

Article

Environmental Compatibility of Lightweight Aggregates from Mine Tailings and Industrial Byproducts

Won Jung Ju ¹ , Doyun Shin ^{2,3,*}, Hyunsik Park ² and Kyoungphile Nam ¹

¹ Department of Civil and Environmental Engineering, Seoul National University, Seoul 08826, Korea; wju888@snu.ac.kr (W.J.J.); kpnam@snu.ac.kr (K.N.)

² Resource Recovery Research Center, Mineral Resources Research Division, Korea Institute of Geoscience and Mineral Resources, Daejeon 34132, Korea; hyunsik.park@kigam.re.kr

³ Department of Mining and Geological Engineering, University of Arizona, Tucson, AZ 85721-0012, USA

* Correspondence: doyun12@email.arizona.edu; Tel.: +1-520-621-0769

Received: 9 August 2017; Accepted: 18 September 2017; Published: 25 September 2017

Abstract: A lightweight aggregate was produced by sintering the mixture of gold mine tailings, red mud, and limestone at 1150 °C. The physical (i.e., skid resistance, abrasion resistance, and bond strength) and environmental (i.e., leachability) feasibility of this aggregate was assessed to consider its potential use as a construction material for bicycle lanes. The skid resistance (British pendulum number of 71) and bond strength (1.5 N·mm^{−2}) of the aggregate were found to be appropriate for this use. However, the abrasion loss value of the aggregate was found to be 290 mg, which exceeds the limit of Korean Standard KS F 281 (200 mg). Heavy metals were found to not leach from the aggregate in various leaching tests. These include Korean (Korea Standard Method for Solid Waste), American (Toxic Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP)), and European (BS EN 12457-1) leaching tests, despite the raw materials containing significant amounts of Pb, As, and F. However, leachate extracted from the aggregate exhibited an aquatic toxicity to *Daphnia magna* of 13.94 TU_{24hr} and 14.25 TU_{48hr}, most likely due to a high pH and Ca concentration originating from the free CaO present in the aggregate. The data suggests that the physical properties of the reconstructed aggregate are appropriate for use in bicycle lane construction, however the dissolution of Ca and the pH level of the leachate need to be controlled to protect aquatic ecosystems.

Keywords: mine tailings; red mud; waste limestone; leachability; toxicity; lightweight aggregate

1. Introduction

In total, there are 5396 mines located in South Korea, and mine tailings from flotation processes accumulate in 345 of these mines [1]. The estimated volume of these tailings was 15 million m³ in 2012 [2]. These tailings can result in severe, long-term environmental and social consequences from tailing spills, dam failures, seepage, unrehabilitated sites, and cases of direct discharge into waterways [3–5]. Meanwhile, a huge quantity of waste limestone having non-practical value of calcite is generated from cement industry. Bauxite residue, referred to as red mud, is also produced from the alumina industry. Current bauxite residue reached an estimated 2.7 billion tons in 2007, increasing at 120 million tons per annum [6,7].

To mitigate the problems associated with the storage of large volumes of tailings, many studies have proposed methods of recycling tailings as valuable resources including cemented paste backfills [8], bricks [9], and road base materials [10]. Since the gold tailing mostly consists of fine quartz particles, its application is highly limited unless an agglomeration or sintering process is employed. Various trials to utilize red mud, including civil and building construction, wastewater and effluent

treatment, recovery of major metals, and steel making and slag additive, were also conducted [6]. Aside from these uses, the production of lightweight aggregates may represent an attractive recycling application for mine tailings because lightweight aggregates have a higher value than normal weight aggregates [11]. Various mineral wastes have been used to produce lightweight aggregates, including reservoir sediment [12], fly ash [13], red mud with a pulverized fuel ash [14], limestone powder with fly ash [15], and sewage sludge [16]. The advantage to utilize mine tailing as a source for lightweight aggregates by using red mud and waste limestone as fluxes is that these three powder-type waste materials can be simultaneously consumed because the major components of tailing, red mud, and waste limestone are quartz, hematite, alumina, and lime, and these four oxides form stable slag composition, as used in the iron and steelmaking processes [17].

When these problematic waste materials are recycled as construction materials, such as lightweight aggregates, the environmental impact should be evaluated to ensure effective environmental management. For example, Petkovic et al. [18] proposed a decision-making tool for determining whether recycled materials such as asphalt waste or vehicle tires are appropriate for use as road construction materials. To assess the environmental impact of the recycled materials, a coupled 8-step procedure was suggested, including a scenario description, recycled material characterization, identification of hazardous elements in the recycled materials, and determining the influence of these parameters on leaching behavior. If the calculated risk is deemed higher than an acceptable level of risk, the materials cannot be recycled for road construction [18]. Chang et al. [19] determined the impacts from the leachability of hazardous toxic elements from lightweight aggregates made of sludge cake obtained from electronics factories. Although lightweight aggregates from the recycled metal sludge contained Cd, Cr, Cu, and Pb, the metals were not found to leach. Consequently, it was proposed that these recycled aggregates do not have a harmful effect on the environment. Maghool et al. [20] evaluated the potential usage and environmental impact of steelmaking slag aggregates as road construction materials. In total and leachable heavy metal tests, the steel slags were found to have no environmental risks for use as aggregates in roadwork applications. Likewise, identifying the leaching behavior of recycled materials is very important to assess the potential environmental impacts associated with recycling wastes or byproducts. However, most studies so far have been focusing on leachable hazardous elements tests, and very few studies have been reported on environmental compatibility of the recycled materials based on leachability and ecotoxicity tests [14].

In a previous study, lightweight aggregates were produced from a mixture of gold mine tailings, red mud, and waste limestone using a high-temperature ceramic sintering process [21]. The mixture of mine tailing, red mud, and waste limestone at 2:1:1 was able to achieve low temperature sintering (1150 °C) and the produced aggregate showed significantly higher compressive strength than the commercial aggregates and improved water resistance. In this study, the physical and environmental feasibility of using lightweight aggregates was analyzed regarding environmental compatibility when used for bicycle lanes, based on hazardous elements leachability and leachate toxicity tests by *Daphnia magna*.

