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STUDY ON ELUTION REDUCTION OF HEXAVALENT CHROMIUM FROM RECYCLED BASE COURSE MATERIAL USING WASTE SYRUP

* Keiichiro Shibata[1], Hidenori Yoshida[2], Hiroki Yokoyama[3], Shinichiro Okazaki[4] and Matsumoto Naomichi[5]

[1] Graduate school of engineering, Kagawa university, [2, 3, 4] Faculty of engineering and design, Kagawa university, Japan, [5] Technical staff, Kagawa university, Japan

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ABSTRACT: In the civil engineering field, the utilization of recycled materials is promoted so as to reduce environmental burden. In particular, the utilization of concrete accessory product generated by the dismantlement of the concrete construct is an urgent issue in the light of both environment conservation and the shortage of repository site. Most concrete accessory products are recycled as the recycled base course material. However, it is at risk of the elution of the trace of hexavalent chromium from the recycled base course material. A major countermeasure to this problem is the reduction treatment to harmless trivalent chromium by reducing substances. There are many different types of the reducing substances. Among them, low cost is required for the reduction material because the recycled base course material is inexpensive. Therefore, in this study, waste sugar syrup is focused on with attention to two points such as reducibility and low cost. The elution test for the hexavalent chromium in cement paste is conducted, and the reducibility of the sugar contained in the waste syrup is verified. As a result of the reduction test using the waste syrup, it becomes clear that the eluted hexavalent chromium concentration decreases below the effluent standard.

Keywords: Waste syrup, Hexavalent Chromium, Recycled base course material, Reducing property

1. INTRODUCTION

The utilization of recycled materials for the purpose of environmental loading reduction is promoted in the civil engineering field in Japan which shifts from the mass production, mass consumption and mass disposal society to the recycling society. Especially, the utilization of concrete by-products generated from the demolition of concrete structures is promoted from the viewpoint of environmental conservation and tightening of disposal sites, and most of them are recycled as in [1]. The transition of the recycling rate of concrete by-products is shown in Fig. 1 as in [2]. More than 99 % of the by-products are recycled, and most of them are recycled as roadbed material. The utilization of recycled roadbed material is expected to be promoted in future from the viewpoint of reduction of environmental load by recycling and low material cost. However, trace of hexavalent chromium (Cr^{6+}) contained in the cement may be detected from the recycled roadbed material as in [3], [4]. It is recommended to confirm the degree of the elution in the case of using recycled roadbed material. In addition, Cr^{6+} may elute from not only recycled roadbed materials but also cementitious solidification materials used for cement-improved soil, when the soil in which the significant inhibition of hydrate formation is occurred such as a volcanic cohesive soil is improved as in [5], [6]. Hexavalent chromium has very strong toxicity, and is specified as a harmful substance in the environmental standard by the Ministry of Environment. On the other hand, it is easily reduced to harmless trivalent chromium. Therefore, hexavalent chromium is often detoxified by reduction treatment using a reducing substance. Though the kinds of reducing substances are various, the low cost is also required for reducing substances due to the cheapness of the recycled roadbed material. Thus, in this study, the discarded sugar syrup is focused on with considering two points, i.e., reducing characteristics and low cost.

There is a past research which verified the reduction of Cr^{6+} elution from regenerated roadbed material by reducing sugar as in [7]. Concretely speaking, the fruit juice and six kinds of sugar solution including reducing sugar are sprayed or immersed in crushed concrete material. The reduction sugar and the fruit juice containing it are confirmed to have the effect of reducing the elution for Cr^{6+}. Among them, fructose and glucose have high reducing ability for Cr^{6+}. In this study, two test methods are devised to verify the reduction of Cr^{6+} elution from the roadbed material is examined with a view to verification of the reduction of Cr^{6+} elution from cement-improved soil in near future. One is a method to immerse crushed concrete in sugar solution as in the past research, and the other is a method to mix sugar solution as admixture in mixing concrete. An availability of the waste syrup on the elution of the Cr^{6+} is examined by each different approach.

