Practical Paper

Deterioration of granular activated carbon collected from post-ozonation upflow fluidized bed contactor—influence of particle diameter

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ABSTRACT

An examination was undertaken of the properties of granular activated carbon (GAC) collected from a post-ozonation upflow fluidized GAC contactor at a full-scale advanced water purification facility operated by the Hanshin Water Supply Authority (HWSA), Japan. Activated carbon (AC) was collected from the upper, middle, and lower layer of the contactor and fractionated by a series of sieves. The amount of manganese, iron and calcium accumulated on each fraction was estimated by hydrochloric acid extraction test. The amount of iodine adsorption (I_N) was also measured.

The amounts of metal accumulated were 1.2–89 ($mg\,Mn\,g^{-1}$), 1.4–4.3 ($mg\,Fe\,g^{-1}$), and 6.6–32 ($mg\,Ca\,g^{-1}$). The amount was affected not only by the layer from which the carbon was collected but also by the average particle diameter of each fraction. I_N was in the range of 119–527 ($mg\,g^{-1}$) and decreased from the lower through the middle to the upper layer. Judging from I_N, the AC collected from the upper layer, the furthest downstream, was subject to particular deterioration. A number of potential factors affecting the deterioration of GAC were suggested.

Key words | adsorption capacity, calcium, granular activated carbon, iron, manganese, particle size

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INTRODUCTION

The Hanshin Water Supply Authority (HWSA) is a public waterworks enterprise supplying 1,128,000 $m^3 day^{-1}$ sourced from the Yodo River to a population of 2,500,000. The introduction of an advanced water purification system consisting of ozonation, GAC adsorption, and coagulation began in 1993. The advanced purification system is a countermeasure against unpleasant smell and taste, synthetic chemicals, and disinfection byproducts. Unique to HWSA is the intermediate ozonation after coagulation and sedimentation, and subsequent upflow fluidized GAC contactor processing. Enhanced aerobic

biological activity is observed as operating time progresses due to the bacteria which attach to the GAC. Some of the microparticles in the contactor are washed out by air flushing once a day and removed by subsequent sand filtration. Although subject to constant stirring by the upflow, the GAC in the contactor is not completely mixed. As the supplied GAC has a specified diameter distribution, larger GAC particles tend to fall to the bottom and smaller ones tend to rise. The exchange plan for the GAC in the contactor foresees the removal of 1/5 of the used GAC and its replacement with roughly the same

amount of new GAC once a year. A temporary rectangular frame with a cross section 1/5 that of the contactor itself is placed on the bottom of the contactor to remove used GAC and the new GAC is introduced after complete removal of the used GAC inside the frame.

In the present study, the properties of GAC collected from the contactor after a lapse of 13 years were examined to evaluate deterioration, especially with reference to the effect of GAC particle diameter. There have so far been no research papers concerning GAC particle diameter and its role in deterioration. In the present study, the collected GAC was fractionated by a series of sieves and the fractions analyzed. The amount of accumulated manganese, iron, and calcium was estimated by hydrochloric acid extraction test. The amount of iodine adsorption (I_N) by the AC was also measured. The deterioration mechanisms and contributory factors are also discussed.

METHODS

The AC for testing was collected from the upper, middle, and lower layers of the upflow fluidized GAC contactor designated A-5-1 in System III at the Inagawa purification plant of HWSA at the time of special cleaning operations at the contactor in November 2006. The contactor had been in operation for 13 years. The specified depth of the filled GAC was 2.14 m under static conditions. The average expansion rate of the fluidized contactor was 45%. GAC was collected using a cylindrical tube of 50 cm length, which was thrust vertically into the bed after water had been drained from the contactor. The GAC collected from the top 50 cm of the bed was designated AC-U, that collected from the bottom 50 cm AC-L, and that from the approximate middle AC-M.

A sieving test was conducted according to Japanese Industrial Standard (JIS) K 1474 (Test methods for AC). Fractionated AC was obtained by the sieving test. The AC was designated according to the mesh size of the sieves which passed and retained it. For example, AC-M that was passed through a 710 μm sieve but was retained by a 600 μm sieve was designated AC-M$_{710-600}$. AC particles of less than 250 μm were designated AC-M$_{250-0}$.

