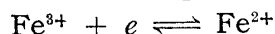


64. Yasushi Mashiko : On the Relation between the Aging of Iron Spring and its Oxidation-Reduction Potential.

(Chemical Institute of Hot Spring Research Center*)

The mineral springs and hot springs are, in general, natural oxidation-reduction systems. It is known that these springs contain hydrogen sulfide, ferrous ion, arsenious acid ion, manganous ion, oxygen, etc. Before the spring wells out, all of these substances are generally in a reduced state, but an oxidation reaction, the so-called aging or Veraltung, begins to proceed immediately after the spring is exposed to air. The aging involves not only the oxidation but other phenomena, but it is well known that oxidation plays an important part in the aging.

Therefore, oxidation-reduction potential measurement of springs was carried out in order to investigate the nature of aging in iron springs. In iron spring, a reversible oxidation-reduction reaction is considered to proceed as follows :



Seki¹⁻³⁾ and Matsumi⁴⁾ reported several studies on the oxidation-reduction potential of many hot springs in Japan by colorimetric method using some indicators. These papers involve very interesting qualitative discussions on hot springs, but some electrochemical potentiometric methods are expected to be more suitable in order to discuss further, quantitatively and more precisely.

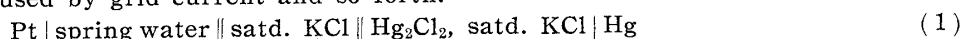
Experimental Method

Indicator Electrode : Platinum plate (about 4 cm²).

Reference Electrode : Saturated calomel electrode.

Potentiometer : Potentiometric circuit of Towa Dempa Co., Model HM-3 pH meter.

The spring water tested was stirred quickly with a magnetic stirrer to prevent unfavorable polarization caused by grid current and so forth.



The sign of the cell potential was defined as follows : If the direction of current is from right to left in the cell (1), in working state, the electromotive force of the cell was regarded as positive. Therefore, half-electrochemical reaction can be written as follows :



and its electromotive force E is given by the following equation :

$$E = E_0 + \frac{RT}{nF} \ln \frac{[\text{Oxid.}]}{[\text{Red.}]} \quad (3)$$

E_0 is the standard potential of reaction (2), R the gas constant, F the farady, n the number of equivalents in reaction (2), and [Oxid.] or [Red.] represents the activity (or concentration) of reacting substance of oxidized or reduced state in spring water.

Standard Potential of $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$ and Formal Potential of Iron Spring.

An accurate value of standard potential, E_0 , between Fe^{3+} and Fe^{2+} , by the measurement of Schumb and Sweeter,⁵⁾ is +0.783 v. vs. N.H.E., but our observations on iron springs in Japan show that the formal potential of mineral springs shifts toward negative direction from the standard potential. Range of the deviation is within several hundred millivolts (mv.). The formal potential mentioned above is defined as the potential of the spring when the concentration of Fe^{2+} is 1/2 the total content of iron in the spring. For example, in the case of Yubatake Spring in

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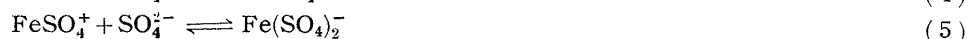
- 1) M. Seki : J. Japan. Balneoclimatol. Assoc., **14**, 86(1949).
- 2) M. Seki, O. Kamisaka : J. Balneol. Soc. Japan, **4**, 18(1950).
- 3) M. Seki : J. Japan. Balneoclimatol. Assoc., **15**, 1(1949).
- 4) H. Matsumi : *Ibid.*, **15** 48(1949).
- 5) W.C. Schumb, S.B. Sweeter : J. Am. Chem. Soc., **57**, 851(1935).

Kusatsu Spa, an acidic vitriol spring, the deviation is 0.06 v., and that in Ikaho Spring, iron carbonated spring, is about 0.6 v.

Without doubt these deviations are caused by the complex formation or hydrolysis of Fe^{3+} . The complex formation mainly occurs between Fe^{3+} and SO_4^{2-} . Cl^- , F^- , and ion of phosphoric acid may also form a complex with Fe^{3+} , and in fact, F^- and ion of phosphoric acid form a complex or insoluble precipitate in mineral springs, but iron(III) chloride complex has lower stability than that of SO_4^{2-} in acidic vitriol springs and the content of Cl^- is generally smaller than that of SO_4^{2-} . F^- and ion of phosphoric acid are present in a very small concentration with SO_4^{2-} or total iron content.