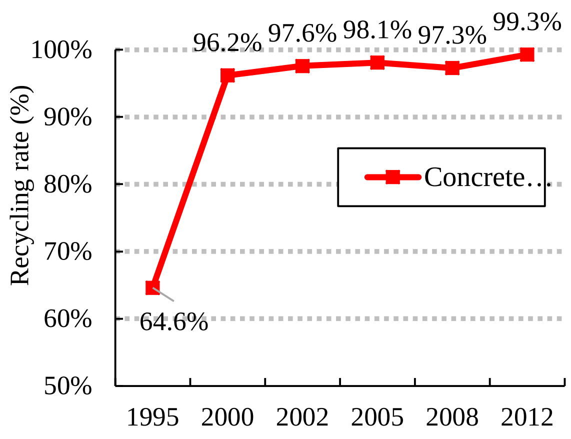

Fig. 1 Transition of recycling rate of concrete by-products

2. ELUTION MECHANISM OF HEXAVALENT CHROMIUM

In nature, chromium exists in a trivalent state as well as in cement raw materials. Trivalent chromium (Cr^{3+}) in the raw material is partly changed to Cr^{6+} in the cement manufacturing process. Previous studies have shown that Cr^{6+} is not only adherent to cement minerals but also present as water-soluble Cr^{6+} as in [8]. Water soluble Cr^{6+} in the cement is dissolved in the liquid phase during the elution process of the hydration reaction and is fixed to the precipitated hydrate. Therefore, the concentration of Cr^{6+} in the liquid phase decreases as the hydrate is formed.

As has described above, the cement contains Cr^{6+}, and Cr^{6+} is eluted with the hydration reaction. On the other hand, when concrete is crushed and used as a recycled roadbed material, Cr^{6+} may be eluted from the recycled roadbed material due to its use under the environment in contact with rain, groundwater, etc., and due to the influence of the particle size of the material. Alternatively, advanced processing such as crushing, grinding and classification is not conducted because there is no regulation in the processing method of recycled roadbed material. According to the past research, the elution amount of Cr^{6+} increases as the grain size decreases. Therefore, it is considered that the possibility of Cr^{6+} elution increases by the mixture of crushed concrete with extremely small grain size. Furthermore, the using site of recycled roadbed material is mainly the topper roadbed or the lower roadbed (see Fig. 2), and the runoff of Cr^{6+} to soil may occur because the recycled roadbed material is in contact with soil. Thus, the elution countermeasure of Cr^{6+} before the usage as recycled roadbed material is very important from a safety point of view.

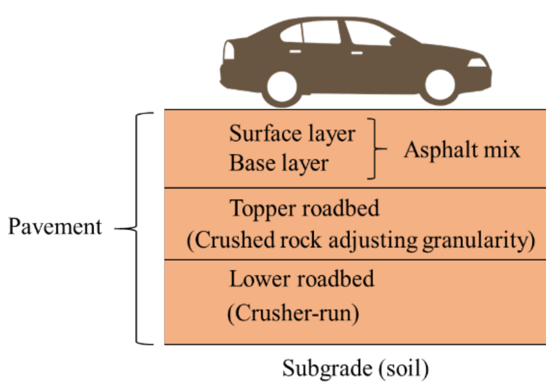

Fig. 2 Materials used for roadbed material

3. WASTE SYRUP AND REDUCING ABILITY OF SUGAR

Waste syrup is selected as a reducing agent for Cr6+ in view of low material costs, reducing ability and waste recycling. The syrup contains several kinds of sugars such as allose, glucose and fructose, and the expired syrup is used in the test. Sugars are divided into reducing and non-reducing sugars. The difference between reducing and non-reducing sugars is the existence or non-existence of reducing group, and it is known that the sugar with aldehyde group in the structure shows reducing property as in [9]. For example, glucose has the structure shown in Fig. 3, in which the aldehyde moiety shows reducing property. On the other hand, the sucrose which is a disaccharide does not show reducing property because the glucose and fructose which belong to the reducing group link together. In the test, the glucose, allose and sucrose are prepared as the reducing agents in addition to the waste syrup in order to confirm the usefulness of the waste syrup and to clarify each reducibility.

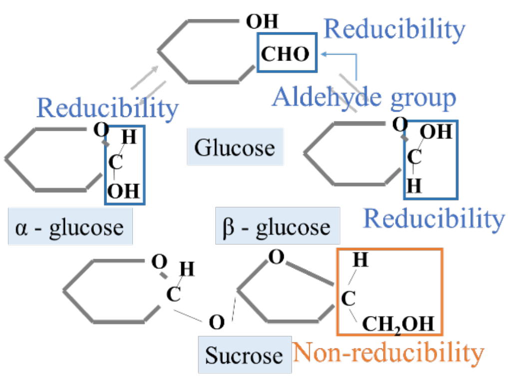

Fig. 3 Examples of reducing sugars and non-reducing sugars

4. TEST METHOD

As has already mentioned above, two kinds of tests are conducted to evaluate the reducibility of sugars to Cr^{6+}. One is a method to mix sugar in cement before solidification, and the other is a method to immerse sample after solidification and grinding in sugar aqueous solution. The former is called the mixing method and the latter is called the reduction test by the immersion method. Each test is conducted by reference to the elution test which is noticed by the Ministry of Environment Notification No. 46 as in [10], and three times of each test are conducted under the same conditions to ensure reproducibility.

