

# A Water-cleaning Effect of Silica-Alumina Sintered Spheres

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## Abstract

Decrease of iron-content in water for daily life during several months was investigated in different places, by employing silica-alumina sintered spheres. It showed a remarkable effect of water-cleaning, which a preliminary basic approach in laboratory seemed to support.

## key words

water-cleaning, silica-alumina, rust, iron

## 1. Introduction

During these years, non-pollutional process to clean up the contaminated water has been emphasized, because every chemical procedure brought about the secondary undesirable pollution.

Some sorts of silica-alumina stone were selected as the raw material of sintered spheres for water-cleaning and several excellent results have been obtained in practice, as seen in the following areas;

- (a) To remove the red rust in water, as well as retard its formation
- (b) To soften the hard water
- (c) To remove the boiler-scale mainly consisting of calcia or silica
- (d) To remove the uric stone and its odor
- (e) To clean the water for daily life, as well as for stockbreeding field

There must be one definite answer to the question on the reason why such a remarkable effect can be observed in so various practical fields. To find out the answer as the

common principle, the cleaning effect on the red rust in water was investigated as the first item, on which the actual satisfactory results are described here. For this application, a fluidized bed consisting of silica-alumina sintered spheres, having enough strength to function with rotation, vibration and friction continuously for a few years, was employed as a practical apparatus with success [1].

Based upon it, a fundamental approach was tried in our laboratory, supporting the practical result mentioned above.

## 2. Result in Practical Use

### 2.1. THE APPARATUS EMPLOYED TO CLEAN THE RED WATER

As an example, Figure 1 is shown, whose conception is as illustrated in Figure 2. The sintered spheres for the fluidized bed consist mainly of silica-alumina. The diameter is determined in response to the pressure applied and flow rate of water, so that the fluidizing procedure can be stabilized in continuous use.

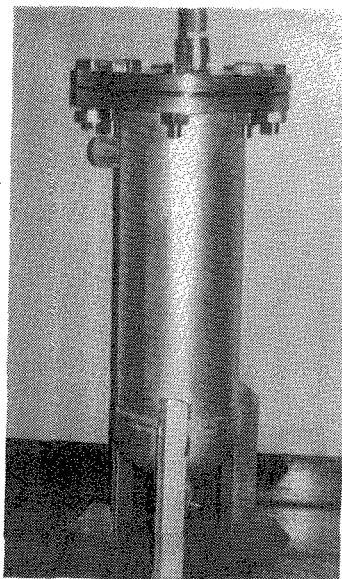


Figure 1. A typical apparatus in practical use.

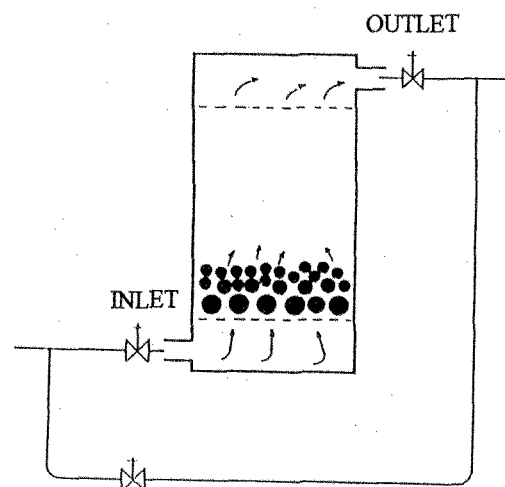


Figure 2. Conception of Figure 1.

## 2.2. RESULT AND DISCUSSION

Figures 3, 4 and 5 show the result of a practical use by employing the apparatus as seen in Figure 1. This result was obtained in three different offices (A, B & C) belonging to NTT (Nippon Telegraph & Telephone Corp., Japan). The iron content (mg/l), together with degree of color and muddiness, was determined in accordance with the Japanese ministerial ordinance on water-supply, issued by the Ministry of Public Welfare, No.69, in 1992.

Recently, quite a similar result to that in Figures 3 - 5 even after 200 days has been found in addition to these figures. All the other analysed values as drinking water such as general bacteria, nitric and nitrous nitrogen, Cl ion, organic materials, pH, taste and odor were much lower than each standard level as prescribed in the ordinance mentioned above.

As observed in Figures 3 - 5, some of decreasing velocity of these analysed values seem to be exponential, where the apparatus is the same. It should be noted that just after determining every first value at the starting time-point, washing treatment was carried out, because the storage tanks and route pipes rusted too much to begin with this long-term test.

In contrast with Figure 5, which is a result obtained at room temperature, Figure 6 shows the change without such a preliminary washing, although the manufacturer of ceramic spheres employed, as well as the user and the temperature applied, was different from the above mentioned. The apparatus used in Figure 6, was for warm water, electrically generated. In this case, it was not so easy to achieve the standard level (less than 0.3mg/l),

though the decreasing rate looked so high, taking about one month from as high as 16mg/l to only 0.56.