Meanwhile, the letter 'A' was used to designate AC that was not fractionated, i.e. AC-M$_A$.

All fractionated AC samples were ground to powder and passed through a 75 μm sieve. The powders were dried at 388 K for 3 hours and kept in a desiccator containing silica gel. A hydrochloric acid extraction test and an iodine adsorption test of the powdered AC were conducted as described below.

Diluted hydrochloric acid for the extraction test was prepared by mixing 1 volume of concentrated hydrochloric acid and 4 volumes of pure water. A 0.2 g sample of the powdered AC and 10 ml of the diluted hydrochloric acid were placed in a beaker and kept on the boil on a hot plate for 10 minutes. After cooling, 1 mol L^{-1} of hydrochloric acid was added to the suspension to a volume of 50 ml using a mess flask. The suspension was filtered through a 0.45 μm membrane filter and subjected to atomic absorption spectrometry to determine the concentration of metals. The amount of manganese, iron, and calcium extracted was calculated according to their respective concentrations in the filtrate. In the present study, the amount extracted was considered to be an index of the amount accumulated on AC. It is nevertheless possible that some accumulated metals are insoluble in hydrochloric acid.

I_N was measured as the remaining adsorption capacity of AC according to a modified version of the standard method for powdered AC for drinking water treatment, i.e., Japan Water Works Association K 113 of 1985. This method, due to a number of revisions, is no longer current, but is adequate to estimate the adsorption capacity of the AC tested here. A 0.3 g sample of AC and 30 ml of 0.05 mol L^{-1} I$_2$ solution were placed in an Erlenmeyer flask with a cap. The suspension was shaken for 30 minutes to achieve adsorption equilibrium and filtered through a 0.45 μm membrane filter. A 10 ml sample of the filtrate was then titrated with 0.1 mol L^{-1} of sodium thiosulfate solution to determine the concentration of remaining iodine after adsorption. I_N was calculated as follows:

$$I_N(\text{mg g}^{-1}) = 12.69 \times (10 - af)/(0.3 \times 10/30)$$

a: amount of titrant (ml), f: factor of 0.1 mol L^{-1} sodium thiosulfate solution.

For AC-U_A, AC-M_A and AC-L_A, the accumulated amounts of calcium, ash content, and volatile content were measured. The hydrochloric acid extraction test was conducted in the same way as for the fractionated ACs, except for the grinding to powder. Ash content and volatile content were measured according to JIS M 8812 (Coal and coke–Methods for proximate analysis). Volatile content is weight loss (wt%, dry-base) when a solid sample is heated for 7 minutes at 1,173 K with air excluded.

RESULTS AND DISCUSSION

Particle size distribution of GAC

Table 1 shows the particle size distribution of AC-U, AC-M, and AC-L. The median diameters were 410, 500, and 1,060 μm respectively. It was ascertained that AC-L consisted of considerably larger particles. It was assumed that particles in the lower layer were less mobile than those in other layers. No microparticles were found in our visual observation of AC-L before sieving, but the results indicated the presence of microparticles of less than 250 μm. These microparticles were presumed to have been formed by the physical impact of the sieving machine. In AC-L, the proportion of particles smaller than 250 μm was 1.4% while that of particles of 300–250 μm was only 0.2%. That is,

AC-L_{250-0} contained more particles derived from the outside surface of AC-L than other fractions.

Ash content and volatile content

The ash content of AC-U_A, AC-M_A, and AC-L_A was 19.8%, 16.1%, and 14.3%, respectively, and the corresponding volatile content 27.3%, 24.9%, and 17.3%. These results indicate that the amount of both inorganic and organic matter accumulated increased in the order of AC-L, AC-M, and AC-U, that is contrary to the flow direction.