2. Materials and Methods

2.1. Sample Preparation and Characterization

A detailed description of the lightweight aggregate production process and thermodynamic analysis has been presented previously [21]. Briefly, gold mine tailings from flotation processes at a domestic mining and mineral processing company; red mud from the Bayer process of a domestic aluminum hydroxide manufacturer; and waste limestone powder from a cement producer in Korea, were prepared to a size of under 100 µm, mixed at the ratio of 2:1:1 (*w/w*), and pelletized. Spherical pellets sized at approximately 10 mm in diameter were prepared by hand rolling with drops of distilled water. The samples were dried at 200 °C for 48 h to remove potential physi-sorbed residual moisture. The prepared pellets were arranged in a dense alumina boat and inserted into a Si-C

electrical resistance heating box furnace. The pellets were heated for 30 min at 1150 °C to produce the lightweight aggregate.

The elemental and mineralogical composition of the aggregate was analyzed using X-ray fluorescence (XRF) (S4 Pioneer, Bruker AXS, Karlsruhe, Germany) and X-ray powder diffraction (XRD) (D8 Advance, Bruker, Karlsruhe, Germany), respectively. The heavy metal content in the mine tailings, the red mud, and the waste limestone was digested using the Korean standard testing method for soil contamination [22]. The digested samples were filtered through a 0.45 µm GHP syringe filter (Pall, Nassau County, NY, USA) for further analysis.

2.2. Physical Feasibility Tests

The physical feasibility of the lightweight aggregate as a material for bicycle lane construction was evaluated by testing skid resistance, abrasion resistance, and bond strength to Korean Standards (KS, available at <http://www.kssn.net>); KS F 2375 (Testing method for measuring surface frictional properties using the British Pendulum Tester); KS F 2813 (Method of abrasion test for building materials and part of building construction (Abrasive paper method)); and KS F 4936 (Coating materials for the protection of concrete), respectively. Skid resistance was measured using the British Pendulum Tester (JI-537, Jeil Precision, Seoul, Korea), abrasion resistance was measured using the Taber Abrasion Tester (WL210T, Withlab, Gyeonggi-do, Korea), and bond strength was tested using the Universal Testing Machine (Z030 TEW, Zwick, Ulm, Germany). The specimens produced for these tests are shown in Appendix A, Figure A1.

2.3. Leachability Tests

The leachability of the hazardous elements comprising the lightweight aggregate were tested using various official standards such as the Korean standard testing methods for solid wastes (KSTM-SW) [23]; the EPA 1311 method “Toxicity Characteristic Leaching Procedure” (TCLP) [24]; and EPA 1312 method “Synthetic Precipitation Leaching Procedure” (SPLP), which is designed to simulate in situ exposure of materials to slightly acidic rainfall [25]. The European standard method “Characterization of waste Leaching compliance test for leaching of granular waste materials and sludges Part 1: One stage batch test at a liquid to solid ratio of 2 L·kg^{−1} for materials with particle size below 4 mm; BS EN 12457-1” was also used [26]. For KSTM-SW, 100 g of the aggregate was passed through a 2.0 mm sieve and mixed with distilled water adjusted to a pH of 5.8 to 6.3 with HCl at a ratio of 1:10 (*w/v*). The mixture was shaken for 6 h at 200 rpm, with 4 to 5 cm amplitude at room temperature. For TCLP and SPLP, the aggregate was passed through a 9.5 mm sieve and mixed with an extracting solution of distilled water adjusted to a pH of 2.88 ± 0.05 with acetic acid for TCLP, and to a pH of 5.00 ± 0.05 with a 60:40 (*w/w*) mixture of H₂SO₄:HNO₃, for SPLP, respectively, at a 1:20 ratio (*w/v*) [24]. These mixtures were shaken on a rotary agitator (30 rpm, 23 ± 2 °C) for 18 h [24]. For the European standard method, BS EN 12457-1, a 0.175 kg of the sample aggregate was passed through a 4 mm sieve, mixed with 0.35 L of deionized water (pH 5–7.5, conductivity <0.5 mS·m^{−1}), and mixed on an end-over-end tumbler (5–10 rpm) for 24 h at 20 ± 5 °C [26]. In these, all procedures, solids and liquids were separated by centrifuging at 12,000 g for 15 min and filtration through a 0.45 µm GHP syringe filter for further analysis.

2.4. Toxicity Tests

The acute toxicity of the leachate obtained from the KSTM-SW leachability tests was determined by exposing *Daphnia magna* to the leachate for 24 h and 48 h using the Acute Toxicity Test Methods for *Daphnia magna* Straus (Cladocera, Crustacea) [27]. The variation of toxic effect was plotted with the variation in the dilution percentages for each leachate. These results were then fitted to a sigmoidal curve using SigmaPlot 10.0 (Systat software, Chicago, IL, USA) to calculate half-maximal effective concentration (EC50) value and the toxic unit (TU).

2.5. Analytical Methods

The concentration of Cr, Fe, Ni, Cu, Zn, As, Cd, Pb, Ca, and Mg in the leachate was obtained from the different leachability tests, and the digested samples were analyzed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (ICAP 7400 DUO, Thermo Scientific, Waltham, MA, USA). Cyanide and fluoride was spectrophotometrically determined using the pyridine-pyrazolone method [28] and Zirconium-SPADNS method [29], respectively.

