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Lightweight aggregate with wet magnetic separated reject ash and dredged soil

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Environmental problems have been arisen from the ash produced from coal power plants. That is the reason that there have been many studies on recycling coal ash by making artificial lightweight aggregates (ALA) from coal ash. Although fly ash among many types of ash is currently being recycled effectively, most of the reject ash (RA) having 5% or more unburned carbon content is being simply reclaimed in the ash pond. In order to recycle RA effectively, various types of aggregate were manufactured and trials for making a porous aggregate by bloating have been made by using RA and dredged soil (DS). As it is, of course, a more economical way to use the raw material itself as a bloating agent compared to adding some bloating agents to ALA to make it light, the reject ash was separated by a magnet into two; one is a magnetic reject ash (MRA) having more ferrous component and the other is a non-magnetic reject ash (NMRA) having more unburned carbon. The magnetic separated ash was mixed with dredged soil to make ALA. As a result, a lightweight aggregate having less than 1.0 specific gravity could be obtained by using MRA which contains more ferrous components than as received RA or NMRA and therefore acts like a bloating agent itself to make ALA lighter.

Key words: Artificial lightweight aggregate, Reject ash, Dredged soil, Specific gravity, Absorption rate, Bloating, Wet magnetic separation.

Introduction

As industry develops, demands for lightweight aggregates which are used to build high-rise buildings and bridges and to make acoustic boards are increasing. As not only the price of high quality natural aggregate becomes high but also its specific gravity is 2 or more, application of it to high-rise buildings and bridges is limited. Therefore, many studies have been actively conducted to make ALA by using various ashes coming from coal power plants for structural and non-structural applications of it [1-5]. ALA has so porous a structure compared to natural aggregate that it is possible to lighten the weight of large scale structures such as high-rise buildings or long span bridges by using it. Because the porous structure of ALA gives us other benefits such as sound absorption and thermal insulation, ALA could be applicable to the fields of making acoustic board, thermal insulation board, etc. [6-7].

Coal power plants produce fly ash and bottom ash as by products which are categorized by general wastes. Reject ash (RA) is separated by a cyclone type separator to distinguish it from the recyclable fly ash for cement subsidiary material. Because RA usually contains 5% or more unburned carbon content, it is simply reclaimed to the ash pond near to the power plant. Generally speaking, refined fly ash having less than 5% carbon could be used as a concrete admixture without any modification and be applied to various types of secondary cement products through active research. Hence, most RA is being reclaimed, causing many problems such as soil pollution and securing of landfill area. Dredged soil (DS) is also a type of waste obtained during the construction of coal power plants and is simply being reclaimed. In fact, million tons of DS is reclaimed near the power plants in Korea. However, it can be used as a raw material for artificial lightweight aggregate (ALA), since it has such good plasticity that high forming strength could be attained with it.

ALA made of RA only has a relatively higher specific gravity than those of other aggregates because of its good plasticity, particle size, and pore distribution. That is why many studies have been conducted by adding effective bloating agents and ferrous materials in it to make ALA [8-10]. In this study, magnetic separation of RA was conducted in order to examine whether ALA can be made by using only RA itself without mixing other bloating agents or additional ferrous materials.

One of the important results in this study is that effective bloating of ALA could be realized using accumulated ferrous materials and unburned carbon attained by magnetic separation of RA itself. Magnetic reject ash (MRA) which sticks to the magnet has relatively more ferrous components than those of as received RA; hence, non-magnetic reject ash (NMRA) which does not stick to a magnet contains relatively much less unburned carbon than those of as an received one. Ferrous materials (ferric oxides) in MRA can emit oxygen gas through a reducing process of

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iron; therefore, it is thought that this is the one of the bloating mechanisms to make ALA light without adding an additional bloating agent.

The purpose of this study is to recycle RA effectively by making ALA. RA was separated as MRA and NMRA using a 2000 Gauss magnet. Dredged soil was also used as a raw material for ALA to enhance the dry strength of a green body, for RA itself has poor plasticity.

Experimental

Table 1 shows chemical composition of the raw materials. RA which is rejected after the refining process of fly ash has 5% or more unburned carbon. Magnetic separation was performed with a 2000 Gauss magnet in a solution of distilled water and RA with a ratio of 10 to 3. DS generally enhances the green body strength of an aggregate because of its excellent plasticity. For plastic molding, it was ground using a fin-mill, and the particle size of it was reduced to under 100 μm.

