

論文

Neutralization of the Tamagawa Thermal Acid Water with Crushed Limestone

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Abstract

The Tamagawa hot-spring, Akita Prefecture, Japan, is a hydrochloric and sulfuric acid hot-spring with a water temperature of 98°C, an artesian flow rate of 9m³ min⁻¹, and a pH of 1.2. In order to cope with a projected dam construction at the downstream, in situ tests for neutralization of the water with crushed limestone were carried out.

A plastic cylinder-cone type reactor reinforced with glass-fiber (with the angle of repose 60°) was used. Hot spring water was introduced into the reactor from its bottom and run as a countercurrent through the reactor. In neutralization tests by use of the crushed limestone with a grain size of 5~25mm, a neutralization percentage (decrease in pH 8.4 acidity) of 80.5% was attained when the acid water containing 1300mg l⁻¹ of SO₄²⁻ was treated at 50°C with the residence time of 5min. If 95% of the water of the Tamagawa hot-spring is neutralized with a neutralization percentage of 75%, then the pH at the point of the dam body 22km downstream can be expected to rise from 3 to over 4.3.

1. Introduction

Many volcanoes and hot-springs are distributed all over Japan. Volcanic hot-springs are mostly of a strong acid type. The inflow of acidic hot-spring waters into rivers has done much damage to agriculture, fisheries, and river constructions around the drainage basins, making district development and water utilization extremely difficult.

The Tamagawa hot-spring, Akita Prefecture, Japan has a water temperature of 98°C and an artesian flow rate of 9m³ min⁻¹, which is the largest discharge from single spring sources in Japan. It is an extremely peculiar hot-spring for its water quality with a pH of 1.2 and high HCl and H₂SO₄ contents (Table 1). This acid water has been called "Tamagawa poisonous water". In an attempt to get nonpoisonous neutral water, a neutralization treatment had been tried in which the acidic water was sprinkled over and permeated into the soil to effect ion-exchange with the soil, but had not lasted long¹⁾. Since 1940, an attempt has been made to conduct the Tamagawa river water, acidified by the inflow of the Tamagawa hot-spring water, into Tazawa Lake to effect dilution with the neutral lake water, but, as the result, the acidification of the lake water has advanced year by year to the present pH of 4.1~4.9, and fish and other living things in the lake have become almost extinct. In 1979, the construction of a dam with a total reservoir capacity of 254,000,000m³

Table 1. Chemical composition of Tamagawa hot spring water

Tw (°C)	pH	8.4Ax (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	F ⁻ (mg/l)	Na ⁺ (mg/l)	K ⁺ (mg/l)
97.8	1.19	5210	2735	1540	103	45.8	29.7
Ca ²⁺ (mg/l)	Mg ²⁺ (mg/l)	T-Fe (mg/l)	Al ³⁺ (mg/l)	Li ⁺ (mg/l)	SiO ₂ (mg/l)	T-As (mg/l)	Sp. Cond. (μS/cm)
95.1	31.5	84.6	109	0.022	257	2.95	30900

at the upper Tamagawa river was decided for the purpose of an increased power supply and for other purposes; and that led to another decision for an everlasting neutralization of the Tamagawa hot-spring acid water to be conducted by the government, with the water quality improvement target of pH 4 at the dam construction site and pH 6 or over at Tazawa Lake (Figure 1).

This report deals with the in situ experiments, carried out during the period 1979~1987, on the effect of neutralizing the Tamagawa hot-spring water with crushed limestone, with the principal object of searching the neutralization conditions and reactor types that are of low cost and the most efficient.

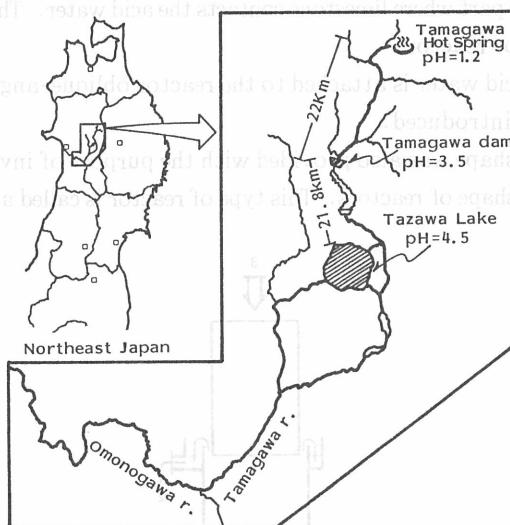


Fig. 1. The location of Tamagawa hot spring and Tamagawa river basin are shown.