Therefore, it may be considered that one of the main factors controlling the oxidation-reduction potential of an iron spring is the complex formation between Fe^{3+} and SO_4^{2-} , as well as the hydrolysis of Fe^{3+} , after some amount of Fe^{3+} has been formed by aging of the mineral spring. This hypothesis can be applied only in a strongly acidic range, because a more stable hydrolysis of Fe^{3+} will occur in a weakly acidic or neutral range.

The iron(III)-sulfate complex⁶⁾ is reported to be as follows:



A more detailed studies⁷⁻⁹⁾ have been reported on the hydrolysis of Fe^{3+} in a solution of simple constituents such as FeCl_3 in dil. HCl. According to these works, the hydrolysis of Fe^{3+} is represented as follows:



Discussions will be made on the oxidation-reduction potential of iron springs during the process of aging, relating the above equilibria.

Oxidation-Reduction Potential of Artificial Iron Spring

The simplest artificial iron spring was prepared by dissolving FeSO_4 in dil. H_2SO_4 . Its character changed continuously from acidic vitriol spring to vitriol spring and then to iron carbonated or carbonated spring by the addition of NaHCO_3 . The oxidation-reduction potential of artificial springs was measured, keeping the ratio of Fe^{2+} to Fe^{3+} constant by bubbling oxygen-free CO_2 , and changing the pH value by the addition of NaHCO_3 . The initial composition of the artificial iron springs used and the results of measurements are shown in Table I and Figs. 1, 2, and 3.

TABLE I. Initial Composition of Artificial Iron Spring

Component ^{a)}	No.1 (mole/L.)	No.2 (mole/L.)	No.3 (mole/L.)
Total SO_4^{2-}	0.0095	0.0441	0.483
Fe^{2+}	0.00165	0.001773	0.00112
Total Fe^{3+}	0.001108	0.00052	0.000831
pH	2.0	1.35	0.8

a) SO_4^{2-} was determined by gravimetry by BaSO_4 method.

Fe^{2+} was titrated with 0.01N KMnO_4 .

Fe^{3+} was determined by iodometry after reduction with Cu_2I_2 .

Analysis of pH-Oxidoreduction Potential Curves of Artificial Iron Springs

Three pH-potential curves shown in Figs. 1~3 have an identical shape, but the higher the formal concentration of sulfate ion in iron spring, the wider the plateau (Part A) of the pH-potential curve. Namely, the steep slope (Part C) shifts to a higher pH value.

1) Part A: The phenomenon, in which the oxidation-reduction potential does not change markedly with a small change of pH values under the fixed formal sulfate concentration and a fixed ratio of formal Fe^{2+} to Fe^{3+} , is observed in the iron spring having strongly acidic pH value.

This phenomenon can be written mathematically as follows:

$$\partial E / \partial \text{pH} = 0 \quad (9)$$

The oxidation-reduction potential, E , of these springs is given by the following equation:

$$E = E_0 + \frac{RT}{F} \ln \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \quad (10)$$

where E_0 is the standard potential of $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$, $[\text{Fe}^{3+}]$ the simple Fe^{3+} concentration or

6) R. A. Whiteker, N. Davidson: J. Am. Chem. Soc., **75**, 3081(1953).

7) N. Bjerrum: Z. physiol. Chem., **59**, 350(1907).

8) W. C. Bray, A. V. Hershey: J. Am. Chem. Soc., **56**, 1889(1934).

9) A. B. Lamb, A. G. Jaques: *Ibid.*, **60**, 967, 1215(1938).

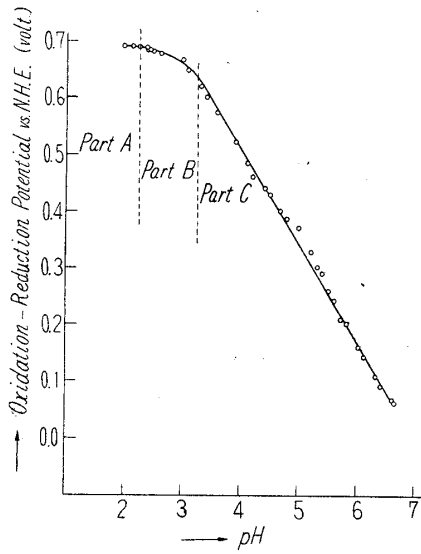


Fig. 1. pH-Potential Curve of Artificial Iron Spring (No. 1)

