Mechanism of Pore Formation in Novel Porous Permeable Ceramics Prepared from Steel Slag and Bauxite Tailings

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Porous permeable ceramics (PPC) were prepared from composite ceramsites (CC) via a single firing process. CC were granulated with steel slag as a core and bauxite tailings in an outer-layer. XRD, SEM, EDS, mercury porosimetry and metallographic microscopy were used to study its properties and the pore formation mechanism. Results showed that during sintering process, gradual diffusion of cations from slag to tailings layers enhanced bonding among CC with formation of new crystals: anorthite and pyroxene. PPC had a wider distribution of pores from 0–300 μm sintered at 1 160°C. With an increase in sintering temperature, ceramics were densified with disappearance of the small pores, which had an increasing threshold diameter values from 45 μm at 1 160°C to 70 μm at 1 190°C. Big pores larger than the threshold values would be remained and enlarged due to shrinkage of CC during the densification process. The decreasing amounts of pores and an increasing pore diameter had contrary effects on its permeable properties. PPC sintered at 1 180°C with porosity of 27.5% and medium pore diameter of 92.7 μm had the optimum properties with bending strength of 10.92 MPa, water permeability of 0.039 cm/s and qualified leaching properties of harmful elements (Mn, Cr, V and Pb). This study would promote a more feasible and economic method for producing porous permeable ceramics and improving added value of steel slag and tailings.

KEY WORDS: pore forming; porous permeable ceramic; steel slag; composite ceramsite; bauxite tailings.

1. Introduction

Steel slags is the largest solid waste during steel-making process. About 0.2 billion tons of steel-slag in 2017 were discharged with output of 1.69 billion crude steel in the world.1) Due to low cementitious reactivity and instability, steel slags was mainly reused as low value-added raw materials in areas, such as concrete, road pavement, water way construction and artificial reefs areas. Improve its values in utilization process became new trends.2) Many new methods such as converting it into glass ceramics,3) building ceramics,4) fertilizes,5) special backfill materials6) and recovery of phosphorus7) were explored.

Porous permeable materials, which have open pores and channels, are in huge demand for municipal construction because of their many special properties, such as water permeability and sound absorption.8,9) Permeable pavement is an essential component in construction of a sponge city.10,11) Permeable pavement allows rainwater to penetrate through to the soil, and the filtered rainwater is then either harvested for later reuse or released slowly into the underlying soil or drainage system. Utilization of steel slag in permeable pavement materials could be a potential high value-added utilization method.

Traditionally, there are two kinds of permeable bricks: cementitious porous permeable bricks (PPB) and sintered porous permeable ceramics (PPC).12–14) Both of these are composed of aggregate and binder but are produced via different preparation processes. For cementitious permeable bricks, cement is used as a binder during the hydration process, and crushed stone or sands with similar particle-size are used as aggregate. For the latter,14,16,17) a mixture of clay and additives is the binder in the sintering process, and discarded ceramics become aggregates with a thermal stability. Compared with cementitious PPB, PPC have a higher production rate, better appearance and higher compressive strength.14) However, resources of clay and discarded ceramics are limited, and lack of raw materials increases production costs and hinders development of PPC.

Research on substitution for clay or discarded ceramics had become a hotspot in this field. A new method of hydrothermal reaction for blast furnace slag was put forward.18) And a lot of reports found that industrial solid waste, such as gangue14,19) and other tailings14,16,20) that contain clay minerals with plastic properties can play the role of clay and replace clay in ceramics.

Making substitutions for discarded ceramics is very difficult. To maintain enough open pores and qualified mechanical properties, aggregates of PPC require good thermal
stability and high strength after the firing process. However, most natural and artificial aggregates (such as marble, sands, and tailings) do not meet these requirements because of their own reaction under high temperature. Ceramsite is a stable aggregate with wide sources of raw materials, but traditionally, it needs to be sintered at high temperature before it can serve as an aggregate, which results in high energy consumption and cost. A chemical foaming method for permeable ceramics is another technology that is capable of avoiding using an aggregate. High temperature foaming agents are mixed into raw materials and release gas during the firing process. The released gas is expected to form open pores and channels. However, it is too hard to control the formation of open and uniform pores in ceramics, and thus, the technologies cannot be put into practice. Therefore, the method using traditional clay and aggregates is still the most promising and feasible for producing PPC. While extending the research to study the substitution of its raw materials for traditional clay and discarded ceramics is significant.