One of the conditions for bloating an aggregate is that oxygen gas should be emitted under the conditions of a reducing atmosphere by ferrous materials or carbon dioxide gas should be emitted by an oxidizing atmosphere of unburned carbon in the RA. In order to bloat an aggregate without an additional bloating agent, it is necessary to separate MRA having more ferrous materials from NMRA having more unburned carbon using a 2000 Gauss magnet.

After the wet separation process, both MRA and NMRA were dried in a drying oven for 48 hours. Then, RA, MRA and NMRA were mixed with DS in various compositions in a ball mill for 24 hours. The mixing ratios are shown in Table 2. Aggregate specimens were molded 8~10 mm in diameter using distilled water and dried in a drying oven for 24 hours. The dried aggregate was directly inserted into an electric furnace maintained at 1050~1200 °C (with 50 °C interval) for 10 minutes. After firing, they were cooled down to room temperature in air. The specific gravity and absorption rate of aggregate were measured using Archimedes' method. The surface and cross-sectional morphology of the specimens were observed through an optical microscope (Camscope^{TM}).

Table 1. Chemical composition of the raw materials.

	RA	MRA	NMRA	DS
Ig. loss	1.88	0.74	0.85	6.07
SiO_2	52.66	42.6	53.16	67.3
Al_2O_3	22.42	16.98	22.66	14.66
Fe_2O_3	4.88	24.62	3.27	4.31
CaO	4.71	5.29	4.72	0.87
MgO	1.23	2.02	1.18	0.95
Na_2O	0.8	0.53	0.81	2.03
K_2O	1.15	0.84	1.18	2.2
TiO_2	1.14	0.89	1.17	0.8
P_2O_5	0.61	0.59	0.6	0.05
MnO	0	0.17	0	0.04
C	9.17	4.67	10.35	0.67
Total	99.94	99.94	99.93	99.93

Results and Discussion

Physical properties of aggregates made of RA and DS

Table 3 shows the calculated values for the selected chemical compositions (Fe_2O_3 and carbon) of aggregates made of various mixtures of RA and DS. Fig. 1 and Fig. 2 show the specific gravities and the water absorption ratios of aggregates manufactured with various mixing ratios of RA and DS at temperatures between 1050 °C and 1200 °C, respectively. As shown in Fig. 1, the specific gravity generally increased from 1050 up to 1150 °C and then decreased from 1150 °C to 1200 °C. However, the specific gravity of RD46 exceptionally started to decrease from 1100 °C. It is speculated that iron oxides would be reduced under the reducing

Table 2. The mixing ratios of specimens by weight percent (wt %).

Specimen symbol	RA	MRA	NMRA	DS
RD46	40			60
RD55	50			50
RD64	60			40
RD73	70			30
RD82	80			20
MRD46		40		60
MRD55		50		50
MRD64		60		40
MRD73		70		30
MRD82		80		20
NMRD46			40	60
NMRD55			50	50
NMRD64			60	40
NMRD73			70	30
NMRD82			80	20

Table 3. The calculated values for the selected chemical compositions of aggregates made of various mixtures of RA and DS.

	RD46	RD46	RD64	RD73	RD82
Fe_2O_3	4.54	4.6	4.65	4.71	4.77
C	4.07	4.92	5.77	6.62	7.47

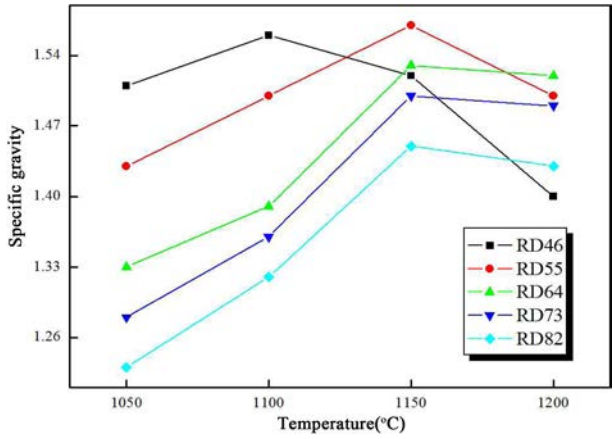

Fig. 1. The specific gravity of aggregates manufactured with various mixing ratios of RA and DS at temperatures between 1050 °C and 1200 °C.

