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STUDY ON PROPERTIES OF CONCRETE MIXED WITH RICE HUSK ASH ADSORBING HEAVY METALS

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ABSTRACT: Goals 12 of the Sustainable Development Goals (SDGs), “Sustainable Consumption and Production”, aims to achieve “Drastic reduction of waste generation through the prevention, reduction, recycling and reuse of waste” by 2030. In Asia, more than 100 million tons of rice husk are discharged annually. Although they are utilized for biomass power generation as reuse, the generation of wastes has not been drastically reduced. Therefore, it is necessary to develop a method to realize a significant reduction of rice husk. The rice husk has the following features; it has the adsorption performance for heavy metals and incinerated rice husk contains a large amount of amorphous silica, which may increase the strength of concrete. Thus, firstly, untreated rice husk is utilized as an adsorbent for heavy metals. After that, it is used for biomass power generation to reduce its volume. Since heavy metals that remained in the rice husk are concentrated at this stage, the rice husk ash used for biomass power generation is mixed as a fine aggregate of concrete instead of being discarded as it is. In this study, fresh properties are examined by slump test and air content test, hardening property is investigated by compressive strength test, and harmful substance elution is evaluated by dissolution test. As the result, the concrete has fresh properties with no problem in construction, the concrete mixed with rice husk ash has a higher compressive strength than ordinary concrete, and no harmful substance is eluted from the concrete mixed with rice husk ash.

Keywords: Rice husk ash, Recycling, Concrete admixture, Heavy metals

1. INTRODUCTION

In recent years, various environmental problems such as environmental pollution and the shortage of waste disposal sites are faced by the mass consumption of resources and energy and the increase of waste discharge associated with the consumption. Therefore, the formation of a recycling-oriented society becomes an urgent problem. As the initiatives to realize a recycling-oriented-society, goal 12, “Sustainable Consumption and Production” which is one of the 17 goals raised in "Sustainable Development Goals (SDGs)" aims to achieve "Drastic reduction of waste generation through the prevention, reduction, recycling and reuse of waste" by 2030. Recently, as a part of the generation control and reduction of wastes, the recycling of food wastes which are regarded as a worldwide problem is promoted due to their enormous generation. In Asia, where rice is the staple food, more than 100 million tons of rice husk are discharged annually as food waste. As reuse, as shown in [1], they are utilized as an energy resource for biomass power generation, which is one of the renewable energies. However, in biomass power generation, the amount of generation waste has not been drastically reduced in the true sense because a large amount of rice husk ash is generated as an energy resource after incinerating rice husk. Therefore, it is necessary to develop a method to realize a significant reduction of rice husk. In addition, it is also necessary to change the rice husk to a resource recycling material with high-added value in recycling the rice husk because it is important to implement the development method in society at an early stage. As reported in [2] and [3], even untreated rice husk has adsorption performance for heavy metals in an aqueous solution. Additionally, as described in [4], the incinerated rice husk contains a large amount of amorphous silica. In this study, at first, untreated rice husk is utilized as an adsorbent for heavy metals, and metals with high value are recovered after adsorption. After that, it is used for biomass power generation to reduce its volume. In this stage, since heavy metals that remained in rice husk ash are concentrated, the rice husk ash in which heavy metals remain is mixed as a fine aggregate of concrete instead of being discarded as it is. Since rice husk ash contains a large amount of amorphous silica, there is a possibility that the merits such as an increase of concrete strength are brought about as shown in [5] and [6] That is to say, in the achievement of zero-emission of rice husk which is a sort of food waste, it is very important whether rice husk ash can be mixed into concrete or not.

Therefore, in this study, the fresh and hardening properties are grasped for concrete mixed with rice husk ash containing heavy metals, and whether it can be used as concrete or not is evaluated. Furthermore, the elution properties of heavy metals from concrete mixed with rice husk ash containing heavy metals are examined to assess environmental loading.

2. MATERIALS

2.1 Cement and Aggregate

Ordinary Portland Cement (density 3.16 g/cm^3) specified in JIS R 5210 Japanese Industrial Standards is used for cement. In addition, the mountain sand and crushed stone 2005 produced in Sanuki City, Kagawa Prefecture, Japan are used for fine aggregate and coarse aggregate, respectively. According to the properties of the used aggregate, the surface dry density and maximum particle size for fine aggregate are respectively 2.57 g/cm^3 and 2.5 mm, and those for coarse aggregate are respectively 2.62 g/cm^3 and 20mm.

