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REMOVING FLUORIDE FROM A HOT SPRING USING AN ELECTROLYSIS SYSTEM

*Yuki Imai[1], Shiori Yanagawa[2], Misa Konishi[3], and Tomonori Kawakami[4]

Faculty of Engineering, Toyama Prefectural University, Japan

*Corresponding Author, Received: 13 June 2016, Revised: 14 July 2016, Accepted: 29 Nov. 2016

ABSTRACT: A high concentration of fluoride in the wastewater from hot springs is an environmental issue in Japan, since some of the wastewater exceeds the national minimum effluent standards of 8 mg/l. However, an effective treatment for fluoride removal has not yet been developed. Accordingly, the temporal effluent standards of 15mg/l - 50 mg/l have, so far, been applied to the wastewater from hot springs.

In this study, an electrolysis system consisting of an anode bath and a cathode bath separated by a diaphragm made of a clay panel was tested for the removal of fluoride. In an electrolysis system, fluoride is removed by co-precipitation with magnesium hydroxide formed in a cathode bath under a high pH condition.

As a pretreatment of wastewater, 100 mg/l of magnesium was added to water from Gero hot spring, Gifu, Japan, to enhance the formation of the precipitation of magnesium hydroxide, since water from Gero hot spring contains less than 1 mg/l of magnesium. Water from Gero hot spring to which 100 mg/l of magnesium had been added was treated by an electrolysis system with a flow rate of 10 l/day and a current of 120 mA. The electrolysis system reduced the fluoride concentration from 16.6 mg/l to 6.4 mg/l, which meets the national minimum effluent standards of 8 mg/l.

Keywords: Gero hot spring, co-precipitation, sequential flow reactor, national minimum effluent standard

1. INTRODUCTION

UNICEF has designated Japan as one of the countries with endemic fluorosis due to excess fluoride in drinking water [1]. The health problem has been remedied by using alternative water sources that are free of fluoride. However, high concentrations of fluoride in the wastewater remain an environmental issue in Japan, since some wastewaters exceed the national minimum effluent standards of 8 mg/l [2]. Since no effective treatment for the removal of fluoride has been developed, temporal effluent standards have been applied to the wastewater of some industries. The operation of hotels with hot springs, very popular with Japanese people for vacations, is one such industry, since the wastewater discharged by the hotels sometimes contains a high concentration of fluoride originating from the hot spring. Different temporal effluent standards for fluoride concentration are applied to hotels with hot springs depending on the amount of the effluent and the type of hot spring. Hotels that have an effluent of more than 50 m^3/day have a temporal effluent standard of 15 mg/l. For the other hotels, different standards, such as 30 mg/l or 50 mg/l, are applied based on the type of hot spring, i.e., pumped out or gushed out naturally, respectively. The possibility of stiffening temporal effluent standards has been discussed by the Japanese Ministry of Environment every three years; however, as decided at the council held in 2015, no changes will be made in the regulation due to the lack of appropriate technologies for effectively removing fluoride [3]. There are some techniques to remove fluoride from drinking water such as reverse osmosis [4], electrodialysis and nanofiltration [5-6], however, these are the techniques just separate fluoride into the solution with higher fluoride concentration and the solution with lower concentration. These techniques are not suitable for wastewater treatment.

To remove fluoride from industrial wastewater, the primary treatment has generally been to add calcium to produce insoluble CaF_2, followed by coagulation. According to the solubility product of CaF_2 (3.9×10^{-11} mol^3/l^3), 8.8mg/l of calcium is sufficient to obtain 8 mg/l of fluoride theoretically; however, in the actual cases, an 8-mg/l concentration of fluoride cannot be achieved even by adding 300 mg/l of excess calcium. As a result, secondary treatments, such as ion exchange or the addition of aluminum, are introduced to meet the regulation [7-9].