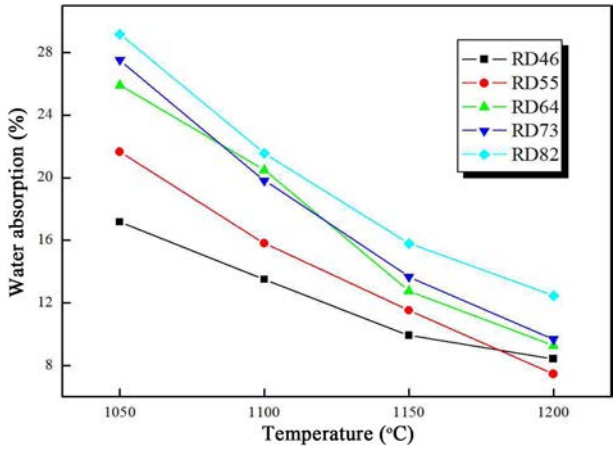

Fig. 2. The absorption rate of aggregates manufactured with various mixing ratios of RA and DS at temperatures between 1050 °C and 1200 °C.

atmosphere inside the aggregate because DS which has excellent plasticity prevented oxygen from entering into the aggregate during the sintering. In addition, oxygen which was produced by reduction of iron oxides would be combined with unburned carbon existing in the aggregate and carbon monoxide or dioxide gas were produced inside the aggregate, which resulted in a decrease in the specific gravity of the aggregate. Generally speaking, the more RA content, the lower the specific gravity with the exception of RD46 and RD55 above 1150 °C, which means micro-cracks should exist on the surface as well as inside the aggregate because it has less plasticity if it contains less DS. While RD46 and RD55 having a relatively small amount of RA show the highest specific gravity at 1050 °C, the specific gravity starts to decrease from 1100 °C to 1200 °C due to the large volume expansion of the aggregate which may be seen in Fig. 3. In particular, RD46 shows the lowest specific gravity at 1200 °C. Although RD46 has less DS, it has an appropriate carbon content to make a black core and to produce carbon dioxide inside the aggregate resulting in its volume expansion. As shown in Fig. 3, the large volume expansion of RD46 and RD55 can be observed above 1150 °C and 1200 °C, respectively. The large cracks which are also observed in the aggregates of RD46 and R55 above 1150 °C and 1200 °C

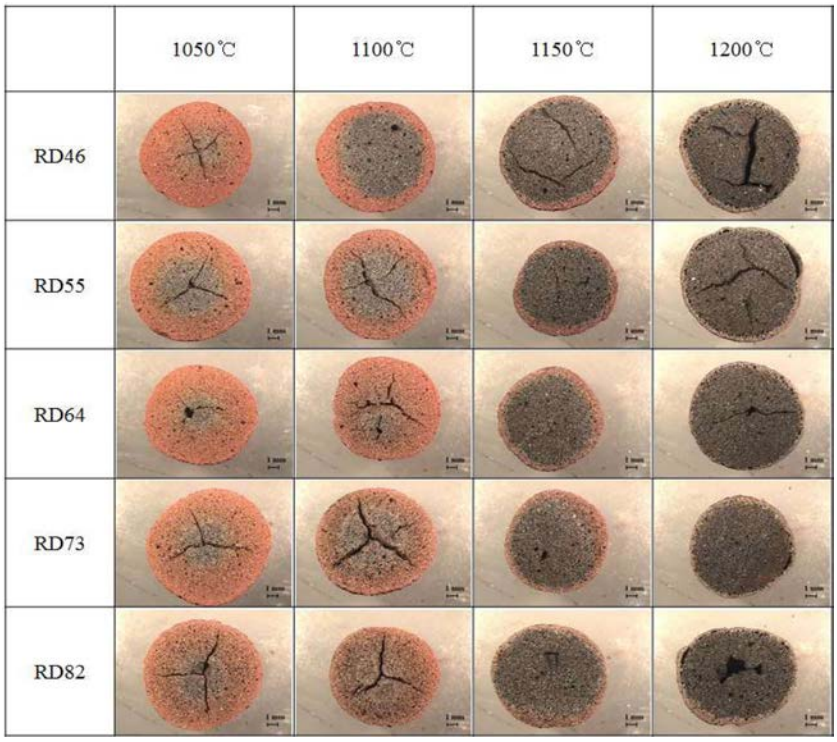

Fig. 3. Cross-sectional morphologies after cutting the aggregates made of RA and DS (The scale bar at the right bottom of each picture indicates 1 mm).

are an evidence of the large volume expansion of them.