It is also noticeable that in all of these cases there could be found out no increase of iron-content, suggesting the retarding effect of rust formation owing to the spheres during such a long-term test. TABLE 1 summarizes an example of the other check-points, by analysing the water treated by another manufacturer's spheres and tested in another user, including the result after 1 year.

As a conclusion, it might have been made clear that such a sort of ceramic sintered spheres has been playing a certain positive rôle in the environmental field of application as a kind of effective water cleaner.

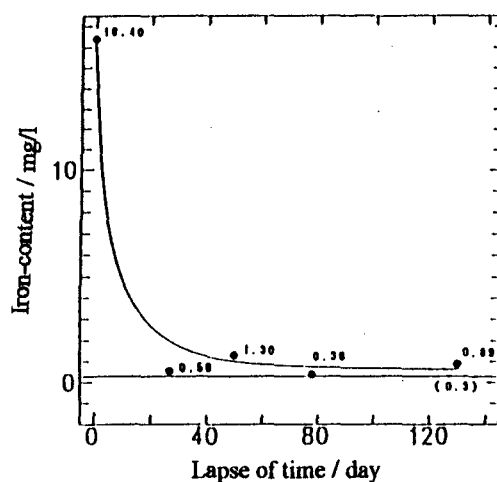


Figure 6. Change in iron-content with the lapse of time in the case of a warm water generator.

TABLE 1. An example of change in water quality by a long-term test

Item	Unit	Standard level	Value at the beginning	Result after (month)			
				6	7.5	10	12
Iron	mg/l	0.3	0.25	0.06	0.05	0.04	0.03
Color	degree	5	6	1*	1*	1*	2*
Muddiness	degree	2	1	1*	1*	0.5*	0.5
Odor	—	N	N	N	N	N	N
Taste	—	N	N	N	N	N	N
pH	—	5.8-8.6	7.2	7.6	7.5	7.4	7.4
Nitric & nitrous nitrogen	mg/l	10	0.21	0.12	0.19	0.25	0.22
Cl ion	mg/l	200	9.0	10.0	8.0	11.0	14.0
Org. mater. (consump. of KMnO <sub>4</sub> )	mg/l	10	0.6	0.8	1.8	1.0*	1.0*
Vapor. residue	mg/l	500	71	130	83	82	95
Hardness (Ca, Mg etc.)	mg/l	300	41	67	45	44	54
Ammoniacal nitrogen	mg/l	none	**	**	**	**	**
No. of general bacteria	pc/l	100	1-2	0	0	0	0

