REMOVAL OF ARSENIC FROM GEOTHERMAL WATER

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ABSTRACT

The coprecipitation techniques using respectively iron(111) hydroxide and iron(III) salt followed by hydrolysis was employed to remove the arsenic from geothermal water in the Ohtake area, Kyushu, Japan. For both methods, the optimum pHs were found to be about pH 3. The Fe requirements to lower the residual arsenic concentration to environmental standard(0.05 ppm) were at least 45 ppm($Fe(OH)_3$ method), and 25 ppm($FeCl_3$ method). In case of the $FeCl_3$ method, the stirring time did not influence the arsenic removal. While for the $Fe(OH)_3$ method, the effect of arsenic removal was influenced by stirring time. Effect of treatment temperature was also examined. In the range of 50-80°C, pH 3 was the optimum and at room temperature, pH 5 was the optimum on arsenic removal. Silicic acid in geothermal water is said to interfere the arsenic removal, but present study showed that it was true in acidic state, but in the alkaline state, the existence of the colloidal silica on iron(III) hydroxide prevented the desorption and/or elution of arsenic.

INTRODUCTION

Recently, owing to the tense international situation and a prospective exhaustion of petroleum resources, the energy problem become more serious. As Japan is poor in natural resources, the finding of energies to substitute for petroleum is urgent. The so-called " Sun Shine Project" started in 1974 with new plans for the utilization of hydrogen energy and the utilization of natural energies such as solar and geothermal energies, and gasification and liquefaction of coal, Japan is a well known volcanic country in the world and geothermal energy is abundant(1.5×10^8 KW). Thus, the development of geothermal energy is a very promising solution of the problem. In the geothermal power production, high-pressure and high-temperature steam from bores are used. These bores are discharging steam-brine mixtures. Usable energy to be found in geothermal water is said to be twice as much as one in geothermal steam. However, there are still problems to be solved in the utilization of geothermal water. The geothermal water in the Ohtake area contains arsenic(2-5 ppm) and as is well known, arsenic is a cumulative poison in the body, so that the direct use of the geothermal water is dangerous. Only a part of the geothermal water is being used to supply hot water to the local people using the heat exchanger and the geothermal water itself is reinjected to the reduction bores. But the reinjection of the discharge water under pressure into the subsurface may cause the earthquake. Still more, reinjection may cause a drop in temperature of the heat reservoir, and it may in its turn reduce an electric power generation. Currently, the reinjection of geothermal water is regarded as a better way of disposing it. But if the pretreatment is required because of the scaling problems, the treatment cost could be very high. Removal of arsenic from geothermal water will be useful for multi-purpose utilization, such as district heating, hot water supply, large-scale gardening and so on. Now, investigations on the reduction of the arsenic concentration to the environmental standard of 0.05 ppm are necessary. At the same time, the effective performance as well as the economical efficiency is required. For the arsenic removal from geothermal water, some studies have been done(Rothbaum, 1975; Buisson et al, 1979). However, the nature of geothermal water varies according to the constituents and the results are not generally applied. In the present work, geothermal water was the one immediately after discharge from the bore. The coprecipitation method using iron(III) salt and iron(III) hydroxide was employed. The method of the direct addition of iron(III) hydroxide was studied from the point of view of the operational conditions such as pH control and filtration, and the comparison of both methods was made.

CONSTITUENTS AND PROCEDURE.

Typical constituents of discharge water in the Ohtake area is shown in Table 1. The $FeCl_3$ method and the $Fe(OH)_3$ direct addition method are shown in Fig.1.

INFLUENCE OF PH

As shown in Fig.2, in case of the $Fe(OH)_3$ addition method, the maximum arsenic removal was obtained at around pH 3, then the extent of arsenic (As) removal decreased to around pH 7.5 linearly, and over pH 8, the extent of As removal seemed to be unchanged or to go up a little. In the region of over pH 8, almost no effect on As removal was found(only 10-20%).Even at pH 3, the residual As concentration exceeded slightly the