2. Experimental

2.1 Limestone

In these experiments, crushed limestone was selected as the neutralizing agent for consideration of economy. Limestone with a grain size in the range of 5~80mm and a purity of 98% or more as CaCO₃ was used (Table 2). Impurities in the limestone consisted mostly of silicates as the gangue and of traces of organic materials, clay, and magnetite.

Table 2. Chemical composition of limestone¹⁾(wt. %)

CaO ²⁾	MgO	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	P ₂ O ₅
55.19	0.40	0.09	0.08	0.42	0.016

¹⁾ HAKURYU SEKKAI KAKO LTD. (JAPAN).

²⁾ as CaCO₃ 98.55%.

2.2 Hot-spring water

The acid water of the Ohbuke hot-spring (Source spring) was conducted by means of polypropylene pipes of 80mm ϕ in diameter for about 1km to the experiment site, and was used for the experiment as such or after dilution with the river water when necessary.

2.3 Experimental setting

The neutralization reactor is schematically shown in Figure 2. The reactor tank, made of glass fiber-reinforced plastic, consists of a cylindrical upper part and a conical lower part (the angle of repose 60°). A perforated plate is placed in the conical part; the diameter of the perforation holes was 3~10mm, varied depending on the volume of the reactor. Four types of reactor, with volumes of 0.01m³, 0.186m³, 0.42m³, and 8m³, were provided, each volume designated herein denoting the volume of the part where limestone contacts the acid water. The type of reactor described above is called a cone type reactor.

The inlet pipe for the acid water is attached to the reactor oblique-angled to effect an agitation by swirling of the water introduced.

A reactor with a cubic shape was also provided with the purpose of investigating neutralization efficiency affected by the shape of reactors. This type of reactor is called a rectangular type reactor.

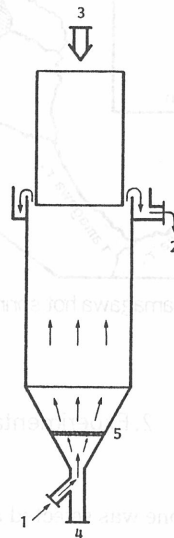


Fig. 2. Schematic diagram of Cylinder-Cone type reactor. (1) inlet of original acid water for reaction; (2) effluent of reacted water; (3) Charging of crushed limestone; (4) drain-pipe; (5) perforated plate.

In order to examine the behavior of the acid water, neutralized with limestone, after overflowing from the reactor, an apparatus as explained below was provided. Seven plastic tanks of 20l capacity were connected in series, with a stepwise difference in level, to the overflow part of the reactor. A polyvinyl chloride cylinder of a size nearly fitting to the tank was inserted into each tank, so that the water introduced from the upper end of the cylinder flowed down to the bottom, then flowed up along the inner wall of the tank, and overflowed.

2.4 Experimental procedures and analyses

The acid water to be used in the reaction was kept in a reservoir tank, which was installed at a level higher than the reactor. The reservoir tank and the reactor were connected to each other with a polypropylene pipe. The acid water was introduced into the reactor from its lower part utilizing the water head, and made to contact limestone and overflow from the upper part of the reactor. Limestone, the neutralizing agent, was charged from the upper part of the reactor. The amount of limestone consumed by neutralization was replenished from time to time.

Samplings of the acid water before neutralization and of the overflow water after neutralization were made at prescribed time intervals, and the samples taken were immediately filtered with filter paper No.5C (Toyo Roshi Co., Ltd., Japan) to be made into specimens for analysis.

Neutralization percentage is expressed by the percentage of the difference between the pH 8.4 acidities ($8.4 Ax$) before and after neutralization²⁾. $8.4 Ax$ denotes the calcium carbonate concentration (expressed in mg l^{-1}) equivalent to the amount of normal sodium hydroxide solution that is needed in titration until the reading of a pH meter reaches 8.4; the relation is expressed in the following equation;

$$\text{Neutralization percentage (\%)} = \frac{8.4 Ax \text{ of original acid water} - 8.4 Ax \text{ of neutralized water}}{8.4 Ax \text{ of original acid water}} \times 100$$

Experiments for the reactors with different shapes were simultaneously conducted for the sake of comparison.

