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Original Research

Environmental Toxicity Analysis and Reduction of Ceramsite Synthesis from Industrial Coal Gasification Coarse Cinder Waste

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Abstract

Coal gasification coarse cinder (CGCC) is the main waste in the coal gasification industry, containing low calorific value but high heavy metal residuals. To achieve environmental toxicity stabilization and waste recycling, we developed a manufacturing method of multiple-functional ceramsite from CGCC by pelletizing and sintering. By altering key parameters during the manufacturing process (including CGCC content, sintering temperature, and time), the physical properties and leaching toxicity of ceramsite were evaluated. Sintering temperature was identified with a significantly positive relationship with ceramsite's compressive strength, whereas CGCC content was negatively correlated with water adsorption. The highest compressive strength (24.00 MPa) and relatively lower water absorption (21.36%) was achieved at 50% CGCC content and 1,150ºC sintering for 30 min. The toxicity tests showed acceptable leaching heavy metals with minimal environmental impact. Considering the energy conservation and the maximal recycling of CGCC, optimal ceramsite manufacturing is suggested as 50% CGCC content and 1,150ºC/10 min sintering temperature/time. Our results indicated that multiple-functional ceramsite manufacturing is a low-cost and environmentally friendly approach for CGCC recycling.

Keywords: ceramsite, coal gasification coarse cinder (CGCC), heavy metals, compressive strength, environmental toxicity

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Introduction

Coal gasification coarse cinder (CGCC) is a by-product during the industrial coal process [1]. Landfill is the traditional CGCC disposal method [2-3], which was not environmental friendly due to the release of heavy metals and polycyclic aromatic hydrocarbons (PAHs) into soils and groundwater [3-4]. Long-term contamination consequently decreases soil quality and threatens human health [5-6]. Thus, to explore a safe and feasible way for recycling CGCC is an urgent need. Recycling for CGCC could achieve the possibility of using this waste which contained heavy metals as a safe resource, avoiding the consumption of raw materials and making a great contribution to the development of the local economy [7]. Many studies therefore addressed alternative approaches for comprehensive utilization of CGCC to reduce the potential environmental risk and recycle it as valuable functional materials.

A previous study on the recycling of coal-based solid wastes predominantly addressed the high calorific and fine particulate matters, such as coal fly ash, lime mud, and wastewater treatment sludge. Qin et al. successfully manufactured ceramsite from lime mud and coal fly ash as a new high-performance product through waste recycling [8]. Via sintering and alkaline hydrothermal reaction, construction and demolition wastes were transferred into zeolite-loaded ceramsite [9]. The green ceramsite from sewage sludge also showed the potential of recycling wastes as the light weight aggregates in industrial practices [10]. However, though CGCC has high yield at the coal processing cites, there were few studies for its reutilization due to such difficulties as low calorific value, large particle size, and high heavy metal concentrations. Given the fact that CGCC has the main components as SiO_2, CaO, Fe_2O_3, and Al_2O_3, it is hypothesized as appropriate raw material for ceramsite manufacturing [8], but its leaching toxicity needs particular attention for environmental risk control and management.

In this study, we developed a manufacturing method of multiple-functional ceramsite from CGCC by pelletizing and sintering. Both physical properties and environmental leaching toxicity of the ceramsite were evaluated and linked to manufacturing parameters as raw material ratio, sintering temperature, and sintering time. The manufacturing conditions were therefore optimized as effective CGCC recycling approach for high-quality ceramsite with minimal toxic risks.

Table 1. Raw material contents for ceramsite manufacturing.

Group	CGCC (%)	Clay (%)	Quartz sand (%)
1	20	40	40
2	35	25	40
3	50	25	25
4	65	10	25

This paper is organized as follows: after the introduction is presented in the first section, the second section covers the materials of manufacturing ceramsite and methods for chemical and morphological analysis, physical analysis, and data analysis. The third section contains the results, discussion, and comparisons with national standards. The conclusions and recommendations for decision makers are presented in the final section.