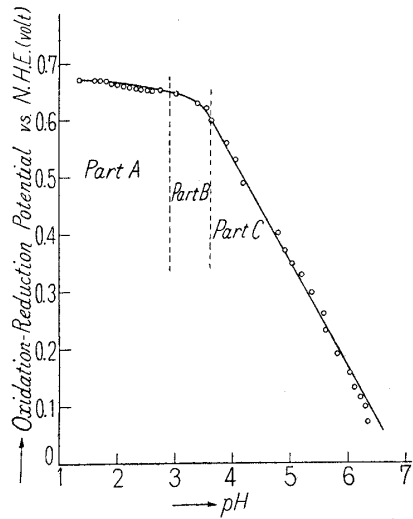


Fig. 2. pH-Potential Curve of Artificial Iron Spring (No. 2)

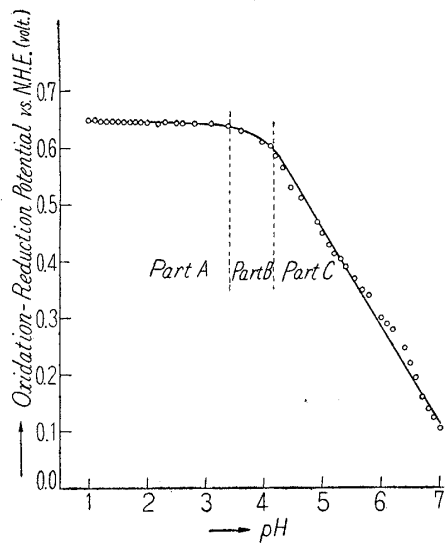


Fig. 3. pH-Potential Curve of Artificial Iron Spring (No. 3)

activity, $[\text{Fe}^{2+}]$ the simple Fe^{2+} concentration or activity. The absence of change of E with the change in pH values shows that practically no hydrolysis occurs in such a pH range.

However, the formal potential of these strongly acidic vitriol springs is not identical with the standard potential of $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$. It is, therefore, suggested that the complex formation between Fe^{3+} and SO_4^{2-} must occur in the spring. Whiteker and Davidson⁶⁾ reported in their paper that Fe^{3+} in solution acidified with H_2SO_4 formed iron(III)-sulfate complex such as $\text{Fe}(\text{SO}_4)^+$ or $\text{Fe}(\text{SO}_4)_2^-$.

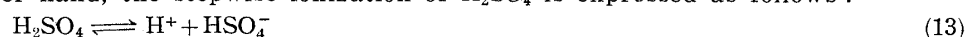
Generally, these complex formations are expressed as follows :



According to the law of mass action, the stability constant of complex ion, K_1 , would be written as follows :

$$K_1 = \frac{[\text{Fe}(\text{SO}_4)_n^{(3-2n)+}]}{[\text{Fe}^{3+}][\text{SO}_4^{2-}]^n} \quad (12)$$

On the other hand, the stepwise ionization of H_2SO_4 is expressed as follows :



The following two equations will then be derived from the above equilibria :

$$K_2 = \frac{[\text{H}^+][\text{HSO}_4^-]}{[\text{H}_2\text{SO}_4]} \quad (15)$$

$$K_3 = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} \quad (16)$$

K_2 or K_3 is the constant of the primary or secondary ionization. If the formal concentration of SO_4^{2-} is represented as $C_{\text{SO}_4^{2-}}$, the following equation will be derived from the equations (10), (12), (15), and (16) :

$$E = E_0 + \frac{RT}{F} \ln [\text{Fe}(\text{SO}_4)_n^{(3-2n)+}] - \frac{RT}{F} \ln K_1 - \frac{RT}{F} \ln [\text{Fe}^{2+}] - n \frac{RT}{F} \ln \{ C_{\text{SO}_4^{2-}} - n [\text{Fe}(\text{SO}_4)_n^{(3-2n)+}] \} + n \frac{RT}{F} \ln \left\{ 1 + \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_2 \cdot K_3} \right\} \quad (17)$$

When the formal SO_4^{2-} concentration is sufficiently larger than the formal Fe^{3+} concentration, as in the case of artificial iron springs No. 2 and 3, equation (17) can be simplified as equation (18).

$$E = E_0 + \frac{RT}{F} \ln C_{\text{Fe}^{3+}} - \frac{RT}{F} \ln K_1 - \frac{RT}{F} \ln [\text{Fe}^{2+}] - n \frac{RT}{F} \ln C_{\text{SO}_4^{2-}} + n \frac{RT}{F} \ln \left\{ 1 + \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_2 \cdot K_3} \right\} \quad (18)$$

$C_{\text{Fe}^{3+}}$ is the formal concentration of ferric ion.