In recent years, more and more researches have reused industrial solid wastes in ceramics. Research on ceramics derived mainly from steel slag and clay has found that ceramics belonging to a SiO₂–Al₂O₃–CaO–MgO–Fe₂O₃ system in composition and can reuse more slags that contain high CaO and Fe₂O₃ contents in the raw materials. Moreover, after sintering, the ceramics had a main mineral of pyroxene or anorthite and had high strength with a flexural strength of about 100 MPa and a water absorption rate of below 0.05%. This type of ceramic is an ideal candidate for the aggregate because of its excellent mechanical property.

Sintered ceramics such as fly ash ceramsite, coal gangue ceramsite and red mud ceramsite were prepared from solid waste. Most of the ceramsites were composed of pyroxene and/or anorthite and had high strength properties from 1.25 MPa to 7 MPa of cylinder compressive strength. However, preparation of porous ceramics from sintered ceramsite has still not been put into practice because of its high cost.

In this paper, a new method for preparing porous permeable ceramics from ceramsites via a single firing process is presented. Unfired composite ceramsites (CC) were prepared using a granulation process from steel slag and bauxite tailings. Homogenous mixture ceramics made from steel slags and tailings with the same composition as PPC and tailing ceramics made from bauxite tailings were studied as references. Mechanical properties, linear shrinkage, and crystal phrases of the novel PPC under different firing temperature were analyzed, and its porosity and pore diameter distribution were also tested and mechanism of pore formation for PPC were discussed.

2. Experimental

2.1. Raw Materials

The raw materials were steel slag and bauxite tailings, which were respectively from ShanDong Iron and Steel Company and ECONES Company in Shandong Province, China. The main chemical compositions (wt%) were determined using X-ray fluorescence (XRF, XRF-1800, Shimadzu, Japan), and the results were given in Table 1.

2.2. Preparation

Different from the traditional mixing process of raw materials (Fig. 2(a)), PPC were produced using novel granulation processes (Fig. 2(b)). CC were granulated by wetting the steel slag as a mother bulb followed by wrapping it in the bauxite tailings, resulting in steel slag as a core and bauxite tailings in an outer layer.

After crushing, the slag was sieved to 900 μm, and after milling, the tailing was sieved to 75 μm. The sieved slags were firstly added into granulator as a mother bulb with 8 wt.% water, and after 60 s, the tailings were added (ratio of tailings-to-slag of 3:2) into the granulator to wrap with the bulb. Extra water was supplied to an amount of 15 wt.% of the solid. The prepared unfired CC were then sieved for particles with size in the range of 1.25–3 mm.

PPC green bodies were then molded from unfired CC and sintered via a single firing process. Batches of ceramics (including rectangular ones with dimensions of 20 mm × 50 mm for bending strength tests and circular ones with φ 100 mm for measuring the permeability rate) were press-molded from unfired CC under a a under a relative smaller pressure of 2.0 MPa, dried at 105°C for 12 h, and fired in a gradient furnace (GR 1300/13S, Nabertherm, Germany) with a heating rate of 1.5°C/min to 150°C and a heating rate of 5°C/min to different sintering temperatures of 1 100°C, 1 150°C, 1 160°C, 1 170°C, 1 180°C, and 1 190°C. After maintaining

**Fig. 1.** Preparation process of permeable ceramics: (a) traditional process and (b) novel process. (Online version in color.)

| Raw materials | SiO₂ | Al₂O₃ | CaO | MgO | Fe₂O₃ | Na₂O | K₂O | P₂O₅ | TiO₂ | MnO | Cr₂O₃ | V₂O₅ | PbO | Total |
|---------------|------|-------|-----|-----|-------|------|-----|------|------|-----|------|------|-----|------|
| Steel slags   | 19.57 | 2.92  | 42.93 | 4.13 | 23.08 | – | 0.11 | 2.52 | 1.03 | 2.6 | 0.23 | 0.34 | 0.09 | 99.55 |
| Bauxite tailings | 60.9 | 22.75 | 1.78 | 0.77 | 7.93  | 0.17 | 4.0 | 0.09 | 1.19 | 0.07 | 0.03 | – | – | 99.68 |

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the sintering temperature for 30 min, the ceramics were cooled to room temperature via natural convection inside the furnace. As a reference, homogenous mixture ceramics (MC) made from steel slags and tailings with the same composition as PPC and tailing ceramics (TC) made from bauxite tailings were molded and sintered respectively from the −75 μm tailings or and −75 μm steel slag.