3. Results and discussion

Conceivable factors to govern the magnitude of neutralization percentage are: (1) the shape of reactors, (2) the grain size of limestone, and (3) the concentration, composition, temperature, and flow rate of the acid water. Examinations of these factors are described below.

3.1 Shape of reactors and grain size of limestone

The effect of grain sizes of limestone on neutralization percentage as measured with reactors of different shapes is shown in Figure 3.

Higher neutralization percentages can be expected with limestone of a smaller grain size, because it has a greater specific surface area to produce a greater contact area with the acid water as compared with the limestone of a larger grain size^{3),4)}. The experimental results as shown for three types of grain size of limestone conform to this prediction. Use of the limestone with the smallest grain size will be a good choice because the unit prices per weight are the same for any limestones of varied

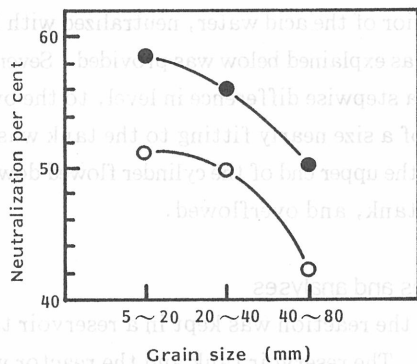


Fig. 3. Relation between the grain size of crushed limestone and neutralization percentage. (●) cone type reactor 8m³; (○) rectangular type reactor 8m³; Ax of acid water 6500mg/l; water temperature 50~58°C; retention time of water 4 min.

grain size. In the experiments hereafter, therefore, limestone with a grain size range 5~25mm was used.

As to the effect of the shape of reactors, the conical reactor gave higher neutralization percentages by 6~8% than the rectangular type reactor as shown in Figure 3.

Flow rate of water is inversely proportional to the cross sectional area of a reactor, and hence, in the conical reactor the acid water introduced has a very large flow rate at the inflow point, the very bottom of the cone-shape, effecting an increased water agitation and limestone dissolution. Limestone particles having dropped through the perforated plate rotated in the spiralling water flow and dissolved completely. When the angle of repose was designed to be 60°, the gravity flow of limestone became smooth enough to take the flow pattern of a mass flow type without any retention in the reactor⁵⁾.

In the rectangular reactor, in contrast to the conical one as above, the water current was inhomogeneous making branched flow paths, with non-uniform flow rates normal to the bottom face. Therefore, the sinking of limestone by dissolution was not constant and the caking of limestone was observed here and there.

Because of these, conical reactors can be considered superior to rectangular ones.

3.2 Acid concentration of the water

Acid concentration in the water was expressed in terms of 8.4 Ax, which implies H⁺ concentration. Fe³⁺ ions oxidized from Fe²⁺, and H⁺ ions produced by the hydrolysis of Al³⁺ ions are involved in the content of 8.4 Ax. In addition, H₂CO₃, H₂SiO₃, H₃PO₄, and organic acids are contained in 8.4 Ax but can be neglected in the case of present experiments⁶⁾.

The relationship between acid concentration of the water and neutralization percentage is shown in Figure 4. Under the present experimental conditions, no considerable variation in neutralization percentages was found for the waters in the 8.4 Ax range of 4,000~4,600mg/l, but the efficiency dropped at 8.4 Ax of 6,500mg/l. This decrease was found to be related to the SO₄²⁻ concentration in the acid water. When 8.4 Ax was 6,500mg/l, SO₄²⁻ concentration was about 2,600mg/l. When an acid water, high in SO₄²⁻ concentration, reacts with limestone, gypsum (CaSO₄·2H₂O) is produced

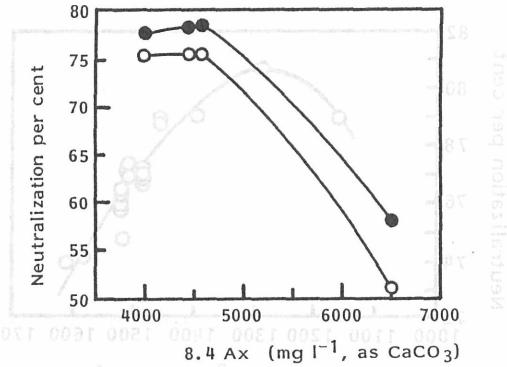


Fig. 4. Relation between acid concentration of water and neutralization percentage. continuous flow test for 10 days; (●) cone type reactor; (○) rectangular type reactor; grain size of limestone 5~25mm; water temperature 60~66°C; retention time of water 5min.