2.2 Rice Husk Ash

According to [7], rice husk ash contains about 90 % silica by mass. The silica content of rice husk ash is higher than that of fly ash, and the content of rice husk ash is comparable to that of silica fume. Moreover, it is reported that silica as the amount of the amorphous state is large, the reactivity of the silica contained in rice husk ash increases. Therefore, as described in [8], it is expected to promote the pozzolanic reaction, which is related to the improvement of concrete strength. Thus, rice husk ash is noticed as a high silica material. Additionally, the research to use rice husk ash as a concrete admixture is studied, because the properties of density and strength of concrete are improved due to amorphous silica. From the result of XRD analysis of rice hull ash incinerated at 600 ~ 1150 ºC conducted by Umeda et al.[9], it is reported that the incinerated at 1000 ºC or less is necessary to maintain the amorphous structure of silica. In addition, as shown in [10], to obtain amorphous silica, it is desirable to incinerate rice husk at low temperature as much as possible and in a minimum of time. Thus, in this study, rice husk is put into an alumina vessel, heated to 600 °C in an electric furnace for 2 hours, then incinerate at 600 °C for 3 hours, and then left to cool. Fig. 1 shows the rice husk ash prepared to use in this study. Then, to confirm whether silica contained in the prepared rice husk ash is amorphous or not, the crystal structure of the prepared rice husk ash is analyzed by XRD (X-ray Diffraction) analysis.

Fig. 2 shows the spectrum of the prepared rice husk ash analyzed by the XRD analysis. From the peak position and peak width of the spectrum obtained by the XRD analysis, it is possible to know the components and crystallinity of the prepared rice husk ash. The horizontal and vertical axes in Fig. 2 are the diffraction angle and the X-ray diffraction intensity, respectively. From Fig. 2, it can be seen that the intensity peak appears in the vicinity of 22 º to 23 º of 2θ. In addition, it is found that the peak width is wide and that the X-ray diffraction pattern (called halo according to [11]) is continuous. As a result of XRD analysis, a broad peak (halo pattern) appeared between 15 º and 30 º around 22.5 º of 2θ, so it can be said that silica in the rice husk ash produced in this study is a typical amorphous state. Such fact is seen to have good accordance with the references [12] and [13].

Fig. 1 Rice husk ash

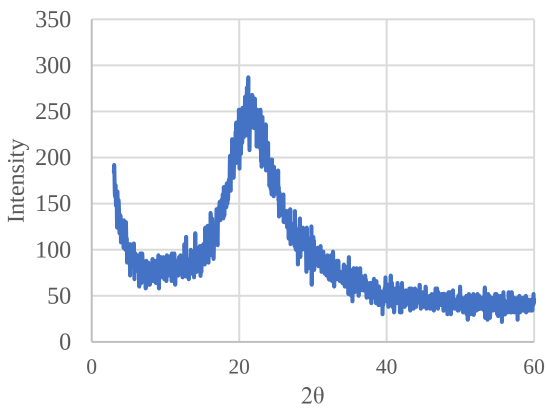

Fig. 2 Spectrum of rice husk ash by XRD

2.3 Chemical Admixture

For chemical admixtures, the air-entraining and high-range water-reducing admixture (AE-HR-WRA) and the air-entraining admixture (AE-A) are used, respectively. Regarding the main components of the used chemical admixture, the main component of AE-HR-WRA is a complex of a lignin sulfonic acid compound and a polycarboxylic acid ether, and the main component of AE-A is a modified rosinic acid compound-based anionic surfactant.