3. Results

3.1. Physical Feasibility of the Lightweight Aggregate as Construction Materials for Bicycle Lanes

The physical feasibility of the lightweight aggregate as a material for constructing bicycle lanes was demonstrated with respect to skid resistance, abrasion resistance, and bond strength. For skid resistance, the energy loss is measured when the surface of the specimen is rubbed against a rubber slider, with the resulting amount of energy lost expressed as the skid resistance, and represented as a British Pendulum Number (BPN). The BPN of the aggregate in this study was 71. When compared with the acceptable minimum for bicycle lanes of 40 [30], the value is appropriate. For abrasion resistance, a machine rotates an abrasion head rubbing an abraded face of the specimen. When the number of revolutions of abrasion head reaches 1000, the loss of specimen is measured. The abrasion value in this study was 290 mg, which exceeds the limit of the KS F 2813 standard (200 mg). For the bond strength test, the maximum tensile load on the specimen was measured, and the bond strength was calculated from the equation (bond strength ($\text{N}\cdot\text{mm}^{-2}$) = $T/1600$, where T is the maximum tensile load (N)). The bond strength of the lightweight aggregate in this study of $1.5 \text{ N}\cdot\text{mm}^{-2}$ satisfies the KS F 4936 standard value of $1.2 \text{ N}\cdot\text{mm}^{-2}$. Overall, the lightweight aggregates tested in this study can be utilized as construction materials for bicycle lanes if reinforcement for abrasion resistance is applied.

3.2. Environmental Compatibility of the Lightweight Aggregate

The environmental impact of the lightweight aggregate when used as a material for bicycle lane construction was demonstrated by leachability and leachate toxicity tests. First, the potentially hazardous elements in the raw materials were analyzed. Table 1 shows the elemental compositions of the mine tailings, the red mud, and the waste limestone analyzed by XRF. The major components of the mine tailings were Si (36.68%); red mud, Fe (26.89%) and Al (13.19%); and waste limestone, Ca (56.43%). Figure A2 also shows the XRD peak patterns of the mine tailings, the red mud, and the waste limestone. The major minerals in the mine tailings, red mud, and the waste limestone was SiO_2 (62.98%), Fe_2O_3 (26.53%), and CaCO_3 (81.73%), respectively. Table 2 shows the total hazardous element concentrations of the raw materials and the lightweight aggregate. In the mine tailings and the red mud, 107 and 40 $\text{mg}\cdot\text{kg}^{-1}$ of Pb and 12.6 and 15.2 $\text{mg}\cdot\text{kg}^{-1}$ of As was detected, respectively. Fluoride was also detected in the all raw materials, in the range of 308–472 $\text{mg}\cdot\text{kg}^{-1}$.

Table 1. Major compositions of the mine tailings, the red mud, the waste limestone, and the lightweight aggregate determined using X-ray fluorescence (XRF) spectrometry.

Element	Content (wt. %)			
	Mine Tailings	Red Mud	Waste Limestone	Lightweight Aggregate
O	50.00	37.50	31.80	36.00
Si	36.38	5.63	4.55	23.06
Ca	0.64	5.02	56.43	15.53
Fe	0.67	26.89	1.97	11.54
Al	7.29	13.19	1.84	7.02
K	3.94	0.05	0.85	2.21
Ti	0.11	4.59	0.16	1.76

Table 1. Cont.

Element	Content (wt. %)			
	Mine Tailings	Red Mud	Waste Limestone	Lightweight Aggregate
Na	0.14	6.32	-	1.36
S	0.30	0.13	0.04	0.46
Mg	0.22	0.14	1.65	0.53
Mn	0.06	0.03	0.51	0.22
Zr	0.01	0.23	-	0.12
Cr	0.02	0.08	-	0.05
Rb	0.02	-	0.01	0.02
Sr	0.01	-	0.1	0.03
Pb	0.01	-	-	-

Table 2. Total concentrations of hazardous elements (As, Cd, cyanide, Cr, Cr(VI), Cu, F, Hg, Ni, Pb, and Zn) in the mine tailings, the red mud, the waste limestone (Unit: mg·kg⁻¹).

Element	Mine Tailings	Red Mud	Waste Limestone
As	12.64 ± 0.24	15.23 ± 0.40	6.91 ± 0.21
Cd	ND	1.32 ± 0.05	ND
cyanide	ND	ND	ND
Cr	87.53 ± 0.55	290.58 ± 2.32	4.18 ± 0.05
Cr(VI)	ND	ND	ND
Cu	13.83 ± 0.32	10.90 ± 0.10	27.83 ± 1.70
F	308.67 ± 28.57	472.00 ± 50.48	424.33 ± 3.51
Hg	ND	ND	ND
Ni	2.27 ± 0.06	19.90 ± 0.10	21.83 ± 0.84
Pb	107.93 ± 2.36	40.27 ± 0.25	5.83 ± 0.40
Zn	28.77 ± 1.34	20.43 ± 0.40	15.50 ± 1.50

ND = not detected.

The leachability of the raw materials and lightweight aggregate were evaluated using standard leaching tests from Korea, the US, and Europe as shown in Table 3. For all raw materials and the lightweight aggregate, no significant leaching of hazardous elements was detected. Similar studies have also reported no leached heavy metals detected from lightweight aggregates from mining residues, heavy metal sludges, and incinerator fly ash, even when the raw materials contained heavy metals [31,32].

Table 3. Leaching characteristics of the mine tailings, red mud, and waste limestone in comparison with regulations from Korea, the US, and Europe.

Element	Mine Tailings	Red Mud	Waste Limestone	Lightweight Aggregate	Regulatory Standards
(A) KSTM-SW (pH 5.8–6.3) (unit: mg·L ⁻¹)					Korea Waste Control Act
As	ND	ND	ND	ND	1.5
Cd	ND	ND	ND	ND	0.3
CN	ND	ND	ND	ND	1
Cr	ND	0.653 ± 0.025	ND	0.045 ± 0.006	-
Cr(VI)	ND	ND	ND	ND	1.5
Cu	ND	ND	ND	ND	3.0
Hg	ND	ND	ND	ND	0.005
Ni	ND	ND	ND	ND	-
Pb	ND	ND	ND	ND	3.0
Zn	ND	ND	ND	ND	
Ca	51.81 ± 0.39	1.67 ± 0.49	6.92 ± 0.14	1116.85 ± 45.50	
Mg	4.35 ± 0.06	0.01 ± 0.00	1.49 ± 0.02	0.03 ± 0.00	
Leachate pH	8.05 ± 0.14	11.85 ± 0.01	9.58 ± 0.13	12.65 ± 0.03	

Table 3. Cont.