on the surface of limestone giving rise to retardation of further neutralization. This is evident from Figure 5, which shows the fact that, when SO_4^{2-} concentration in acid water exceeds $1,400mg l^{-1}$, the amount of gypsum deposited on the surface of limestone begins to increase remarkably. Chloride concentration was as large as $3,200mg l^{-1}$, but chlorides, generally being soluble, do not retard the progress of reaction.

Based on the finding that SO_4^{2-} concentration relates to the neutralization efficiency, an investigation was made on the effect of SO_4^{2-} concentration (Figure 6). This experiment was carried out by use of a conical reactor of $0.01m^3$ capacity, and each point in the figure represents an average of 90 analytical values obtained by three measurements per day during a run of continuous water supply for a period of 30 days. As shown in Figure 5, the peak for the maximum neutralization percentage is found near the SO_4^{2-} concentration of $1,300mg l^{-1}$. From calculation in view of water quality management, however, a neutralization percentage exceeding 75% is found to meet the

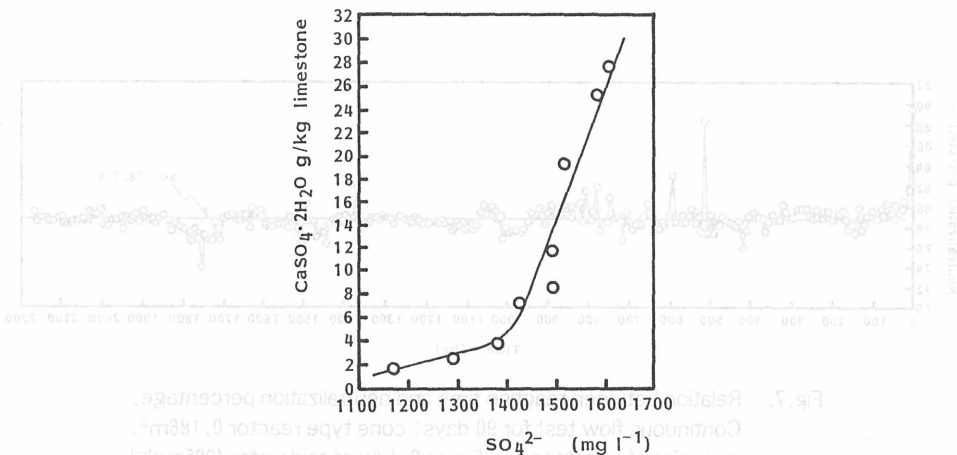


Fig. 5. Relation of the amount of the deposited gypsum to the sulfate ion concentration.

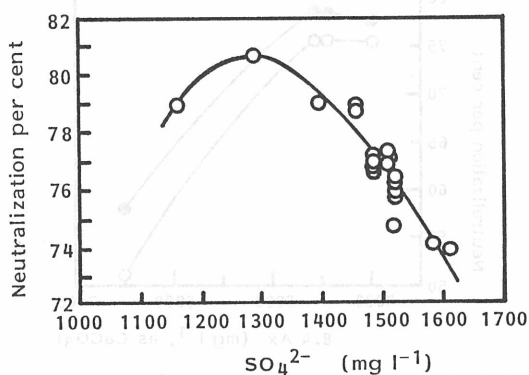


Fig. 6. Relation between sulfate ion concentration in acid water and neutralization percentage. continuous flow test for 30 days; cone type reactor 0.01m³; grain size of limestone 5~25 mm; weight ratio of Cl/SO₄²⁻ in acid water 1.51~1.88; retention time of water 5min.

purpose; hence, an acid water with SO₄²⁻ concentration below 1,500mg l⁻¹ is considered to be satisfactory.