Fig. 2 shows the water absorption rate of aggregates according to the temperature variation. A decrease in the absorption rate is in good accordance with the increase in density in Fig. 1 up to 1150 °C, and thereafter a further decrease in absorption rate can be explained by the formation of glassy phases on the surface above 1150 °C. On the whole, it shows that the higher the temperature is, the lower the water absorption rate is. That is because the density of an aggregate increases through a general sintering process, so the extent of pores absorbing water becomes smaller. This shows also that the absorption rate also increases with an increase in RA content. The reason is that an aggregate containing a high RA content has less DS having excellent plasticity, so that minute cracks were created during the forming process. These cracks might be the cause of an increase in the absorption rate of the aggregates with more RA content. The specific gravity and absorption rate graphs show an opposite tendency in general as shown in Fig. 1 and Fig. 2; however, RD46 and RD55 are exceptions. Although the specific gravity of RD46 and RD55 decreased with an increase in the temperature between 1100 and 1200 °C, the absorption rate of them still decreased with an increase in the same temperature range. It is thought that a glassy phase is formed on the surface of aggregates at this temperature range, and these glassy phases blocked open pores, resulting in a further decrease in the absorption rate.

Fig. 3 shows cross sectional morphology of aggregates by the Camscope observations. Aggregates were cut by a low speed diamond saw before observation. This figure shows that the area of the black core which formation is known to be due to a reducing atmosphere inside the aggregate increased with an increase in the temperature. This means that as the temperature increased, more irons were reduced inside the aggregates, and it is thought that this makes more cracks inside the aggregates by being bloated due to carbon dioxide gas emitted by the reaction of unburned carbon and oxygen from the reductive reaction of ferrous materials. The aggregates are divided into a shell part and a core part. The shell is red because it consists of ferric oxides which were oxidized during the sintering process, while the core becomes black because a dense oxide layer of the shell prevents oxygen from entering inside the aggregate, making a reducing atmosphere inside the aggregate during the sintering process [11-14]. Hence, oxygen produced by the reduction of ferrous materials in the core region of an aggregate might react with unburned carbon from the RA, producing carbon monoxide or carbon dioxide gas which makes the aggregate bloat at high temperature. However, RD82 having a relatively large amount of RA has a relatively large amount of unburned carbon. Therefore, its plasticity is not so good that minute cracks were created in and on the surface of the aggregate. Because of these cracks, oxygen can easily penetrate into the inside of aggregate, so the area of the black core of it is relatively smaller than that of the others.

Physical properties of aggregates using MRA and DS

Table 4 shows the calculated values for the selected chemical compositions (Fe_2O_3 and C) of aggregates made of various mixtures of MRA and DS. Fig. 4 and Fig. 5 show the specific gravities and the water absorption rates of aggregates manufactured in various mixing ratio of MRA and DS at temperatures between 1050 °C and 1200 °C, respectively. As shown in Fig. 4, the specific gravity of aggregates rapidly decreased in

Table 4. The calculated values for the selected chemical compositions of aggregates made of various mixtures of MRA and DS.

	MRD46	MRD46	MRD64	MRD73	MRD82
Fe_2O_3	12.43	14.47	16.5	18.53	20.56
C	2.27	2.67	3.07	3.47	3.87

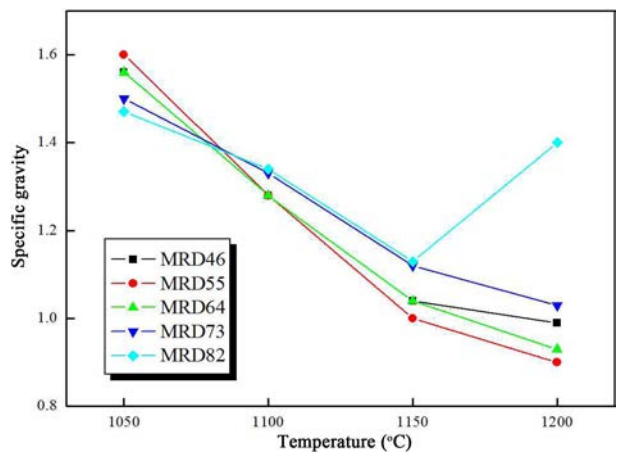

Fig. 4. The specific gravity of aggregates manufactured in various mixing ratios of MRA and DS at temperatures between 1050 °C and 1200 °C.

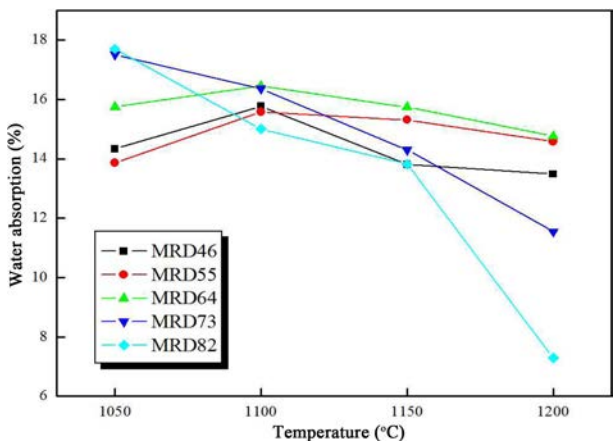

Fig. 5. The absorption rate of aggregates manufactured in various mixing ratios of MRA and DS at temperatures between 1050 °C and 1200 °C.