The potentials, E_2 and E_3 , of the artificial iron springs No. 2 and 3 shown in Table I in strongly acidic range at 20° are expressed as follows :

$$E_2 = E_0 + 0.059 \times \log 0.00052 - 0.059 \times \log K_1 - n \times 0.059 \times \log 0.0441 + n \times 0.059 \times \log \left\{ \frac{[\text{H}^+]^2}{K_2 \cdot K_3} + \frac{[\text{H}^+]}{K_3} + 1 \right\} - 0.059 \times \log 0.00177 \quad (19)$$

or

$$E_3 = E_0 + 0.059 \times \log 0.000831 - 0.059 \times \log K_1 - n \times 0.059 \times \log 0.483 + n \times 0.059 \times \log \left\{ \frac{[\text{H}^+]^2}{K_2 \cdot K_3} + \frac{[\text{H}^+]}{K_3} + 1 \right\} - 0.059 \times \log 0.00112 \quad (20)$$

At the same pH value as those of the iron springs No. 2 and 3, equation (21) is derived from (19) and (20) :

$$n = \frac{(E_2 - E_3) + 0.024}{0.061} \quad (21)$$

The coordinate number, n , of SO_4 ion to iron(III)-sulfate complex ion can be calculated from this equation (21). The n calculated from the potentials in Figs. 2 and 3 are shown in Table II.

TABLE II.

pH	E_2	E_3	n
1.35	0.668	0.646	0.8 } ≈ 1
1.5	0.668	0.646	
2.0	0.661	0.644	0.7
2.5	0.652	0.642	0.6

The result of calculation for n shows that the complex formation in strongly acidic vitriol spring (namely at pH 1.35~1.5 in Table II) is suggested as follows :



Therefore, the oxidation-reduction potential of strongly acidic vitriol spring at 20° can be represented as follows:

$$E = E_0 + 0.059 \times \log C_{\text{Fe}^{3+}} - 0.059 \times \log K_1 - 0.059 \times \log [\text{Fe}^{2+}] - 0.059 \times \log C_{\text{SO}_4^{2-}} + 0.059 \times \log \left\{ 1 + \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_2 \cdot K_3} \right\} \quad (23)$$

The fact that the value of $\partial E/\partial \text{pH}$ from equation (23) is not zero, and further that the experimental results show the value of $\partial E/\partial \text{pH}$ to be almost zero, suggest that the following relation must be established in strongly acidic range usually observed in acidic vitriol spring:

$$1 \gg \frac{[\text{H}^+]}{K_3} + \frac{[\text{H}^+]^2}{K_2 \cdot K_3} \quad (24)$$

Relation of (24) means that the ionization of sulfuric acid in such pH range of acidic vitriol spring is large by interaction of coexisting ions and so it may be regarded almost as complete ionization. Equilibrium (22) and the values of $\partial E/\partial \text{pH}$ of natural acidic vitriol springs in Japan will be discussed in the following section again with another experiment.

2) Part C: $\partial E/\partial \text{pH} = 0.177$ volt/pH at 20°.

Now the analysis of section C will be made. The stepwise hydrolysis of Fe^{3+} mentioned above occurs in weak acidic vitriol, iron carbonated, or iron carbondioxated spring. The practical and theoretical studies on this hydrolysis have been made by Rabinowitch and Stockmeyer,¹⁰⁾ Lamb and Jacques,⁹⁾ Bray and Hershey,⁸⁾ and by other investigators. As a result of this hydrolysis in such small hydrogen ion concentration of iron springs as in Part C, sparingly soluble $\text{Fe}(\text{OH})_3$ is separated from the spring, and the oxidation-reduction potential of such iron spring is controlled by the solubility of $\text{Fe}(\text{OH})_3$ deposited. Therefore, when the solubility product of $\text{Fe}(\text{OH})_3$ is expressed as (25), the oxidation-reduction potential of such iron spring can be written as equation (26).

$$[\text{Fe}^{3+}][\text{OH}^-]^3 = S \quad (25)$$

$$E = E_0 + \frac{RT}{F} \ln S \cdot K_w^{-3} - 3 \times \frac{RT}{F} \ln \frac{1}{[\text{H}^+]} - \frac{RT}{F} \ln [\text{Fe}^{2+}] \quad (26)$$

From equation (26), the value of $\partial E/\partial \text{pH}$ is

$$\frac{\partial E}{\partial \text{pH}} = -0.177 \text{ v./pH} \dots \dots \text{at } 20^\circ \quad (27)$$

The experimental results shown in Figs. 1, 2, and 3 are in good agreement with the theoretical values from equation (26). As an example in which oxidation-reduction potential of natural spring is expressed as equation (26), Arima Spring will be cited (cf. following section).