Figure 7 shows the data of neutralization percentages obtained when an acid water with an average SO₄²⁻ concentration of 1,440mg l⁻¹ were continuously supplied for 90 days to conical reactor of 0.01m³ capacity. The arithmetic average of the neutralization percentages for the reactor is 78.7%, which is high enough. The salient high values of neutralization percentage at some periods of time originate in relatively greater contents of finer limestone particles adhering on the grains. On the other hand, the salient low values of neutralization percentage were observed in periods with rainfalls, when finer limestone particles were washed away by the rain and the temperature of the acid water dropped. In view of the above, it was verified that, for an acid water with a SO₄²⁻ concentration below 1,500mg l⁻¹, satisfactory neutralization percentages can be expected even with a continuous supply of the water for a long time.

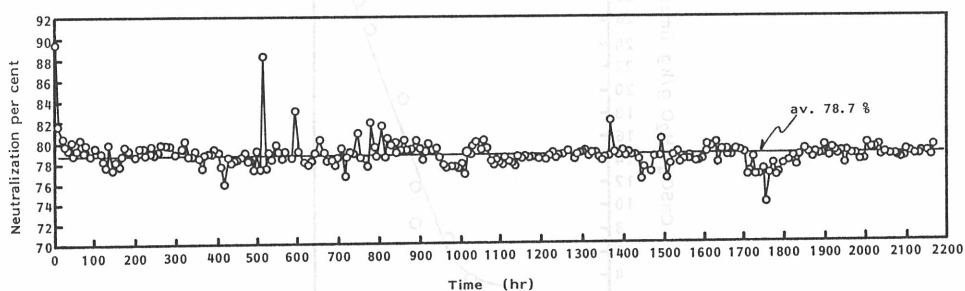


Fig. 7. Relation between reaction time and neutralization percentage. Continuous flow test for 90 days; cone type reactor 0.186m³; grain size of limestone 5~25mm; 8.4 Ax of acid water 4995mg l⁻¹ (pH 1.24, SO₄²⁻ concentration 1440mg l⁻¹); water temperature av. 65.7°C; retention time of water 5 min.

3.3 Composition of the acid water

For the Ohbuke vent thermal acid water in Tamagawa hot-spring, an annual variation in Cl^- and SO_4^{2-} concentrations is observed as shown in Figure 8. Hence, neutralization percentages affected by the composition ratios of $\text{Cl}^- : \text{SO}_4^{2-}$ were examined. Acid waters with prescribed composition ratios were prepared by addition of hydrochloric acid to the hot-spring water to produce a variety of $\text{Cl}^-/\text{SO}_4^{2-}$ ratios and by dilution with the river water to produce various 8.4 Ax values. The results are shown in Figure 9.

As far as SO_4^{2-} concentrations of the acid water did not exceed $1,500\text{mg l}^{-1}$ too much, higher neutralization percentages were observed with higher Cl^- concentrations. It is suggested that a neutralization percentage of over 80% can be attained with a $\text{Cl}^-/\text{SO}_4^{2-}$ ratio of 2 or more.

3.4. Temperature of the acid water

As described above, the magnitude of SO_4^{2-} concentration of the acid water was found to affect the neutralization percentage. When its SO_4^{2-} concentration is high, therefore, the acid water must be diluted with the river water to an appropriate concentration. The dilution, however, is accompanied by a decrease in the temperature of the acid water. An experiment was carried out to find the effect of temperatures on neutralization percentages of the acid water that was adjusted to an appropriate 8.4 Ax of $4,500\text{mg l}^{-1}$. The result is shown in Figure 10.

To ensure a neutralization percentage of more than 75%, a water temperature below about 60°C has to be maintained according to Figure 10. On the actual location, the temperature of the acid water that is 98°C at the source spring will decrease to about 70°C when the water is conducted through insulated pipes to the neutralization site about 1km away. On the assumption that the acid water had 8.4 Ax of $5,500\text{mg l}^{-1}$, the water was diluted to 8.4 Ax of $4,500\text{mg l}^{-1}$ with a neutral river water of 5°C , the temperature of the water would decrease further to 58°C . Because this temperature

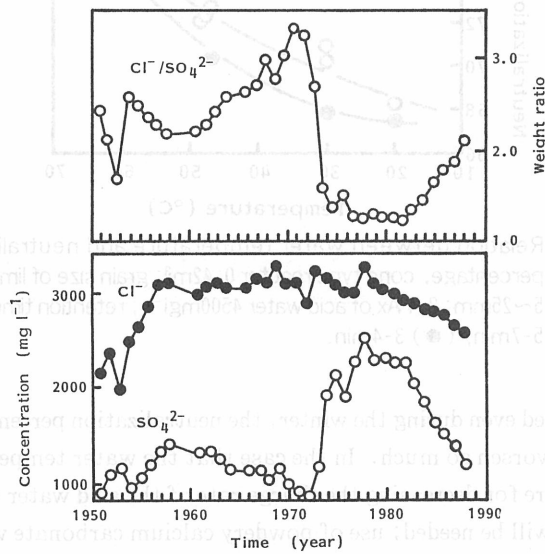


Fig. 8. Seasonal variation of chloride ion concentration and sulfate ion concentration in the Ohbuke vent thermal acid water at Tamagawa hot spring head, 1951-1988.