4.1 Mixture method

The purpose of this method is to reduce the elution amount of Cr^{6+} by mixing the sugar which has the reducibility as an admixture. Cement paste of 70 % water-cement ratio is produced, and the mold for cement is removed after 7 days and sealed curing is carried out for 21 days. Samples are prepared by mixing Cr^{6+} standard solution and waste syrup. There are nine patterns of specimens, and the test conditions are shown in Table 1. After curing, the specimen is finely crushed with a hammer, and the sample having grain size of less than 2 mm is collected by sieving. Thereafter, the concentration of Cr^{6+} in the solution obtained by the elution test is measured. The concentration of Cr^{6+} is determined by diphenylcarbazide adsorptiometry coupled with collecting on membrane filter. The mixture method is shown in Fig. 4. The operation added to the mixture method is shown in the figure. The Cr^{6+} is reduced by mixing in advance before cement is set. The advantage of this method is that there is not necessary to treat for sample after construction.

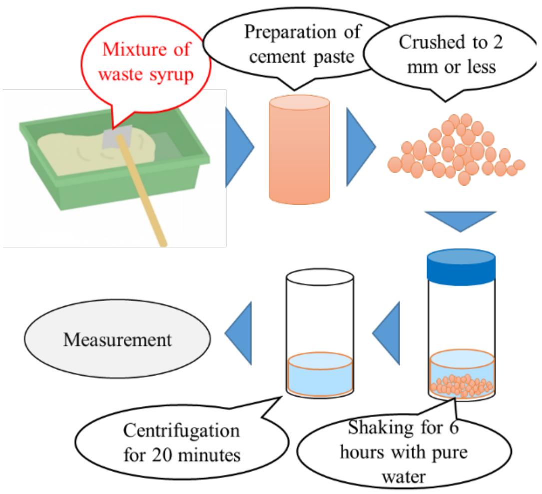

Fig. 4 Mixture method

Table 1 Test condition (Mixture method)

Water-cement ratio	70 %
Formwork size	ϕ 5 * 10 cm
Form removal	After 7days
Sealed curing	21 days
Adding Cr^{6+}	0, 1, 2 ppm
Waste syrup concentration	0.000, 0.125, 0.250 % (/cement)

4.2 Immersion method

The purpose of the immersion test is to reduce Cr^{6+} by immersing the crushed sample in a sugar solution. Though the test procedure is almost the same as that described in 4-1, the sugar is not mixed. Four kinds (waste syrup, glucose, allose, and sucrose) of sugar aqueous solution are respectively adjusted at three kinds of concentrations, and the crushed sample is immersed in the sugar solution for 24 hours. There are 12 patterns of specimens. Test conditions in the immersion method are shown in Table 2. Also, the mixture method is shown in Fig. 5. The operation added to the immersion method is shown in the figure. Most of Cr^{6+} remains in the concrete by hydration of cement. However, immersion in sugar solution may reduce Cr^{6+} which is slightly eluted from the concrete.

Table 2 Test condition (Immersion method)

Water-cement ratio	70 %
Formwork size	ϕ 5 * 10 cm
Form removal	After 7days
Sealed curing	21 days
Adding Cr^{6+}	0, 1, 2 ppm
Sugar solution concentration	0.1, 0.5, 1.0 % (/water)

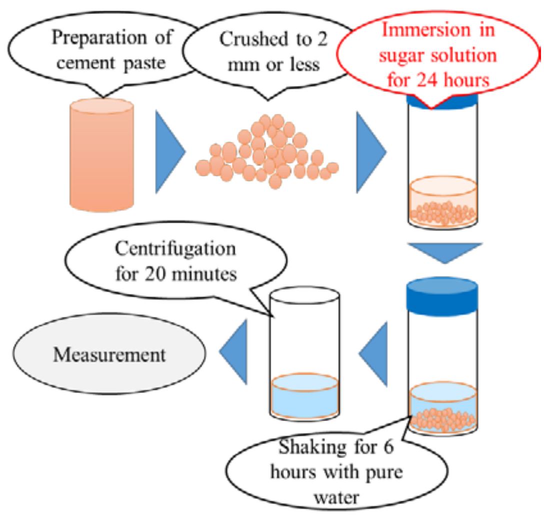

Fig. 5 Immersion method

5. TEST RESULTS

The test results for each method are shown in graphs. Each test is conducted three times to ensure a reproducibility, and the average value for three batches is listed in the graphs.