Note: \* = less than, \*\* = less than 0.1mg/l, N = normal

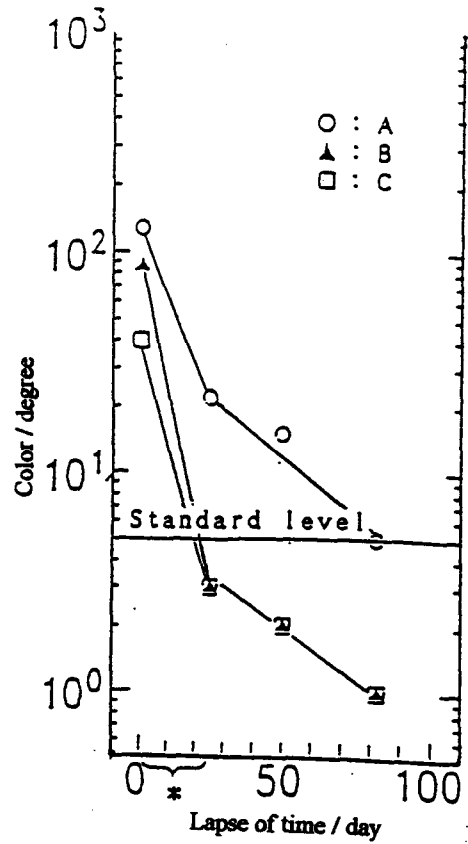


Figure 3. Change in color

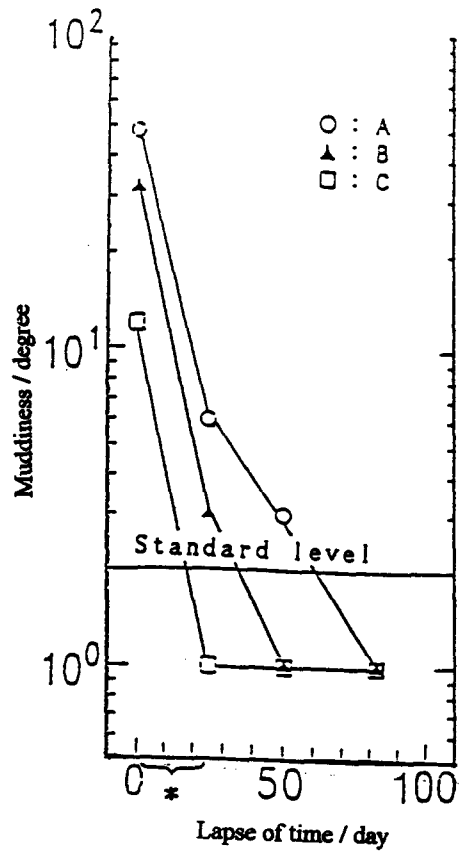


Figure 4. Change in muddiness

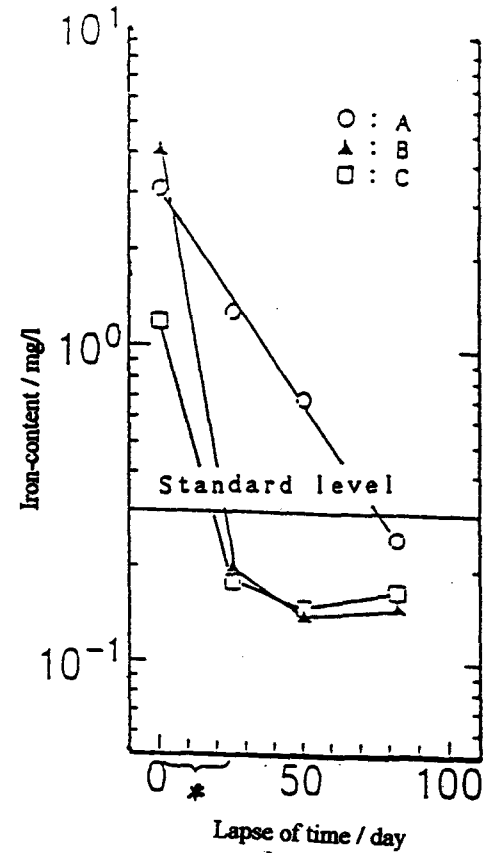


Figure 5. Change in iron-content

Note; \* means the fact that washing was carried out.

TABLE 2. Chemical composition (%) of silica-alumina sintered spheres employed in laboratory

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	MgO	CaO	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>
45.81	43.40	1.58	1.41	0.30	0.74	4.52	2.00	0.05	0.04

Note: Cd and Pb were less than the limit of detection, 0.2 and 20mg/kg respectively.

TABLE 3. Physical properties of the spheres in TABLE 2

ITEM	Diameter of ball (mm)	
	15	5
True density (g/cc)	3.01	3.02
Appar. density (g/cc)	2.85	2.83
Bulk density (g/cc)	2.07	2.27
Appar. porosity (%)	35.4	30.2
Surface area (cm <sup>2</sup> /l)	2341	6217
Space volume (cc/l)	428	396
Compres. strength (kgf/pc)	254	86
(N/pc)	2490	843
Filled up density (kg/l)	1.184	1.370

TABLE 4. Weight change in iron in the settled water

	No.1	No.2	No.3
Wt. of spheres	0 (no use)	60.05g	60.05g
Stirring	no	no	288rpm
1st run	-0.96%	-1.30%	-0.46%
2nd run	-0.73%	-1.06%	+1.07%

### 3. A Preliminary Fundamental Experiment in Laboratory

Following the conclusion of the last section, a basic approach was carried out as a tentative and preliminary experiment in our laboratory. In reality, the fluidizing of spheres could not be performed, since the size of them for fluidizing depends on the actual condition and water pressure and flow-rate was not enough to make supplied spheres fluidize.

#### 3.1. SINTERED SPHERES EMPLOYED

TABLE 2 summarizes the chemical composition of the spheres manufactured by A Co., Ltd., Japan. TABLE 3 shows the basic physical properties of the same spheres as those in TABLE 2. Important points may be mostly their stable chemical composition and strength, as well as their constant porosity owing to a strict quality control such as a severe temperature control for sintering. It is said that the

shortage of strength caused the water-flow to be stopped due to mechanical cracking of fluidizing spheres in use, being closely related with chemical composition followed by every control of processing. The standard deviation of compressive strength in TABLE 3 is known to be 34 and 18kgf/pc, respectively, where  $n = 10$  and test speed = 0.5mm/min.

#### 3.2. APPARATUS

Glass beakers for 500ml filled with 500ml of regular water for daily life were set in a thermostat kept within the temperature range of 39.5 - 40.5°C, where a stainless-steel-made mechanical stirrer was partly used for comparison.

Specimens of pure iron plate stocked in acetone, having appropriate size and weight of 0.25 × 20 × 30mm and 1.2g respectively, were used. The sintered spheres had 5mm in diameter as shown in TABLE 3.