Gero hot spring is located 35°48'N and 137°14'E in Gifu Prefecture, Japan. It is widely regarded as one of the three best hot springs in Japan [10]. More than 40 hotels offer rooms and hot spring baths. Hot water is pumped out to deliver to the hotels. Temporary effluent standards of 30 mg/l and 15 mg/l are applied to small and large hotels, respectively. The fluoride concentration, which is officially reported to be 16.5 mg/l [11], exceeds regulations for large hotels.

However, the above-mentioned treatments to remove fluoride are quite prohibitive for the hotel business due to the high cost compared to their business scale.

In the current study, a new electrolysis system was examined as a cost-effective system for removing fluoride from wastewater from hotels with hot springs to the level of the national minimum effluent standard of 8 mg/l. We focused on the water of Gero hot spring as a model.

2. MATERIALS AND METHODS

2.1 Gero hot spring

Raw hot spring water from Gero was used for fluoride removal. The objective of the current research is the removal of fluoride from wastewater; however, raw hot spring water was used for the experiments, since it has the highest concentration of fluoride without dilution. Fluoride removal was examined in a laboratory using a batch reactor and a sequential flow reactor.

2.2 Batch reactor

Electrolysis using a batch reactor was performed to remove fluoride. The batch reactor shown in Fig. 1 consisted of two electrolysis baths separated by a membrane filter into a cathode bath and an anode bath. Each bath had a volume of 300 ml. In an electrolysis system, fluoride is removed by co-precipitation with magnesium hydroxide formed in the cathode bath under a high pH condition. Magnesium was added to the water from Gero hot spring to enhance the formation of magnesium hydroxide, since the magnesium concentration of water from Gero hot spring, less than 1 mg/l, is too low for the formation of magnesium hydroxide. The magnesium concentration was adjusted to 50 mg/l with magnesium chloride. A constant current power supply, adjusted to 80 mA, was used for the electrolysis. Electrolysis was performed for 1 hour.

Since it was found that alkalinity (HCO_3^-) interfered with the formation of magnesium hydroxide by forming magnesium carbonate, alkalinity was removed before electrolysis.

Alkalinity was removed from the solution by adding sulfuric acid in accordance with the following equation:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O.$$

CO_2 formed and dissolved in the solution was removed by aeration.

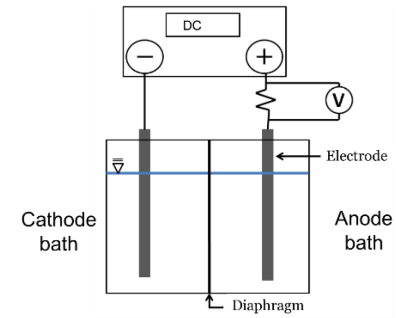

Fig.1 Schematic diagram of the batch reactor

Using the solution mentioned above, the first of a two-series electrolysis was performed. After the first electrolysis, part of fluoride was co-precipitated with magnesium hydroxide in the cathode bath. At the same time, part of the fluoride was transferred to the anode bath by the Coulomb force. Since one- and two-sided treatments are both required for wastewater treatment, a second electrolysis was performed to treat the solution in the anode bath. The solution taken out of the anode bath was mixed with the same amount of the raw hot spring water to which magnesium had been added. The second electrolysis was performed with this solution. The addition of sulfuric acid was not needed because the solution taken out of the anode bath was sufficiently acidic to remove alkalinity.

2.3 Sequential flow reactor

As a sequential flow reactor, a reactor with an anode bath and a cathode bath separated by a clay panel was used (Fig. 2). The volume of each bath was 420 ml. An aeration bath was installed at the inlet of the cathode, where alkalinity was removed by the acid solution formed in the anode bath. Water from Gero hot spring to which magnesium had been added in advance was introduced to the anode and aeration baths. The total flow rate was set at 10 l/day, which is equivalent to a retention time of 2 hours. In the experiments, the flow ratio of Gero hot spring water into the aeration bath (b) to the anode bath (a) was varied with 4 ratios, i.e., b:a=0:10, 5:5, 8:2, and 9.4:0.6. The Mg concentration was adjusted to 100 mg/L. One hundred twenty mA was applied for electrolysis with a constant current power supply.