5.1 Test results of mixing method

Fig. 6 shows the results of the elution test on a specimen mixed with waste syrup as a mixture agent. The vertical axis of the graph represents the concentration of detected Cr^{6+}, and the horizontal axis represents the concentration of mixed waste syrup. Focusing on the concentration of Cr6+ in the sample without waste syrup, it is revealed that the added concentration of Cr^{6+} does not affect the concentration of Cr^{6+} eluted from the sample. According to the past research, an amount of water soluble Cr^{6+} in cement is about 5 ~ 10 mg/kg, which means that 0.3 -0.6 ppm is contained according to the present test conditions. This suggests that most of the Cr^{6+} is immobilized in the cement setting process, and that the elution amount of water-soluble Cr^{6+} form the cement does not change. The detected concentration of Cr^{6+} decreases in the specimen to which waste syrup is added. Furthermore, the detected concentration of Cr^{6+} decreases as the concentration of waste syrup increases. From these results, it is clarified that mixing waste syrup is effective for the reduction of elution amount of Cr^{6+}. When waste syrup was mixed by 0.25%, the concentration of Cr6+ is lower than the environmental quality standards for soil as well as the effluent standard. The waste syrup is a highly effective admixture, because it has sufficient reducibility in a small amount and leads to the recycling of waste. In order to establish the waste syrup as an admixture, it is necessary to examine not only reducibility but also workability factors such compressive strength and slump value. Alternatively, only the specimen using waste syrup is prepared and the elution test is performed in the mixing method. Therefore, in the future, the test in which other sugar solutions are mixed is conducted in order to investigate the effects of each type of sugar. In addition, it is necessary to examine the usage as a cement-based solidifying agent since the reduction effect by mixing is confirmed. The detected concentration of Cr^{6+} and kinds of immersed sugar solution are shown in the vertical and horizontal axes, respectively. The graph also includes the elution results from the blank test, i.e., the elution results from the test for samples which is not immersed in the sugar solution, as the reference value.

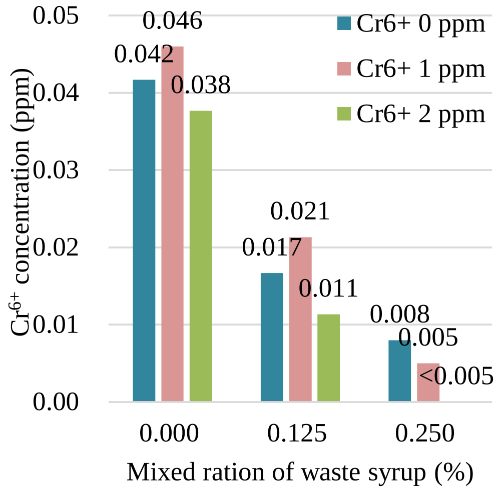

Fig. 6 Test results of elution test by mixture method

5.2 Test results of immersion method

Fig. 7, 8 and 9 show the results of the elution test of the test specimen which is immersed in each sugar solution. The elution amount of Cr^{6+} is summarized in the graph when three kinds of Cr^{6+} are added in each RSS addition amount. As in the test of the mixing method, there is no effect of the concentration of Cr^{6+} on the elution amount in the

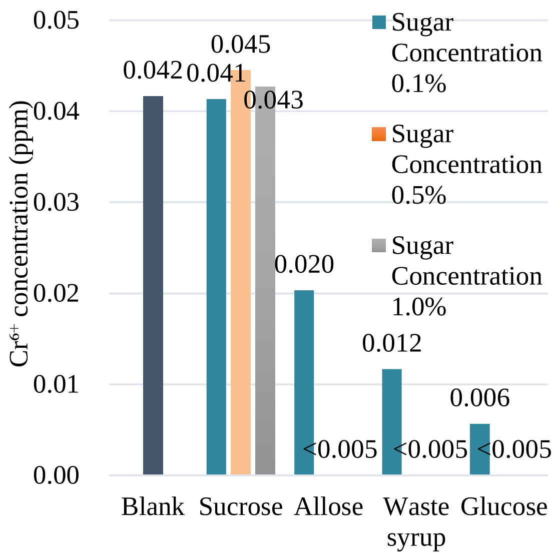

Fig. 7 Test results of elution test by immersion method (adding Cr^{6+} concentration of 0 ppm)

