

## Development of volcanic-ash-derived new flocculation agent

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The flocculation method is one of the main process of the water treatment. Flocculation agent is used in the coagulation process. In general, flocculation agent is artificially manufactured, and the discharged sludge in the water processing plant contains in relatively considerable quantity of aluminum that is the component of the flocculation agent. Therefore, recycling of the sludge is difficult, and it is mainly disposed as industrial waste. For the similar reasons, it is difficult to use this flocculation agent in the treatment of environmental turbidity of dam lakes.volcanic-ash-derived new flocculation agent is developed<sup>1)</sup>. This agent contains the natural mineral without an artificial material, and has the equal cohesion to conventional flocculation agent. The turbid water treatment by this new flocculation agent such as at water treatments and dam lakes is highly expected in situ.

### *Condensation method and flocculation agent*

Purification of water means to remove turbid and contaminants from water; and the main method is the condensation method. First, to make the target material a solid, then second, to separate it from water is the condensation method. For this separation, the sedimentation method is entirely used. Turbidity is categorized as comparatively big materials such as sand or clay mineral such as small colloidal particles (about  $1\text{nm} (10^{-9}\text{m}) \sim 1\text{ }\mu\text{m}(10^{-6}\text{m})$ ). The contaminant adheres to colloidal particle or is soluble in water. In case of dissolution, as a preprocessing, the contaminant is changed into a solid material (colloidal particle) by the oxidation or is adsorbed by putting the adsorptive material (colloidal particle) in the contaminant.

The influence of gravity voluntarily settles out greatly to a big material such as sand. However, the colloidal particle doesn't settle out easily because it greatly undertakes an influence Brownian motion (\*1). compared with gravity. It is this colloidal particle that becoming the object of the cohesion method.

Van der Waals attraction (\*2) always works as power to attract against each other between colloid particles. If the particle attracts against each other mutually according to this

power, it flocculates. If the particle grows, the influence of gravity strengthens and it subsides. Then, why does not the colloidal particle flocculate? It is because the surface of the colloidal particle usually is electrically-charged of the plus or the minus; therefore, due to the particles next to each other are like charges, they mutually repulse. Since this repulsion surpasses Van der Waals' forces, the colloidal particle keep floating without agglutinate.<sup>2)</sup>

Therefore, in the process of condensation method, to reduce the repulsion power by this charge, flocculation agent is poured in. The component of the flocculation agent is electrolyte that becomes an ion in water. The charge of the colloidal particle is neutralizes by this ion. If it makes neutralized, the influence of the Van der Waals force grows, and the colloidal particle agglutinate and subside.

There are an inorganic flocculation agent and an organic polymer coagulant. PAC (polyaluminum chloride) and the sulfuric acid band (sulphonated aluminum) are well known in the inorganic flocculant. Polyacrylamide is well known in the organic polymer coagulant. Both an inorganic flocculant and an organic polymer coagulant can make neutralize the colloidal particle. Especially an organic polymer coagulant has cross-linking action in which the colloidal partial are linked by polymer; therefore, the agglutinate force is very high. Both of these flocculant are chemical compounds. The reactivity is well and they can demonstrate the effect to any types of turbid water. However, the unreacted elements may remain in the treated water in case of using it voluminously. Moreover, because sediment after the process includes aluminum and the high polymer, it is detrimental to recycle. Flocculation agent that is made from natural mineral was developed in order to make up this disadvantage. However, most of these natural minerals are made from alkali earth metal by which the pH in the treated water is raised, and the cohesive force is low. Moreover, the sediment is likely to be alkalify that remains the difficulty of recycling. Therefore, pulverized powder of volcanic ash and the pumice-weathering stone is developed as a flocculation. However, because the cohesive force of this type of flocculation agent is also low, several thousands of ppm is necessary for the process and this amount is not practicable.

### *New flocculation agent and the cohesion mechanism*

To solve the above-mentioned problem, a volcanic-ash-derived flocculation agent is developed. The volcanic ash is distributed Tohoku, Kanto, San-in, and the Kyushu region and it is from a lower part with low organic substance. The main clay mineral of the volcanic ash is aqueous aluminum silicate.

The procedure for manufacturing flocculation agent from the volcanic ash are : put

volcanic ash through a sieve and control its size    add water to size-controlled volcanic ash and disperse the mineral particle    According to circumstances, add pH adjuster to the compound liquid .

The most important point in the process of    and    is to disperse the mineral particles without destroying them but with keeping them close to unit particle. The difference between our flocculation agent and the natural mineral flocculation agent is in this excellent dispersibility.    Resulting properties of the flocculation agent are shown in Table 1, and the elements are shown in Figure 1, and photograph is shown in Photograph 1.

There are two cohesion mechanism by the developed flocculation agent:    neutralization of surface charge of the colloidal particle that is the component of turbidity.    the physical incorporate of the colloidal particles by the self-cohesion of flocculation agent.

