Preparation and environmental toxicity of non-sintered ceramsite using coal gasification coarse slag

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Abstract: In this study, non-sintered ceramsite was prepared using coal gasification coarse slag obtained from a methanol plant. The basic performance and heavy metal leaching toxicity were analyzed. The results showed that seven out of nine non-sintered ceramsite groups were in accordance with the national standard of compressive strength (5 MPa), while only three groups met the national standard of water absorption index of less than 22%. The heavy metal concentrations in these three groups were found to be lower than that specified in National Class IV of surface water environment standards. The concentration of Cr was found to be 16.45 μg/L, which represents only 1% of the IV standard. The optimum mixing ratio, which showed high compressive strength (6.76 MPa) and low water absorption (20.12%), was found to be 73% coal gasification coarse slag, 15% cement, and 12% quartz sand. The characterization using Fourier transform infrared spectroscopy showed that the formation of gelatin in ceramsite enhances the performance of the ceramsite base and increases the immobilization of heavy metal. The study proved that the preparation of non-sintered ceramsite using coal gasification coarse slag reduces its environmental risk and achieves efficient utilization of the slag. Therefore, it can be concluded that it is a feasible and environmental friendly method for the disposal of coal slag.

Introduction

The rapid development in the coal chemical industry has played an important role in the adjustment of China’s energy structure (Xie et al. 2010). However, the large quantities of industrial waste produced, such as coal ash, fly ash, and coal gangue, have caused a series of environmental problems (Dermatas and Meng 2003, Sharma et al. 2008). The residue of coal chemical industry mainly consists of fly ash and coal gasification slag, which are produced in large quantities and have low utilization rate. On the other hand, traditional disposal methods, such as landfill and storage in ash dumps, cause pollution to the atmosphere, ground water, soil, and farmland, which in turn affects human health (Civeira et al. 2016, Steffan et al. 2018). This causes a waste of resources, in addition to the environmental pollution. Therefore, it is necessary to carry out the disposal and treatment of these residues in a comprehensive and efficient manner.

Currently, research conducted worldwide on coal chemical residues is mostly focused on the disposal of fly ash through using as building materials, adsorbent materials, and new wall materials (Ahmaruzzaman 2010, Blissett and Rowson 2012, Cheng et al. 2017, Yao et al. 2015). Few studies have investigated the disposal of coal gasification coarse slag. There are major differences between coal slag and fly ash, which are reflected in their primary components, heat value, and toxicity (Ismail et al. 2014, Saafi et al. 2015, Wu et al. 2014, Wu et al. 2015). However, similar to fly ash, coal gasification coarse slag also has a certain chemical activity (Guo-jun et al. 2005). As the preparation of ceramsite using fly ash, this is considered a new direction for the disposal of coal gasification residue. Ash slag ceramsite, which is a kind of man-made light aggregate, is widely used in construction, decoration, horticulture, sewage treatment, and other similar applications (Li et al. 2016, Li et al. 2018, Qin et al. 2015).

Sintered ceramsite production requires high temperature, a complicated procedure, large investment in equipment, and high energy (Jian et al. 2017). On the other hand, non-sintered ceramsite production is a simple process that requires low energy and makes it possible to recycle a large amounts of coal gasification coarse slag, reduce the emissions and save energy. Compared to the high-temperature sintering process in the case of sintered ceramsite makes fixation of harmful heavy metals, non-sintered ceramsite may pose a risk of high toxicity, because there is no fixation of heavy metals through sintering. Therefore, careful attention should be paid to the
environmental toxicity and safety of non-sintered ceramsite produced using coal gasification coarse slag. In this study, the effects of different mixing ratios of raw materials on the performance of non-sintered ceramsites produced using coal gasification coarse slag were studied to determine the optimal mixing ratio. In addition, the leaching toxicity of the ceramsites was tested to determine their environmental safety. Finally, the optimal material allocation ratio was determined based on both aspects.

