

REMOVING ARSENIC AND FLUORIDE FROM HOT SPRING WATER BY ELECTROLYSIS

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ABSTRACT: Currently in Japan, there are many hot springs containing fluoride and arsenic with high concentration. Although the national minimum effluent standard for arsenic and fluoride is 100 µg/L and 8 mg/L, respectively, they are not applied to the hotels with hot spring since no appropriate treatment techniques are available. The objective of this research is to reduce fluoride and arsenic in hot spring wastewater by using electrolysis technique to meet the national minimum effluent standards. The electrolysis system with an anode bath and a cathode bath separated by a diaphragm was adopted. Fluoride and arsenic co-precipitate with magnesium hydroxide formed in the cathode bath in which pH value increases as the electrolysis progresses. The Gero hot spring containing fluoride and arsenic as 17 mg/L and 120 µg/L, respectively, was used as a model effluent. Since Gero hot spring water contains almost no magnesium, magnesium chloride was added as a magnesium source. The addition of 100-200 mg/L could reduce the fluoride concentration to less than 8 mg/L. The arsenic concentration decreased to less than 10 µg/L. 1040 C/L of electricity was required for the operation. The electrolysis system successfully reduces the fluoride and arsenic concentrations below the national minimum effluent standards.

Keywords: Hot spring wastewater, Arsenic, fluoride, Electrolysis, National minimum effluent standard

1. INTRODUCTION

Intake of drinking water containing high concentrations of fluoride for a long term could cause fluorosis, such as dental fluorosis and skeletal fluorosis. In order to prevent human health from fluorosis, the standard for drinking water and the national minimum standards were set as 0.8 mg/L and 8 mg/L, respectively. Currently in Japan, however, there are many hot springs containing fluoride in excess of the national minimum effluent standards. A temporal standard is applied to hotels with hot springs since no appropriate treatment techniques are available. Adsorption, ion exchange and reverse osmosis (RO) techniques can be used for removing fluoride from drinking water, however, co-existing contaminants in hot springs degrade their effectiveness [1,2]. In addition, RO is not available for wastewater treatment due to rejected water with concentrated contaminants [3]. Even though the Japanese Ministry of Environment invited private companies to compete for the treatment technique for the wastewater, no effective technology has been developed yet [4]. Accordingly, the ministry decided to extend the term of validity of the temporal provisional standard for 2001 after reviewing the regulation in 2016 [5].

On the other hand, long-term exposure to arsenic from drinking water and food could cause cancer and skin lesions. Arsenic is naturally present at high levels in the groundwater of a number of

countries, and it is highly toxic in its inorganic form. The national minimum effluent standards of arsenic have been set at 100 µg/L. In Japan, many hot springs contain arsenic exceeding the national minimum effluent standard such as Kusatsu hot spring (250–1260 µg/L) [6], Gero hot spring (140 µg/L) [7], and Yudanaka hot spring (1240 µg/L) [8]. Hot spring inns are exempted from arsenic regulations. This is also due to the lack of effective technologies to remove arsenic.

The authors have been developing technologies to remove fluoride from drinking water in developing countries. In developing countries, inexpensive and easy-to-operate equipment is required. Fluoride removal by an electrolysis system is one of the technologies applicable to hot spring wastewater. The electrolysis system consists of electrolysis baths separated by a diaphragm. When electrolysis progresses, magnesium contained in well water in a cathode bath precipitates as a form of magnesium hydroxide as the pH increases and fluoride co-precipitates with magnesium hydroxide [9,10]. Moreover, arsenic was found to be removed efficiently by this electrolysis method. With this electrolysis method, fluoride and arsenic can be removed simultaneously. In drinking water, it is rare that fluorine and arsenic exist at the same time in high concentrations; however, the waters of both Kusatsu and Gero hot springs have higher concentrations of fluoride and arsenic than the minimum effluent standards. It is

preferable that they should be treated and removed.

The objective of this research was to remove fluoride and arsenic simultaneously from hot spring wastewater using an electrolysis system to meet the national minimum effluent standards.

2. MATERIALS AND METHODS

For the simultaneous removal of fluoride and arsenic, an electrolysis system was used. The electrolysis system consists of an anode bath and a cathode bath separated by a diaphragm. When water containing magnesium is electrolyzed in the electrolysis system, magnesium precipitates as a form of magnesium hydroxide by increasing the pH value of the cathode bath. Fluoride and arsenic co-precipitate with magnesium hydroxide when the electrolysis progresses.

