DEVELOPMENT OF WATER TREATMENT DEVICE BY FLUIDIZATION ELECTROLYSIS USING GRANULAR CERAMICS

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ABSTRACT

In recent years, with the increase in the consumption of natural resources and energy, global environmental problems have appeared. This is a very serious environmental load on worldwide food production. For this reason, innovative techniques for production of low entropy by using effectively the energy for the ecosystemic agriculture have been expected. In this study, granular ceramics of 2 to 3 mm in diameter having electrical charges at the surface were produced, using the natural raw materials of silicate minerals haing excellent moldabilities and sintering properties. Production of water having functions was attempted by effective use of the electrochemical energy of the ceramics with an efficient water treatment apparatus in which the ceramics were fluidized in water, differently from conventional systems. In the experimental results, the EC of water treated with the ceramics was not changed, but the ORP and also the pH and the DO were changed. The speed of oxidation−reduction reaction was high, and the ceramics− treated water enhenced the vigor of seeds. It can be expected that this treatment system, by which the ORP of water can be moderately controlled, is advantageous in controlling the growth of plants.

Keywords: granular ceramics, ecosystemic agriculture, electrochemical energy, ORP, silicate mineral, fluidization electrolysis, water treatment

INTRODUCTION

The deterioration of the cultivation environment such as soil contamination and water pollution has been one of the factors in the reduction in the vigor of seeds or crops, such as soil disease injury and physiological hindrance to roots. In nutriculture in greenhouses, the assurance of good quality raw water and environmental protection are important problems to be solved. In this study, stable granular ceramics having electrical charges at the surface were produced, using the natural raw materials of silicate minerals having excellent moldabilities and sintering properties. The functions of water were examined through effective use of the electrochemical energy of the ceramics.

MATERIALS AND METHODS

Granular Ceramics

The tested raw materials of silicate minerals are produced at Hoori district of Miyazaki in Japan, and are presumed to have erupted 400 to 500 million years ago (Fig.1). The particles of the powder have massive structure of 2×10^{-6} to 240×10^{-6} m in size. The granular ceramics of 2 to 3 mm in diameter are made by using the powder and the natural soil as the bonding agent, and sintering at 1200 ℃ (Fig.2). The granular ceramics are especially called "龍玉 ; Ryu–gyoku" in Kanji (Chinese Han's writing) after Hoori district in Japan.

Immersion Experiment

In this experiment, in order to reveal the effects of the granular ceramics immersed in water, the change in the state of air–saturated distilled water as a sample under a constant temperature condition (25 ℃) placed in an incubator was examined. For the preparation of the air–saturated distilled water, distilled water was placed into a 300–ml beaker, and air was fed into the water under pressure with an air pump. Thereby, oxygen and carbon dioxide were dissolved in equilibration with the atmosphere. Accordingly, it is supposed that chemical species such as H_2O, O_2, CO_2, H^+, OH^-, CO_3^{2-}, HCO_3^-, and H_2CO_3 were present in the air–saturated distilled water. Into the water, a magnetic stirrer was placed, and the beaker was placed onto a magnetic starter. The stirrer was then rotated at 500 rpm. The state of the water was monitored with a thermometer, a pH meter, a DO meter, a EC meter, and a ORP meter. After stable measurements were obtained, 10 g of the ceramics was placed into the beaker, and the measurement was continued.

Water Treatment Apparatus

Granular ceramics have a surface structure that can easily carry charges (electrons, e^-). Therefore, it can be much expected that frictional electricity and piezoelectricity are generated, and accompany that, electrochemical reactions take place. In this study, the apparatus for water treatment as shown in Fig.3 was experimentally produced. The upper and lower sides of a fluidization layer (280 mm in length, 75 mm in diameter) made of polyvinylchloride were sectioned with stainless steel nets. Into the section, the granular ceramics of 800 g were inserted. With a magnetic pump, water flow was directed from the lower to the upper side so that the ceramics could be fluidized. For the apparatus, a circulation system was employed, by which water passing through the fluidization layer was fed back into the water tank, and the flow rate could be controlled with a valve.

RESULTS AND DISCUSSION

Immersion Effect

A ceramic immersion section and a blank section (not charged with ceramics) were provided. The change in the physical properties of the water was examined at intervals of 10 minutes after the test was started.

As the results, the pH rose immediately after the test was started and after that remained at a nearly constant value. More particularly, the pH was 5.51, measured immediately before the start of the test, 5.63 for the ceramics immersion section (10 to 20 minutes), 5.57 (10 minutes) and 5.59 (20 minutes) for the blank section. Accordingly, the increments caused by the action of the ceramics were 0.03 to 0.06. The oxidation reduction potential (ORP) was 311 mv when measured immediately before the start of the test.