**Material and methods**

*Experiment material*

The coal gasification coarse slag used in this study was sampled from a methanol plant in northwest China. The appearance of the sample was similar to that of pulverized coal. After drying and sifting, the slag was passed through a 245 μm-sieve. The color of the sieved sample was carbon black. The sample mineral composition mainly consisted of amorphous minerals, such as quartz and calcite. The X-ray diffraction (XRD) quantitative analysis showed that the calcite and quartz contents (mass percentage) in the sample are 72% or more, and 11%–21%, respectively. Table 1 shows the results of the elemental quantification (X-ray fluorescence spectrometry (XRF), Thermo electron corporation ARLADVANT XP+) of coal gasification coarse slag, which was performed to determine the main components of the coarse slag.

It was found that the main components of coal gasification coarse slag were CaO, SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O, and unburned carbon. The main components of the glassy phase, which are the active ingredients used in the ceramsite production, are SiO₂ and Al₂O₃. The results showed that the concentrations of both components were low in the sample, and thus a certain amount of quartz sand had to be added as an admixture to supplement the source of glassy phase. Fe₂O₃, MgO, and Na₂O were present in the sample as fluxes in the glassy phase with levels adequate for the formation of ceramic materials (Xu 2012, Zishu et al. 2012).

Table 2 shows the comparison between the contents of heavy metals in the coal gasification coarse slag and coal fly ash, as well as their properties. The main difference was mainly in their heavy metal content, moisture content, calorific value, and particle size, which show that it is not possible to use the same disposal method for both wastes. The results of the analysis of heavy metals in coal gasification coarse slag indicated that chromium (920.821 mg/kg) and arsenic were the main heavy metal pollutants. This shows the importance of the heavy metal fixation in ceramsite production, since the coal gasification coarse slag was used as a raw material.

The quartz sand used in the test was analytical grade quartz sand that was passed through a 245 μm-sieve after grinding and screening (produced by the Beijing Chemical Plant). The cement used was benchmark cement (produced by Shandong Lucheng Cement Co., Ltd. for: GB8076-2008).

*Preparation of non-sintered ceramsite*

The content of SiO₂ in coal gasification coarse slag was not sufficient for the ceramsite production, thus, a certain amount of quartz sand was needed to replenish the glassy phase content. According to previous studies, the amount of quartz sand added should be limited to 8–12% of the mixture. On the other hand, as the coal gasification coarse slag ceramsites have low strength and high water absorption tendency, which makes it difficult for them to form a ball, a certain amount of cement can be added to increase their hardening speed and strength. The recommended amount of cement, taking into consideration all economic aspects, should be limited to 15–25%. Variance analysis was used to design different test groups for different raw material ratios (Table 3) in order to determine the mixing ratio that delivers the ceramic materials with best performance.

The coal gasification coarse slag was pretreated with alkali, the raw materials were mixed according to the proposed ratios, and then the raw materials were pelletized on a disk pelletizer (ZL-5 disc pelletizer, Zhengzhou Hehai Machinery Equipment Co., Ltd.). The inclination angle of the pelletizer disk was adjusted to 60°, and the rotation speed was first set to 30–35 rpm for about 30 s to convert the mixture into a large number of granular cores, and then it was increased to 70–80 rpm for another 30 s. The evenly stirred mixture was pelletized into balls, and when the pellets were no longer adhered to each other, they were covered with moist gauze for 24 hours at room temperature. The newly cultivated ceramsite was steam cured at 40°C for 12 h using steam curing equipment. Finally, the ceramsites granules (particle size of 3 to 8 mm) were sieved and dried in the oven for 30 min to obtain non-sintered ceramsites.
Table 3. The raw material ratio of each experimental group

<table>
<thead>
<tr>
<th>Group</th>
<th>Coal gasification coarse cinder [%]</th>
<th>Cement [%]</th>
<th>Quartz sand [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>63</td>
<td>25</td>
<td>12</td>
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<td>2</td>
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<td>9</td>
<td>77</td>
<td>15</td>
<td>8</td>
</tr>
</tbody>
</table>