3) Part B: The connexion between Parts A and C, namely Part B, seems to result from the fact that oxidation-reduction potential of iron spring having such pH value, SO_4^{2-} , and ionic strength as those in Part B is controlled not only by the occurrence of complex formation between Fe^{3+} and SO_4^{2-} , but also by the first and second hydrolysis of Fe^{3+} accompanied with the complex ion formation mentioned above. Therefore, the form of Fe^{3+} dissolved in the spring will be FeSO_4^+ , FeOH^{2+} , and $\text{Fe}(\text{OH})_2^+$. The relation of the concentration between these ions will be shown by the following equations:

$$\frac{[\text{FeSO}_4^+]}{[\text{FeOH}^{2+}]} = [\text{H}^+][\text{SO}_4^{2-}]K_1 \cdot K_{h_1}^{-1} \quad (28)$$

$$\frac{[\text{Fe}(\text{OH})_2^+]}{[\text{FeSO}_4^+]} = [\text{H}^+]^2[\text{SO}_4^{2-}]K_1 \cdot K_{h_1}^{-1} \cdot K_{h_2}^{-1} \quad (29)$$

where K_{h_1} and K_{h_2} are expressed as

$$\frac{[\text{H}^+][\text{FeOH}^{2+}]}{[\text{Fe}^{3+}]} = K_{h_1} \quad (30)$$

$$\frac{[\text{H}^+][\text{Fe}(\text{OH})_2^+]}{[\text{FeOH}^{2+}]} = K_{h_2} \quad (31)$$

According to this view, the oxidation-reduction potential of the spring in which Fe^{3+} is mainly dissolved as FeSO_4^+ , FeOH^{2+} , and $\text{Fe}(\text{OH})_2^+$ is expressed by equation (32).

$$E = E_0 + \frac{RT}{F} \ln C_{\text{Fe}^{3+}} - \frac{RT}{F} \ln \left\{ [\text{SO}_4^{2-}]K_1 + [\text{H}^+]^{-1} \cdot K_{h_1} + [\text{H}^+]^{-2} \cdot K_{h_1} \cdot K_{h_2} \right\} - \frac{RT}{F} \ln [\text{Fe}^{2+}] \quad (32)$$

10) E. Rabinowitch, W.H. Stockmeyer: J. Am. Chem. Soc., **64**, 335(1942).

where
$$C_{\text{Fe}^{3+}} = [\text{FeSO}_4^+] + [\text{FeOH}^{2+}] + [\text{Fe}(\text{OH})_2^+] \quad (33)$$

$\partial E/\partial \text{pH}$ and $\partial E/\partial(-\log C_{\text{SO}_4^{2-}})$ of Natural Iron Springs in Japan

Iron springs in Japan can be classified into two types. The one is a cold spring which contains Fe^{3+} at welling and the other is a volcanic hot spring which contains practically no Fe^{3+} at welling.

Therefore, the foregoing knowledge is useful to the analysis of a cold iron spring at welling, and is also useful to that of the hot spring after certain extent of Fe^{2+} has been oxidized by aging. In order to examine the nature of the spring containing certain amount of Fe^{3+} , aging was prevented by bubbling oxygen-free CO_2 before the measurement of potentials. The pH value of the spring was varied stepwise by the addition of NaHCO_3 and its potential was measured at each pH value. The results obtained from several iron springs in Japan are described below.

1) Yubatake Iron Spring in Kusatsu Spa (Gumma Pref., northern Kwanto area):

Yubatake Spring belongs to H_2S -acidic vitriol-alum spring, and its pH value is 1.45, the temperature 63.5° , and it contains 105.9 mg./kg. of total iron ion at welling.¹¹⁾ The pH-potential curve of Yubatake Spring obtained by the foregoing method is shown in Fig. 4. The spring water used showed a ratio of 0.71 of Fe^{3+} to Fe^{2+} as the formal concentration.