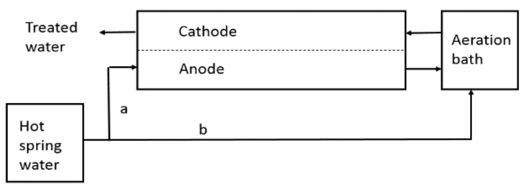

Fig.2 Schematic diagram of the sequential flow reactor

Table 1 Water quality of Gero hot spring. The concentration for 2013 is from the official record

Date Y/M/D	pH	EC mS/m	Na mg/l	NH_4 mg/l	K mg/l	Mg mg/l	Ca mg/l	F mg/l	Cl mg/l	NO_3 mg/l	SO_4 mg/l	Alkalinity meq/l
2015/ 9/11	8.9	35	107.2	0	1.0	0.1	0.6	17.7	75	0	10.8	1.66
2013/11/ 5	9.5	52.2	108.9	0	1.2	0	1.9	16.5	75	0.1	10.9	1.65

2.4 Analyses

Major ions were measured by an ion chromatography after samples were filtered by a membrane filter with a pore size of 0.45 µm. The pH was measured by a glass electrode method. Titration to the endpoint of pH=4.8 by sulfuric acid was used to measure alkalinity.

3. RESULTS AND DISCUSSION

3.1 Gero hot spring

The quality of water from Gero hot spring sampled on September 11, 2015, is shown in Table 1, together with the official record sampled on November 5, 2013. The official record is the analytical concentrations of chemical components registered in Gifu Prefecture based on Japan's Hot Spring Law.

The concentrations of the major ions, including alkalinity, of our analysis were quite similar to those of the official record, with the exceptions of calcium and fluoride. The concentration of fluoride fluctuated in the other samples between 15.8 mg/L and 18 mg/L. In the sample from September 11, 2015, the fluoride concentration was as high as 17.7 mg/L, which is approximately twice the national minimum effluent standard of 8 mg/L. The Mg was contained slightly, the pH was 8.9, and the alkalinity was 1.66 meq/L.

3.2 Batch reactor

Table 2 shows the fluoride removed by electrolysis from the hot spring water with alkalinity. The pH decreased in the anode bath while it increased in the cathode bath. The fluoride concentration decreased in the cathode bath; however, it increased in the anode bath, indicating that fluoride was transferred from the cathode bath to the anode bath by the Coulomb force. Accordingly, the decrease in the fluoride concentration was very small when the averaged concentration of both baths (14.7 mg/l) after electrolysis is compared with the initial concentration (16.9 mg/l). Even when the average magnesium concentration decreased from 45.9 mg/l to 19.7 mg/l and white precipitation appeared in the cathode bath, there could be little co-precipitation of fluoride with magnesium hydroxide, due to the formation of magnesium carbonate.

The fluoride removed from the hot spring water without alkalinity by the first electrolysis is shown in Table 3. Due to the addition of sulfuric acid to remove alkalinity, the pH value of the initial solution was low. The fluoride concentration decreased in the cathode bath but increased in the anode bath, indicating that fluoride was transferred in the same manner as with alkalinity. However, some amount of fluoride was found to have been removed by precipitation during electrolysis, since

Table 2 Fluoride removed by electrolysis with alkalinity

	pH	F (mg/L)	Mg (mg/L)
Initial	8.83	16.9	45.9
Anode	2.43	22.3	37.7
Cathode	11.1	7.0	1.7
Average		14.7	19.7

Table 3 Fluoride removed by the first electrolysis without alkalinity

	pH	F (mg/L)	Mg (mg/L)
Initial	3.9	15.8	47,1
Anode	2.3	19.6	28.7
Cathode	11.6	5.2	0.0
Average		12.4	14.4

Table 4 Fluoride removed by the second electrolysis without alkalinity

	pH	F (mg/L)	Mg (mg/L)
Initial	2.8	17.2	49.2
Anode	2.3	19.4	42.3
Cathode	11.0	8.3	0.4
Average		13.9	21.4

the average concentrations of fluoride in both baths after treatment were well below that of the initial solution. When the average concentrations of the anode and cathode baths are compared, electrolysis without alkalinity was showed to more effectively remove fluoride than electrolysis with alkalinity.

