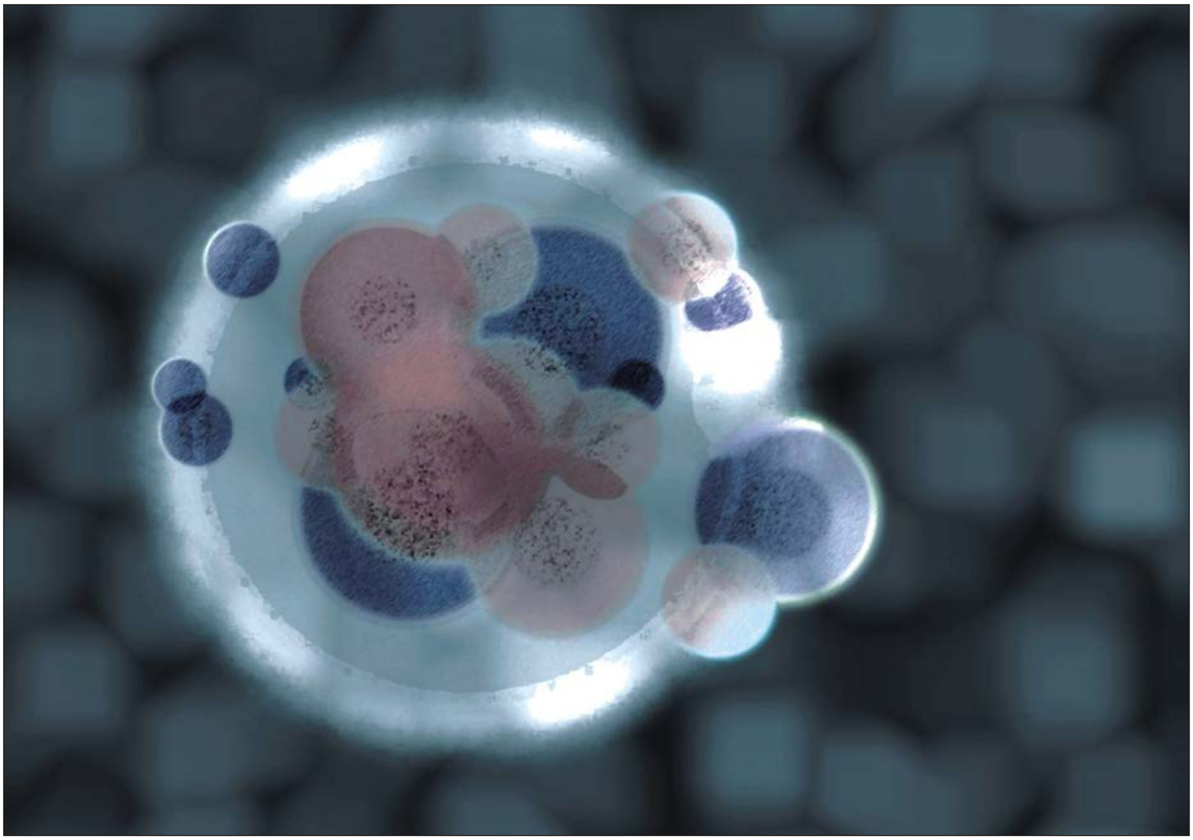

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Role of Ceramics Treatment in Fluidization Method to Remove Scale from Hot Spring Water

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Abstract: In recent years, hot springs have become a part of modern medical rehabilitation and recuperation. Furthermore, hot springs are said to speed recovery from illness and protect against further ailment. The hot springs are inherited natural resource and it is necessary to preserve them for future generations. The study was carried out for the removal test of scale in hot spring by use of the ceramics fluidization treatment device in two locations of the Shiohitashi hot spring and the Obama hot spring in Japan. The results showed that scale of Shiohitashi hot spring was characteristic of containing large amount of iron ion and small amounts of calcium ion. The color of scale was reddish brown under the influence of them. However, the scale of Obama hot spring contained large amount of calcium ion, which increased twice as much as that before treatment and the color was white. These results made clear that removal of scale in hot spring by ceramics fluidization took effect on calcium ion. Although chloride in the sea might increase effects, it should be proved by the continuous experiments.