Experiments were carried out in a continuous flow system. Fig.1 (a) shows the flow diagram of the continuous electrolysis system, and Fig.1 (b) shows a photo of the electrolysis system used in the experiment. The diaphragm of the electrolysis system shown in Fig.1 (b) is made of an uncalcined plate. An aeration bath is added to the electrolysis system. The sizes of the anode and cathode baths were 7 cm (H) × 40 cm (L) × 1 cm (W) and 7 cm (H) × 40 cm (L) × 2 cm (W), respectively. The volumes of the anode and cathode baths were 280 mL and 560 mL, respectively. As shown in Fig.1 (a), a constriction plate to restrict the mixing of the solution before and after was provided in the flow in the anode and cathode tanks. A plastic (PVC) plate 0.5 mm thick was used as the constriction plate. The constriction plate provided an open area 1 cm deep from the bottom. In this study, the compartments in the anode bath were named the “+1 cell” and the “+2 cell” from upstream to downstream. The compartments in the cathode bath were named the “-1 cell” and the “-2 cell” from upstream to downstream. A platinum wire (purity 99.99%, diameter 0.6 mmφ, length 1 m) was used as the electrode for the anode, and a stainless steel wire (SUS 304, diameter 1.0 mmφ, length 1 m) was used for the cathode.

Table 1 shows the water quality of the Gero hot spring. The Gero hot spring, which contains fluoride and arsenic, was used as a model effluent. Since Gero hot spring water contains almost no magnesium, magnesium chloride was added as a

magnesium source when electrolysis was carried out.

In the laboratory, the water taken from the Gero hot spring was put in a bucket, and magnesium chloride was added to adjust the magnesium concentration. The hot spring water (Mg added) was introduced into the anode bath and the aeration bath of the electrolysis cell. Carbonate and bicarbonate, which interfere with the formation of magnesium hydroxide, were removed from the raw water by introducing the effluent water from the anode bath with low pH into the aeration bath. The size of the aeration bath was 6.5 cm (H) × 6.5 cm (L) × 6.5 cm (W), and the volume was 275 mL. The generated carbon dioxide was expelled to the atmosphere by aeration. As the operating condition, the treatment capacity was 10 L/day. The residence time in the cathode bath was 80 minutes. Electrolysis was carried out at a constant current by using a constant current power supply (TAKASAGO ZX-400 M).

We investigated the effect of the flow rate ratio, which is the ratio of the flow rate to the anode bath (a): aeration bath (b), magnesium concentration, and current on the removal of fluoride and arsenic.

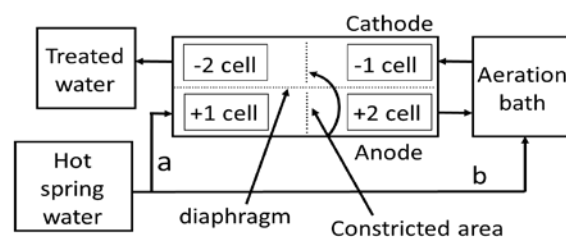


Fig.1 (a) Schematic diagram of the sequential flow reactor

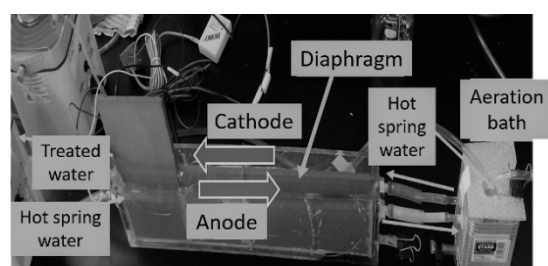


Fig.1 (b) The electrolytic equipment used for the experiment

Table 1 Water quality of the Gero hot spring

	pH	Na ⁺ (mg/l)	K ⁺ (mg/l)	Mg ²⁺ (mg/l)	Ca ²⁺ (mg/l)	F ⁻ (mg/l)	Cl ⁻ (mg/l)	SO ₄ ²⁻ (mg/l)	As (mg/l)	Alkalinity (μeq/l)
Literature[11]	9.5	108.9	1.2	0	1.9	16.5	75	10.9	140	-
Measured value	9.2	105.2	0.6	0	0	16.9	75	11.4	114	1329

2.1 Effect of The Flow Rate Ratio

The flow rate ratio of the hot spring water supplied to the anode bath (a) and the aeration bath (b) was varied— $a:b=10:0$, $5:5$, $2:8$, or $0.6:9.4$ —under conditions in which the magnesium concentration and the current were set at 100 mg/L and 120 mA, respectively.