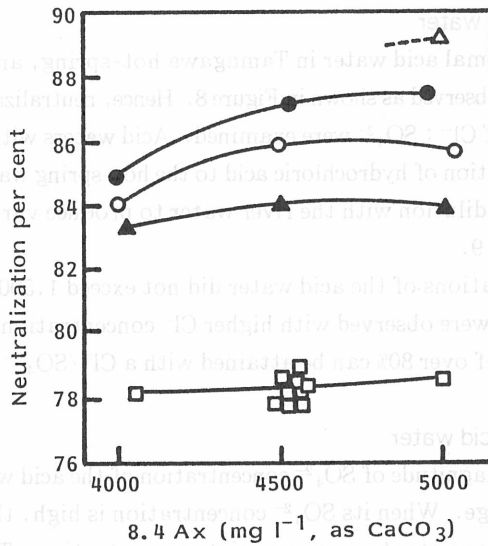


Fig.9. Effect of the composition ratio of chloride ion to sulfate ion on neutralization percentage. Continuous flow test for 30 days; cone type reactor 0.01m³; grain size of limestone 5~25mm; retention time 5min. weight ratios of Cl⁻/SO₄²⁻, □=1.48-1.57, ▲=2.11-2.16, ○=2.46-2.62, ●=3.41-3.44, △= 4.28.

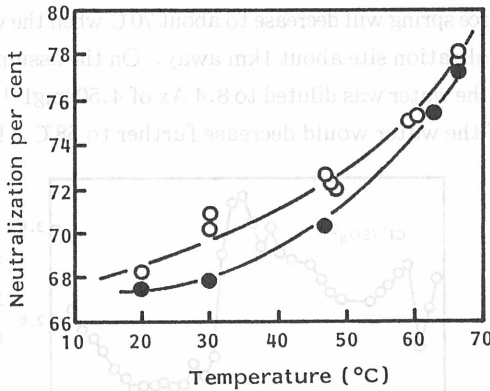


Fig.10. Relation between water temperature and neutralization percentage. cone type reactor 0.42m³; grain size of limestone 5~25mm; 8.4 Ax of acid water 4500mg l⁻¹; retention time, (○) 5-7min, (●) 3-4min.

can possibly be maintained even during the winter, the neutralization percentages during the winter can be expected not to worsen so much. In the case that the water temperature will decrease to far below 60°C, a measure for decreasing the charge rate of the acid water to prolong the time for contact with limestone will be needed; use of powdery calcium carbonate will be required in some cases.

3.5 Charge rate

Neutralization proceeds through the contact of the acid water with the surface of limestone. Charge rates, therefore, will be expressed in terms of contact times. Based on the charge rate and the gap volume in the reactor, calculated from the volume of the reactor and the weight and the density of the packed limestone, the apparent contact time for the acid water with limestone was determined.

The averages of all values obtained by the measurements of three times per day during a continuous run for 10 days are plotted in Figure 11 for both conical and rectangular reactors for comparison. From the result that the reaction efficiencies are nearly the same for the contact time of 2 min and 5 min, the case of 2 min seems to be preferable in view of the water treatment capacity per unit time. But in this case there is a tendency that unreacted fine limestone particles are carried away from the reactor, and hence, the contact time of about 5 min can be estimated to be practically good. Figure 11 also indicates that the conical reactor clearly exceeds the rectangular one in neutralization percentage by about 4%.

3.6 Qualities of the overflow water after neutralization

Qualities of the overflow water after neutralization are illustrated in Figure 12, which the location A represents the point of overflow from the reactor, and the locations B to H represent the points of overflow from subsequent tanks, respectively. The other conditions of the experiment are as indicated in the figure.