In Fig. 4, the tangent of the curve is horizontal at initial pH (natural value of Yubatake spring water). So it is clear that hydrolysis of Fe^{3+} in this spring is negligible and it corresponds to Part A described in the preceding section. Therefore, it is deduced that Fe^{3+} forms iron(III)-sulfate complex cation, $\text{Fe}(\text{SO}_4)^+$.

Existence of iron(III)-sulfate complex cation in this spring can be recognized more precisely by plotting $(\log C_{\text{SO}_4^{2-}})$ against oxidation-reduction potential, because $\partial E/\partial(-\log C_{\text{SO}_4^{2-}})$ of the curve should show $+0.059 \text{ v./}(-\log C_{\text{SO}_4^{2-}})$ and $-\log C_{\text{SO}_4^{2-}}$ potential curve a straight line from equation (23). In order to examine this relationship, conc. H_2SO_4 was added into the spring under the bubbling of oxygen-free CO_2 , the pH value of the sample was adjusted to the initial point by the addition of NaHCO_3 , using a glass-electrode pH meter, and the oxidation-reduction potential was measured with Pt electrode before and after the foregoing treatment. Total SO_4^{2-} concentration was also determined gravimetrically by BaSO_4 method at each plotting. The result of the experiment is shown in Fig. 5.

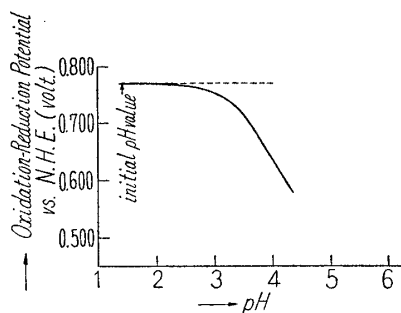


Fig. 4. pH-Potential Curve of Yubatake Spring

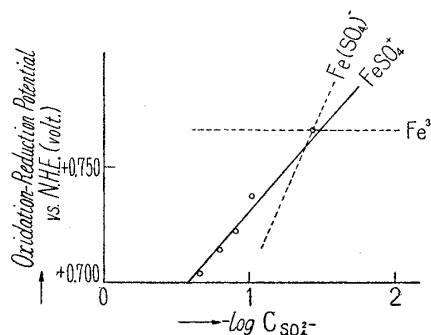


Fig. 5. $(\log C_{\text{SO}_4^{2-}})$ -Potential Curve of Spring

The Curve in Fig. 5 is in good agreement with the theoretical value and so it is clear that Fe^{3+} changed from Fe^{2+} by aging in Yubatake Spring exists mainly in the form of iron(III)-sulfate complex cation, such as $\text{Fe}(\text{SO}_4)^+$.

2) Maka Spring in Hokkaido:

Maka Spring belongs to the common salted, acidic-alum-vitriol spring. It is a cold mineral spring having pH 2.20 and containing 24,920 mg./kg. of total solute, the total sulfate ion being 20,446 mg./kg. and total iron ion 2,447 mg./kg.¹²⁾

The pH-potential curve is plotted in Fig. 6 and the $(-\log C_{\text{SO}_4^{2-}})$ -potential curve showed a shape identical to that of Yubatake Spring.

From these data, it can be concluded that Fe^{3+} in Maka Spring mainly forms iron(III)-sulfate complex cation, $\text{Fe}(\text{SO}_4)^+$, as in the case of Yubatake Spring in Kusatsu Spa.

3) Tsurugi Spring (Ishikawa Pref., near Noto Peninsula in northwest coast on Japan Sea):

It shows 20.5° at welling and belongs to acidic vitriol spring containing 1,816 mg./kg. of solute,

- 11) "Nippon Kôsen-shi" (Mineral Springs in Japan), Ministry of Health and Welfare, Japan, 299 (1954),
 12) *Ibid.*, 34(1954).

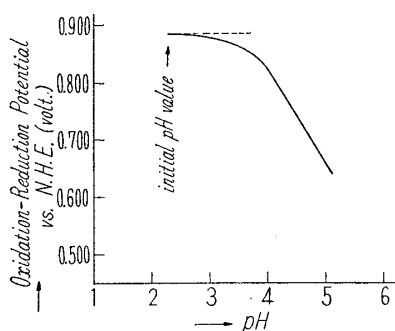


Fig. 6. pH-Potential Curve of Maka Spring

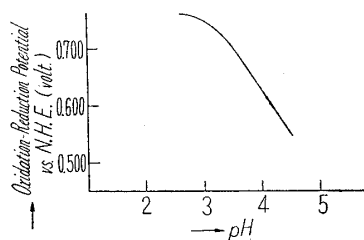


Fig. 7. pH-Potential Curve of Tsurugi Spring

101 mg./kg. of total iron ion, and 1,312 mg./kg. of total sulfate ion. The pH of the spring is 2.6 at welling.¹³⁾ The pH-potential curve of this spring is shown in Fig. 7.