Materials and Methods

Manufacturing Ceramsite from Coal Gasification Coarse Cinder

The CGCC and coal fly ash were collected from the methanol plant of Yulin Energy and Chemical Industry, Yanzhou Coal Corporation, China (N38°34’41.9”, E109°55’50.4”). After being dried at 105ºC for two hours, smashed by a grinder for three minutes, and sieved by 60-mesh sieve, the CGCC was then mixed with clay/quartz (the CGCC content listed in Table 1) and sintered in a silicon molybdenum furnace. Sixteen treatments were carried out to optimize the physical properties of ceramsite, including sintering temperature from 1,000°C to 1,150ºC, sintering time from 10 min to 90 minutes, and CGCC content from 20% to 65% (Table 2). The raw meal ball could not form a meal ball structure when CGCC content was 65%, so No. 1-12 treatments were available.

Table 2. Orthogonal treatments.

Treatments	CGCC content (%)	Temperature (ºC)	Time (min)
1	20	1,000	10
2	20	1,050	30
3	20	1,100	60
4	20	1,150	90
5	35	1,000	30
6	35	1,050	60
7	35	1,100	90
8	35	1,150	10
9	50	1,000	60
10	50	1,050	90
11	50	1,100	10
12	50	1,150	30
13	65	1,000	90
14	65	1,050	10
15	65	1,100	30
16	65	1,150	60

Table 3. The main components in CGCC.

Components	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	C
Contents (%)	20.12	8.23	30.08	18.17	2.14	1.93	16.12

Chemical and Morphological Analysis

The key components in CGCC were analyzed by x-ray fluorescence spectroscopy (XRF, ARLADVANT XP+, Thermo, USA). The key components are listed in Table 3. The leaching trace elements (Cr, As, and Hg) were detected by inductively coupled plasma mass spectrometry (ICP-MS, 7500A, Agilent, USA). The morphology was analyzed by a scanning electron microscope (SEM, S-4800, Hitachi, Japan). The surface functional groups of CGCC and ceramsite were characterized by a Fourier transform infrared spectrometer (FTIR, TENSOR II, Bruker, Germany).

Ceramsite Physical Analysis

The compressive strength of ceramsite was analyzed by pressure tester from 0 to 125 MPa with three individual replicates. Water absorption was measured by drying the ceramsite to constant weight, soaking for two hours, transferring into the container with water, and finally evacuating for 10 min. Water adsorption was calculated following Equation (1).

$$W = \frac{G_1 - G_0}{G_0} \times 100\% \quad (1)$$

…where W represents water absorption (%), and G_0 and G_1 refer to ceramsite weight (g) before immersion in water and after evacuation, respectively.

Data Analysis

The environmental toxicity analysis of original CGCC and manufactured ceramsite followed the National Solid Waste Method for Leaching Toxicity Industry Standards