Table 1. Chemical composition (ppm) of geothermal waters

	Ohtake		Hatchobaru	
	9	10	4	7
Na	1050	1030	2250	2140
K	132	124	277	266
Li	4.79	4.73	10.9	10.2
Ca	28.4	29.7	60.2	76.3
Mg	0.01	0.21	1.21	1.21
F	2.95	2.35	4.05	3.80
Cl	1774	1738	3954	3651
HCO_3	57	77	12	11
SO_4	145	193	138	95
HBO_2	a4	78	191	170
SiO_2	531	433	679	746
As	2.0	2.1	3.2	3.6
pH	8.57	8.44	6.99	7.04

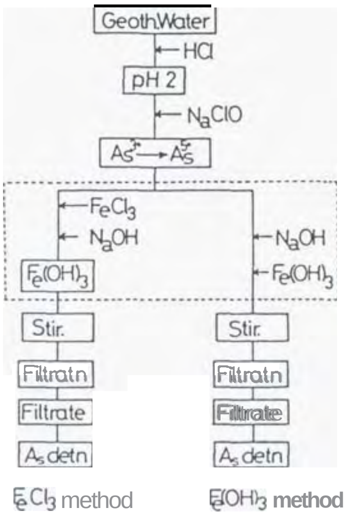

Fig. 1 Procedure for the estimation of arsenic removal.

environmental standard(0.05 ppm), and to get through the standard level, at least 45 ppm(as Fe) of iron (111) hydroxide will be required. For the $FeCl_3$ method, nearly the same tendency as the $Fe(OH)_3$ method was obtained, i.e., at pH 3, maximum arsenic removal was obtained and then the percent arsenic removal decreased to pH 7 linearly, and over pH 7, the residual As concentration was nearly constant (below 0.4 ppm, and the percentage arsenic removal =86%). Although it is not shown in the figure, iron (III) hydroxide does not dissolve in the pH 3 solution(lower limit calculated by solubility product), but at pH 2, almost all the iron(III) hydroxide will be dissolved in the solution, that is , below pH 3, the effect of arsenic removal decreases. The comparison of the residual As concentration between these methods tells us that at optimum pH(=3), the $FeCl_3$ method is superior to the $Fe(OH)_3$ method by a factor of about 5.7 and at pH 9, by a factor of about 6.5 using a Fe concentration of 40 ppm at 80°C.

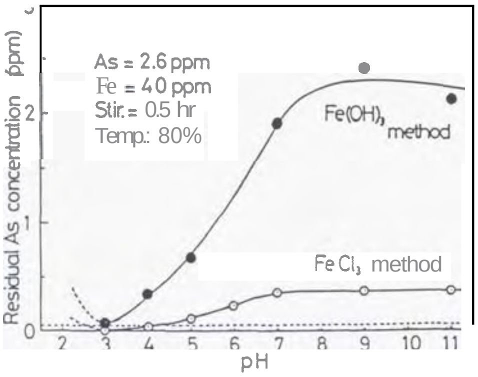

Fig. 2 The relation of residual arsenic concentration and pH.

INFLUENCE OF IRON(III) CONCENTRATION

The residual As concentration vs. Fe(III) concentration curves for the Ohtake geothermal water using the $FeCl_3$ method and the $Fe(OH)_3$ method are shown in Fig.3. The fact that the effect of arsenic removal at pH 3 is higher than that at pH 4 was confirmed as for the relatively wide range of Fe(III) concentration(20-100 ppm) too. The $Fe(OH)_3$ method has a lesser effect on arsenic removal than the $FeCl_3$ method for the Fe (111) concentration of 20-100 ppm at the same pH. For both methods, minimum amounts of Fe(III) requirement to attain the environmental standard were estimated to be 24 ppm(pH 3) and 35 ppm(pH 4) for the $FeCl_3$ method, and 46 ppm(pH 3) and 108 ppm (pH 4) for the $Fe(OH)_3$ method. Thus, the $Fe(OH)_3$ method requires about two times(pH 3) or about three times(pH 4) as much iron(III) as the $FeCl_3$ method. (Incidently, the phenomenon of coprecipitation is observed when the main precipitate is formed, And a precipitate once precipitated is experimentally known to have less capacity to coprecipitate. Coprecipitation mechanism will be classified into the following categories;

(a) Adsorption on the surface of the main precipitate.