The $\partial E/\partial \text{pH}$ value is -17 mv./pH at the initial point of the curve. It can be considered from this experiment that Fe^{3+} forms FeSO_4^+ with SO_4^{2-} , FeOH^{2+} by hydrolysis, and perhaps a small amount of $\text{Fe}(\text{OH})_2^+$ is also present.

4) Ichinoyu Spring in Arima Spa (Hyogo Pref., near Kobe):

The Ichinoyu Spring belongs to earthy, common salted, iron carbondioxated spring containing 14,717 mg./kg. of NaCl, 2,896 mg./kg. of CaCl_2 , and 608.8 mg./kg. of $\text{Fe}(\text{HCO}_3)_2$.¹⁴⁾ The pH-potential curve of the spring is shown in Fig. 8.

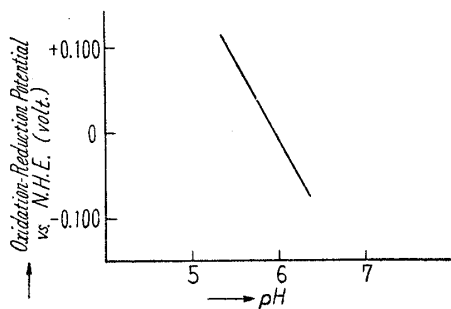


Fig. 8. pH-Potential Curve of Ichinoyu Spring

It is shown from this experiment that Fe^{2+} was oxidized by air in aging process to Fe^{3+} , which was further hydrolysed into $\text{Fe}(\text{OH})_3$ in the case of Ichinoyu spring.

Changes of Oxidation-Reduction Potential of Acidic Vitriol Springs by Aging

In connection with several equilibria controlling the oxidation-reduction potential of iron springs, some discussions have already been given with the experiments on artificial and natural springs. In this section, an explanation will be made on the fact that there exists some difference between the changes of oxidation-reduction potential of natural, strongly acidic vitriol hot springs, such as the Yubatake Spring, and that of artificial spring prepared according to the table of chemical analysis of natural spring, when both are stood in air.

Oxidation-reduction potential of Yubatake Spring was about -0.1 to $+0.05$ volt vs. N.H.E. at room temperature, when it was sealed in a glass vessel immediately after welling and brought to this laboratory. The ferric ion in the spring was negative by thiocyanate test in such a state. Therefore, it contained practically no ferric ion. The potential of the spring drifted toward positive direction in several minutes, probably because of the evaporation of hydrogen sulfide gas by stirring in a glass beaker. When the same sample was left to stand at room temperature, the odor of hydrogen sulfide was lost after two days.

13) "Onsen Bunseki Kenteisho" (Analysis of Mineral Springs), Hot Spring Research Center, Tokyo (1956).

14) "Zenkoku-Kôsen-Chôsa" (Investigations of Mineral Springs in Japan), Sanitation Bureau, Ministry of Home Affairs, Japan, 218(1935).

The oxidation-reduction potential of this sample showed +0.55 volt vs. N.H.E.

After a few more days, the thiocyanate reaction of the spring turned positive and the oxidation-reduction potential drifted to a more positive direction, as shown in Fig. 9. With the artificial spring, which was prepared according to the table of Yubatake Spring already cited, the same change of potential was observed until the odor of hydrogen sulfide disappeared, but further deviation of the potential to a more positive value than 0.55 volt vs. N.H.E. could not be observed.

Sulfuric acid solution of ferrous sulfate, holding the same pH value as the Yubatake Spring and showing 0.56 volt vs. N.H.E. of oxidation-reduction potential, kept its potential after standing for two weeks, as shown in Fig. 9.