Key words: Hot spring water, ceramics, scale

INTRODUCTION

As in other places of the world, also in Japan the thermal waters have been created by local geothermal and volcanic activities in certain geological, hydrological and tectonic structures. On account of distribution of 83 active volcanoes along Japan island arcs, Japan is blessed with so many hot springs through out the country from north to south[1] and there are roughly 150 hot springs with 14000 individual springs. Hot springs are not only water lines that are based on rain water being heated by earth's magma. Many of the hot springs are virgin water springs (in some of areas when the earth's core is cooled down and it releases gases and water vapor which turns into hot water) or fossil liquid (when ancient live forms died at the beginning of time the remains dissolved and turned into oil or water). There are various kinds of hot springs in Japan such as acidic, alkaline, sulfuric, ferric, carbonic and so on. White[2], Oki and Hirano[3], Ellis and Mahon[4] and Truesdell[5] attempted chemical classification for hot spring source, respectively. Nakamura[6], Sato[7] and Matsubaya[8] individually presented 2 to 5 sources with common names for natural waters.

Japanese likes taking the baths from ancient times like ancient Roman and believes its medical effect at any rate[1]. Since mid 1980's hot spring bathing has become boomed all over the country[9]. These hot springs have also been found to have medicinal properties. The content of gypsum and low salinity make the water ideal for healing bruises, rheumatism, neuralgia, skin diseases, gynecological ailments and other chronic problems.

Formation of scale on the outer layer of bath-tub and sometimes inner side of circulation pipe by which hot spring water is supplied to the bath-tub, becomes a big problem. Usually, scale is formed due to passing of water for long time through a same pipe and staying of water for long duration of time in the bath-tub. It is an urgent social problems to be solved to secure safety and cheaper water and to utilize it. The samples were collected to examine from two different places of Shiohitashi hot spring, Makizono-cho, Aira-gun, Kagoshima prefecture and the Obama hot spring, Obama-cho, Minamitakaki, Nagasaki prefecture, Japan by using fluidization treatment with granular ceramics of which raw materials were originated from natural silicate minerals.

MATERIALS AND METHODS

Quantify of mineral spring

Shiohitashi hot spring: Hydrogen carbonate mineral spring (low tonicity-neutral-high hot spring)

Obama hot spring: Sodium chloride mineral spring (isotonicity-weak alkali-high hot spring)

Granular ceramics: The main chemical components of granular ceramics were silica (70.0%) and aluminium

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oxide (11.9%). The particles of the powder have massive structure of 2×10^{-6} to 240×10^{-6} m in size. The granular ceramics of 2 mm in diameter with hardness of 7 were made by using the powder and the clay as the bonding agent and sintering at 1200°C[10].

Experimental apparatus: The treatment device was mounted at the entrance of water storage tank in the hot spring. Water was sampled in it before and after treatment and in a bathtub.

Electrical Conductivity (EC), pH, water temperature and dissolved oxygen concentration (DO) were measured by HORIBA U-10 water quantity checker and the oxidation reduction potential (ORP) by TOA ELECTRONICS PHL-10. The following items of dissolved components were measured.

Suspended materials: JIS industrial water test method.

Fe^{2+}, Fe^{3+}: Phenanthrolin absorption spectro photometry
Ca^{2+}, Mg^{2+}, K^+, Na^+: Flame atomic absorption method
Cl^-, SO_4^{2-}: Ion chromatography
SiO_2: Molybdenum blue absorption spectrophotometry

Test pieces were fitted before and after treatment and the conditions of adhesive scale in hot spring were observed by them.

RESULTS AND DISCUSSION

If any kind of water meets two criteria such as water temperature needs to be higher than 25°C and water must contain a pre-required amount of minerals in 1 kg of hot spring water, that water can be claimed as a hot spring.