Element	Mine Tailings	Red Mud	Waste Limestone	Lightweight Aggregate	Regulatory Standards		
(B) TCLP (pH 2.88) (unit: mg·L ⁻¹)					USEPA Land Disposal Restrictions Regulations		
As	ND	ND	ND	ND	5.0		
Cd	ND	ND	ND	ND	1.0		
CN	ND	ND	ND	ND	-		
Cr	0.263 ± 0.057	0.244 ± 0.015	ND	0.055 ± 0.011	5.0		
Cr(VI)	ND	ND	ND	ND	-		
Cu	0.967 ± 0.695	ND	0.474 ± 0.099	0.133 ± 0.192	-		
Hg	ND	ND	ND	ND	-		
Ni	ND	ND	0.134 ± 0.189	ND	-		
Pb	ND	ND	ND	ND	5.0		
Zn	0.591 ± 0.046	0.005 ± 0.000	0.105 ± 0.035	ND	-		
Leachate pH	3.37 ± 0.01	5.27 ± 0.02	5.73 ± 0.01	12.62 ± 0.02			
(C) SPLC (pH 5) (unit: mg·L ⁻¹)					USEPA Land Disposal Restrictions Regulations		
As	ND	ND	ND	ND	5.0		
Cd	ND	ND	ND	ND	1.0		
CN	ND	ND	ND	ND	-		
Cr	ND	0.417 ± 0.021	0.010 ± 0.014	0.036 ± 0.001	5.0		
Cr(VI)	ND	ND	ND	ND	-		
Cu	0.129 ± 0.183	1.399 ± 2.384	0.199 ± 0.305	ND	-		
Hg	ND	ND	ND	ND	-		
Ni	ND	ND	ND	ND	-		
Pb	ND	ND	ND	0.106 ± 0.139	5.0		
Zn	ND	0.097 ± 0.158	ND	ND	-		
Leachate pH	8.61 ± 0.11	11.67 ± 0.01	9.60 ± 0.01	12.84 ± 0.01			
(D) EU Method (pH 5–7.5) (unit: mg·kg ⁻¹)					European Legislation for Solid Wastes		
					Inert Waste	Non-Hazardous Waste	Hazardous Waste
As	ND	0.071 ± 0.000	ND	ND	0.5	2	25
Cd	ND	ND	ND	ND	0.04	1	5
CN	ND	ND	ND	ND	-	-	-
Cr	ND	0.034 ± 0.006	ND	0.032 ± 0.009	0.5	10	70
Cr(VI)	ND	ND	ND	ND	-	-	-
Cu	ND	0.260 ± 0.175	0.023 ± 0.000	ND	2	50	100
Hg	ND	ND	ND	ND	-	-	-
Ni	ND	ND	ND	ND	0.40	10	40
Pb	ND	ND	ND	ND	0.5	10	50
Zn	ND	0.060 ± 0.009	0.005 ± 0.000	ND	4	50	200
Leachate pH	7.78 ± 0.09	12.32 ± 0.00	9.39 ± 0.03	12.84 ± 0.01			

ND = not detected.

The results show that the leachate of the red mud and the lightweight aggregate showed a relatively high pH of more than 11, with the exception of the red mud leachate from the TCLP test. The high pH of red mud is because of its caustic nature [33]. The residual NaOH in the red mud reacts with silicate and forms Na₂SiO₃ at high temperatures [34], therefore, in the aggregate after the sintering process, the alkaline characteristics of red mud would be gone. The high pH of the leachate from the aggregate may originate from CaO. The high Ca concentration in the leachate supports this assumption. As shown in our previous study [21], during the sintering process of the lightweight aggregate, CaCO₃ (calcite) decomposes at 897 °C, and is no longer observed for samples heated above 1050 °C, 1050 °C, and 1100 °C, where SiO₂ (quartz), Fe₂O₃ (hematite) and CaO were the main phases present within the heated sample, respectively. Even though the CaO content of the aggregate decreases at 1150 °C, there is still CaO remaining as analyzed by Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM/EDX). The CaO in the aggregate generates alkaline leachates, and free CaO dissociates to form Ca²⁺ and OH⁻ to increase the pH. Similarly, steel slag contains free CaO and generates an alkaline leachate with a pH of 10 to 13 [35], containing heavy metals that are passively treated by storage in a wetland [36]. Proctor et al. [37] analyzed the potential ecological risk of three types of steel-industry slags and concluded there is potential for impacts to aquatic life due to a high pH.

As an indicator of impact on the surrounding environment, the ecotoxicity of the KSTM-SW leachate was analyzed by using water fleas, *Daphnia magna* (Table 4). The toxicity is presented as toxic units (TU, 100/EC₅₀). The TU value of red mud was very high (i.e., 30.4 at 48 h), possibly because of a

high pH value. The TU value of the lightweight aggregate leachate was also significantly higher than the raw material leachate except for the leachate from the red mud. Rendal et al. [38] showed that toxicity measured by *Daphnia magna* significantly increases at pH values above 8. Also, as shown in Table 3, in the lightweight aggregate leachate, a very high concentration of Ca was observed. To remove this calcium, the leachate was left in contact with air for two days to allow the Ca to precipitate as CaCO_3 (Figure A3). The precipitate was collected by filtration using a $0.45\ \mu\text{m}$ filter and identified as CaCO_3 by XRD analysis (Figure A4). The pH of the as-is leachate was adjusted to 6. Then the toxicity of the leachate including as-is leachate, pH-adjusted leachate, Ca-removed leachate, and Ca-removed and pH-adjusted leachate was tested (Table 5). The toxicity of the pH-adjusted leachate greatly reduced, and the toxicity of the leachate after removing Ca was also down by about half. By removing Ca and adjusting pH, the TU value of the leachate was also significantly reduced. The remaining toxicity of the leachate with the Ca removed may be attributed to the residual Ca ($96.3\ \text{mg}\cdot\text{L}^{-1}$) or high pH, as the LC_{50} of Ca is $52\ \text{mg}\cdot\text{L}^{-1}$ [39].