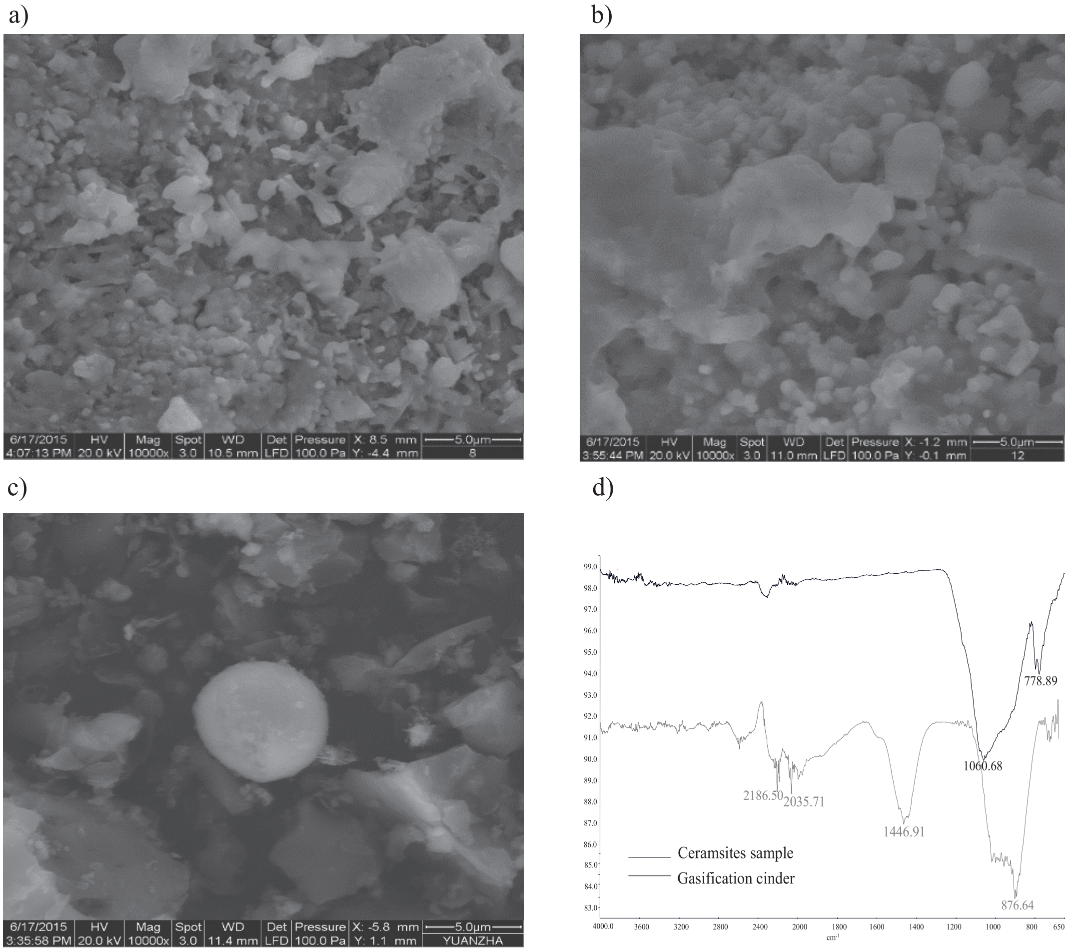

Fig. 1. SEM (10,000× magnification) of original CGCC c) and two ceramsites (a) for 35%/1150ºC/10min and b) for 50%/1150ºC/30min). FTIR spectrum of CGCC and ceramsite d).