2.3. Testing

Bending strength of the fired rectangular samples were tested with a ceramic tile flex tester and the cross-sectional height (h), width (b), and fulcrum distance (l) of the specimen were measured using a digital vernier caliper and calculated according to formula (1).

Moreover, the circular samples for the permeability test were cut into cylinders and were measured using a tester given in Chinese national standard (29) GB/T 25993-2010 for permeable materials. The volume of escaped water at a specific time was measured using a graduated cylinder. The water level difference (H) was measured with a Vernier caliper, and the thickness (L) and surface area (A) were calculated according to formula (1).

To calculate the permeability coefficient according to Eq. (2). Each result is the average value of three measurements.

\[ f = \frac{3Fl}{2bh^2} \]  

\[ K_r = \frac{QL}{2AHl} \]

Element-leaching properties of PPC green body and sintered at 1 180°C were conducted in accordance with the Chinese National Standard HJ 557-2010. One part of PPC sintered at 1 180°C was crushed into size of less than 5 mm for keeping most of CC particles in its shapes. Another part of PPC sintered at 1 180°C and PPC green body were pulverized to particles with the size of less than 75 mm in order to highlight the effect of leaching properties. Leaching solutions were detected by inductively coupled plasma optical emission spectrometry (ICP-OES) (ICP-OES730, Agilent, USA). In this research, harmful elements including Cr, Mn, V and Pb were selected to analyze according to the amounts of its oxide in raw materials in Table 1.

Crystalline phases of the samples were identified using an automated X-ray diffractometer (XRD) (21X, MAC Science Co. Ltd., Japan) at 40 KV and 30 mA utilizing CuKα radiation on powder samples sieved with < 300 grade mesh. The detector was scanned at a step size of 0.02°, a dwell time of 2 s per step was used, and the scan range was from 10° to 90°. The pore size distribution was measured using a Mercury Porosimetry (Auto Pore IV 9500, Micromeritics, US) with a scan range from 0.49 psia to 59 954.04 psia. A metallographic microscope (DM4M, Leica, Germany) was used to observe the microstructures of samples after the samples were inlaid and polished. SEM analysis was conducted using an EVO18 Special Edition (Carl Zeiss, Germany) operating at 25 kV. Before the SEM tests, the samples were etched with 0.5% HF for 100 s at room temperature and coated with Au.

3. Results

3.1. Mechanical and Permeable Properties

Unfired CC, green bodies of PPC, and PPC sintered at 1 180°C are shown in Fig. 2. After sintering, PPC became denser with a brown color, which changed from the orange color of the green body and unfired CC. The sintered PPC showed an excellent water permeable property (Fig. 2(c)).

Bending strength and permeability of different PPC were shown in Fig. 3. With increasing temperature from 1 160–1 190°C, the strength of PPC continued to raise, but an adhesion phenomenon at the bottom of the PPC sintered at 1 190°C was observed. While its permeability reach a maximum values at 1 180°C and decreased at 1 190°C.

The optimum sintering temperature of PPC was chosen to be 1 180°C. PPC sintered at this temperature had a bending strength of 10.92 MPa and a permeability coefficient of 0.039 cm/s, which were significantly above the supreme grade in quality available for Chinese national standard (29) (GB/T 25993-2010), bending strength of 4.5 MPa and permeability coefficient of 0.02 cm/s.

3.2. Pore Structure

Porosity, median pore diameter data and permeability of PPC sintered at different temperatures were shown in Fig. 4. With an increasing sintering temperature from 1 160 to 1 190°C, the median pore diameter increased from 17.5 μm to 105.9 μm, whereas the porosity decreased from 30.2% to 23.3%. However, the permeability increased to the maximum at 1 180°C and then decreased.

Cumulative volumes of pores in PPC sintered from 1 160 to 1 190°C are given in Fig. 5, which shows that pores with diameter larger than 215 μm in all of the samples were less than 10%. Also, the cumulative percent of pores with diameter between 215–118 μm increased rapidly in samples.
sintered from 1 160 to 1 170°C, whereas the cumulative percent of pores with diameter between 118–45 μm increased more rapidly in samples sintered from 1 170 to 1 180 and 1 190°C. Also, the cumulative percent of pores with diameter less than 0.6 μm in samples sintered 1 190°C were the largest proportion. In fact, pores less than 0.6 μm were very small, and this indicates that the pores almost disappeared with a densification process.