2.2 Effect of The Magnesium Concentration

The magnesium concentration was varied—0, 50, 100, or 200 mg/L—under conditions in which the flow rate ratio and the current were set at $a:b=0.6:9.4$ and 120 mA, respectively.

2.3 Effect of The Electrolysis Current

The current was varied—80, 120, or 200 mA—under conditions in which the flow rate ratio and the magnesium concentration were set at $a:b=0.6:9.4$ and 100 mg/L, respectively.

2.4 Analyses

Sampling was conducted at the raw water exit, +1 cell, +2 cell, aeration bath, -1 cell, and -2 cell after continuing to operate for 24 hours or more for stabilizing.

The concentration of As was analyzed by ICP-MS (Agilent 7700 Series).

The ionic component concentrations of F^- , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Na^+ , K^+ , NH_4^+ , Mg^{2+} , and Ca^{2+} were analyzed by ion chromatographs.

(Cation: Thermo ICS 1500, separation column IonPac CS 12A, eluent methanesulfonic acid 30 mmol/L, suppressor CERS 500)

(Anion: Thermo ICS 2000, separation column IonPac AS 18, eluent KOH 23–40 mmol/L (gradient), suppressor AERS 500)

The pH was measured by a glass electrode method with a BECKMAN ϕ 32 pH Meter (electrode: BECKMAN 511070).

3. RESULTS AND DISCUSSION

3.1 Effect of The Flow Rate Ratio

Fig.3.1 (a) shows the effect of the flow ratio on the removal rate of fluorine and arsenic. When the anode side had a small flow rate, a higher removal rate was observed. The fluoride concentrations in each cell with various flow rate ratios are shown in Fig.3.1 (b), and the arsenic concentrations are shown in Fig.3.1 (c). When the flow rate ratio was $a:b=10:0$, the entire amount of raw water was supplied to the anode. On the other hand, when $a:b=0.6:9.4$, the majority were supplied to the mixed aeration tank.

When the flow rate ratio $a:b=10:0$, no significant change in fluorine concentration was observed in each cell. On the other hand, in the case of $a:b=0.6:9.4$, the fluoride concentration increased slightly due to the Coulomb force in the +1 cell and the +2 cell; however, the fluoride concentration was close to that of the raw water in the aeration bath to which the majority of the raw water was supplied. Thereafter, the fluoride concentration rapidly decreased in -1 and -2 cells. For arsenic, even when the flow rate ratio was $a:b=10:0$, the arsenic concentration decreased in the -1 and -2 cells. The highest removal ratio of arsenic was also recorded when the flow rate ratio was $a:b=0.6:9.4$.

The pH and magnesium concentrations in each cell at various flow rate ratios are shown in Fig.3.1 (d) and Fig.3.1 (e), respectively. The pH in the aeration bath was less than 4 irrespective of the flow rate ratio, indicating that carbonate and bicarbonate had been removed. When the flow rate ratio was $a:b=10:0$ and $a:b=0.6:9.4$, there was a difference in pH in the -1 and -2 cells. In the former case, the pH in the -2 cell was 8.10, while in the latter case, it was 10.05. When taking the solubility of magnesium as 16.6×10^{-5} mol/L [12], the solubility product is calculated to be $K_{sp}=[Mg^{2+}][OH^-]^2 = [16.6 \times 10^{-5}][33.2 \times 10^{-5}]^2 = 1.83 \times 10^{-11}$. When the same solubility product is assumed, a magnesium concentration of 35 mg/L in the solution is obtained at $pH=10.01$, which almost coincides with the measured value of 34 mg/L. At pH 8.10, if the same solubility product of magnesium hydroxide is assumed, the solubility is $(10^{(10.05-8.10)})^2=7900$ times higher than that at $pH=10.05$, indicating that theoretically, no precipitation occurs. In fact, slight precipitation was found only in the vicinity of the electrode. Consequently, the magnesium concentration did not decrease greatly, as shown in Fig.3.1 (e). The difference in the pH value in the -2 cell affects the formation of $Mg(OH)_2$ and the removal of arsenic and fluoride.