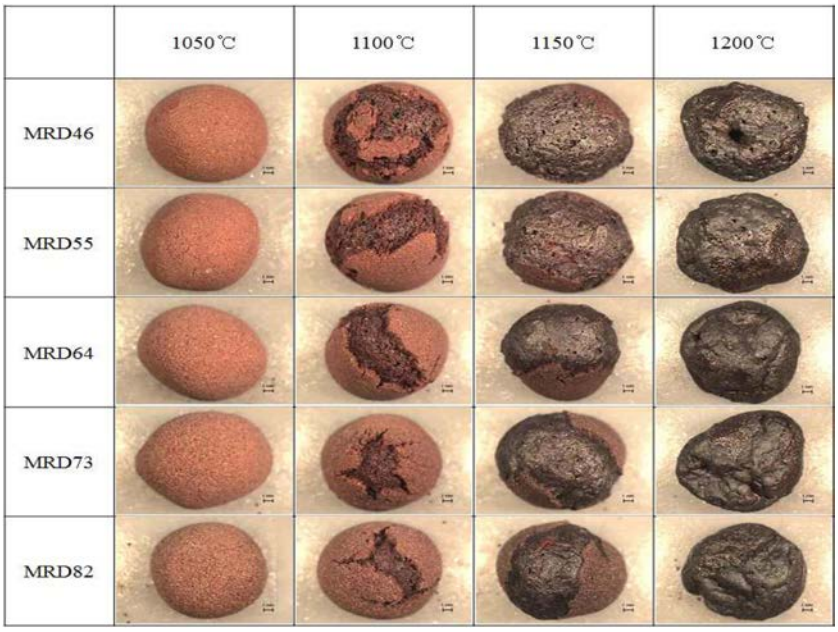

Fig. 6. Surface morphologies of aggregates made of MRA and DS (The scale bar at the right bottom of each picture indicates 1 mm).

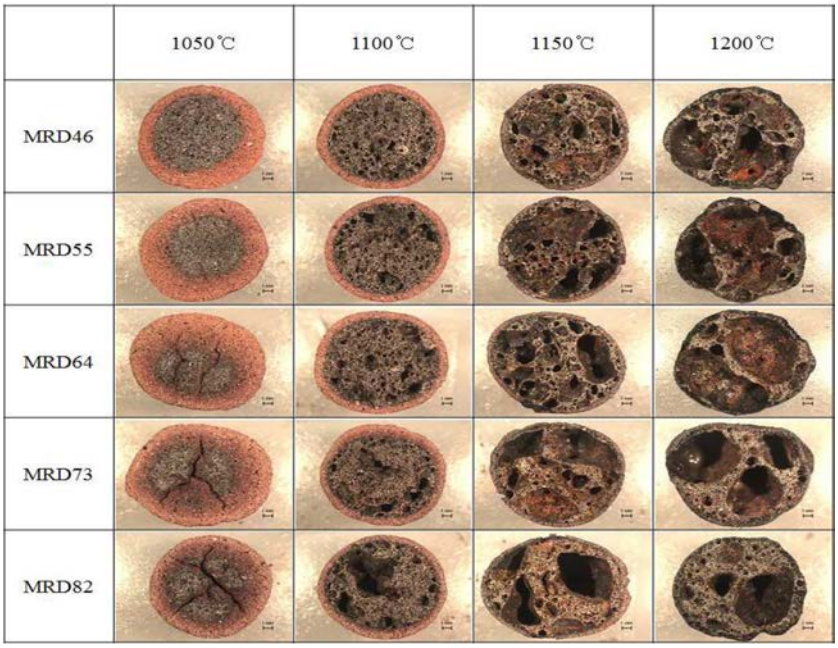

Fig. 7. Cross-sectional morphologies of aggregates made of MRA and DS (The scale bar at the right bottom of each picture indicates 1 mm).