Manganese

The amount of manganese accumulated in the fractionated AC is plotted as the ordinate and the average diameter of each fraction as the abscissa in Figure 1. The average diameter was the arithmetical mean of the upper and lower sieve mesh sizes. The amount of manganese accumulated was 1.2–89 (mg Mn g^{-1}). Considerably more manganese was accumulated on AC-U_{250-0}, AC-M_{250-0}, and AC-L_{250-0} than on particles in the next biggest fraction from which data was obtained, i.e. AC-$U_{300-250}$, AC-$M_{355-300}$, and AC-$L_{355-300}$. This observation suggests that some particles smaller than 250 μm were formed by the sieving test and that more manganese was detected on the microparticles. As the amount on AC-L_{250-0} was much greater than on other

Table 1 | Particle size distribution of activated carbon

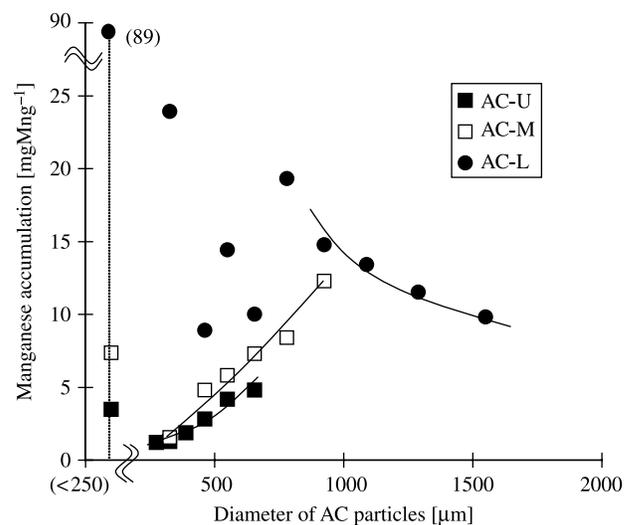| Diameter [μm]	Distribution [%]		
	AC-U	AC-M	AC-L
>1700	0.0	0.0	0.6
1700 ~ 1400	0.0	0.1	15.6
1400 ~ 1180	0.0	0.1	23.2
1180 ~ 1000	0.0	0.2	19.7
1000 ~ 850	0.0	0.4	12.4
850 ~ 710	0.3	2.6	15.1
710 ~ 600	1.6	16.5	6.9
600 ~ 500	12.9	30.8	2.5
500 ~ 425	28.4	26.5	1.2
425 ~ 355	37.6	17.6	0.8
355 ~ 300	14.2	3.9	0.3
300 ~ 250	3.9	0.7	0.2
250 >	0.9	0.5	1.4

Figure 1 | Relation between manganese accumulation and diameter in AC particles.

grades, it was hypothesized that more manganese accumulated on the outside surface of AC-L.

Regarding the effect of the diameter of AC-L, in the range over 850 μm, the amount of manganese accumulated became less as the diameter increased. In the range under 850 μm, no tendency was discerned from the inconsistent plots. Meanwhile, the amount of manganese accumulated on AC-M and AC-U became less as the diameter decreased, except at less than 250 μm. This observation suggests that the main mechanism of manganese accumulation on AC-L was different from that on AC-M and AC-U.

The outside surface area per unit of weight generally increases as the diameter of the particle decreases Adhesion to the outside surface is suggested by the results in the range over 850 μm in AC-L. The results observed in AC-U and AC-M were opposite. Manganese in raw water is oxidized to permanganate by ozonation (Reckhow *et al.* 1991) and reduced to insoluble manganese dioxide by certain reducing compounds such as humic substances (Ma & Graham 1999). The main mechanism of manganese accumulation on AC-L in the range over 850 μm may be adhesion of already produced manganese dioxide to AC. On AC-U and AC-M, a chemical reaction of some kind seemed to produce in the vicinity of AC particles an insoluble manganese which, instead of becoming separated, adhered directly to them, as the various conditions in bulk water were mostly common to all the particles within each layer. Residual ozone is

one of the probable species concerned. Partial concentration of ozone in the vicinity of AC may be different for particles of different diameter, as ozone is consumed rapidly on the surface of AC.