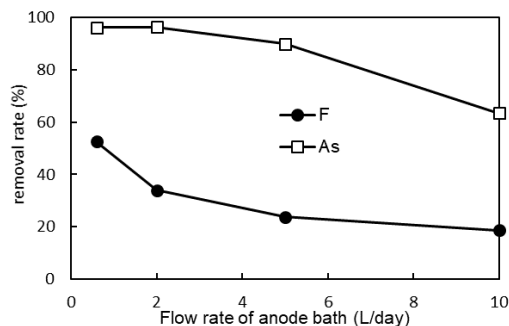


Fig.3.1 (a) Effect of the flow rate ratio on the removal rates of fluoride and arsenic

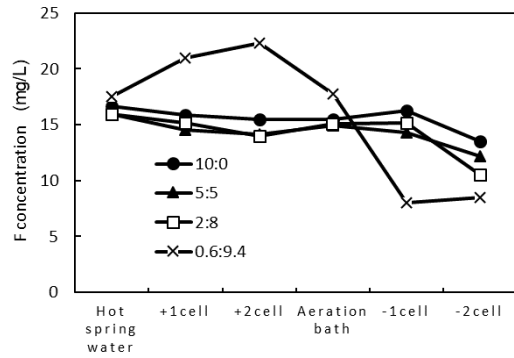


Fig.3.1 (b) Change in the fluoride concentration in each cell

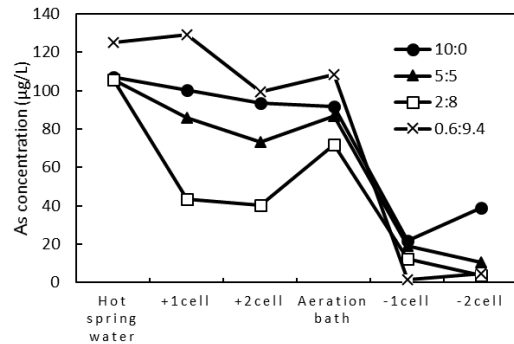


Fig.3.1 (c) Change in the arsenic concentration in each cell

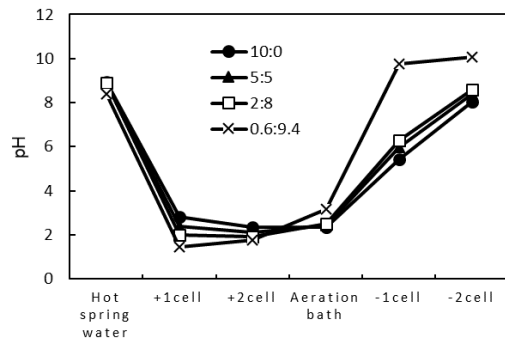


Fig.3.1 (d) Change in the pH in each cell

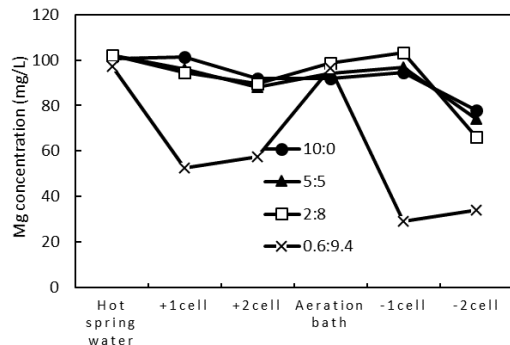


Fig.3.1 (e) Change in the Mg concentration in each cell

3.2 Effect of The Magnesium Concentration

Fig.3.2 (a) shows the influence of fluoride and arsenic on the removal rate when the magnesium

concentration in the raw water was varied. The higher the magnesium concentration, the higher the removal rate of fluoride and arsenic. However, when the magnesium concentration was 50 mg/L or more, the removal rate of arsenic stayed within 90 to 100%.

Fig.3.2 (b) and (c) show the fluoride concentration and the arsenic concentration, respectively, in each cell when the magnesium concentration was varied. In the legend of the figures, Mg 0, Mg 50, Mg 100, and Mg 200 indicate when the magnesium concentration in the raw water was 0 mg/L, 50 mg/L, 100 mg/L, and 200 mg/L, respectively. When the magnesium concentration was varied between 100 and 200 mg/L, 8 mg/L (removal rate 53%) of the fluoride concentration in the treated water (-2 cell) was obtained. The arsenic concentration in treated water (-2 cell) was less than 10 µg/L when the magnesium concentration was 50 mg/L or more.

Fig.3.2 (d) and (e) show the pH and the magnesium concentration, respectively, in each cell when the magnesium concentration was varied. When 200 mg/L of magnesium was added, about 100 mg/L of magnesium remained in the treated water (-2 cell). The reason is that the pH did not increase sufficiently. However, the magnesium reduction from the raw water in treated water (-2 cell) was largest when 200 mg/L of magnesium was added, leading to the highest removal of fluoride.