all temperature ranges except for MRD82 at 1200 °C. The cause of the rapid decrease in the specific gravity would be explained as follows. The various ferrous compounds were reduced to FeO and emitted oxygen gas. Because the melting point of FeO is 1100 °C, a glassy phase of FeO was formed from 1100 °C [15-17]. Riley [18] suggested that when manufacturing aggregates, if the temperature of gas emission corresponds with the forming temperature of a glassy phase on the surface of the aggregate under a condition where there are sufficient bloating substances, gas generated during the sintering process cannot escape to the outside; it therefore, expands, forming lots of air holes inside. The result shown in Fig. 4 is in good agreement with Riley's suggestion. MRD55 and MRD64 above 1150 °C showed a specific gravity less than 1.0, which means they are floating on water. In these cases, because DS having excellent plasticity blocked the entrance of oxygen effectively during the sintering, ferrous compounds inside the aggregates were reduced and protective glassy layers of FeO were created inside the aggregate. At the same time, some of the emitted oxygen gas by reduction of ferrous compounds reacted with unburned carbon in the aggregate, emitting carbon

monoxide or carbon dioxide gas, which accelerated bloating the aggregate and made large pores in it. However, glassy phase sintering would occur if too much ferrous components existed in the aggregate as the case for MRD82 in Fig. 4. It is speculated that too much glassy phase would not help bloating but cause abnormal sintering, resulting in a relatively high specific gravity. Fig. 5 shows the water absorption rates of aggregates having various mixing ratio of MRA and DS at temperatures between 1050 °C and 1200 °C. In general, the water absorption rate gradually decreased with an increase in the temperature. In the case of most ceramics, the absorption rate increases with a decrease in the specific gravity, because a lower specific gravity means more pores in the aggregate. However, the specific gravities in Fig. 4 gradually decreased with an increase in the temperature because glassy phases blocked open pores of the aggregate. In particular, MRD82 having a relatively large amount of MRA shows a rapid decrease of absorption rate between 1150 and 1200 °C, for it has too much glassy phase.

Fig. 6 shows surface morphologies of aggregates and Fig. 7 shows cross-sectional morphologies of aggregates observed after cutting the cross-section of aggregates using a low-speed diamond saw. As shown in Fig. 6, more cracks on the surface were observed with an increase both in the temperature and in the content of dredged soil. The glassy phases in the aggregate were apparently bloated from the inside of the aggregate. The higher the temperature and the more content of dredged soil, the more bloating phenomenon. Fig. 7 shows cross-sectional images of aggregates manufactured in various mixing ratios and at various temperatures. As shown in Fig. 7, the area of black core inside the aggregates increased with an increase in the temperature. The pore size and glassy phases also increased with an increase both in the temperature and in the content of magnetically separated reject ash. The cracks formed inside aggregates at 1150 °C as shown in the left most column in Fig. 7 are evidence of no glassy phase at this stage. By contrast, no cracks was found in the aggregate above 1100 °C. The presence of a glassy phase in the aggregates did not enable making any crack inside the aggregates, but to create large pores in them. The cross-sectional image of MRD82 at 1200 °C can explain the abnormal behavior of specific gravity and absorption rate in Fig. 4 and Fig. 5. It seems like that it would rather be sintered by liquid aided sintering than become bloated. More glassy phase would be helpful in making an aggregate lighter; however, it would raise a serious problem in a mass production process because aggregate can stick together and make a large lump of aggregate. Therefore, it was speculated that the manufacturing conditions of MRD 46, MRD 55, and MRD 64 at 1100 °C were the best and suitable for making aggregates of which the specific gravity is about 1.3 for the application of a non-structural purpose.

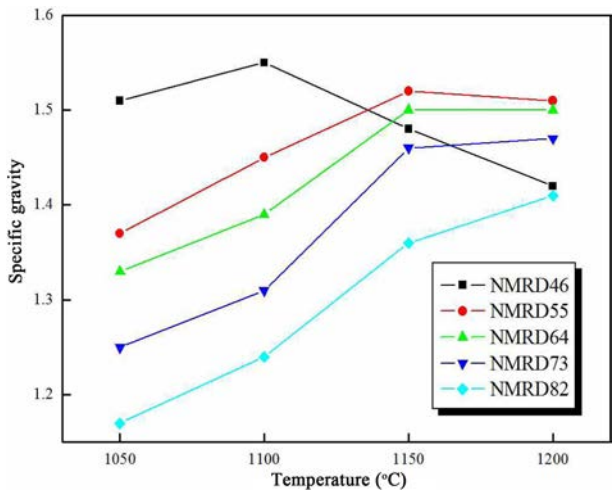

Fig. 8. The specific gravity of aggregates manufactured in various mixing ratios of NMRA and DS at temperatures between 1050 °C and 1200 °C.