3. TEST METHOD

3.1 Concrete Mix Design

On the concrete in the tests, the mix proportion is designed at a water-cement ratio of 55 % and a fine aggregate ratio of 46 %. Table 1 shows the mixed proportions of concrete in the test. “Blank” is ordinary concrete (concrete without rice husk ash), “RHA” is concrete mixed with rice husk ash, and “RHA(Cd)” is concrete mixed with rice husk ash adsorbing cadmium. The heavy metal which is mixed in the concrete of the test is cadmium which is known as a causative substance of pollution diseases in Japan and is a toxic heavy metal that affects living organisms and the environment. The mixing method of rice husk ash into concrete is so-called "outer percentage mixing" in which fine aggregate is replaced by the rice husk ash, and the replacement rate is 5 % for the volume of fine aggregate. 1.9 % (RHA and RHA(Cd)) for the cement mass, respectively. Then, the addition amount of AE-A is 0.001 % (all specimens) for the cement mass. Furthermore, as shown in [14], there are studies on the elution behavior of heavy metals from mortar-containing heavy metals. However, there are few studies on the elution of heavy metals from concrete mixed with rice husk ash as admixture. Thus, in the test, a predetermined concentration of cadmium is adsorbed on the rice husk ash in advance. Concretely, the adsorption test (shaking test) of rice husk ash for cadmium is carried out using the cadmium nitrate solution prepared at the initial concentration of 1 ppm, and the residual concentration of cadmium is analyzed by ICP-AES after the shaking test. From the results, it is found that about 0.9 ppm of cadmium is adsorbed on the rice husk ash used in the tests. Therefore, this concentration (about 0.9 ppm) shall be taken as the initial concentration of cadmium in rice husk ash. In addition, mixing is carried out according to the following procedure. First, half of the aggregate (coarse aggregate, fine aggregate, rice husk ash), cement, and the rest of the aggregate are put to the mixer in that order. Rice husk ash is mixed with the fine aggregates in advance. After putting the materials into the mixer for 30 seconds, rotate the mixer to mix the materials. Then, pure water with a chemical admixture is poured into the mixer and mixed for 60 seconds for the Blank specimen and 90 seconds for RHA and RHA(Cd) ones.

3.2 Fresh Properties Test for Concrete

Regarding the fresh properties tests, each material (cement, aggregate, rice husk ash, and so on) is mixed using a mixer to prepare a concrete sample. After that, the slump test and air content test are carried out according to JIS A 1101 Japanese Industrial Standards and JIS A 1128 Japanese Industrial Standards, respectively. In the slump test, first, the slump cone is filled with three layers of fresh concrete. In each time, approximately one-third of fresh concrete is filled into the slump cone, and the fresh concrete is struck 25 times with a rod. After filling the slump cone with fresh concrete, the fresh concrete which protrudes from the upper part of the slump cone is made flat in alignment with the upper-end surface of the slump cone. After that, the slump cone is lifted vertically for 2 to 3 seconds, and the slump is measured. In the air content test, the air content measuring instrument is filled with fresh concrete in the same procedure as the slump test described above. After that, the side of the container is hit with a wooden hammer, fresh concrete protruding from the upper part of the container is removed and the upper part of the container is leveled. Next, the lid is gently attached to the container with the exhaust port opening, and four fasteners are tightened. Then, after the exhaust port and the pressure control valve are closed, the pressure in the container is raised using a pump and the pointer of the pressure gauge is adjusted to the scale of the initial pressure. Afterward, the actuated valve is opened for about 5 seconds, and the scale of the air content of the pressure gauge is recorded to one decimal place. In the test, the target slump and air content values are set to 12±2.5 cm and 4.5±1.5 %, respectively.

3.3 Preparing Of Test Specimens For Concrete

A cylindrical specimen of ϕ100 × 200 mm is prepared by JIS A 1132, the Japanese Industrial Standard. Two patterns of cylindrical specimens are prepared for compressive strength test and dissolution test. After preparing the specimens, they are cured in water for 28days. The upper surface of the specimen is ground by a polishing grinder so that the specimen loading surface (upper surface) of the test specimen becomes flat.

3.4 Hardening Properties Test for Concrete

After the specimens are cured in water for 28 days, the compressive strength test is carried out as a physical property test of concrete by JIS A 1108 of the

Table 1 Mix proportions of concrete (kg/m^3)

	Water	Cement	Rice Husk Ash	Fine Aggregate	Coarse Aggregate	AE-HR-WRA	AE-A
Blank	175	318	0	785	940	2.86	0.003
RHA	175	318	32	746	940	6.05	0.003
RHA(Cd)	175	318	32	746	940	6.05	0.003

Japanese Industrial Standard. In the procedure of the compressive strength test, the specimen is placed in the universal testing machine, and the specimen is loaded at a uniform speed so as not to give an impact to it. After that, the maximum load indicated by the testing machine is recorded and the compressive strength is calculated. The compressive strength is defined by the following equation (1).

$$\boldsymbol{f_c(N/mm^2) = \frac{P}{\pi d^2/4}} \qquad (1)$$

where "*fc*" is the compressive strength, "*P*" is the maximum load and "*d*" is the measuring diameter of the cylindrical test specimen. To ensure reproducibility, the mean value of three tests is adopted as a test result in the tests.