The pH gradually decreased after the overflow from the reactor, owing to the increase in H^+ liberated by hydrolysis of Fe^{3+} , that is an oxidation product of Fe^{2+} . The decrease in the SO_4^{2-} content was caused by the precipitation of $CaSO_4 \cdot 2H_2O$ which resulted natural cooling. The decrease in concentrations of Fe^{2+} and SO_4^{2-} resulted from the precipitation of iron compounds and gypsum in tanks. The amount of gypsum precipitated on neutralization of the Tamagawa hot-spring water, when estimated on the basis of this experiment, was found to be about 1 ton day^{-1} with installation of a reservoir tank to give a residence time of 50 min. To cope with this huge amount, some way of the precipitate processing will have to be studied.

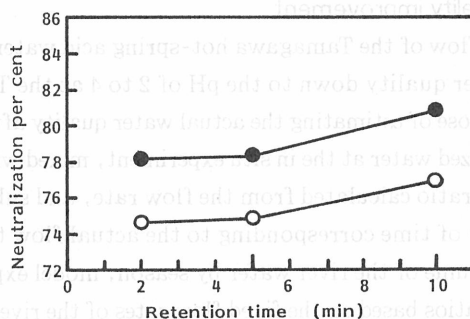


Fig. 11. Relation between retention time of acid water and neutralization percentage. Continuous flow test for 10 days; (●) cone type reactor 0.186m^3 , (○) rectangular type reactor 0.186m^3 ; grain size of limestone $5\sim 25\text{mm}$; 8.4 Ax of acid water 4400mg^{-1} ; water temperature $60\sim 66^\circ\text{C}$.

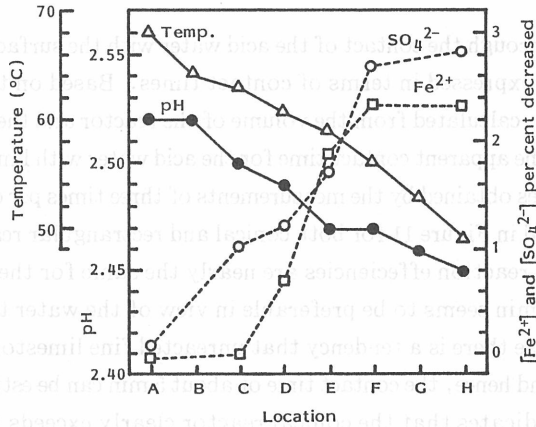
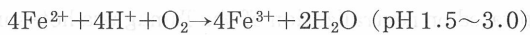


Fig. 12. pH and water temperature changes, ferrous ion concentration and sulfate ion concentration reduction rates, of the flowing water. Original acid water, $[\text{Fe}^{2+}] = 85.5 \text{ mg l}^{-1}$, $[\text{SO}_4^{2-}] = 1627 \text{ mg l}^{-1}$; retention time of each tank (B to H) 10min.

Owing to the low pH value, the Al^{3+} ions in the water flowed out without forming any precipitate.

In addition, silica-based compounds, the gangue of limestone, precipitated in the tank, but could be almost completely trapped in the first tank owing to their relatively large particles size.

By oxidizing Fe^{2+} to Fe^{3+} and then neutralizing the acid water with limestone, most of the Fe^{3+} ions in the water can be precipitated. A process utilizing *Thiobacillus ferrooxidans*⁷⁾, which is of the lowest cost and high efficiency, has been considered as the way of oxidizing Fe^{2+} . The oxidation can be described by the equation:



However, to be unapplicable was this method concluded, because it was confirmed that the high Cl^- concentration and high temperature of the Tamagawa hot-spring water do not permit proliferation of these bacteria, leading to their failure in oxidation.

3.7 Estimation of water quality improvement

Presently, in 1988, the inflow of the Tamagawa hot-spring acid water into the river throughout its course converts the water quality down to the pH of 2 to 4 at the Tamagawa dam site under construction. With the purpose of estimating the actual water quality after neutralization, samples were taken from the neutralized water at the in situ experiment, mixed with the water of tributaries of the Tamagawa river in a ratio calculated from the flow rate, and subjected to a water analysis after agitation for a period of time corresponding to the actual flow time in the river. Because of the fluctuation of the volume of the river water by season, model experiments were carried out by determining the mixing ratios based on the fixed flow rates of the river water as follows: $8.14 \text{ m}^3 \text{ sec}^{-1}$ in the low water discharge season, and $9.74 \text{ m}^3 \text{ sec}^{-1}$ in the ordinary water discharge season. The results are shown in Figure 13.