The potential gradually decreased and was 302 mv at 60 minutes for the ceramics immersion section. On the other hand, the potential gradually increased and then exhibited a peak value of 323 mv at 20 minutes for the blank section. Accordingly, with the action of the ceramics, the ORP was decreased by 11 to 16 mv. The changes in electrical conductivity (EC) for the ceramics immersion section and the blank section were small, that is, 0.08 to 0.12 μ s/cm and 0.24 to 0.38 μ s/cm, respectively. Thus, no evidence of the ion dissolution, caused by the immersion of the ceramics, was observed. The dissolved oxygen concentration (DO) was 8.31 mg/ ℓ measured immediately before the test was started and 8.21 mg/ ℓ at 60 minutes for the blank section, though the value was indefinite to some degree. On the other hand, the tendency for the ceramics immersion section was that the concentration decrease with time was larger to some degree compared with that of the blank section; that is, the ceramics immersion section exhibited 8.10 mg/ ℓ at 60 minutes. Accordingly, the decrement in DO, caused by the caramics, became higher with the immersion time. The decrements were 0.03 mg/ ℓ (10 minutes) and 0.11 mg/ ℓ (60 minutes).

The above results suggest that the ceramics had a considerable effect on the ORP, the DO, and the pH. It is presumed that the decreases in ORP, observed in this experiment, were related to the decreases in DO, and the increase in the pH was attributed to the decrease in H^+ in the water because no changes in conductivity were observed.

Effect of Fluidization Treatment

As shown in Table 1, the pH increased linearly with the increase in the treatment time at the flow rate of 12 ℓ /min. The increments in pH, caused by the action of the ceramics, were 0.01 (5 minutes) to 0.06 (60 minutes). The DO increased with the treatment time. That is, the concentration were 6.88 mg/ ℓ , measured immediately before the test was started, and 7.66 mg/ ℓ (60 minutes) for the fluidization section and 7.42 mg/ ℓ (60 minutes) for the control section. Accordingly, the increments in DO, attributed to the ceramics, were 0.18 mg/ ℓ (10 minutes) to 0.30 mg/ ℓ (60 minutes). The EC was unchanged compared with the value (0.220 mS/cm) measured immediately before the test was started, exhibiting a constant value of 0.220 mS/cm for both the control and the fluidization sections. This means that no ions were dissolved from the ceramics using this treatment system. The ORP increased for both the fluidization and the control sections. Especially, the change in potential was remarkable for the fluidization section. The increments in ORP attributed to the action of the ceramics were 76 mv (5 minutes) to 150 mv (60 minutes). The relation between the time T(min) after fluidization treatment and the ORP P(mv) is expressed as following equation. where, A and B are experimental coefficient (−).

$$\log P = A - B \cdot e^{-4T}$$

The potential of tap water for the control, measured immediately after the sampling, was 462 mv, and that of the tap water treated for 20 minutes was 549 mv. At this time, the potential for the fluidization section was about 87 mv higher. However, the oxidation−reduction speed for the fluidization section was high. The value was 464 mv on the first day after the treatment and after that decreased by 85 mv/day. On the other hand, the change in the potential for the control was slow (450 mv, a decrement of 12 mv/day). On and after the fifth day, the potentials for both sections remained stably at about 230 mv. Generally, the water molecule is expressed as H_2O. However, the molecules do not exist separately in water, but n molecules are bonded through hydrogen bonds to form a cluster (mass of molecules). When the water is subjected to pressure, vibration, or a magnetic field, electricity, the state of the molecule mass is changed (Kubo, 1989). Statistically, the following dissociation takes place.

$$H_2O = H^+ + OH^- \qquad (1)$$

$$O_x + ne^- = Red \qquad (2)$$

The oxidation−reduction reaction is expressed as formula (2) in which O_x is an oxidant, Red is a reductant, e^- is an electron, and n is the number of transfer electrons. Thus, as the change in the state of water, the following relation between the formation reaction and the ORP of the $H_2O - O_2$ system (Morinaga, 1976;Tamura, 1982) taking place when water undergoes oxidation– reduction action should be taken into account.