A large amount of colloidal particles that are the causes of turbidity consist of the clay mineral, and their surface hold negative charge with pH 3 or more, and they repulse and disperse each others in water.    Moreover, the surface of algae that occur in lake and reservoir are also electrically charged by the carboxyl group. On the other hand, our flocculation agent includes plentiful of clay minerals that surface is plus charged. Beside, more plus charges are added to agent in the process of manufacturing. Therefore, when our flocculation agent is poured in water, dispersed minus charges in clay minerals and algae are neutralized and are cohered.

On the other hand, our flocculation agent coheres voluntarily in water because it has self-cohesive property (\*3). To be paid attention is that it physically incorporates the floating colloidal particle when cohering, and then it forms the fluck. The formed fluck settle out. This action occurs in any condition of the colloidal particle charges, and it is a similar physical agglutinative action even it is different from the action of cross-linkage process of the organic polymer coagulant. Moreover, due to this self-cohesive property of the flocculation agent, the unreacted agent doesn't remain in the treated water in case of excessive amount of flocculation agent is poured in. This is confirmed its safety of    treat water in a fish acute toxicity testing by killifish.

Figure 2 shows pattern diagrams of the cohesion mechanism of above-mentioned our flocculation agent. The relationship between the additive amount and the turbidity of our flocculation agent to china clay (clay mineral) murky waters is shown in Figure 3, and Figure 4 shows an outcome of an experiment. The experiment indicate the result that the same amount of our flocculation agent and the pulverized volcanic ash are poured in the low density simulated murky waters made by the red clay of Okinawa Prefecture. These figures clarify that our flocculation agent has great cohesive force. Photograph 2 shows the

cohesion situation when our flocculation agent is added to the red clay murky waters.

### *Application cases to the dam lake turbid water*

Turbidity in a river or a reservoir happens after heavy rain, and it continues for a long period. In many cases, negatively charged clay mineral causes these types of turbidity. The impurity becomes a problem visually or, in case of stocking turbidity with the downstream, it becomes an environmental preservative issue. Although agglutinating and subsiding turbidity is the most appropriate treatment; as previously stated, there is a problem in using existing flocculation agent. So that usage of the flocculation agent is low.

Here is the verification test using our flocculation agent. The murky water of this test was the dam lake where turbidity did not disappear for a long term of period, and the cause of impurity was the mica minerals with the minus charge. In this verification test several experimental tanks were set up in the vicinity of the intake of the reservoir, and 10 m<sup>3</sup> of impure lake water were pumped up into each tank. Each of the follows: our flocculation agent, natural mineral flocculation agent, PAC, and natural mineral flocculation agent+PAC, was mixed with each water tank, and the water quality afterwards was observed. For the comparison, the water tank with raw water entered was prepared (control plot). Figure 5 shows the result. The turbidity of the murky water mixed with our flocculation has decreased the turbidity rapidly. On the other hand, the both electric conductance and the pH indicate almost the same numerical value as the raw water. What this test proved is that our flocculation agent can keep excellent cohesive force without changing the water quality.

Regarding the cohered treat water (supernatant water), the followed items are analyzed: 5 items concerning the environmental standards on the maintenance of living conditions (lakes and marshes), 26 items concerning environmental standards on the protection of human health, and 6 items concerning fisheries water quality criterion. As a result of the analysis, beside the slight increase in pH and BOD, any of declining water quality or increase of the noxious substance were not been confirmed.

Table 3 shows the analysis result of elution volume and contained amount of cohesion sediment. The analysis items of elution volume include 26 items of environmental standards that is similar to the treat water, and copper and aluminum. As a result, it was not detected in 26 items in the precipitation of our flocculation agent as well as others, and lead was detected slightly as well as raw water. However, aluminum was detected from all precipitation comparatively in a high density. The density of both our flocculation agent and natural mineral flocculation agent was as same as that of raw water; however, the density of flocculation agent using the natural mineral flocculation agent and PAC together showed

several times higher density than that of the raw water. As a result of the analysis of the contained amount, each item of the sediment by our flocculation agent was almost equal to the precipitation of the raw water. On the other hand, precipitation that used the natural mineral flocculation agent with PAC indicated a high value with the ignition loss, the moisture weight percentage, and aluminum.

It was confirmed that our flocculation agent had an effective cohesive force for the impurity of the dam lake, and that it did not aggravate the treated water or no changes were seen on precipitation.

Our flocculation agent demonstrates the cohesive force for not only murky water, but also blue-green algae of lakes. Moreover, the volcanic ash that is the raw material of our flocculation agent is confirmed that the adsorption ability of heavy metals is high. These suggest that our flocculation agent has a various performance. By our flocculation agent, the dispersibility of the naturally exist clay mineral was improved, and it is again emphasized that environmental load in manufacturing and use of our flocculation agent is extremely low.

*Note)*

\*1 An irregular movement of the colloidal particle. It happens because solvent molecules (water) that are surrounding particles, collides from unpredictable directions with irregular speed.

\*2 Universally worked gravity besides the intermolecular chemical linkage

\*3 The character to cohere by sensitively reacting to even little electrolyte concentration in water. It coheres even in water with little suspended solid (colloidal particle), even in natural water or membrane filtered water with few suspended substances.

*Reference*

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