The values of cumulative percent of characteristic pore diameters in different PPC samples are summarized in Table 2. Samples sintered at 1 160/1 170°C had only about a quarter/one-third of pores larger than 70 μm, and about two-thirds/half of the pores were less than 45 μm. However, in samples sintered at 1 180°C/1 190°C more than two-thirds of the pores were larger than 70 μm, and only one-tenth/28 v.% of the pores were less than 45 μm.

For samples sintered at 1 180°C, there were only 5 v.% of pores with diameters between 45–0.6 μm, and at 1 190°C, there 7 v.% of pores had diameters between 70–0.6 μm. In contrast, for samples sintered at 1 160°C, about 66 v.% of the pores had diameters between 45–0.6 μm and at 1 170°C, about 43 v.% of the pores had diameters between 45–0.6 μm.

Therefore, with an increase in sintering temperature, samples were densified with disappearance of the small pores. For samples sintered at 1 180°C, the amount of pores in the range of 45–0.6 μm almost disappeared. For samples sintered at 1 190°C, the amount of pores in the range of 70–0.6 μm almost vanished as well. So there were a different maximum threshold diameter values for densification of pores from 45 μm at 1 180°C to 70 μm at 1 190°C.

Changes in the pores can be seen from metallographic microscope images of PPC sintered at 1 160, 1 170, 180, and 1 190°C, as shown in Fig. 6. Big pores (BP) were mainly derived from the intersection of three or more ceramsites, and small pores (SP) were mainly from the intersection of two ceramsites. With an increase in temperature, part of the pores disappeared (shown as DP) in the intersection of two ceramsites which were bonded because of a sintering reaction and diffusion between their outer surfaces. In contrast, most of the BP were enlarged. When samples were sintered at 1 190°C, most of the SP disappeared, but BP still remained.

The overall shrinkage of PPC depended on two factors, shrinkage of a single ceramsite itself and densification of different ceramsites. When sintered from 1 170–1 180°C, densification among ceramsites ensured the overall shrinkage and strength. Densification of ceramsite itself around the area of big pores resulted in the force of shrinkage along the inward radial direction enlarging sizes of the pores. It
could be deduced that the single ceramsite shrank because of both densification during the sintering process and crystal transformation to high density crystals, such as esseneite that has a density of 3.2–3.6 g/cm³. As diffusion enhanced at 1180°C, both densification and crystal transformation were improved with increasing shrinkage.

It was inferred that the disappearance of small pores resulted in reduce of the amount of whole pores in PPC and decrease of its porosity as well. Meanwhile, big pores larger than the threshold values were hard to be densified, and would enlarged. Because of the disappearance of small pores and larger diameter of remained big pores, the value of medium pore diameter of PPC become bigger from 1160–1190°C.

As shown in Fig. 4, PPC had a decreasing porosity and increasing medium pore diameter with the increasing temperature respectively due to the less pores but larger pore, which had respectively negative and positive effects on its permeability. When sintered from 1160 to 1180°C, PPC had an increasing permeability indicating a larger effect of the increasing medium pore diameter than that of the decreasing porosity. But the effects changed inversely during the higher sintering temperature from 1180 to 1190°C.

3.3. Evolutions of Crystalline Phases

XRD pattern of raw materials, tailings ceramics, and PPC are shown in Figs. 7–9. Crystalline phases of bauxite tailings were quartz (SiO₂), muscovite (KAl₂Si₃O₁₀(OH)₂), hematite (Fe₂O₃), and the clay minerals illite ((K, H₃O)Al₂Si₃AlO₁₀(OH)₂) and kaolinite (Al₂(Si₂O₅)(OH)₄). Steel slags had crystals of calcium silicate (Ca₂SiO₄), RO (MgO, FeO), calcium oxide (CaO), and srebrodolskite (Ca₂Fe₂O₄).

As seen in Fig. 9, the peaks of quartz and other minerals in the raw materials decreased and disappeared at 1100°C, indicating that they participated in reaction below 1100°C. Also, peaks of hematite significantly increased, and these peaks were stronger than those of hematite in tailings ceramics (Fig. 8). This means that in PPC, Fe³⁺ in steeling slag mainly exists in the RO phase (solid solution phase of FeO, MgO, and MnO) and was oxidized to Fe₂O₃.