$$O_2 + e^- = O_2^- \tag{3}$$

$$O_2 + H^+ + e^- = HO_2 \tag{4}$$

$$2H^+ + 2e^- = H_2 \tag{5}$$

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{6}$$

$$O_2 + 2H^+ + 2e^- = H_2O_2 \tag{7}$$

$$HO_2 + H^+ + e^- = H_2O_2 \tag{8}$$

$$H_2O_2 + 2H^+ + 2e^- = 2H_2O \tag{9}$$

In the experiment in which the granular ceramics were immersed into the air saturated distilled water, the ORP was reduced, and the pH increased. The mechanism is suggested as follows. As expressed by the above formulas, the electron e^- of the ceramics reacts with dissolved oxygen O_2 so that hyperoxide ion O_2^-, reduced with one electron, is formed. As the dissolved oxygen is a paramagnetic substance, the O_2^- acts as an active species to react with H^+ so that HO_2 is produced. In this process, the dissolved oxygen and H^+ are consumed. In the fluidization experiment, the pH and the ORP increased. Probably, this is attributed to the formation of OH^- and H_2O_2. In the processes of the respective formation reactions, dissolved oxygen is consumed. The phenomena in which the dissolved oxygen is increased as observed in the fluidization treatment will be useful for increased physiological activity in plants and will supplement the lack of dissolved oxygen in water. As to the level of the ORP of water which is related to the production of plants, it has been experimentally revealed that physiological hindrance occur in the case of the oxidized water with a high potential (higher than 800 mv), and also, for the reduced water with a lower potential, the growth is inhibited. It can be expected that this treatment system, by which the ORP of water can be moderately controlled, is advantageous in controlling the growth of plants.

Effect on Vigor of Rice Seeds and Growth

Before seeding rice seeds in nursery box, the soaking of seeds for hastening of germination and disinfection was performed, as the seed pretreatment, using fluidization–treated (one passed) water. The germination test in nursery box was carried out in an incubator at 25 ℃ . As shown Table 2, the germination rates were differentiated on the third day after seeding in the box, and a significant difference at a significance level of 1 % to the control was observed. The above result shows that the ceramics−treated water enhanced the vigor of the seeds, that is, displayed a germination promotion effect. As the result of growth test of rice after transplanting in paddy field, irrigation using the fluidization treatment system showed the promotion of a tillering capacity and a differentiation of young panicle of rice as compared with that of the control (Fig.4).

CONCLUSIONS

Stable granular ceramics having electrical charges at the surface were produced using the natural raw materials of silicate minerals. Production of water having functions was attempted by effective use of the electrochemical energy of the ceramics with an efficient water treatment apparatus in which the ceramics were fluidized in water, differently from conventional systems. In the experimental results, improvements in water quality and proper ORP of water, which will contribute to global environmental protection and ecosystemic agriculture, were obtained.

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Table 1. Physical properties of fluidization-treated water

Test section	Fluidization treatment time(min)	pH (-)	ORP (mv)	DO (mg/ ι)	EC (ms/cm)
Fluidization					
	0	7.14	564	6.88	0.220
	10	7.20	684	7.28	0.220
	20	7.25	701	7.38	0.220
	30	7.29	711	7.50	0.220
	40	7.34	714	7.58	0.220
	50	7.38	714	7.62	0.220
	60	7.42	713	7.72	0.220
Control					
	0	7.14	564	6.88	0.220
	10	7.17	601	7.10	0.220
	20	7.22	601	7.18	0.220
	30	7.25	601	7.26	0.220
	40	7.29	594	7.32	0.220
	50	7.32	583	7.38	0.220
	60	7.36	569	7.42	0.220

Flow rate: 12 ι /min

Table 2. Comparison of germination rate of days after seeding in nursery box

	Day after seeding in nursery box 3	4	5	6	7
	Mean germination rate (%)				
Fluidization-treated water	60.0 **	86.5 **	91.3 **	95.0 **	97.5 **
Control	21.3	61.3	65.0	67.2	72.5

** : Significant difference from control at 1 %

Fig.1 Layer of silicate minerals
(Hoori district in Miyazaki Pref.)