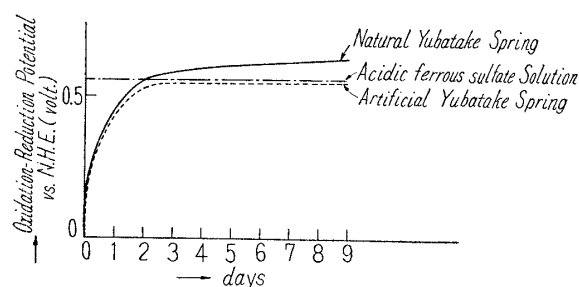
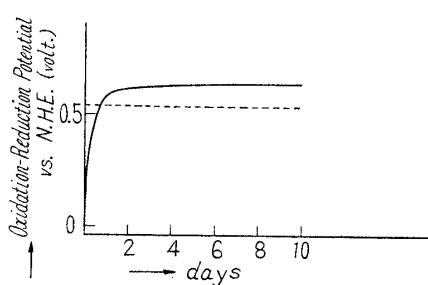
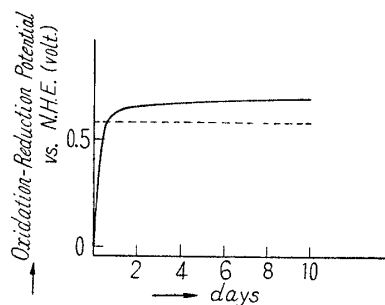


Fig. 9.
Time-Potential Curve

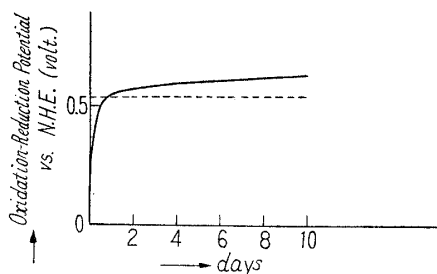
It may be recognized that the observations mentioned above have much in common with a research by Fredenhagen¹⁵⁾ who studied the stability of acidic ferrous chloride solution against oxidation by air. He also reported that the addition of a small amount of Bredig's platinum solution caused a rapid oxidation of ferrous ion by air in 0.1N hydrochloric acid solution. In lieu of his experiments, a small amount of 17 elements, Cu, Mn, Ni, Co, Zn, Pt, Pb, Bi, La, V, Zr, U, Th, Cs, Ce, Sb, and Li, was each added to artificial Yubatake Spring for the same expectation, but it was found that none of these



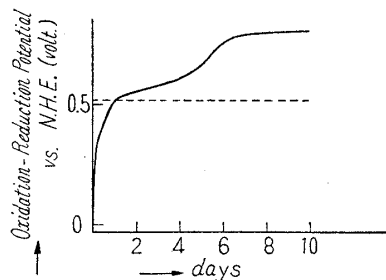
Nigayu Spring in Manza Spa



Hokkosen Spring in Manza Spa



Tetsuyu Spring in Manza Spa



A thermal Spring in Nasu-Chausu Volcano

— Acidic vitriol spring

----- Acidic ferrous sulfate solution

Fig. 10. Time-Potential Curves of Several Acidic Springs

15) C. Fredenhagen : Z. anorg. allg. Chem., **29**, 396(1902).

elements, except copper, platinum, and vanadium were effective. Of these three elements, vanadium was the most effective and copper the weakest. Therefore, it can be assumed that the coexistence of a small amount of vanadium, platinum, copper, and the like may catalyze the aging of acidic vitriol springs. As a reference to this assumption, several time-potential curves (namely, aging effect) of acidic iron springs in Japan are given in Fig. 10.

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Summary

From the analysis of the relation between pH and oxidation-reduction potential of artificial iron springs, the following facts were revealed.

1) In natural, strongly acidic vitriol spring, ferric ion exists mainly in the form of a complex cation, FeSO_4^+ with sulfate ion, and its potential is given by equation (23).

2) In natural, weakly acidic vitriol spring, ferric ion forms FeSO_4^+ , FeOH^{2+} , and $\text{Fe}(\text{OH})_2^+$, and its potential is given by equation (32).

3) In natural iron spring, much more weakly acidic than the above two cases, such as iron bicarbonated or iron carbondioxated springs, ferric ion deposits mainly as $\text{Fe}(\text{OH})_3$, and its potential is given by equation (26).

Ferrous ion in natural strongly acidic vitriol springs is easily oxidized by air to ferric sulfate complex cation, the oxidation velocity of which is more rapid than that of the artificial spring.

Based on the test of artificial springs, it was assumed that a trace of vanadium, platinum, copper, and the like may catalyze the oxidation of ferrous ion by air in natural acidic vitriol springs.

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