(b) Formation of insoluble complex or compound with the main precipitate.

(c) Occulusion into the inner-part of the main precipitate.[Solid solution, mixed crystal etc.])

The data for Fig.3 were applied to Freundlich's adsorption isotherm. In case of the $Fe(OH)_3$ method, the data indicated a straight line exactly. The data for $FeCl_3$ method also revealed a linear plot. From the above results, it may be concluded that the mechanisms of As removal from geothermal water in both methods are substantially explained by the adsorption. However, the difference between the $FeCl_3$ method and the $Fe(OH)_3$ method is obviously regarded as significant.
In the present study, another possibility to explain the mechanism of arsenic removal is the formation of insoluble compounds such as $FeAsO_4$ and $Fe(AsO_3)_3$. The relatively better performance of the $FeCl_3$ method than the $Fe(OH)_3$ method will be explained by the partial contribution of the insoluble compound coprecipitated. Although the

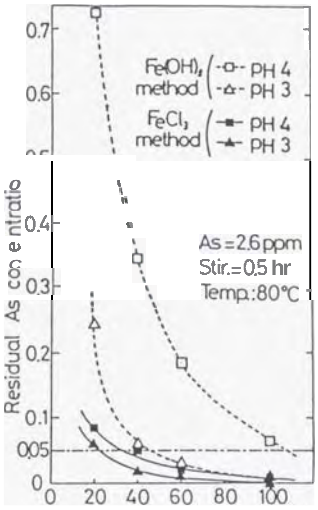

Fig. 3

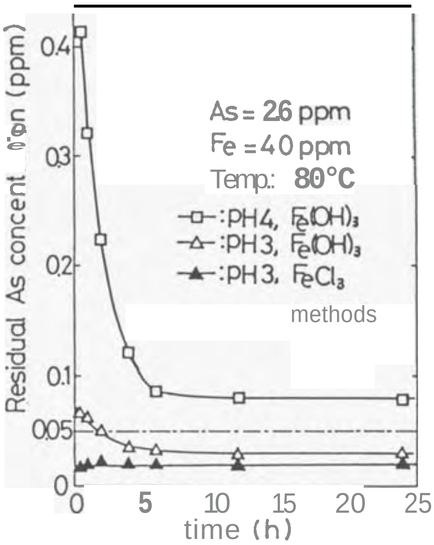

Fig. 4 The relation of residual arsenic concentration and stirring time.

residual As concentration by the $Fe(OH)_3$ method is about six times higher than that by the $FeCl_3$ treatment, the values of percentage arsenic removal are nearly comparable(the $Fe(OH)_3$ method: 73-100 %, the $FeCl_3$ method: 96-100%, at pH 3-4 and [Fe]= 20-100 ppm). Concerning the treatment of the arsenic removal for waste solution containing arsenic, Miyamoto et al(1973) found the existence of iron (III)-arsenic compound(probably $FeAsO_4$) by the analysis of IR spectra,

INFLUENCE OF STIRRING TIME

The relation of residual As concentration and the stirring time for the $FeCl_3$ method and the $Fe(OH)_3$ method is shown in Fig.4. As the figure shows, in case of the $FeCl_3$ method, the residual As concentration is almost constant irrespective of the stirring time(0.5-24 hours). However, in case of the $Fe(OH)_3$ method, the residual As concentration decreases with the passage of time. Still more, for the $Fe(OH)_3$ method the effect of pH seems relatively large, For example, at pH 4, the residual As concentration are 0.413 ppm(at 0.5 hour) and 0.07 ppm(at 24 hours), while at pH 3, they are 0.06 ppm(at 0.5 hour) and 0.031 ppm(at 24 hours). The comparison of both methods at pH 3 shows that the ratio of the residual As concentrations ($Fe(OH)_3$ method /$FeCl_3$ method) was about 4 at 0.5 hour and about 1.5 at 10 hours stirring. Thus, when the Fe concentration of 40 ppm is used, the $Fe(OH)_3$ method also could sufficiently attain the environmental standard after stirring it for 10 hours, This stirring time dependence in arsenic removal may be interpreted by the mechanical dispersion of the secondary(large size) flocculant to the primary (small size) flocculant which might have a wider surface than the secondary one.