In both springs, the concentrations of calcium ion were about 130 mg L^{-1}. More than 1000 mg L^{-1} bicarbonate was contained in Shiohitashi which was 8 times as much as that of Obama hot spring. The concentrations of sodium chloride in Obama were 2345 and 4600 mg L^{-1}, which values were 11 and 26 times as much as that of Shiohitashi, respectively (Table 1).

Shiohitashi hot spring: It has less than 1 g of radical carbon and other mineral elements in each liter of hot spring water. Basically, it is close to the simple spring water as it contains a huge amount of bicarbonate (HCO_3^-) ions. Many of them are low temperature water springs. It is good for heart diseases, blood circulation disorders, neurological disorders, female disorders etc. (Table 2).

As Shiohitashi hot spring is neutral and hydrogen carbonate mineral spring, pH and DO values increased and the suspended materials decreased after passing through the device during the experimental periods. These facts were agreed with that the water quality became muddy before treatment, but it became clear little by little after treatment[11]. Moreover, almost dissolved components had a tendency to decrease after passing through the device. The test pieces of scale proved that the scale became soft after treatment (Table 3).

Table 1: Different components in water of hot springs

Components	Shiohitashi hot spring (mg/1 kg)	Obama hot spring (mg/1 kg)
Cation		
Na^+	210	2345.0
K^+	43.9	268.3
NH_4^+	1.6	2.6
Mg^{2+}	92.5	154.0
Ca^{2+}	129.0	129.2
Fe^{2+}	1.8	0.8
Anion		
F^-	0.3	05
Cl^-	172.0	4588.0
Br^-	1.0	7.2
SO_4^{2-}	93.8	337.0
PO_4^{3-}	0.3	0.4
HCO_3^-	1068.0	130.4
CO_3^{2-}	0.6	15.0
NO_3^-	0.1	0.0
Metasilicate	245.6	232.4
pH ()	67 (53.5)	7.8 (66.0)
Residue on evaporation	1.448 (g kg^{-1})	8.881 (g kg^{-1})

Table 2: Difference of components in scale (X-ray micro analyzer)

	Shiohitashi hot spring		Obama hot spring	
Components (%)	Before	After	Before	After
Mg^{2+}		3.6	8.3	2.6
SiO_2	11.3	12.0	18.6	5.8
Ca^{2+}	4.1	4.1	41.6	87.2
$Fe^{-2,3-}$	58.6	51.4	4.9	3.2
Al^{3+}			1.5	
Cl^-			5.0	1.2

Obama hot spring: Usually, it contains more than 1 g L^{-1} of mineral elements. If the water contains more than 1 g but less than 5 g of salt it is weak saltine spring if less than 10 g then it is a salt spring, if more than 10 g then it is strong salt spring (Table 2). Since highly sufficient in keeping temperature it is called warm hot water.

Table 4 shows that pH has a tendency to decrease in contrast with that of Obama hot spring by the treatment. Dissolved oxygen concentration and suspended solid increased, namely the suspension phenomena were observed in the clean bath-tub. Increase of calcium ion indicated the release phenomena of scale.

Granular ceramics have electrical charges at the surface. When water is allowed to pass through ceramics in the fluidization process, friction and collisions are considered to occur continuously among the molecules of water and granular ceramics. It can be presumed that electrochemical reaction takes place in water in form of frictional electricity and piezoelectricity[11]. Moreover,

Table 3: Change of water qualities before and after treatments by fluidization with ceramics (Shiohitashi hot spring)