Because tailings contained minerals with more SiO₂ and Al₂O₃ and the slag with more CaO, FeO, and MgO, it was inferred that there was reactions between tailings and slag at 1100°C, and newly generated mullite and increased hematite respectively contributed to decomposition of clay minerals in tailings and oxidation of RO in slags.

At 1170°C, peaks of anorthite and augite were obviously generated, although they appeared in 1100°C with weak peaks. With an increase in sintering temperature, anorthite remained unchanged, whereas peaks of esseneite and augite-aluminian formed and increased, and peaks of quartz and hematite decreased.

Augite Ca(Mg, Fe)Si₂O₆, esseneite CaFe₂[(Al, Si)₂O₆], and augite-aluminian Ca(Mg, Fe, Al)(Si, Al)₂O₆ belong to pyroxene group minerals. Pyroxene minerals have the general formula M₂M1T₂O₆, but there is a wide isomorphism phenomena between ions, such as Ca²⁺, Na⁺, Mn²⁺, and Mg²⁺ at position M2, Fe²⁺, Mg²⁺, Mn²⁺, Ni²⁺, Li⁺, Al³⁺.
Fe$^{3+}$, Cr$^{3+}$, and Ti$^{3+}$ at position M1, and Si$^{4+}$ and Al$^{3+}$ at position T. To distinguish changes among augite, esseneite, and augite-aluminian, the XRD patterns in the black dotted box were magnified and are shown in the panel on the right in Fig. 9.

Compared with the characteristic peaks of individual crystals, it was found that the three red right-leaning arrows in the pattern at 1 180°C indicate characteristic peaks of augite, the two red left-leaning arrows in the pattern at 1 180°C indicate characteristic peaks of esseneite, and at 1 190°C there were characteristic peaks of augite-aluminian.

This indicates that augite Ca(Mg, Fe)Si$_2$O$_6$ formed first at lower temperature, and 1 170°C was mainly due to the great diffusion abilities of Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$ in slag. Also, esseneite CaFe(Al, Si)$_2$O$_3$ was obviously generated at 1 180°C. Because the most metal cations were Ca$^{2+}$ and Fe$^{3+}$, their full diffusion resulted in esseneite becoming the main crystals. Augite-alumina [Ca(Mg, Fe, Al)(Si, Al)$_2$O$_5$] formed at 1 180°C and increased at 1 190°C, whereas the characteristic peaks of augite decreased and disappeared from 1 180 to 1 190°C. These changes mean that Al$^{3+}$ mainly in the tailings layer enter the structure of augite crystals during the liquid sintering process, and this results in transformation of augite into augite-alumina. The evolution of pyroxene group minerals from augite, esseneite, and augite-aluminia also indicates the diffusion process from the slag core to the outer tailing layer.

3.4. Micro-structure and Micro-composition

CC sintered at different temperatures were studied using SEM and a metallographic microscope. Figures. 10(1a), 10(2a) and 10(3a) are images of CC sintered at 1 100°C. In Fig. 10(2a), the outer tailings layer (with orange color marked O) and the inner slag (with black color marked I) can be clearly distinguished. The side of the CC was projected into dark orange areas marked S, and the S areas could not be observed using SEM because it was not in the observed cross-section.

As shown in Table 1, most of CaO, MgO, and Fe$_2$O$_3$ came from the slag, and most of the SiO$_2$ and Al$_2$O$_3$ came from the tailings. Therefore, Fig. 10(1a) indicates that the areas of corresponding CaO, MgO, and Fe$_2$O$_3$ enrichment were in the slag, and the areas of SiO$_2$ and Al$_2$O$_3$ enrichment were in the tailings. The slag areas were distributed mainly in the inner area and partly in the outer layer, and this shows that during the granulation process, many slag particles as mother bulbs were adhered to and enclosed by tailings.

In Fig. 10(3a), a horizontal and diagonal narrow gap along the interface between the bottom of slag areas and tailings were observed, and each had a length of about 200 μm. This indicates that in unfired CC, many pores and gaps formed, especially in the interface of slag and tailings.

As seen in Fig. 10(2b), when the sintering temperature was increased to 1 170°C, four white spots marked m in the cross-section appeared in the outer tailing layer, and there are three yellow areas indicated by dashed circles near the areas of black slag. The corresponding location in Fig. 10(2a) shows that the positions of the four spots with black arrows were enriched in Al$_2$O$_3$, and according to XRD analysis of PPC sintered at 1 170°C (Figs. 8 and 9), this was deduced to be mullite.