Physical properties of aggregates using NMRA and DS

Table 5 shows the calculated values for the selected chemical compositions of aggregates made of various mixtures of NMRA and DS. Fig. 8 and Fig. 9 show the specific gravities and the water absorption rates of aggregates manufactured in various mixing ratio of NMRA and DS at temperatures between 1050 °C and 1200 °C, respectively. As shown in Fig. 8, the specific gravity, on the whole, increased with an increase in the temperature except NMRD46. It seems very probable

Table 5. The calculated values for the selected chemical compositions of aggregates made of various mixtures of NMRA and DS.

	NMRD46	NMRD46	NMRD64	NMRD73	NMRD82
Fe_2O_3	3.89	3.79	3.69	3.58	3.48
C	4.54	5.51	6.48	7.45	8.41

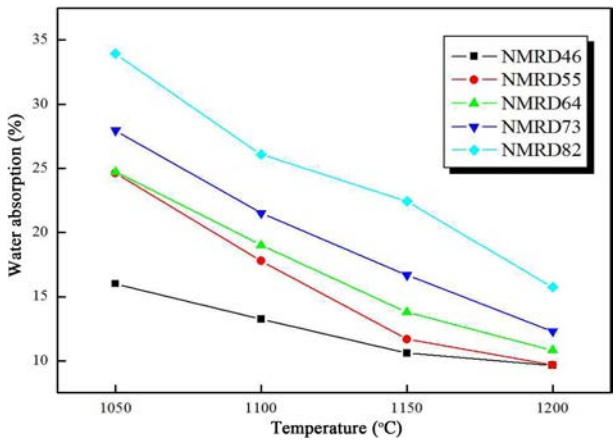

Fig. 9. The absorption rate of aggregates manufactured in various mixing ratios of NMRA and DS at temperatures between 1050 °C and 1200 °C.

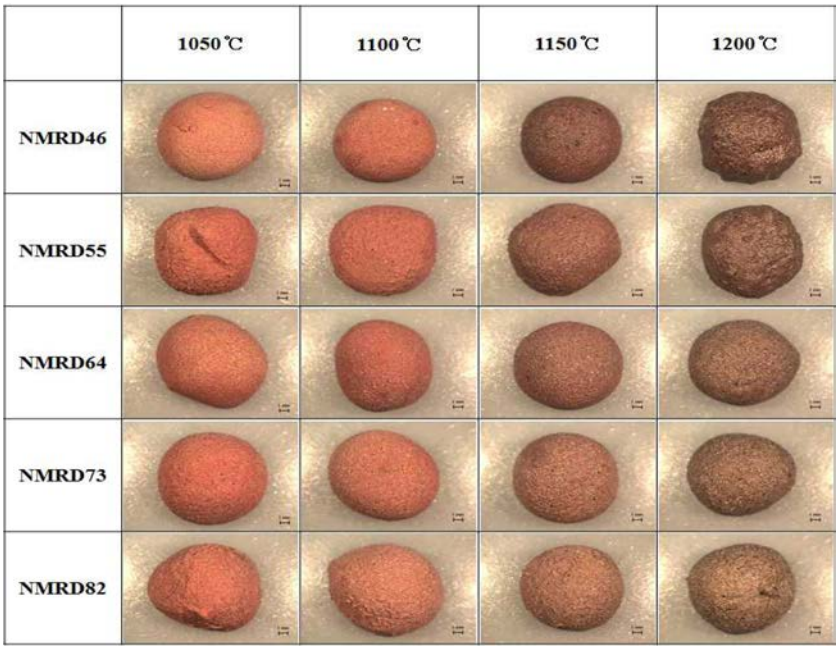

Fig. 10. Surface morphologies of aggregates made of NMRA and DS (The scale bar at the right bottom of each picture indicates 1 mm).