Time after installation	pH Before	pH After	DO (ppm) Before	DO (ppm) After	SS (ppm) Before	SS (ppm) After	Ca^{2+} (ppm) Before	Ca^{2+} (ppm) After	Mg^{2+} (ppm) Before	Mg^{2+} (ppm) After	SiO_2 (ppm) Before	SiO_2 (ppm) After
10 min	6.24	6.57	5.08	5.08	20.0	23.0	120	112	60	60	86	86
7 h	6.25	6.49	4.22	4.22	7.0	2.7	121	119	60	59	85	84
24 h	6.22	6.28	5.21	5.07	5.5	1.3	122	116	60	59	105	83
32 h	6.31	6.34	4.84	5.05	5.3	1.0	121	118	60	59	88	86
48 h	6.18	6.37	4.92	5.41	10.2	2.4	122	119	61	59	84	83
56 h	6.27	6.39	4.70	4.97	6.3	2.3	123	120	61	60	85	84
72 h	6.30	6.35	4.50	4.92	5.1	1.1	123	119	64	63	82	82
96 h	6.34	6.44	4.43	5.28	6.0	1.0	126	116	64	60	86	82
120 h	6.40	6.49	4.28	4.65	14.2	1.8	124	125	63	76	87	85
216 h	6.28	6.39	4.56	4.92	4.6	1.9	125	122	70	68	85	85
264 h	6.13	6.16	4.59	4.74	12.4	2.0	127	125	77	77	86	85
384h	6.33	6.38	5.01	5.28	12.0	3.3	126	123	75	74	84	84
528 h	6.48	6.50	4.78	5.34	17.7	1.7	125	121	58	67	84	83

DO is dissolved oxygen; SS is suspended solid

Table 4: Change of water qualities before and after treatments by fluidization with ceramics (Obama hot spring)

Time after installation	pH Before	pH After	DO (ppm) Before	DO (ppm) After	SS (ppm) Before	SS (ppm) After	Ca^{2+} (ppm) Before	Ca^{2+} (ppm) After	Mg^{2+} (ppm) Before	Mg^{2+} (ppm) After	SiO_2 (ppm) Before	SiO_2 (ppm) After
10 min	7.95	7.80	4.63	5.20	4.9	23.5	132	172	151	143	49	50
1 h	8.00	7.95	4.71	4.93	6.0	6.8	35	367	187	165	48	48
2 h	8.01	7.87	4.72	5.14	6.0	5.0	135	176	320	294	47	45
3 h	7.99	7.80	5.27	5.16	5.2	4.6	201	235	165	147	49	34
4 h	7.99	7.83	5.24	5.41	5.3	4.5	233	412	180	161	49	38
5 h	7.95	7.86	5.18	5.16	9.4	4.2	650	141	159	150	45	37
6 h	8.06	7.84	4.83	4.93	6.2	4.7	212	272	385	149	46	39
7 h	7.90	7.80	5.50	5.33	3.7	8.0	249	895	143	151	47	35
24 h	7.72	7.64	4.17	6.25	5.8	5.7	153	396	134	142	48	40
28 h	7.75	7.88	5.66	6.52	6.2	5.2	204	171	137	150	38	36
32 h	7.68	7.60	7.62	6.50	5.3	77.0	186	187	165	156	48	49
484 h	7.72	7.88	6.32	6.90	6.5	30.7	118	141	131	143	48	49
56 h	7.73	7.75	4.84	5.03	5.3	7.5	166	91	154	150	49	49
72 h	7.84	7.92	4.65	6.06	5.1	12.8	94	665	161	158	31	48
80 h	7.88	7.82	5.20	5.03	6.8	5.7	123	557	159	135	35	34
96 h	7.74	7.77	3.90	5.62	5.5	55.7	133	132	150	143	38	36
104 h	7.55	7.67	4.63	4.12	4.7	8.0	134	182	135	142	38	48
120 h	7.96	7.95	4.00	4.74	6.0	41.9	142	423	149	150	47	43
128 h	7.90	7.91	5.05	5.81	5.7	6.2	376	605	154	174	47	47
144 h	7.62	7.90	3.70	4.44	5.8	6.5	179	127	169	147	49	48

DO is dissolved oxygen; SS is suspended solid

some physical properties have already been changed with the treatment of ceramics in water[12]. Therefore, the ceramics treated water seemed to increase the activation of water[13] which resultant the reduction of suspended materials causing its resistance against formation of scale inside the water pipe and the outer layer of bath-tub.

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