immersion test. The Cr^{6+} is not reduced regardless of the concentration of sucrose since sucrose is a non-reducing sugar. On the other hand, the concentration of Cr^{6+} decreases in all cases and the concentration of Cr^{6+} decreased as the concentration of sugar solution increased when the waste syrup, allose and glucose with reducing groups are used. Additionally, the concentration of Cr^{6+} decreases as the concentration of sugar solution increases. When the sugar concentration exceeded 0.5%, the concentration of Cr^{6+} falls below the detection limit of 0.005 ppm. Among them, the glucose solution

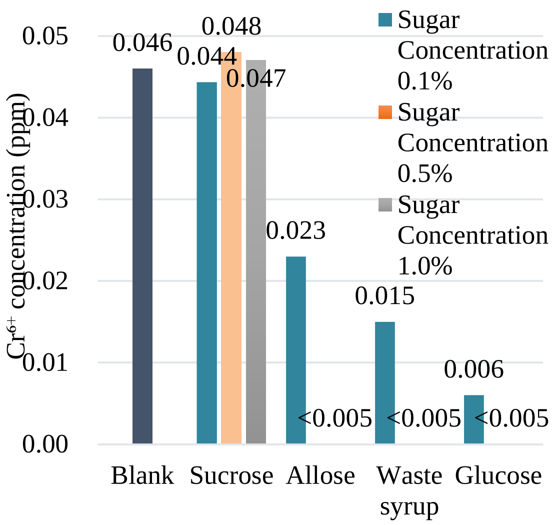

Fig. 8 Test results of elution test by immersion method (adding Cr^{6+} concentration of 1 ppm)

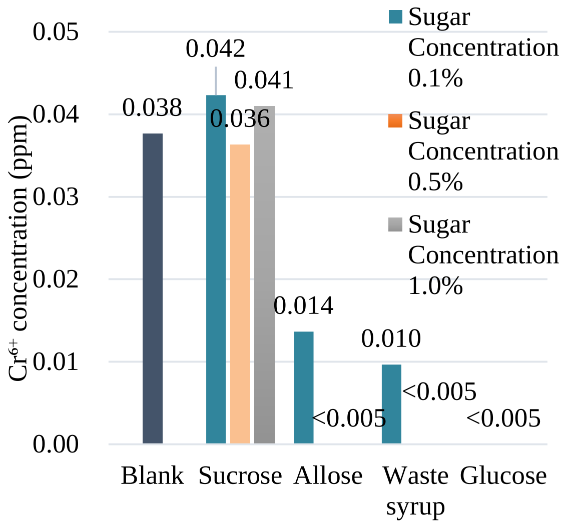

Fig. 9 Test results of elution test by immersion method (adding Cr^{6+} concentration of 2 ppm)

has the highest reducing ability, followed by glucose, waste syrup, allose and sucrose in order of decreasing ability. Since most of the components of the waste syrup are glucose, it is considered that the waste syrup has higher reducing ability than the allose solution. In both the mixing method and the immersion method, the elution amount of Cr^{6+} is deceased, and it is clarified that the waste syrup has an enough ability as the elution reducing material for Cr6+ in the recycled base material.

6. CONCLUSIONS

・The elution amount of Cr^{6+} eluted from the cement paste is roughly determined according to the amount of cement, and the elution amount of Cr^{6+} does not change even if Cr^{6+} is added.

・In the elution test by the mixing method using waste syrup, the detected concentration of Cr^{6+} decreased with the increase of the mixed concentration. The reducibility of the waste syrup is confirmed, and the possibility of the application to cement-based fixation agent is suggested.

・In the elution test by immersion method in the sugar solution, some sugar solutions show reducing property to Cr^{6+}. Sucrose solution does not show reducing property, while the waste syrup, allose and glucose solution show high reducing property.

・The relative merits in reducibility are confirmed in the Reducing sugars, and it is necessary to exam its cause.

・The reducing effect is higher test using immersion method than mixing method when the two methods are compared with the specimens using waste syrup. In addition, it is revealed that the waste syrup is the recycled material that has a reducing effect on the elution of Cr^{6+} from recycled roadbed material by two methods.

7. ACKNOWLEDGMENTS

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