Table 4. Toxic units (TU) of the KSTM-SW leachates determined by using *Daphnia magna*.

Sample	Mine Tailings	Red Mud	Waste Limestone	Lightweight Aggregate
24 h TU	1.36	12.8	0.17	10.67
48 h TU	1.46	30.4	1.50	10.67

Table 5. Toxic units (TU) of the KSTM-SW leachates before and after adjusting pH or removing Ca determined by using *Daphnia magna*.

Sample	As-Is Leachate	pH-Adjusted Leachate	Ca-Removed Leachate	Ca-Removed and pH-Adjusted Leachate
Ca Concentration ($\text{mg}\cdot\text{L}^{-1}$)	1116.85 ± 45.50	1116.85 ± 45.50	96.32 ± 1.49	96.32 ± 1.49
pH	12.65 ± 0.03	5.97 ± 0.02	11.72 ± 0.01	6.00 ± 0.01
24 h TU	10.67	1.31	3.47	0.60
48 h TU	10.67	1.33	6.67	1.50

Both of high pH and Ca content of the lightweight aggregate leachate should be controlled when used for bicycle lanes. Some studies on the use of steelmaking slag recycling as cement have reported that some cementing materials such as blast furnace slag or fly ash were used to consume free CaO [40]. By decreasing the content of free CaO , the high pH and Ca problem may be minimized. Also, since a high free- CaO content may cause volume expansion of the bicycle path by hydration [41], it may be more beneficial to use these additives to consume the free CaO when the lightweight aggregate is produced. Increasing sintering temperature and time may be another option to control the free CaO content because the CaO content decreases with temperature as mentioned above. If the aggregates were produced at temperatures below $1100\ ^\circ\text{C}$, more CaO would remain in the aggregate, and the leachate toxicity to *Daphnia magna* would increase.

The heavy metal leachability of the recycled materials including lightweight aggregates has been assessed in many studies [14,19,31,42], however, this is very first study showing ecotoxicity of the leachate and the potential effect of free CaO contained in the aggregates. Aside from the leachable heavy metal contents, after the sintering process, the composition of the aggregates can be changed and unexpected hazardous materials can be generated. Until now, for construction use, only the leachability test has been used to assess hazardous heavy metal dissolution from the recycled materials. However, if the aggregates are contacted to water, the alkaline leachate containing Ca from the aggregate may generate and contaminate the environment even though the leachate does not contain any heavy metals. Thus, these findings suggest that it is important to assess the alkalinity and toxicity of the leachate from the lightweight aggregate as well as heavy metal leaching.

In conclusion, the lightweight aggregate in this study was evaluated concerning its physical feasibility and environmental leachability and leachate toxicity. The results showed that the use of this

aggregate is feasible for bicycle lanes except for a relatively weak abrasion resistance. Therefore additives, such as nanoparticles, may be added to enhance the abrasion resistance [43]. In the leachability tests, no leached hazardous elements were detected, while the toxicity determined by water fleas increased. The cause of this toxicity may be from high pH and Ca because of the residual free CaO in the aggregate. To control the CaO content in the lightweight aggregate, the sintering temperature and time may be increased, through changing the ratio of limestone addition, or adding other CaO-consuming materials. If the lightweight aggregate is used without treatment, it may generate leachates toxic to aquatic life. These results will be useful for designing an environmentally-sound recycling process of mine tailing, red mud, and waste limestone.

4. Conclusions

In this study, the potential use of a lightweight aggregate made from mine tailings and industrial byproducts was investigated as a construction material for bicycle lanes based on physical feasibility, leachability, and ecotoxicity tests. Overall, it was shown that recycling mine tailings and industrial byproducts as a lightweight aggregate is acceptable but needs reinforcement of abrasive resistance to appropriately control toxic leachates.

Acknowledgments: This research was supported by the Basic Research Project (16-3241) of the Korea Institute of Geoscience and Mineral Resources (KIGAM) funded by the Ministry of Science, ICT, and Future Planning of Korea.

Author Contributions: Won Jung Ju, Doyun Shin, Hyunsik Park, and Kyoungphile Nam conceived and designed the experiments; Won Jung Ju performed the experiments; Won Jung Ju and Doyun Shin analyzed the data; Kyoungphile Nam and Hyunsik Park contributed reagents/materials/analysis tools; Won Jung Ju and Doyun Shin wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest. The funding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, and in the decision to publish the results.

Appendix A

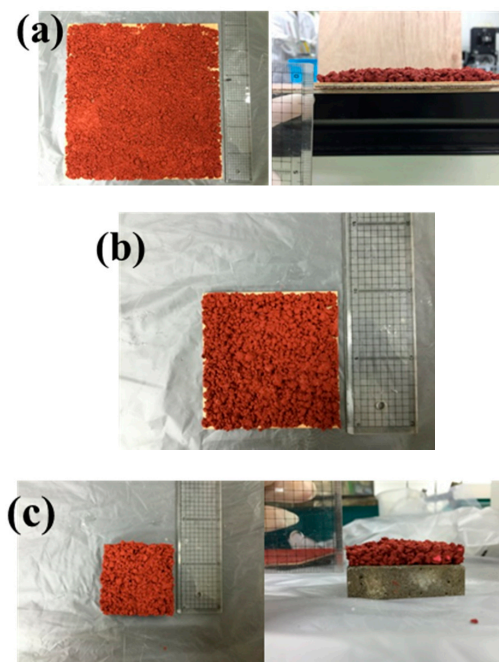


Figure A1. Specimen preparation for (a) skid resistance, (b) abrasion resistance, and (c) bond strength tests.