3.5 Heavy Metals Elution Test From Concrete

In the test, the elution test of cadmium from concrete is conducted based on the Environment Agency Notification 46. First, the specimen is crushed to 5 mm or less with a hammer, and the crushed blocks passed through a sieve (mesh opening 2 mm) defined as a sample. Next, 50 mL of pure water is poured into a centrifuge tube, and 5 g of the sample is also added into the centrifuge tube. They are defined as the specimen in the test. The ratio of pure water to the sample in the specimens is 10 % of the weight-volume ratio. Then, the test specimens are shaken for 6 hours at 200 rpm at 20 °C. After shaking, the specimens are allowed to stand for 10 to 30 minutes, and they are centrifuged at 3000 rpm for 20 minutes. After centrifugation, the supernatant solution of the specimen is filtered through a membrane filter (pore size: 45 μm), and the concentration of cadmium in the filtered solution is analyzed by an ICP-AES. To ensure reproducibility, the mean value of the tests is calculated from the results obtained by three tests as well as the compressive strength test.

4. RESULTS AND DISCUSSION

4.1 Result of Fresh Properties Test for Concrete

Table 2 shows the slump value and air content value for the three cases of Blank, RHA, and RHA(Cd) samples. From Table 2, it can be seen that the slump value and air content value achieve the target values in all the fresh concrete. Although the air content values of all the fresh concrete are within the allowable value, they are lower than the standard value of 4.5 %. In the tests, it is considered that the amount of air was not entrained than expected, because the amount of AE-A added in all the concretes was considerably small (0.001 % of cement mass). In all the samples, the slump value reaches the target one. However, compared to the slump value of Blank, RHA, and RHA(Cd) sample and the slumped shape of that (see Fig. 3 to Fig. 5), regarding the Blank sample, it can be seen that the slump value is the largest and that the slumped shape also collapses from the top. This is because material separation occurs in the fresh concrete of the Blank sample due to the uneven mixing of materials. In the RHA sample, the collapse of the slump from the top can be confirmed, though it is not as much as the blank sample. According to this fact, it can be seen that the material separation occurs even in fresh concrete of the RHA sample. On the other hand, the slump of the RHA(Cd) does not collapse. Additionally, it is found that the fresh concrete of the RHA (Cd) specimen has a higher

Fig. 3 Slump of the Blank

Fig. 4 Slump of the RHA

Table 2 Result of fresh properties test for concrete

	Slump value (cm)	Air content value (%)
Blank	14.3	3.0
RHA	13.0	3.6
RHA(Cd)	10.3	3.1

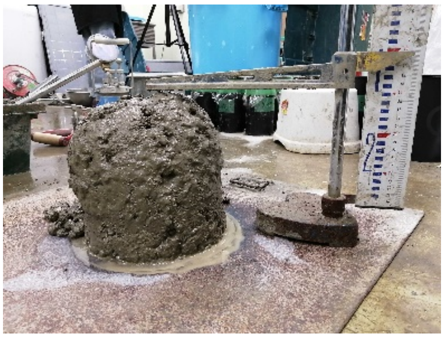

Fig. 5 Slump of the RHA(Cd)

viscosity than that of other specimens. Further examinations are needed to obtain more detailed information on the fresh property of the RHA(Cd) specimen.

4.2 Result of Hardening Properties Test for Concrete

Fig. 6 shows the compressive strength of Blank, RHA, and RHA(Cd) concrete. From Fig. 6, it is found that the compressive strength of the RHA sample is much higher than that of the Blank one. This is due to the pozzolanic reactivity by amorphous silica contained in the rice husk ash. Additionally, according to [15], it is reported that the concrete mixed with rice husk ash with the addition of superplasticizer shows much higher compressive strength than that without superplasticizer. This is because the water-binding ratio decreases due to the addition of a superplasticizer. In the test, since the addition amount of AE-HR-WRA to the RHA is more than twice that to the Blank, the unit water content of the RHA decreases more than that of the Blank. As the water-cement ratio decreases, concrete strength increases. Therefore, it is considered that the compressive strength of the RHA is higher than that of the Blank. Additionally, there is not much difference between the compressive strength of the RHA(Cd) and that of the RHA. It is suggested that the presence or absence of Cd in rice husk ash has little effect on the strength of concrete in the low concentration of Cd in rice husk.