In the case of using water-flow, not being kept just in

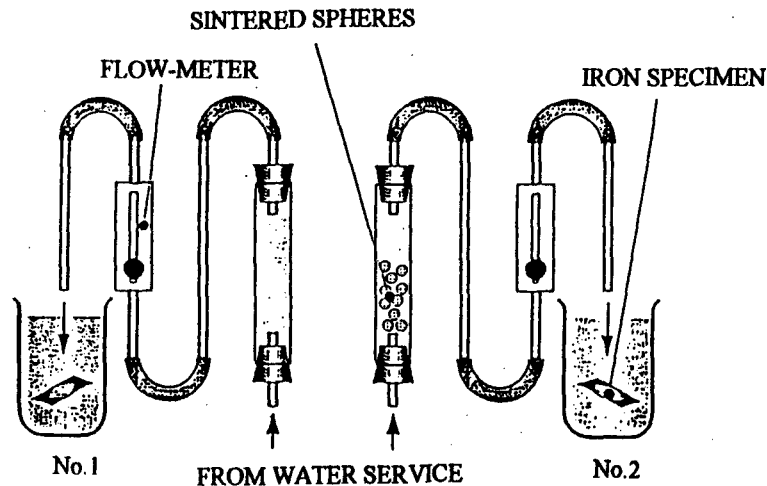


Figure 7. Apparatus for the experiment in the water-flow.

the settled water as above mentioned, the apparatus is as illustrated in Figure 7; where the flow-rate of water with and without spheres was carefully controlled to be the same each other, since the flow with the spheres was slower. The temperature, however, could not be kept constant as in the above case, carried out in a thermostat, but inevitably limited by the temperature of flowing water, 5 - 11°C (room temperature = 15 - 25°C), because recycled water was not suitable for this experiment considering the result obtained in the settled water, having been carried out prior to this approach. The weight decrease in iron plate after every exposure in the flowing water was enough to be able to estimate the effectiveness of the sintered spheres.

### 3.3 RESULT AND DISCUSSION

#### 3.3.1 Experiment in the Settled Water

The result after the first 48h at 40°C is as summarized in TABLE 4.

It is of interest to compare the specimens shown in No. 1 - 3 in TABLE 4 with each other, where both surfaces of No.3 and one surface of No.2 directly contacting with the spheres looked mainly black, and the both of No.1 as well as another surface of No.2 looked completely red and soft, perhaps typical ferrous oxide. A possibility for the spheres to be apt to make up the fixed black rust, perhaps ferric oxide, can be considered. Weight change observed in No.3 is obviously different from the others.

However, it was found out after 72h at 40°C that there seemed to be almost no difference from each other, although the iron specimen was hung so that it could not directly contact with the spheres, since the surface of specimen could not be shaven by the vibration of hard spheres.

#### 3.3.2. Experiment in the Water-Flow

By employing an apparatus as shown in Figure 7, weight decrease of iron specimens was measured to find the effect of spheres. Figure 8 summarizes the result, showing a clear difference. Just formed red rust in water looked surely softer than the black, but there was no apparent

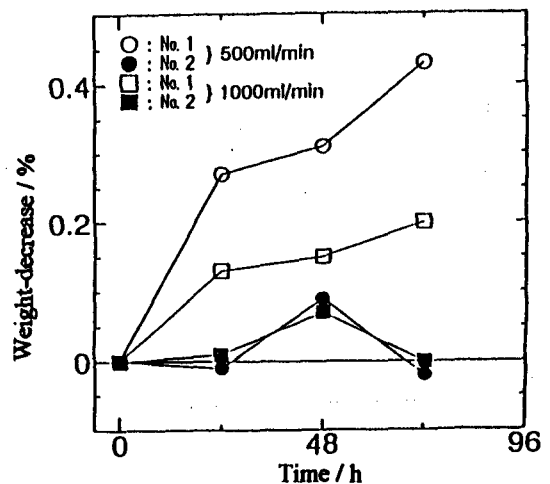


Figure 8. Weight decrease of iron plate in water-flow.

difference in the surface of both specimens, having been treated with and without the spheres, perhaps because such a high speed water-flow must have removed the hard black rust just formed. More detailed and systematic investigation has to be carried out, taking into account of the daily difference of water quality.

### 4. Conclusion

Decrease of iron-content in water for daily life during several months, was investigated in different practical users, by employing different sorts of silica-alumina sintered spheres. It showed a remarkable effect of water-cleaning. A preliminary basic approach in laboratory seemed to support this effect, suggesting the need of furthermore detailed systematic research work.

### Reference

- [1] Yamada, S. and Iwatani, H. (1995) Water-cleaning effect of silica-alumina sintered spheres, *Preprint for 8th Autumn-Symposium of Ceram. Soc. Japan*, p.263

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