Basic performance test of non-sintered ceramsites

In this study, the size of the ceramsite grains produced by the experiment was 5–8 mm. The compressive strength of the ceramsite produced was measured using a servo material pressure tester (WH-5000, Ningbo Zhenhai Weiheng Testing Instrument Co., Ltd.). Three samples were randomly obtained from each group of ceramsite products for testing. The compressive strength value was measured by calculating the arithmetic average of the three measurements for each group. According to the China national standard (GB/T 17431.1-2010), the highest standard cylinder compression strength of industrial waste light aggregate is 4 MPa, and the results of the literatures (Li 2012, Yu 2004, Zou Zhengyu 2013) showed that if the compressive strength of the ceramsite material is higher than 5 MPa, the compression strength of ceramsite cylinders can reach 4 MPa or more.

The prepared sample was dried to a constant weight \((G_f)\) and placed in a suction filter bottle that is continuously filled with water, where it soaked for two hours. After the soaking step was completed, a vacuum pump was used to vacuum the suction filter bottle, maintaining vacuum on the immersion system for 10 minutes. The vacuum pump was then turned off, and the sample was removed from the suction bottle. A saturated cloth with water was used to remove the adhered water on the surface of the ceramsite material, and the samples were weighed again to obtain \(G_i\). The following water absorption formula (1) was used to obtain the ceramsite material water absorption index \(W\).

\[
W = \frac{G_i - G_0}{G_0} \times 100\%
\]

where \(W\) is the water absorption (%), \(G_0\) is the dry weight of sample (g), and \(G_i\) is the weight of the sample after absorption.

According to the Chinese standard (GB/T 17431.1-2010), the water absorption index of ceramsite materials should be less than 22%.

Environmental toxicity test of non-sintered ceramsite

Based on China national industry standard (HJ/T299-2007), the leaching toxicity test was carried out using sulfuric and nitric acids method. The method involves adding a mixture of concentrated sulfuric and nitric acids in a 2:1 ratio to the reagent water (approximately 2 drops of the mixture in 1L of water) to obtain the extraction agent at pH of 3.20±0.05. The samples were broken up and passed through a 9.5 mm-sieve. 150 g of the sieved sample were placed into a 2L-extraction bottle. The bottle was filled with the extractant, whose volume was calculated based on the moisture content of the sample, at a liquid-solid ratio of 10:1(L/kg). The bottle cap was then tightened, and the bottle was fixed on the rotary oscillating device, in which the rotation speed was set to 30±2 rpm and oscillated at 23±2°C for 18±2 h. Afterwards, the filter was installed on the pressure filter and rinsed with dilute nitric acid. The eluent was then discarded, and the sample was filtered. Finally, the leachate was collected and stored at 4°C for testing.

Based on previous studies and the risk level of heavy metals on human health, the main elements that should be detected in the leaching toxicity test are Be, Cr, As, Cd, and Pb. Inductively coupled plasma mass spectrometry (ICP-MS, type 7500a, Agilent Technologies, U.S.A.) was used to test the leaching concentration of heavy metals in the selected ceramsite samples.

Fourier transform infrared (FTIR) spectroscopy

One to two milligrams of the sample were mixed with 200 mg of pure KBr, ground uniformly (to particle size of less than 2 microns), placed in a mold, and pressed on a hydraulic press to form a transparent sheet. The assay was carried out using TENSOR II, Bruker, Germany.

Results and discussion

Effect of raw material distribution ratio on basic properties of ceramsite

Compressive strength

Figure 1 shows the compressive strength of non-sintered ceramsites prepared by coal gasification coarse slag, which was tested according to the ratio of raw material listed in Table 3.