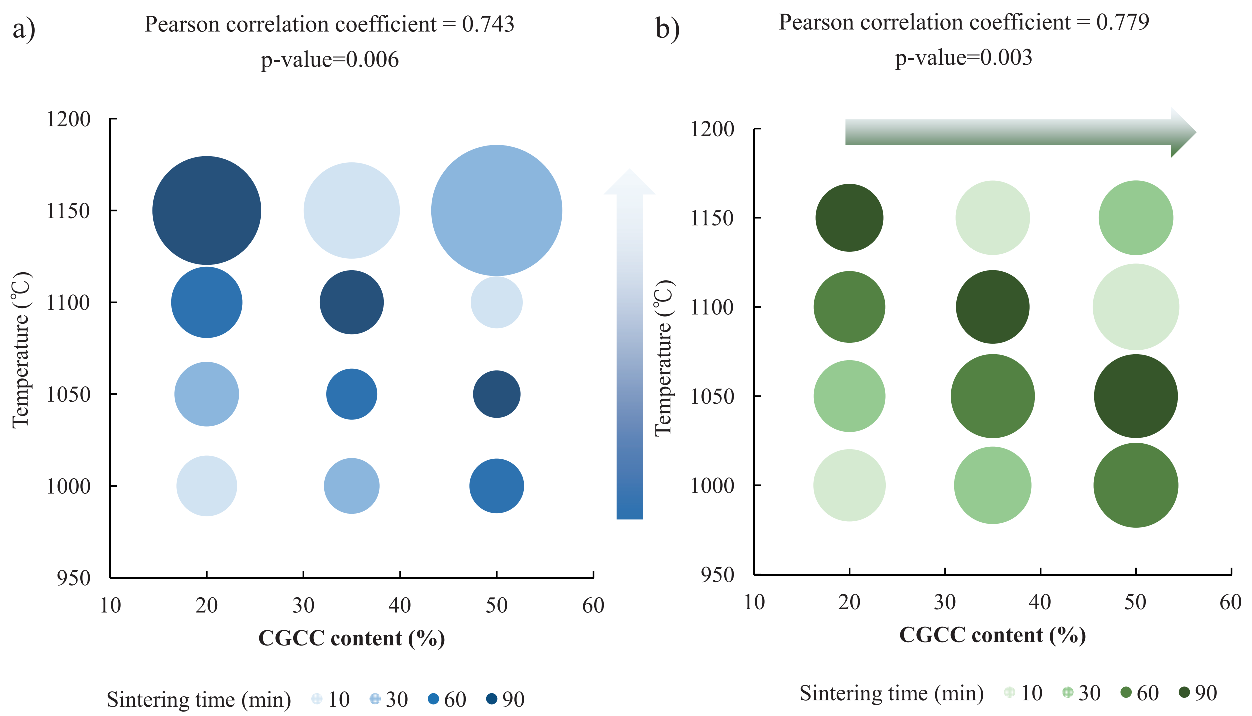

Fig. 2. Ceramsite compressive strength a) and water absorption b). The diameter of the air bubble is positively correlated with compressive strength or water absorption, and the various shades represent different sintering times.

(HJ/T299-2007). SPSS software (version 17.0.0) was used for statistical analysis.

Results and Discussion

The surface morphology by SEM illustrated a better crystallization of ceramsite (Figs 1a-b) than raw CGCC (Fig. 1c). Sintered at 1,150ºC, the formation of spherical structure showed the molten reaction between clay CGCC, forming the glass phase and further the stable crystal lattice structure, different from the anorthite in fly ash ceramic [8, 11]. Thus, the ceramsite morphology change indicated the smooth space structure and the mutual adhesion after sintering with improved compressive strength, instead of the loose and coarse grain structure of raw CGCC. The FTIR spectrum (Fig. 1d) illustrated the existence of C ≡ C stretching vibration (2,186.5 and 2,035.71 cm^{-1}) in

Table 4. The compressive strength and water absorption of ceramsite under different manufacturing conditions.

Samples			Compressive strength (MPa)	Water absorption (%)	Results
CGCC content (%)	Temperature (ºC)	Time (min)	> 5	<22	-
20	1,000	10	5.14	20.03	Qualified
20	1,050	30	5.83	19.82	Qualified
20	1,100	60	7.09	19.70	Qualified
20	1,150	90	16.55	17.66	Qualified
35	1,000	30	4.34	22.96	Unqualified
35	1,050	60	3.64	27.09	Unqualified
35	1,100	90	5.74	20.74	Qualified
35	1,150	10	12.93	21.24	Qualified
50	1,000	60	4.19	27.60	Unqualified
50	1,050	90	3.15	26.94	Unqualified
50	1,100	10	3.77	28.77	Unqualified
50	1,150	30	24.00	21.36	Qualified

Table 5. Properties comparison of CGCC and coal fly ash.