The result of the second electrolysis is shown in Table 4. After treatment, the fluoride concentration in the cathode bath decreased to 8.3 mg/l. The fluoride concentration in the anode bath was 19.4 mg/l, which was similar to the concentration of fluoride in the anode bath with the first electrolysis. This indicates that the fluoride concentration could be decreased to approximately 8 mg/l when batch electrolysis is repeated.

3.3 Sequential flow reactor

According to the experimental results of the batch reactor showing that repeated batch electrolysis could remove fluoride, a sequential flow reactor was tested for removing fluoride.

The effect of the flow ratio on the removal of fluoride is shown in Fig. 3. In the figure, the flow ratios of b:a=0:10, 5:5, 8:2, and 9.4:0.6 are expressed in flow rates of the anode bath of 10, 5, 2, and 0.6 l/day, respectively.

A lower flow ratio resulted in higher fluoride removal. In the case of the ratio of 9.4:0.6, the fluoride removal rate was 62%, and the fluoride concentration after treatment was 6.4 mg/l; as a result, the national minimum effluent standard of 8 mg/l was achieved. The relationship between pH and fluoride concentration and the relationship between pH and magnesium in the cathode bath are shown in Fig. 4. When pH was higher, the fluoride removal rate increased and the magnesium concentration decreased. The change in pH, the concentration of fluoride, and the magnesium concentration in the hot spring water, the anode bath, the aeration bath, and the cathode bath are shown in Figures 5, 6, and 7, respectively, at flow ratios of b:a=0:10 and 9.4:0.6.

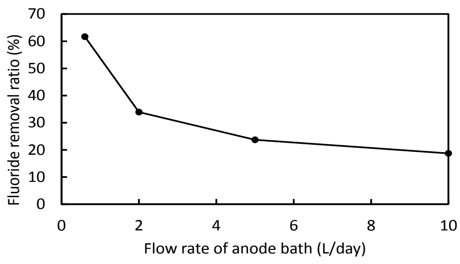

Fig.3 Effect of the flow ratio on the removal of fluoride

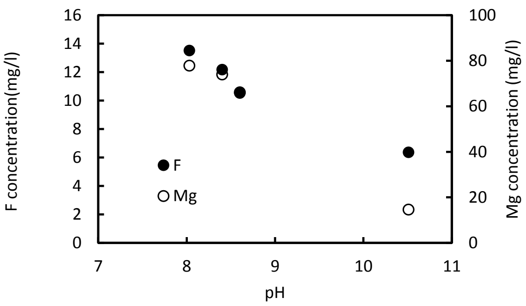

Fig.4 Relationship between pH and fluoride concentration and the relationship between pH and magnesium in the cathode bath