Iron

Figure 2 shows the amount of iron accumulated on AC. The amount of iron accumulated was 1.4–4.3 (mg Fe g^{-1}). On all grades of AC, the amount of iron accumulated became less as the diameter decreased in the range under 600 μm except for the range under 250 μm. While there was no clear difference between layers with iron, the results were similar to those for manganese in AC-U and AC-M in the range under 850 μm.

Calcium

The amount of calcium accumulated on AC-U$_A$, AC-M$_A$, and AC-L$_A$ was 20.7, 14.5, and 9.2 (mg Ca g^{-1}), respectively, increasing in the order of AC-L$_A$, AC-M$_A$, and AC-U$_A$. Figure 3 shows the amount of calcium accumulated on AC. The amount of calcium accumulated was 6.6–32 (mg Ca g^{-1}). The tendency, observed in manganese and iron, for the amount of metal accumulated to become less as the diameter grew smaller was not noted in the case of calcium. The stable oxidation number of calcium is only +2. This means that the accumulation mechanism is not
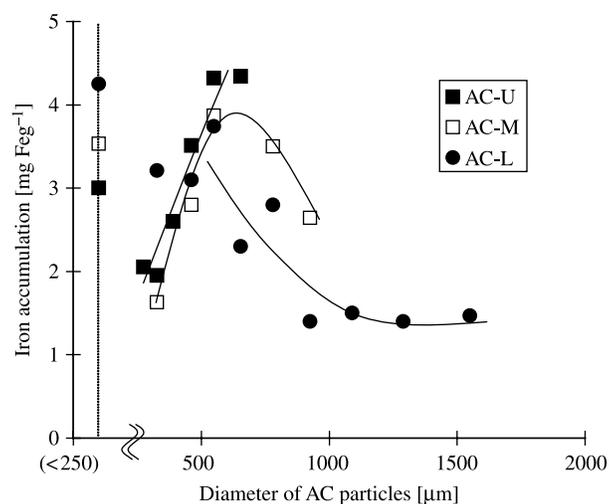

Figure 2 │ Relation between iron accumulation and diameter in AC particles.
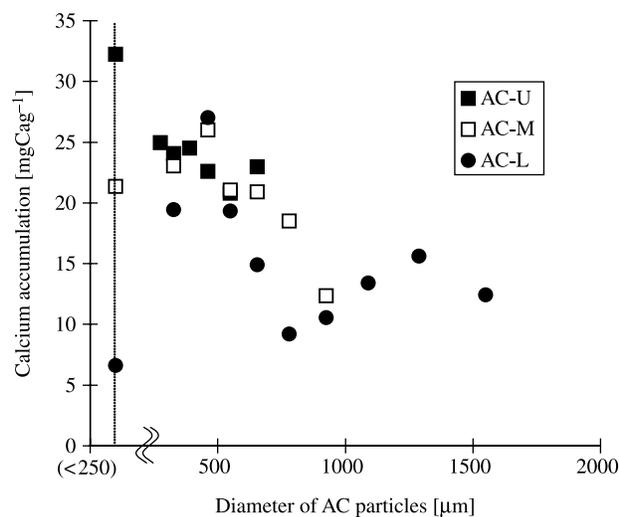

Figure 3 │ Relation between calcium accumulation and diameter in AC particles.

affected by the oxidation and reduction reaction of calcium. This is considered to be a major difference from manganese and iron.

On microparticles of under 250 μm, the amount of calcium accumulated decreased in the order of AC-U$_{250-0}$, AC-M$_{250-0}$, and AC-L$_{250-0}$. As mentioned above, AC-L$_{250-0}$ seemed to contain more broken particles derived from the outside surface of AC-L. This suggests that the accumulation of calcium was rather small in the lower layer.

Iodine adsorption amount, I$_N$

I$_N$ measured as the adsorption capacity of AC was in the range of 119–527 (mg g^{-1}), as shown in Figure 4. I$_N$ of common commercial AC is around 1,000 (mg g^{-1}). Some grades of AC displayed adsorption capacity of around 1/2 that of new AC in spite of having been through about one year of utilization since the previous replacement of GAC.