Components	Trace elements (mg/kg)					Total water (wt%)	Fixed carbon (wt%)	Dry basis calorific value (kcal/kg)
	As	Cr	Hg	Cd	Cu			
CGCC	84.24	920.82	3.8	0.12	22.66	28.94	16.12	757.0
Coal fly ash	24.51	139.88	0.001	0.80	53.73	64.65	47.01	2465.4

CGCC, but weakened after sintering. Besides, the peaks of 1,446.91 cm^{-1} and 8,76.64 cm^{-1} represented the -CH$_3$ deformation vibration of aliphatic hydrocarbons and out-of-plane wag of vinyl compounds, respectively [12]. These characteristic peaks indicated the richness of unsaturated organic compounds in CGCC, and their strength was significantly reduced in ceramsite due to oxidation during the high-temperature sintering. Instead, the formation of 1,060 cm^{-1} and 778.9 cm^{-1} in ceramsite, referring to the stretching vibration of Si-O-Si [13] and Al-O [14], were attributed to the inorganic functional groups from clay components.

Ceramsite compressive strength and water absorption are illustrated in Fig. 2 and Table 4. Correlation analysis identified sintering temperature as the key factor affecting compressive strength (p-value = 0.006; Fig. 2a). The increasing compressive strength with sintering temperature was explained by the more molten and glassy phase at higher temperatures [8, 15]. Compared to the national standard (GB/T 17431.1-2010) that the qualified ceramsite should achieve compressive strength above 5 MPa, the suggested sintering temperature is more than 1,100ºC. The CGCC content (raw material ratio) was positively correlated with water absorption (p-value = 0.003; Fig. 2b). The lowest water absorption was obtained (19.7%) when the CGCC content was 20%, fitting with the national qualified water absorption standard (<22%, GB/T 17431.1-2010). Attributed to the strong water adsorption capacity of CGCC, high CGCC content consequently resulted in more water adsorption and reduced ceramsite quality, which needs particular attention during the sintering process. From principle component analysis, sintering time has limited impact on the physical properties of ceramsite, whereas sintering temperature and CGCC content contributed over 80%.

The heavy metal elements (Cr, As, and Hg) in CGCC are significantly higher than those in coal fly ash (Table 5), similar to a previous report [16]. They are stabilized within the glassy phase and crystal lattice structure of ceramsite and might be released into the environment [17]. It is therefore important to evaluate the heavy metal leaching and toxicity of ceramsite manufactured from CGCC and to assess its potential risk to human health [17]. The concentrations of trace elements leaching from various ceramsites were illustrated in Fig. 3 and Table 6. The leaching chromium (Cr) was negatively correlated with the sintering temperature (p-value = 0.014; Fig. 3a), whereas arsenic (As) was the opposite (p-value = 0.037; Fig. 3b). High temperature (>1,000ºC) benefited the formation of crystalline structure in ceramsite, significantly improved the interaction between heavy metal cations and negatively charged clay particles, and ineluctably enhance their stability [9-10]. The leaching mercury (Hg) had a negative relationship with CGCC content (Fig. 3c), explained by the reduction and improved evaporation by the organic matters in clay. Due to the homogeneous oxidation of combustion, the dominant Hg speciation in CGCC or fly