"The amount of water taken (%)" in the abscissa denotes the percentage of the volume to be neutralized to the total flow rate of the Tamagawa hot-spring. The estimation was made under the assumption that the 8.4 Ax neutralization percentage of the acid water was 75%.

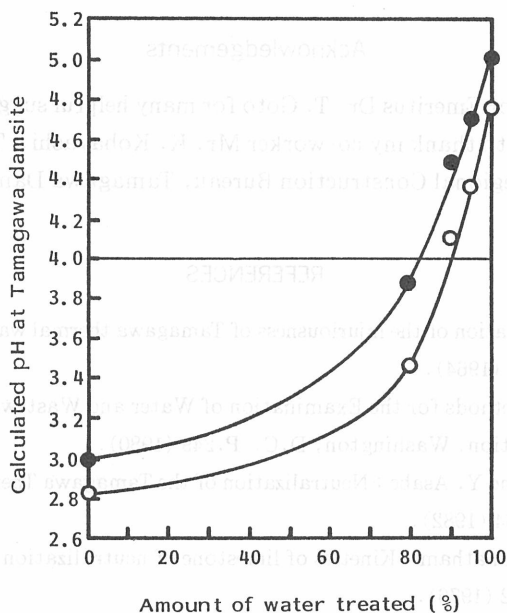


Fig.13. pH at the dam site, predicted from the rate of the amount of water to be taken for neutralization from its source spring water, where the neutralization percentage is 75%. (●) ordinary water discharge season ($9.74\text{m}^3\text{sec}^{-1}$), (○) low water discharge season ($8.14\text{m}^3\text{sec}^{-1}$).

Figure 13 suggests that, in a low water discharge season, neutralization of about 90% of the Tamagawa hot-spring water will suffice to maintain pH 4.0 at the Tamagawa damsite. According to the above estimations, neutralization of the Tamagawa hot-spring water with limestone at a treatment percentage as high as 95% will be expected to give a pH higher than 4.3 at the Tamagawa damsite and to attain a greatly improved water quality and the prevention of acid-caused damage of the dam body.

4. Conclusion

A cone-cylinder type reactor, with an angle of repose 60° and made of thermostable acid-resistant material, is suitable for efficient neutralization with crushed limestone of the Tamagawa hot-spring acid water, 98°C , pH 1.2, having an artesian flow rate of $9\text{m}^3\text{min}^{-1}$. The grain size of the limestone is preferably 5~25mm in view of economy. The neutralization percentage, calculated from the decrease in acidity in terms of 8.4Ax , is affected by the SO_4^{2-} concentration of the acid water; and the SO_4^{2-} concentration of the acid water to be charged must be below the tolerable level of $1,500\text{mg}\text{l}^{-1}$ in order not to precipitate out by the produced gypsum. When the concentration is over this level, the acid water must be diluted by the river water, with an attention not to decrease the water temperature to far below 60°C . The charge rate of the acid water should preferably be about 5min in terms of the contact time. When the above conditions are fulfilled, the water quality at the Tamagawa dam site, under construction at 22km downstream from the Tamagawa hot-spring, can be improved from the current pH of 3~4 to the predicted pH of 4~5.

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4. Conclusion

A cone-cylinder type reactor, with an angle of repose 60° and made of thermostable acid-resistant material, is suitable for efficient neutralization with crushed limestone of the Tamagawa hot-spring acid water, 38°C, pH 1.3, having an artesian flow rate of 30m³/min. The grain size of the limestone is preferably 5~25mm in view of economy. The neutralization percentage, calculated from the decrease in acidity in terms of SO₄²⁻ concentration of the acid water, is affected by the SO₄²⁻ concentration of the acid water to be charged must be below the tolerable level of 1,500mg/l in order not to precipitate out by the produced gypsum. When the concentration is over this level, the acid water must be diluted by the river water, with an attention not to decrease the water temperature to far below 60°C. The charge rate of the acid water should preferably be about 5min in terms of the contact time. When the above conditions are fulfilled, the water quality at the Tamagawa dam site, under construction at 25km downstream from the Tamagawa hot-spring, can be improved from the current pH of 3~4 to the predicted pH of 4~5.