In AC-L, a plateau was seen in the range over 850 μm, while decrease was observed with decreasing diameter in the range under 850 μm. In AC-M and AC-U, the minimum value of I$_N$ was observed at around 500 μm, with increase noted in the range under 500 μm. As for AC of the same diameter, I$_N$ was largest in AC-L and decreased in the order of AC-M, AC-U.

Deterioration mechanism of GAC

The relation between I$_N$ and particle diameter, as shown in Figure 4, did not show a uniform tendency in all AC grades.
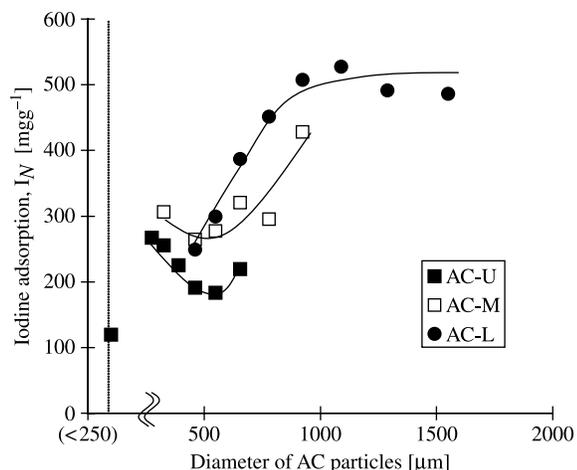

Figure 4 | Relation between iodine adsorption and diameter in AC particles.

Moreover, although AC-U was the most deteriorated, it was placed the furthest downstream in the upflow contactor, judging from the I$_N$, ash and volatile content. The following were suggested as probable factors affecting the deterioration of GAC adsorption capacity:

(1) The stronger fluidization of smaller particles may enhance the external diffusion of contaminants around AC particles. This would explain why AC-U was the most deteriorated and why I$_N$ increased in the range of 500–1,000 μm in all AC grades.

(2) Exfoliation loss from the outside surface of GAC particle by friction with other particles, water, and flushed gas may affect adsorption capacity. Loss of GAC depth with operating time was indeed observed at the actual plant. The deterioration of adsorption capacity may be uneven within an AC particle, i.e., parts near the outside surface may suffer more deterioration than the inner part. Exfoliation must occur as time progresses, as the hardness of GAC gradually decreases through prolonged contact with ozone (Fukuhara & Nakano 2000). If an exfoliated particle is small enough to be washed out from the contactor, the adsorption capacity per weight of residue must consequently be improved. Moreover, this improving effect may be larger in smaller particles if the size of the exfoliated particle is the same. This phenomenon may have contributed to the finding that I$_N$ increased in the range under 500 μm.

(3) Calcium accumulation on AC may influence adsorption capacity. Lee *et al.* (2003) reported that calcium accumulation on GAC reduces adsorption capacity for a synthetic organic chemical. Randtke & Jepsen (1982) showed that fulvic acid combined with calcium is more readily adsorbed by GAC. As stated above, the amount of calcium accumulated increased in the order of AC-L, AC-M, and AC-U. The fact that AC-U was the most deteriorated may be explained by calcium accumulation, although the mechanism cannot yet be identified.

CONCLUSIONS

In the present study, the properties of AC collected from a contactor after a lapse of 13 years were examined to

evaluate deterioration. The specific results are summarized as follows:

(1) The amount of manganese accumulated was 1.2–89 (mg Mn g^{-1}). More manganese was accumulated on the outside surface of AC-L. The main mechanism of manganese accumulation on AC-L was different from that in AC-M and AC-U.

(2) The amount of iron accumulated was 1.4–4.3 (mg Fe g^{-1}).

(3) The amount of calcium accumulated was 6.6–32 (mg Ca g^{-1}) and increased in the order of AC-L, AC-M, and AC-U.

(4) I_N of AC was in the range of 119–527 (mg g^{-1}). Some AC grades displayed adsorption capacity of around 1/2 that of new AC in spite of having been through about one year of utilization since the previous replacement of GAC.

(5) Suggested as probable factors affecting the deterioration of GAC adsorption capacity were the stronger fluidization of smaller particles, exfoliation loss of the outside surface of GAC particles, and calcium accumulation on AC.

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