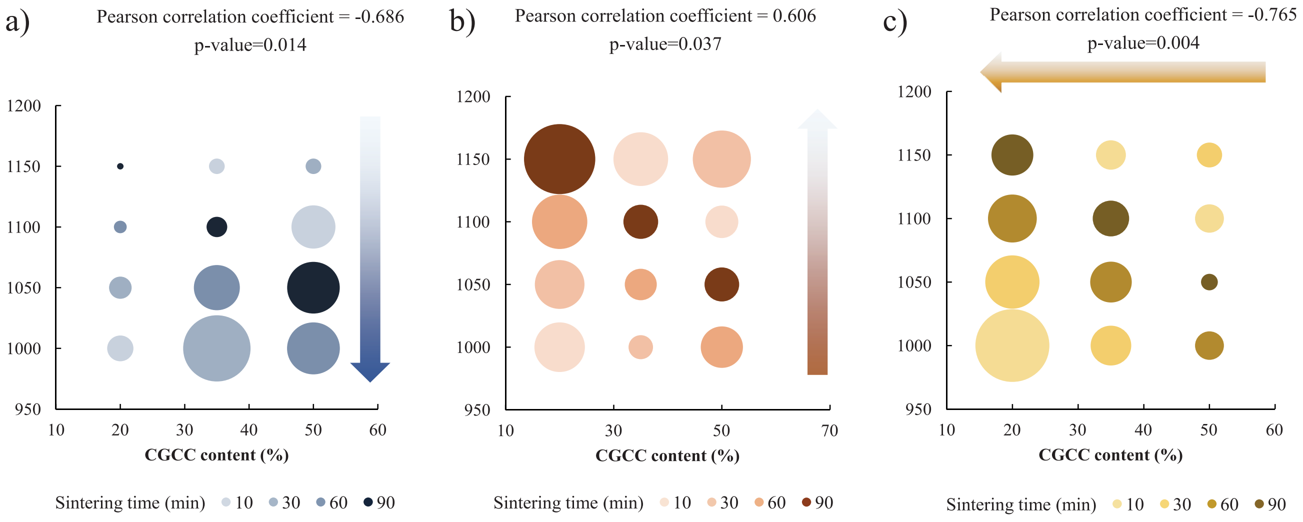

Fig. 3. The leaching toxicity of ceramsite as Cr a), As b), and Hg c). The diameter of the air bubble is positively correlated with the concentrations of trace elements (Cr, As, and Hg), and the various shades represent different sintering times.

Table 6. The leaching trace elements of ceramsite (μg/L) under different manufacturing conditions.

Samples			Cr	As	Hg	Results
CGCC content (%)	Temperature (ºC)	Time (min)	<15000	<5000	<100	-
20	1,000	10	622.1	55.4	2.16	Qualified
20	1,050	30	461.1	53.5	1.16	Qualified
20	1,100	60	147.2	66.4	0.94	Qualified
20	1,150	90	38.6	110.5	0.69	Qualified
35	1,000	30	4,106.0	13.0	0.65	Qualified
35	1,050	60	1,908.0	22.3	0.68	Qualified
35	1,100	90	387.1	26.2	0.53	Qualified
35	1,150	10	224.7	64.9	0.35	Qualified
50	1,000	60	2,524.0	38.8	0.33	Qualified
50	1,050	90	2,503.0	26.1	0.11	Qualified
50	1,100	10	1,746.0	23.7	0.33	Qualified
50	1,150	30	221.6	73.7	0.25	Qualified

ash is Hg^{2+} [18]. The clay is rich in organic matters, which possibly act as reducers to convert Hg^{2+} to Hg^0 [19-20], consequently causing more Hg evaporation during the sintering process and the lower Hg residual in ceramsite with high CGCC content. Similar to physical properties, there was no significant effect of sintering time on ceramsite leaching toxicity. All the leaching heavy metals (Table 6) matched the identification Standard for Leaching Toxicity from Hazardous Waste in China (GB5085.3-2007), showing the feasibility and minimal ecological impacts to recycle CGCC by ceramsite manufacturing.

Conclusions

Of the three parameters, CGCC content and sintering temperature play key roles in both physical properties and leaching toxicity of ceramsite, whereas the impact of sintering time is minimal. Though high concentrations of heavy elements (Cr, As, and Hg) were found in raw CGCC material, the sintering manufacturing process effectively improved the thermodynamic stability of heavy metals by crystalline structure formations at high temperatures, showing limited human health risk. Considering the energy conservation and the maximal recycling of CGCC, optimal ceramsite manufacturing is suggested as 50% CGCC content, 1,150ºC sintering temperature, and 10-min. sintering time. Our study proved the concept of CGCC being sustainable and environmentally friendly recycling. Manufactured into ceramsite, the CGCC wastes from the coal gasification industry are successfully reutilized for civil and construction purposes. Finally, the local authorities and the coal gasification plants should give more financial support for the recycling of CGCC, which is important for promoting the development of manufacturing ceramsite from CGCC waste.

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