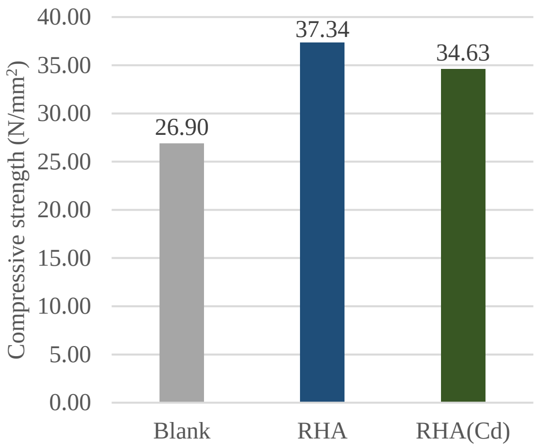

Fig. 6 Result of compressive strength test (28 days)

4.3 Result of Heavy Metals Elution Test from Concrete

Fig. 7 shows the eluted concentration of Cd from Blank, RHA, and RHA(Cd) concrete. The effluent standard for Cd in Japan is 0.03 ppm. From Fig. 7, the eluted concentration of Cd was less than 0.03 ppm for all concrete specimens, and the elution of Cd could hardly be confirmed. It is considered that Cd does not elute from concrete even when rice husk ash adsorbing Cd is mixed with concrete. Therefore, even if rice husk ash containing Cd at a low concentration is used as a concrete mixture, it can be said that there is no impact on the environment.

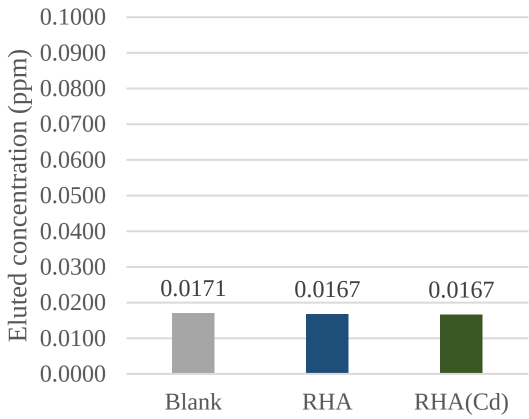

Fig. 7 Result of elution test

5. CONCLUSIONS

In this study, the fresh and hardening properties were grasped for concrete without rice husk ash (Blank), concrete mixed with rice husk ash (RHA), and concrete mixed with rice husk ash containing cadmium (RHA(Cd)), respectively, and whether RHA(Cd) can be used as a concrete or not was evaluated. Furthermore, to assess environmental loading, whether cadmium elutes from RHA(Cd) or not was examined. The results obtained are as follows.

- The slump value and air content value achieved the target values (slump: 12±2.5cm and air content: 4.5±1.5%) in all the fresh concrete of Blank, RHA, and RHA(Cd).
- From the slumped shape of each fresh concrete, it was confirmed that the fresh concrete of the RHA (Cd) specimen has a higher viscosity than that of other specimens. Further examinations are needed

to obtain more detailed information on the fresh property of the RHA(Cd) specimen.

- The compressive strength of the RHA sample was much higher than that of the Blank one. This is due to the pozzolanic reactivity by the amorphous silica contained in the rice husk ash and the decrease of the RHA unit water volume by adding AE-HR-WRA.
- On the other hand, there is not much difference between the compressive strength of the RHA(Cd) and that of the RHA. It is suggested that the presence or absence of Cd in rice husk ash has little effect on the strength of concrete in the low concentration of Cd in rice husk.
- The elution of Cd could hardly be confirmed for all concrete specimens of Blank, RHA, and RHA(Cd). Therefore, even if rice husk ash containing Cd at a low concentration is used as a concrete mixture, it can be said that there is no impact on the environment.

From these results, it is necessary to investigate the fresh properties of RHA(Cd) by changing the concentration of Cd adsorbed on the rice husk ash. In addition, it is needed to verify the long-term intensity expression of RHA(Cd) by extending the curing period.

6. ACKNOWLEDGMENTS

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