The results indicate that the compressive strength of all non-sintered ceramsite samples met the standard except for those with 77% and 70% slag. However, there was no clear linear
relationship between the amount of coarse slag added and the compressive strength. The alkaline liquor used in the pretreatment of slag can significantly stimulate the potential activity of coal gasification coarse slag powder. The Si-O and Al-O bonds in the coal gasification coarse slag broke and the glassy structure disintegrated, under the effect of OH-. Therefore, the degree of polymerization of the Si-O-Al network polymer was reduced, and the active material was eluted to form gel materials, such as hydrated calcium silicate, and hydrated aluminum silicate, which increase the strength of the ceramsite particles (Guo-jun et al. 2005, Zhang et al. 2015, Zishu et al. 2012). Moreover, the hydration reaction inside the material continued for a period of time after the steam curing was finished and the strength of ceramics increased with the progress of hydration. This increase in the compressive strength is also a major advantage of non-sintered ceramsites. Compared to the sintered ceramsite (Jia et al. 2017), the compressive strength of non-sintered ceramsites was basically the same. The strength of some non-sintered ceramsites was lower than that of sintered ceramsites; however, the continued increase in the strength of non-sintered ceramsites after curing resulted in a compressive strength comparable to that of the sintered ceramics.

**Water absorption**

The water absorption phenomenon in the ceramsite particles is caused by the presence of capillaries and pores in the particles. When ceramsite particles are immersed in water, their capillary pores begin to absorb it as a result of the micropump and the vacuum effects (Lau et al. 2017, Jian-cheng 2009).

The water absorption ability and the effect of raw material distribution ratio on the water absorption were tested in the nine groups of unburned coal gasification coarse slag ceramsites (Figure 2). These results, combined with the results of the compressive strength, were used to determine the optimum ratio of the raw materials under the same curing conditions.

Figure 2 shows that the water absorption index of the samples was relatively large. Only three (with ratios of 75%, 73%, and 63% coarse slag) out of the nine groups had water absorption values within the range specified by the standard.

In addition to group 1 (with ratio of 63% coarse slag), the remaining two groups out of three groups which met the standard had higher slag content. This suggests that the increase in the content of coarse slag reduces water absorption in the ceramsite. When these results were compared to those of sintered ceramsites (Jia et al. 2017), they were found to be comparable. However, taking into consideration the large investment, complicated technology, and high energy consumption of the sintering process, the non-sintered ceramsites can be considered more advantageous. Therefore, this production process is considered an efficient and cost-effective method of disposal of coal gasification coarse slag.

**Environmental toxicity test**

Ceramsite materials are widely used in practical engineering applications, and hence their environmental safety and effects on the human health must be carefully tested. In this study, the ceramsite’s raw material mainly consisted of the coal gasification coarse slag discharged from a methanol plant, which contains toxic heavy metal pollutants. In the process of preparing ceramsite, these harmful substances are likely to be immobilized and sealed in the ceramsite material. When the manufactured ceramsite materials are put into use, these harmful substances are likely to migrate to the surrounding environment through rainwater, which poses high risk to the environment and human health (Karayannis et al. 2017). As mentioned, non-sintered ceramsites pose higher environmental toxicity risk compared to sintered ceramsites. Therefore, the leaching toxicity of produced ceramsites and their environmental safety need to be evaluated. In addition, the optimal raw material ratio of ceramsites, which causes the least environmental toxicity and meets the standard, is determined.

Figure 3 shows the results of leaching toxicity of the three groups (slag contents of 75%, 73%, and 63%) selected in the previous steps.

From the five elements that were of interest in this study, only Cr and As had significant concentrations in the samples compared to those of the other three heavy metals (Figure 3), with Cr being the metal with the highest content in the leachate and in the coal gasification coarse slag. However, the Cr concentration of leachate was only 16.45 μg/L, which represents 32.9% of the concentration stated in National Class IV of surface water environment standards (50 μg/L). The

![Fig. 2. The water absorption rate of the non-sintered ceramsite](image)

![Fig. 3. The heavy metal leaching concentration of the non-sintered ceramsite](image)
concentration of the other four heavy metals was far lower (about 1%) than that specified by the national standard for surface water.