INFLUENCE OF TREATMENT TEMPERATURE

In the present work, the treatment temperature was kept at 80°C, because the temperature of geothermal water discharged at the bore was about 80-90°C. However, the distribution and solubility of polymeric silicic acid in geothermal water varies according to the temperature, and the formation of the iron(III) hydroxide also will be influenced by the temperature. Here, for the $FeCl_3$ method, the effect was examined. The results were shown in Fig.5. Figure 5 tells us that the results at 80°C and 50°C show a slight difference between them, but the result at 20°C shows a clear difference to the other ones in the acidic region, i.e., the optimum pH was shifted to pH 5. As stated above, there is a relatively large difference concerning optimum pHs between the room temperature treatment and high temperature treatment. The reason might be explained by the difference in the condition of the $Fe(OH)_3$ colloidal particle growth(aging) and the change of reactivity of polymeric silica in geothermal water.

INFLUENCE OF SILICIC ACID AND THE SALTS

As geothermal water contains relatively much silicic acid and the salts(colloidal silica), arsenic removal using iron(III) hydroxide is considered to be influenced by them(Rothbaum, 1975; Reardon, 1979; Yokoyama et al, 1979; Kaneko, 1981). To examine the effects of colloidal silica, three kinds of sample solutions were prepared; (A) Geothermal water, (B) Modified geothermal water from which colloidal silica was removed using iron(III) hydroxide and the arsenic removed was compensated by adding arsenic solution, (C) Pure arsenic solution in which arsenic concentration was adjusted to the As concentration in the geothermal water in question,

These samples were compared by using the $FeCl_3$ method. Figure 6 shows the results that for these three kinds of solution, the optimum pH is quite

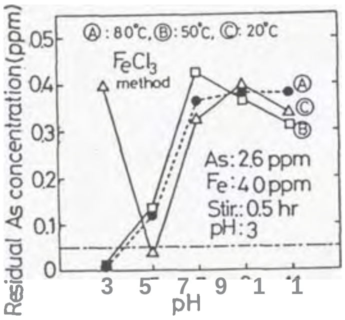

Fig. 5 Influence of treatment temperature on arsenic removal,

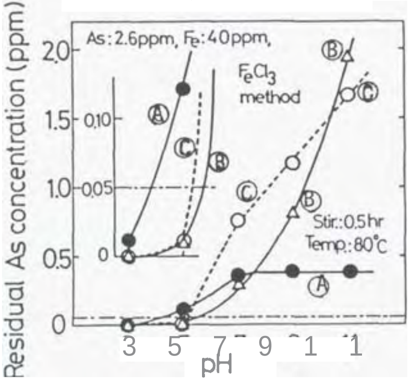

Fig. 6 Influence of silicic acid on arsenic removal,

the same(pH 3) and in the region of pH 3 to pH 5, geothermal water is inferior to the other two solutions concerning the As removal, but in the range of about pH 8 or over, the effect is reversed. Silicic acid is considered to combine with iron (111) ion or iron(III) hydroxide irrespective of the monomeric or polymeric states, and to interfere the arsenic removal by the coprecipitation method using iron(III) hydroxide or iron(III) salts. However, present work tells us that although in the acidic region of pH 3 to pH 5 the arsenic adsorption is certainly interfered, the relative arsenic removal at pH 8 or a higher pH region from nontreated geothermal water is better than the other two solutions. This phenomenon seems to indicate that geothermal water has a kind of buffer action both in acidic and alkaline regions as to As removal owing to a colloidal silica adsorbed.

It might be explained as follows: In general, in the acidic region, the adsorption of anion(such as AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$) on iron(111) hydroxide easily takes place, but in the presence of colloidal silica, colloidal silica also is competitively adsorbed or coated on the iron(III) hydroxide. Thus, the arsenic adsorption on the surface of the iron(III) hydroxide is restricted. But in the alkaline state, the arsenic once adsorbed is desorbed and eluted from the surface of the iron(III) hydroxide, then reaches the adsorption-desorption equilibrium and the coated colloidal silica on iron(III) hydroxide prevents the elution or the desorption of arsenic as the results.

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