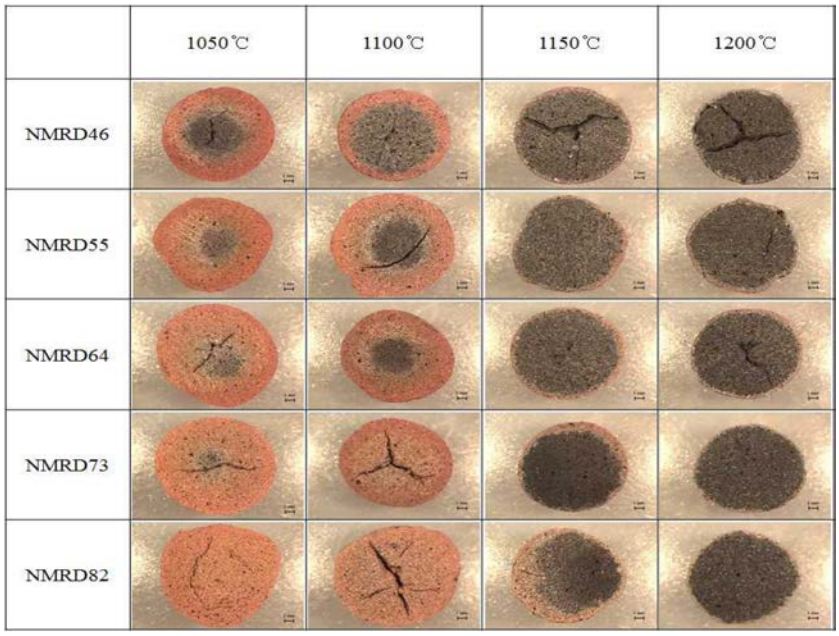

Fig. 11. Cross-sectional morphologies of aggregates made of NMRA and DS (The scale bar at the right bottom of each picture indicates 1 mm).

that all the specimens except for NMRD46 did not form any grassy phase (as seen from Fig. 10) because the NMRD series has little ferrous components from the magnetic separation so that they showed a typical sintering behavior, where the specific gravity increases with an increase in the temperature, rather than bloating. However, NMRD46 which contains more dredged soil having good plasticity has enough component to make a glassy phase in the aggregate even though NMRD has almost no ferrous component to make a glassy phase, resulting in a decrease of specific gravity above 1100 °C. It may be clearly observed in Fig. 8 that the more NMRA, the less the specific gravity. This indicates that the contents of DS greatly affect the sintering of aggregates and the specific gravity increases with an increase in the temperature up to the content limit (here, 60 wt%) of dredged soil for bloating. It is speculated that the less DS was contained, the more minute cracks formed on and in the aggregate, resulting in a lower specific gravity (Fig. 8). Fig. 9 shows the water absorption rate of aggregates manufactured in various mixing ratios of NMRA and DS at temperatures

between 1050 °C and 1200 °C. According to Fig. 9, the water absorption rate decreased with an increase in the temperature. In the case of NMRD46, a decrease in the water absorption above 1100 °C can also be explained by the existence of a glassy phase as mentioned above.

Fig. 10 and Fig. 11 show surface and cross-sectional images of the aggregates made of NMRA and DS by the Camscope. From these figures, it is clearly seen that the area of the black core increased with an increase in the temperature. As shown in Fig. 10 and Fig. 11, all the specimens except NMRD46 at 1200 °C have no pores in the aggregate because most of the ferrous components in the NMR were removed by the magnetic separation. However, it is apparent as shown in Fig. 11 that a few small pores in the specimen of NMRD46 at 1200 °C were observed just underneath the surface which was covered by a thin layer of glassy phase, blocking the open pores and capturing the gas produced inside the aggregate. These pores are attributed to a decrease in the specific gravity of the NMRD46 above 1100 °C.

Conclusions

In this study, artificial lightweight aggregates were manufactured and evaluated for the effective recycling of RA which contains 5% or more unburned carbon. RA was classified as MRA having more ferrous materials and as NMRA having more unburned carbon by the magnetic separation. Both MRA and RA were mixed with DS in various compositions and sintered at various temperatures. The physical properties of aggregates were measured and optical morphologies of aggregates were observed.

It is apparent that the ferrous components in RA play a very important role for bloating of an aggregate. Because DS having excellent plasticity blocked the entrance of oxygen effectively during the sintering, the various ferrous compounds in MRA concentrated by the magnetic separation were reduced and protective glassy layers of FeO were created inside the aggregate. At the same time, some of the emitted oxygen gas by reduction of ferrous compounds reacted with unburned carbon in the aggregate, emitting carbon monoxide or carbon dioxide gas, which accelerating bloating an aggregate and making large pores in it. However, too much glassy phase would not help the bloating but cause abnormal sintering, resulting in a relatively high specific gravity.

Through a comparison of RD55, MRD55 and NMRD55, it is clearly seen that the ferrous components in MRA concentrated by the magnetic separation are essential to make a lightweight aggregate with a specific gravity of 1.3 or less. It was speculated that manufacturing conditions of MRD 46, MRD 55, and MRD 64 at 1100 °C were the best and suitable to make an aggregate of which the specific gravity is about 1.3 for application of non-structural purposes.

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