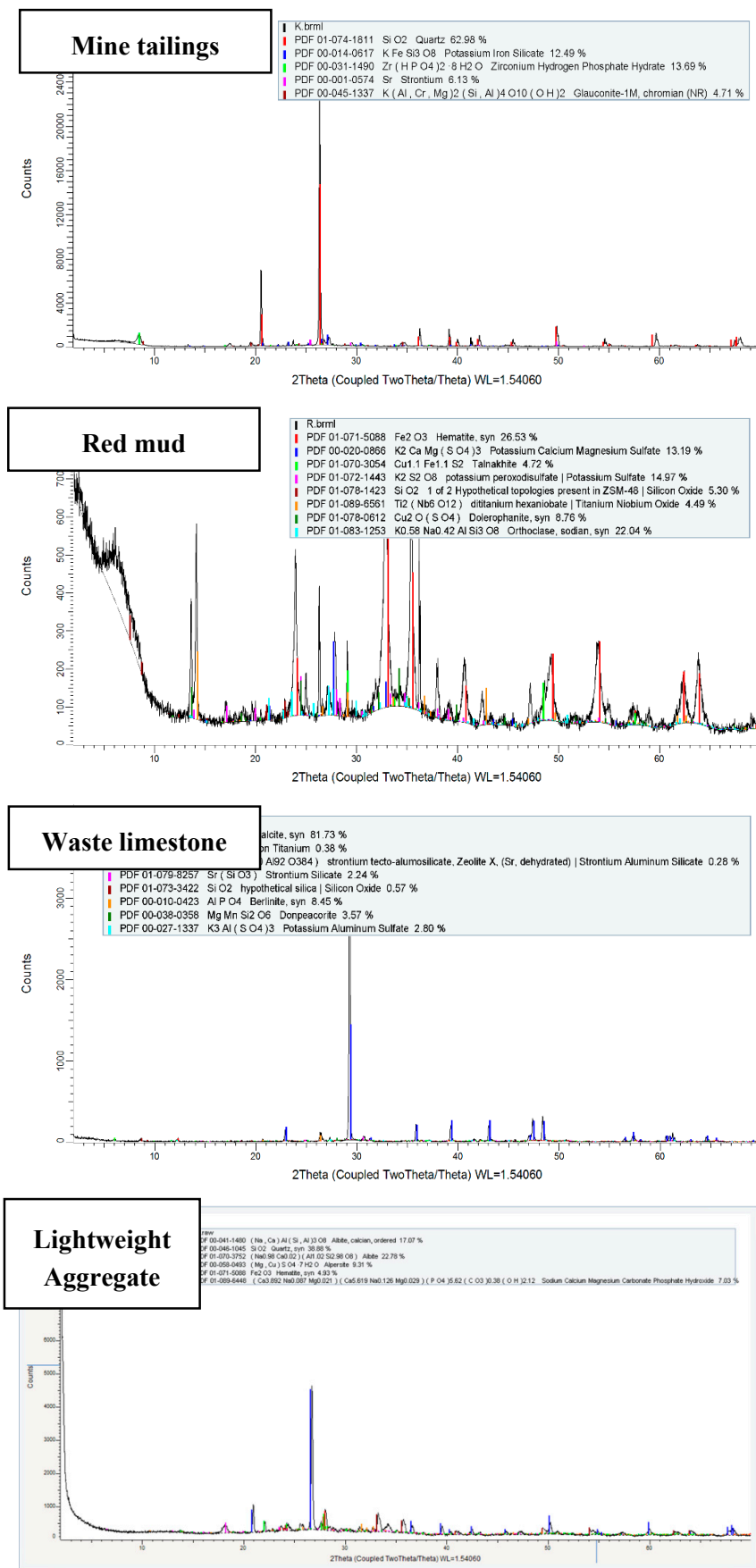


Figure A2. Peak patterns of the mine tailings, red mud, waste limestone, and lightweight aggregate determined using X-ray diffraction (XRD).

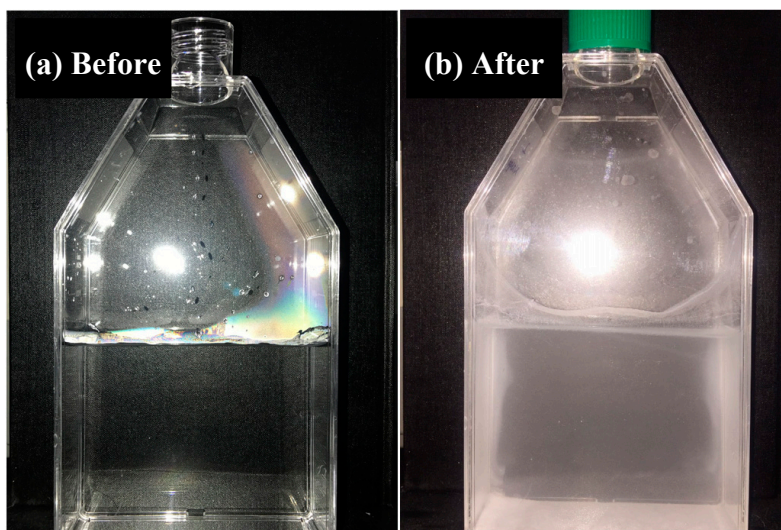


Figure A3. (a) The KSTM-SW leachate and (b) the leachate after CaCO_3 precipitation.