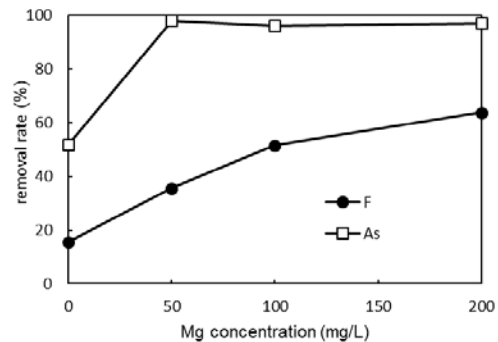


Fig.3.2 (a) Effect of the magnesium concentration on the removal rates of fluoride and arsenic

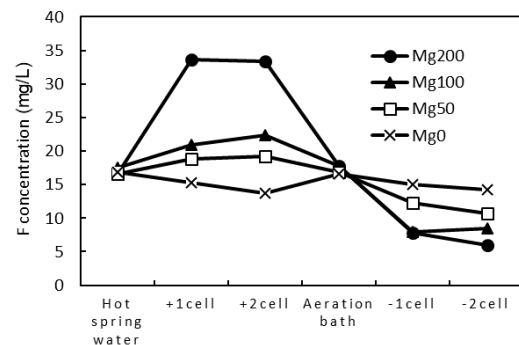


Fig.3.2 (b) Fluoride concentration for different Mg concentrations

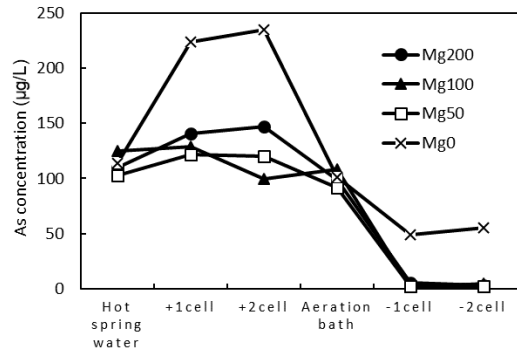


Fig.3.2 (c) Arsenic concentration for different Mg concentrations

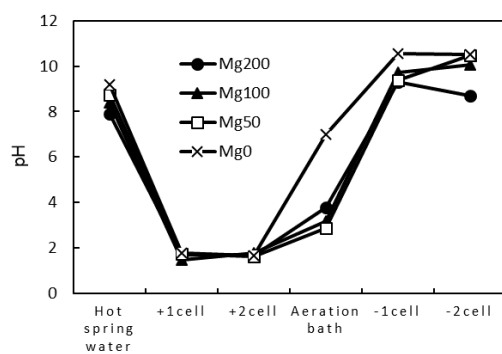


Fig.3.2 (d) pH for different Mg concentrations

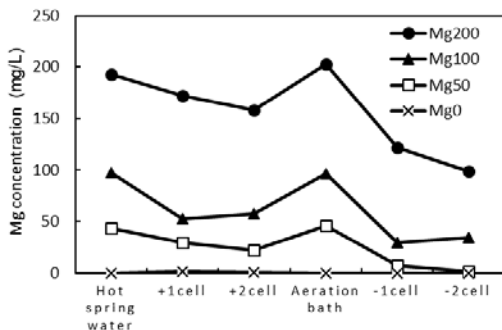


Fig.3.2 (e) Magnesium concentration for different Mg concentrations

3.3 Effect of The Electrolysis Current

Fig.3.3 (a) shows the influence of the current on the removal rates of fluoride and arsenic. Fig.3.3 (b) and (c) show the fluorine concentration and the arsenic concentration, respectively, when the electrolysis currents were varied. Electrolysis currents larger than 120 mA did not increase fluoride removal but did increase arsenic removal. As shown in Fig.3.3 (c), when the current was 120 mA or more, an arsenic concentration of less than 10 µg/L was obtained. The pH and magnesium of each cell are shown in Fig.3.3 (d) and Fig.3.3 (e), respectively. Changes in pH due to different currents were hardly observed; however,

differences in magnesium concentrations were observed in each cell. With a current of 80 mA, magnesium was not sufficiently precipitated, which could be the cause of the low removal rates of fluoride and arsenic.

When the current was 120 mA, the fluoride removal rate was the highest, and the fluoride concentration met the national minimum effluent standard. The arsenic concentration was also less than 10 µg/L.