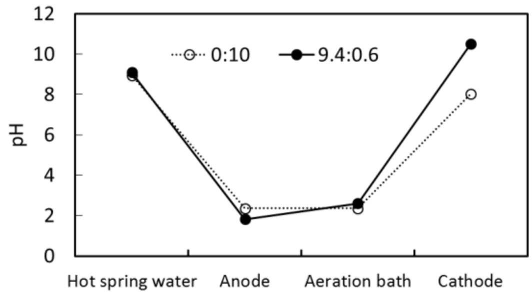

Fig.5 Change in the pH along the flow

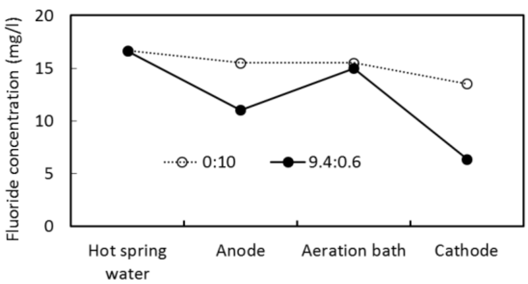

Fig.6 Change in the fluoride concentration along the flow

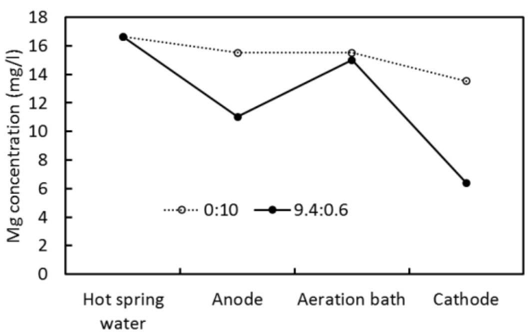

Fig.7 Change in the Mg concentration along the flow.

When the flow ratio was 0:10, the fluoride concentration in the treated water slightly decreased from that in the hot spring water. When compared with the batch reactor, the pH was as low as 8.0 in the cathode bath, and the concentration of dissolved magnesium was high. The reason is that the pH did not recover in the cathode bath after the pH in the mixing bath decreased to 2.35. Therefore, magnesium hydroxide did not form well, and co-precipitation with fluoride did not take place. When the flow ratio was 9.4:0.6, acidic solution with a pH value of 1.8 was formed in the anode bath. However, due to smaller volume of the acid solution that flowed into the aeration bath, a higher pH value of 2.60 was obtained in the aeration bath. As a result, pH increased to 10.5 at the outlet of the cathode bath, and the fluoride concentration decreased to less than the standard concentration of 8 mg/l. The concentration of dissolved magnesium decreased to 14.6 mg/l, as well. The difference in the pH values of 2.60 and 2.35 in the aeration bath between cases with flow ratios of 9.4:0.6 and 0:10, respectively, seems not to be significant. However, this is because pH is expressed in a logarithmic scale. When pH values are converted into hydrogen ion concentrations, a pH of 2.35 is equivalent to 4.5 mmol/l of H^+, while a pH of 2.60 is equivalent to 2.5 mmol/l of H^+. The difference in the concentrations of H^+ as 2.0 mmol/l was large enough to cause a difference in the OH^- concentration in the cathode bath of 0.3 mmol/l, which was calculated from the difference between pH=8.0 and pH=10.5.

3.4 Cost and maintenance

We proved that with this electrolysis system, it is possible to remove fluoride from hot spring wastewater. In the proposed electrolysis system, the devices can be made inexpensively, since the diaphragm of the electrolysis baths is made of a clay panel that would be robust against fouling, as well. Electric consumption for the electrolysis was approximately 1 W, excluding consumption by the water pumps, indicating that 24 Wh would be required for the treatment of 10 L of Gero hot spring water in one day. Supposing that 1 kWh=17 Japanese yen, the treatment of 10 L would require only 0.4 Japanese yen.

It could be possible to reuse magnesium by lowering the pH to dissolve the precipitation. The recovery ratio of magnesium as precipitation was as high as 85%, indicating that most of the magnesium added to the solution might be reused. When the hot spring water contains magnesium naturally, it is not necessary to add magnesium; however, the precipitation that does not need to be reused, in this case, will generate sludge. Nevertheless, the amount of sludge would be much less than that when a Ca-adding method is used, since excess Ca should be added to the solution. In spite of this, reducing electricity, magnesium usage, and sludge would be challenges for the future.

4. CONCLUSION

The electrolysis system for treating Gero hot spring water to remove fluoride was tested in a laboratory. The sequential flow reactor could remove fluoride to a level of 6.4 mg/l, which meets the national minimum effluent standards of 8 mg/l. It would be a cost-effective method for removing fluoride from wastewater.

5. ACKNOWLEDGEMENTS

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