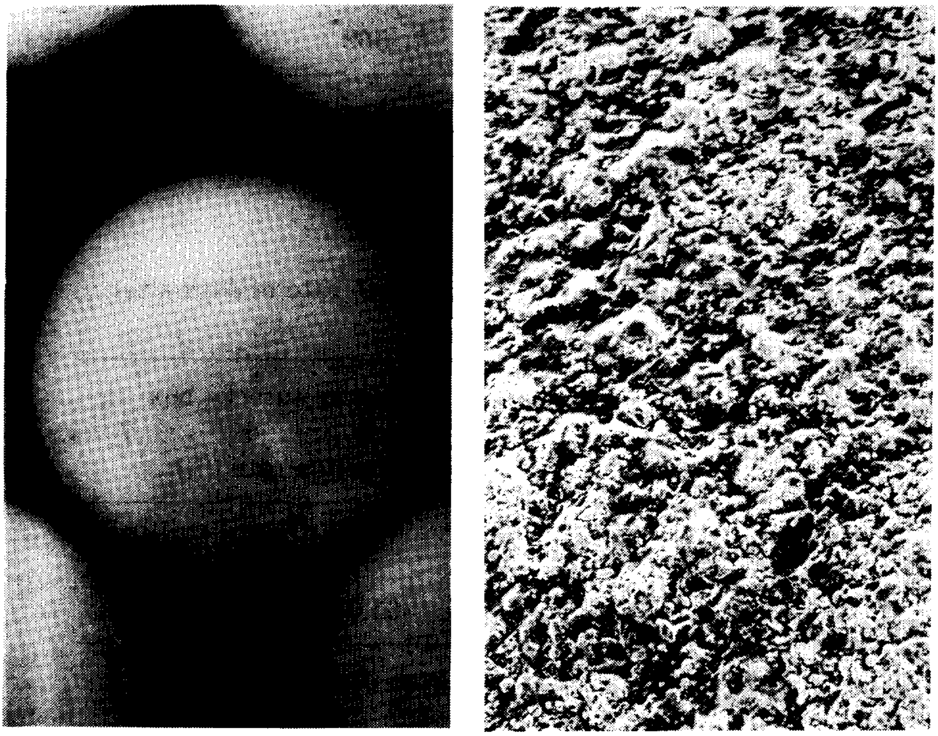

Fig.2 Surface of granular ceramics "Ryu−gyoku"

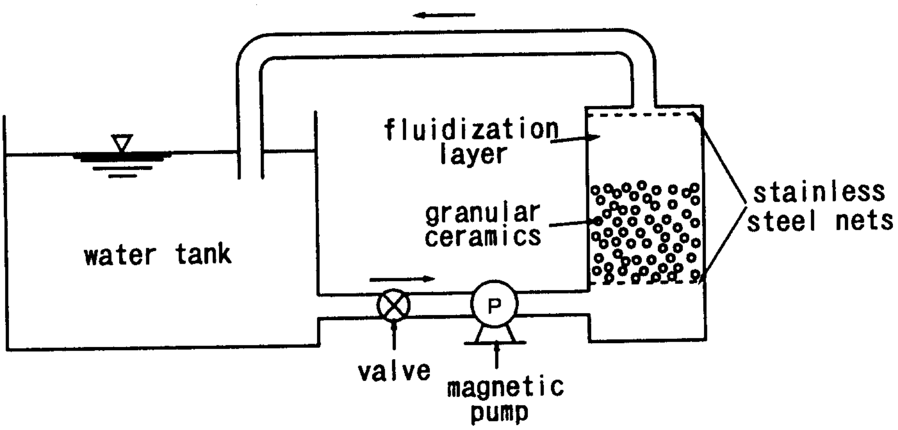

Fig.3. Water treatment apparatus

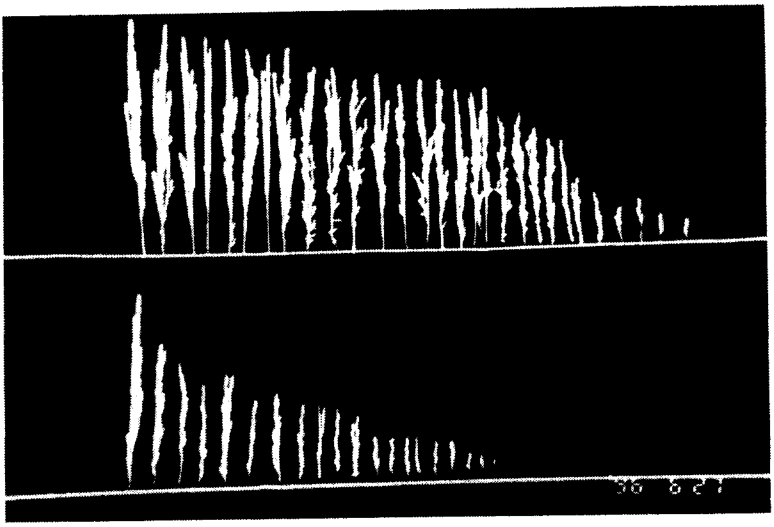

Fig.4 Comparison of differentiation of young panicle of rice per 1 hill
(top: fluidization treatment section)
(bottom: control section)