The amount of electricity per day with a current of 120 mA was calculated to be 10400 C/day. Since the flow rate was 10 L/day, the electricity required per 1 L was 1040 C/L.

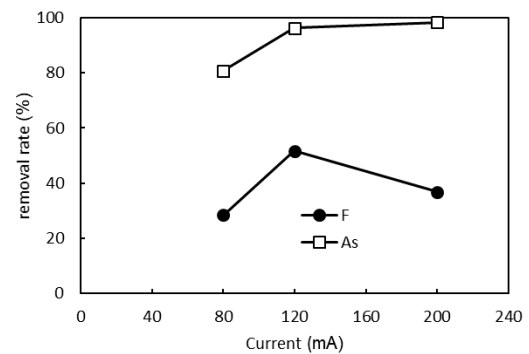


Fig.3.3 (a) Effect of the current on removal rates of fluoride and arsenic

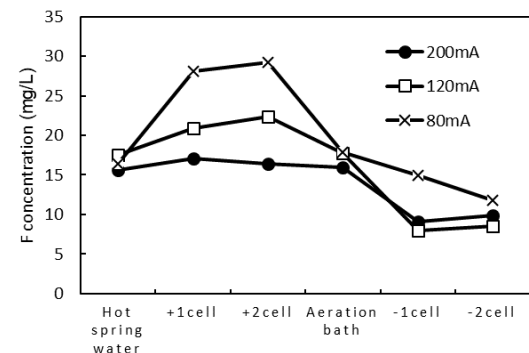


Fig.3.3 (b) Fluoride concentrations in different currents

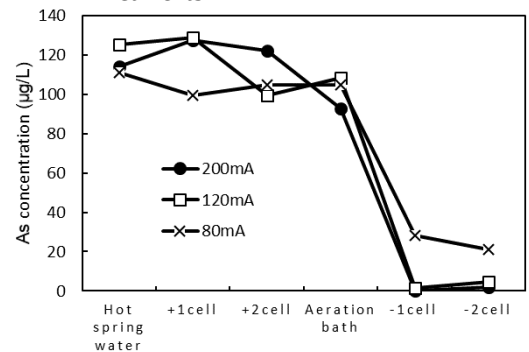


Fig.3.3 (c) Arsenic concentrations in different currents

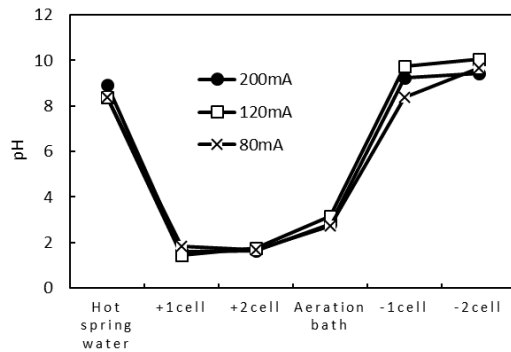


Fig.3.3 (d) pH in different currents

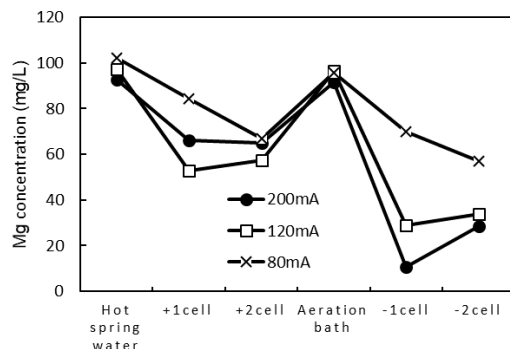


Fig.3.3 (e) Magnesium concentrations in different currents

4. CONCLUSION

An electrolysis system was operated with the aim of simultaneously removing fluorine and arsenic from hot spring wastewater. The electrolysis system consisted of electrolytic cells separated by a diaphragm made of an uncalcined plate. The electrolysis system was used to remove arsenic and fluoride by the co-precipitation of magnesium hydroxide on the cathode side with fluoride or arsenic.

The wastewater of the Gero hot spring was used as a model. Since the Gero hot spring did not contain magnesium, magnesium was added externally. The addition of 100–200 mg/L could reduce the fluorine concentration in raw water from 16.9 mg/L to 8 mg/L or less. Simultaneously, the arsenic concentration could be reduced from 114 µg/L to 10 µg/L or less.

5. ACKNOWLEDGMENTS

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