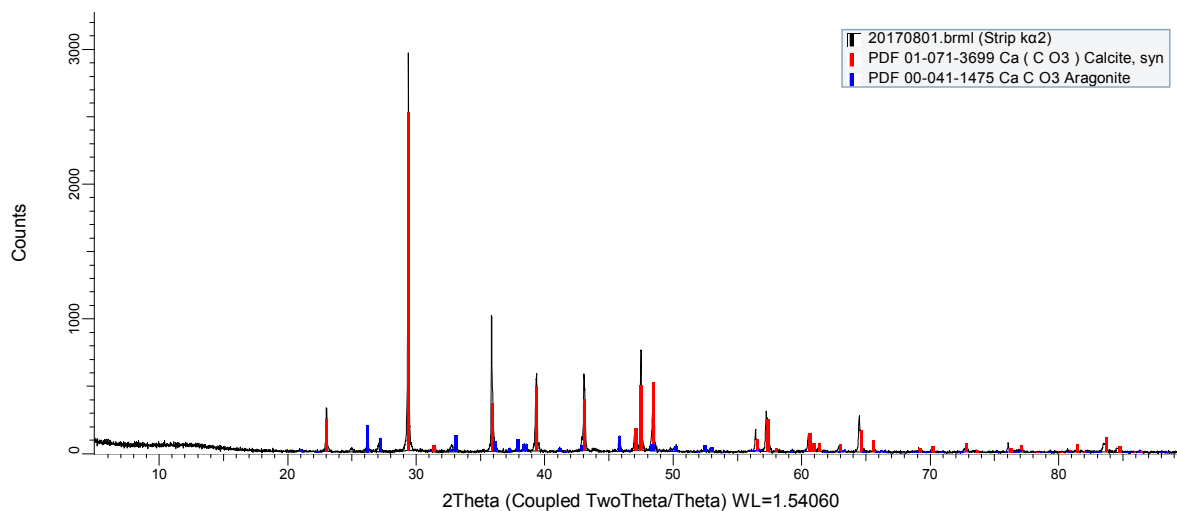


Figure A4. XRD peak patterns of the precipitate from the KSTM-SW leachate from the lightweight aggregate.

References

1. Mine Reclamation Corporation. *Yearbook of MIRECO Statistics*; Mine Reclamation Corporation: Seoul, Korea, 2015.
2. Mine Reclamation Corporation. *Development of Characterizing Method for Mine Tailing*; Mine Reclamation Corporation: Seoul, Korea, 2012.
3. Ritcey, G.M. *Tailings Management: Problems and Solutions in the Mining Industry*; Elsevier Science: Amsterdam, The Netherlands, 1989.
4. Van Zyl, D. Mine waste disposal. In *Geotechnical Practice for Waste Disposal*; Daniel, D.E., Ed.; Springer: Boston, MA, USA, 1993; pp. 269–286.
5. Fourie, A. Preventing catastrophic failures and mitigating environmental impacts of tailings storage facilities. *Proc. Earth Planet. Sci.* **2009**, *1*, 1067–1071. [[CrossRef](#)]
6. Klauber, C.; Gräfe, M.; Power, G. Bauxite residue issues: II. Options for residue utilization. *Hydrometallurgy* **2011**, *108*, 11–32. [[CrossRef](#)]
7. Power, G.; Gräfe, M.; Klauber, C. Bauxite residue issues: I. Current management, disposal and storage practices. *Hydrometallurgy* **2011**, *108*, 33–45.

8. Benzaazoua, M.; Bussière, B.; Demers, I.; Aubertin, M.; Fried, É.; Blier, A. Integrated mine tailings management by combining environmental desulphurization and cemented paste backfill: Application to mine Doyon, Quebec, Canada. *Miner. Eng.* **2008**, *21*, 330–340. [CrossRef]
9. Roy, S.; Adhikari, G.R.; Gupta, R.N. Use of gold mill tailings in making bricks: A feasibility study. *Waste Manag.* **2007**, *25*, 475–482. [CrossRef] [PubMed]
10. Ahmari, S.; Chen, R.; Zhang, L. Utilization of Mine Tailings As Road Base Material. In Proceedings of the GeoCongress, Oakland, CA, USA, 25–29 March 2012; pp. 3654–3661.
11. Owens, P.; Newman, J. Structural lightweight aggregate concrete: The future? *Concr. Lond. Concr. Soc.* **1999**, *33*, 45–47.
12. Tang, C.-W.; Chen, H.-J.; Wang, S.-Y.; Spaulding, J. Production of synthetic lightweight aggregate using reservoir sediments for concrete and masonry. *Cem. Concr. Comp.* **2011**, *33*, 292–300. [CrossRef]
13. Chen, H.-J.; Wang, S.-Y.; Tang, C.-W. Reuse of incineration fly ashes and reaction ashes for manufacturing lightweight aggregate. *Constr. Build. Mater.* **2010**, *24*, 46–55. [CrossRef]
14. Molineux, C.J.; Newport, D.J.; Ayati, B.; Wang, C.; Connop, S.P.; Green, J.E. Bauxite residue (red mud) as a pulverised fuel ash substitute in the manufacture of lightweight aggregate. *J. Clean. Prod.* **2016**, *112*, 401–408. [CrossRef]
15. Shafigh, P.; Nomeli, M.A.; Alengaram, U.J.; Mahmud, H.B.; Jumaat, M.Z. Engineering properties of lightweight aggregate concrete containing limestone powder and high volume fly ash. *J. Clean. Prod.* **2016**, *135*, 148–157. [CrossRef]
16. Mun, K.J. Development and tests of lightweight aggregate using sewage sludge for nonstructural concrete. *Constr. Build. Mater.* **2007**, *21*, 1583–1588. [CrossRef]
17. Turkdogan, E.T. *Fundamentals of Steelmaking*; Maney Publishing: Leeds, UK, 1996; Volume 614.
18. Petkovic, G.; Engelsen, C.J.; Håøya, A.-O.; Breedveld, G. Environmental impact from the use of recycled materials in road construction: method for decision-making in Norway. *Resour. Conserv. Recycl.* **2004**, *42*, 249–264. [CrossRef]
19. Chang, F.-C.; Lo, S.-L.; Lee, M.-Y.; Ko, C.-H.; Lin, J.-D.; Huang, S.-C.; Wang, C.-F. Leachability of metals from sludge-based artificial lightweight aggregate. *J. Hazard. Mater.* **2007**, *146*, 98–105. [CrossRef] [PubMed]
20. Maghool, F.; Arulrajah, A.; Du, Y.-J.; Horpibulsuk, S.; Chinkulkijniwat, A. Environmental impacts of utilizing waste steel slag aggregates as recycled road construction materials. *Clean Technol. Environ. Policy* **2017**, *19*, 949–958. [CrossRef]
21. Park, H.; Ha, M.; Shin, D.; Kim, M.; Sohn, I. Potential utilization of hazardous mining wastes in the production of lightweight aggregates. *Miner. Process. Extr. Metall.* **2017**, 1–10. [CrossRef]
22. Korea Ministry of Environment. Korea Standard Testing Methods for Soil Contamination. Available online: <http://www.law.go.kr/> (accessed on 1 October 2015).
23. Korea Ministry of Environment. Korea Standard Testing Methods for Solid Wastes. Available online: <http://www.law.go.kr/> (accessed on 1 October 2015).
24. United States of Environmental Protection Agency. *T.C.L.P. EPA Method 1311*; United States of Environmental Protection Agency: Washington, DC, USA, 1990.
25. United States of Environmental Protection Agency. *S.P.L.P. EPA Method 1312*; United States of Environmental Protection Agency: Washington, DC, USA, 1994.
26. British Standards Institution. *British Standards. BS EN 12457-1. Characterisation of Waste. Leaching. Compliance Test for Leaching of Granular Waste Materials and Sludges. One Stage Batch Test at a Liquid To Solid Ratio of 2 L/kg for Materials with High Solid Content and with Particle Size below 4 mm (without or with Size Reduction)*; British Standards Institution: London, UK, 2002.
27. Korea Ministry of Environment. Korea Standard Testing Methods for Water Quality. Available online: <http://www.law.go.kr/> (accessed on 1 October 2015).
28. Epstein, J. Estimation of microquantities of cyanide. *Anal. Chem.* **1947**, *19*, 272–274. [CrossRef]
29. American Public Health Association. *Standard Methods for the Examination of Water and Wastewater, Method 4500 FD*, 20th ed.; American Public Health Association: Washington, DC, USA, 1998.
30. Department of Planning, Transport and Infrastructure. Guide to Bikeway Pavement Design Construction & Maintenance for South Australia. Available online: https://www.dpti.sa.gov.au/__data/assets/pdf_file/0006/149964/DPTI_Bikeway_Pavement_Guidelines_2.pdf (accessed on 10 August 2016).