Therefore, it can be concluded that the proposed method has a good ability to fix heavy metal. As mentioned, coal gasification coarse cinder is pretreated by alkaline solution to enhance its ability to form hydrogels, such as calcium silicate and hydrated aluminum silicate, which in turn increases the strength of ceramsite and enhances the fixation of heavy metals. Xiaoming Liu et al. indicated that hydration products adsorb Pb and Cr ions, and hence heavy metals are fixed inside the gel (Liu et al. 2018). Some studies also pointed out that the addition of cement, which is an inorganic gel material, could consolidate heavy metals as a result of its solidification ability (Cerbo et al. 2017, Wang et al. 2015). The mechanisms are as follows: (1) the gel with small pores generated by the hydration of cement efficiently coats the heavy metals, which reduces their permeability; (2) adsorption of heavy metal ions on a large number of fine particles produced through cement hydration increases the stability of heavy metals; (3) adding the raw material with water enhances the cement hydration, which in turn improves the alkalinity of the solution and causes heavy metals in coal gasification coarse cinder to form water-insoluble precipitates, making it difficult for heavy metals to leach; (4) the hydration of cement produces a layered silicate gel, in which Ca²⁺, Al³⁺, and Si⁴⁺ in the lattice can be replaced by heavy metal ions, which causes the entrapment of heavy metals inside it (Jianhuan 2013). The results of the leaching toxicity test proved the environmental safety of the non-sintered ceramsite and clarified the safety of using it in practical applications.

The FTIR characterization of coal gasification coarse slag and ceramsites

The results of the FTIR characterization of un-sintered ceramsite (Figure 4) show that the peak at 2100 cm⁻¹ in the coal gasification coarse cinder was significantly weakened in the ceramsite. Therefore, according to the IR spectrum analysis, the potential structure of the coal gasification coarse cinder contained C≡C or C=C=C bonds. It is proposed, however, that the pretreatment of the coal gasification coarse cinder with NaOH breaks these bonds, resulting in no peak in the ceramsite. The fingerprint area below 1300 cm⁻¹ mainly illustrates the characterization of Si-O or Al-O (Chun-hui et al. 2012, Dingemans et al. 2012). The peak at 1300 cm⁻¹ proved the presence of gel material in the non-sintered ceramsites, which played an important role in increasing the compressive strength of ceramsite and the fixation of heavy metals.

![FTIR spectra](image)

Fig. 4. Fourier Transform infrared spectroscopy (FTIR) of coal gasification coarse cinder (a) and non-sintered ceramsite (b)
Conclusions

The optimal ratio of coal gasification coarse slag added as the raw material for ceramsite production was determined through testing compressive strength and the water absorption index in the produced materials. The results of the tests proved that the non-sintered method used in the ceramsites preparation from coal gasification of coarse slag was an effective and environmental friendly way of slag disposal. In addition, coal gasification coarse slag was used as a resource instead of being a waste material. The results of ceramsites leaching indicated that the Cr concentration ranged from 6.43 μg/L to 16.45 μg/L, and the concentration of As was between 1.02 μg/L and 1.6 μg/L, while the concentrations of Pb, Be, and Cd were very low. These low concentrations of heavy metals ensure the safe use of ceramsites. It was also found that the compressive strength of non-sintered ceramsites meets the national standard of 5 MPa in most of the samples. However, the compliance rate of water absorption index with the national standards was only 33% under the same process conditions. After the completion of the steam curing, the strength of the ceramsite continued to increase with time. This proved that the non-sintered process was suitable for the preparation of high-strength ceramsite. However, the produced ceramsites are not suitable for the preparation of ultra-light ceramic granules, because of their high water absorption index. The results also proved that cement, as an additive, plays an important role in the preparation of non-sintered ceramsite, because it enhances the compressive strength of ceramsite and the fixation of heavy metals in coal gasification coarse slag.

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Reference


