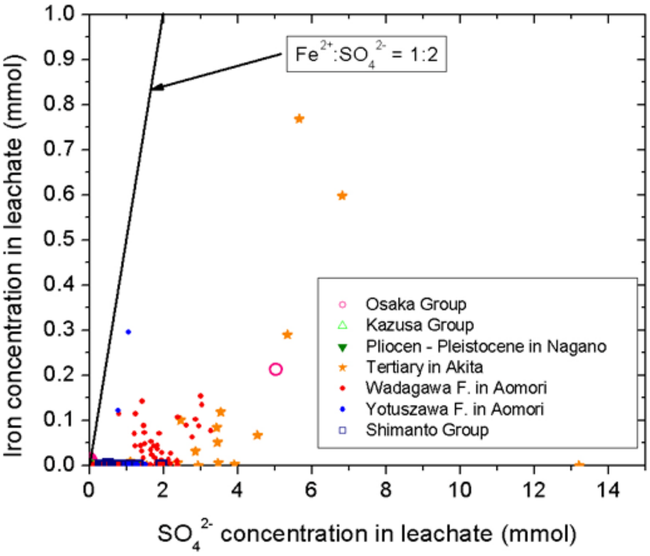

Figure 12. The iron concentration against the sulfate concentration in leachate

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2H_2O \qquad (4)$$

$$Fe^{3+} + 3OH^- = Fe(OH)_3 \qquad (5)$$

If the leachate becomes acid, the ferric hydroxide is dissolved according to the following reaction equation.

$$Fe(OH)_3 + H^+ = Fe^{2+} + HCO3^- \qquad (6)$$

It is assumed that iron like other metal elements are precipitated as a hydroxide in neutrality condition and dissolved in acid condition.

The relationship between bicarbonate concentration and sulfate concentration do not agree with the equation 3. It is presumed that decomposition of sodium-bearing minerals influence the concentration of bicarbonate, because of its relationship with the sodium concentration.

Reaction process

There is a relationship between the sulfate concentration in leachate and the sulfur content in mud sediment (Figure 9). However, the concentration of other elements such as calcium has nothing to do with the content in sediment

(Figure 10). These facts indicate that the sulfate concentration is determined by an amount of pyrite in sediment, and that the calcite volume in sediment does not control the calcium ion concentration. Therefore, we estimate the process of the reaction between mud sediment and water as follows.

1) Sulfate and hydrogen ion are released from mud sediment as the reaction of equation 1. The amount of these ions is related to the pyrite volume in sediment.

2) Calcite in sediment is decomposed by the reaction with hydrogen ion as shown in equation 2. The decomposed volume of calcite is suitable for the amount of hydrogen ion present. This reaction consumes hydrogen ion and released calcium ion and neutralizes the leachate.

3) While both pyrite and calcite exist in the sediment, the reaction of equation 3 will continue and the leachate will be kept in neutrality.

4) If calcite disappears before extinction of pyrite, the reaction system follows equation 1 only and the hydrogen ion concentration increases. On the other hand, when calcite remains in spite of pyrite disappearance, only the reaction between calcite and water is advanced and the pH of leachate increases due to release of hydroxyl ions.

5) The pH of leachate is determined by the process as detailed above. The metal element concentration is controlled by pH of the leachate.

CONCLUSIONS

We examined acid water drainage mechanism of mud sediments that is distributed around the big Japanese cities. From the results, the reaction mechanism between mud sediments and water is concluded as follows:

1) The pH of leachate from mud sediment depends on the quantitative relation between pyrite and calcite.
2) An amount of metal elements in leachate is controlled by the leachate pH.

The mechanism of acid water and metal elements drainage from mud sediments could be clearly described. However, we could not establish a concept of evaluation and prediction of the pollution caused by acid water drainage in the urban ground. In this study, we dealt with only the equilibrium problems in the mud–water reaction system. To make the concept for evaluation and prediction of pollution, we must consider some the following:

1) Kinetic problems in mud–water reaction system.
2) Advection and diffusion problems of acid water and metal elements.

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