31. Huang, S.-C.; Chang, F.-C.; Lo, S.-L.; Lee, M.-Y.; Wang, C.-F.; Lin, J.-D. Production of lightweight aggregates from mining residues, heavy metal sludge, and incinerator fly ash. *J. Hazard. Mater.* **2007**, *144*, 52–58. [[CrossRef](#)] [[PubMed](#)]
32. Cheeseman, C.R.; Makinde, A.; Bethanis, S. Properties of lightweight aggregate produced by rapid sintering of incinerator bottom ash. *Resour. Conserv. Recycl.* **2005**, *43*, 147–162. [[CrossRef](#)]
33. Liu, Y.; Lin, C.; Wu, Y. Characterization of red mud derived from a combined Bayer Process and bauxite calcination method. *J. Hazard. Mater.* **2007**, *146*, 255–261. [[CrossRef](#)] [[PubMed](#)]
34. Guo, Q.; Qu, J.K.; Qi, T.; Wei, G.Y.; Han, B.B. Activation pretreatment of limonitic laterite ores by alkali-roasting using NaOH. *Int. J. Min. Met. Mater.* **2012**, *19*, 100–105. [[CrossRef](#)]
35. Mayes, W.M.; Younger, P.L.; Aumônier, J. Hydrogeochemistry of Alkaline steel slag leachates in the UK. *Water Air Soil Pollut.* **2008**, *195*, 35–50. [[CrossRef](#)]
36. Mayes, W.M.; Younger, P.L. Buffering of alkaline steel slag leachate across a natural wetland. *Environ. Sci. Technol.* **2006**, *40*, 1237–1243. [[CrossRef](#)] [[PubMed](#)]
37. Proctor, D.M.; Shay, E.C.; Fehling, K.A.; Finley, B.L. Assessment of human health and ecological risks posed by the uses of steel-industry slags in the environment. *Hum. Ecol. Risk Assess.* **2002**, *8*, 681–711. [[CrossRef](#)]
38. Rendal, C.; Kusk, K.O.; Trapp, S. The effect of pH on the uptake and toxicity of the bivalent weak base chloroquine tested on *Salix viminalis* and *Daphnia magna*. *Environ. Toxicol. Chem.* **2011**, *30*, 354–359. [[CrossRef](#)] [[PubMed](#)]
39. Biesinger, K.E.; Christensen, G.M. Effects of various metals on survival, growth, reproduction, and metabolism of *Daphnia magna*. *J. Fish. Res. Board Can.* **1972**, *29*, 1691–1700. [[CrossRef](#)]
40. Shi, C. Steel Slag—Its production, processing, characteristics, and cementitious properties. *J. Mater. Civ. Eng.* **2004**, *16*, 230–236. [[CrossRef](#)]
41. Shi, C.; Day, R.L. Early strength development and hydration of alkali-activated blast furnace slag/fly ash blends. *Adv. Chem. Res.* **1999**, *11*, 189–196. [[CrossRef](#)]
42. Cusidó, J.A.; Cremades, L.V. Environmental effects of using clay bricks produced with sewage sludge: Leachability and toxicity studies. *Waste Manag.* **2012**, *32*, 1202–1208. [[CrossRef](#)] [[PubMed](#)]
43. Li, H.; Zhang, M.H.; Ou, J.P. Abrasion resistance of concrete containing nano-particles for pavement. *Wear* **2006**, *260*, 1262–1266. [[CrossRef](#)]



© 2017 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).