From Figs. 10(1b)–10(4b), the yellow areas marked with dashed circles appeared and were larger with an increase in sintering temperature. Thereby, they were deduced to be reaction products between tailings and slag. Compared with Fig. 9, those products were new generated pyroxene and anorthite.

In Fig. 10(1a), high concentrations of Ca$^{2+}$Mg$^{2+}$Fe and Si$^{4+}$Al were nearly separate and respectively existed in slag areas and the tailings layer. With an increase in sintering temperature from Figs. 10(1a)–10(1d), the distributions of these elements became more and more uniform in the corresponding positions of the yellow areas and black slag areas, and this indicated that most of Ca$^{2+}$, Mg$^{2+}$, and Fe$^{2+}$ diffused from slag areas to the outer tailings layer and mixed with Si$^{4+}$Al ions. Such diffusion processes contributed to the formation of pyroxene and anorthite.

Moreover, the yellow areas in the corresponding positions
shown in Figs. 10(1b)–10(1d) show that more pores were generated in the areas. The pores result from the original gaps or pores in unfired CC or/and from volume shrinkage of reaction in the generation of pyroxene and anorthite. However, this led to a densified structure in the yellow areas (except for pores), as seen in Figs. 10(3b)–10(3d).

Meanwhile, mullite and quartz formed in the tailings layer sintered at and above 1 170°C, and these were respec-

![Fig. 10. Different images of CC sintered at (a) 1 100°C, (b) 1 170°C, (c) 1 180°C, and (d) 1 190°C. (1a)–(1d) Images from EDS plane scans of CC; (2a)–(2d) Metallographic microscope images of sintered CC; (3a)–(3d) SEM images of sintered CC.](image)

| ELEMENTS | O  | Si | Al | Ca  | Mg | Fe | K   | TOTLE |
|----------|----|----|----|-----|----|----|-----|-------|
| 1        | 50.88 | 21.61 | 26.38 | 0.00 | 0.13 | 0.27 | 0.73 | 100.00 |
| 2        | 43.19 | 0.00 | 0.36 | 0.25 | 0.37 | 55.84 | 0.00 | 100.01 |
| 3        | 54.85 | 20.41 | 17.65 | 0.47 | 0.48 | 1.99 | 4.15 | 100.00 |
| 4        | 47.30 | 22.59 | 11.90 | 12.60 | 1.19 | 2.91 | 1.50 | 99.99 |
| 5        | 47.00 | 17.30 | 5.57 | 19.08 | 5.16 | 5.84 | 0.05 | 100.00 |

![Fig. 11. SEM and EDS analysis of CC sintered at 1 180°C. (a) Metallographic microscope image of CC, (b) corresponding SEM image of CC, (c) magnified SEM image of parts in white dotted rectangle in panel (b), (d)–(f) respective areas in white dotted rectangles in panel (c), table of EDS results for points (1)–(5) in panels (b) and (d)–(f).](image)
tively white spots in Figs. 10(2b)–10(2d) and gray spots in Fig. 10(2d). Also, hematite in slag areas were black spots in Fig. 10(2c).

Because PPC at 1 180°C had the best properties in terms of both bending strength and permeability ratio, PPC were further researched using SEM and EDS. A typical area in a ceramsite (Fig. 11(b)) was selected, and three micro areas in the tailings layer, yellow areas, and slag areas were magnified and were respectively shown in Figs. 11(d)–11(f). Results of EDS analysis for points 1–3 showed typical compositions in the three areas. From the inner slag areas to outer tailings layer, Ca\(^{2+}\), Mg\(^{2+}\), and Fe\(^{3+}\) gradually decreased, which meant that there was a diffusion process of the three metal cations from slag areas. EDS analysis for points 4 and 5 in Fig. 11(a) confirmed that the white and black spots were respectively mullite and hematite.

3.5. Leaching Properties

As PPC sintered at 1 180°C had the most excellent properties, its leaching properties was further analyzed. Leaching results of Mn, Cr, V and Pb were shown in Table 3. Maximum contaminant level (MCL) limitations of US EPA (United States Environmental Protection Agency) about primary drinking water\(^{31}\) shown in the last line of the table were employed to evaluate leaching results.

The bulk sample of PPC-5mm (with size of less than 5 mm) had the lowest Mn, Cr, V and Pb leaching concentration of 0.0342 mg/l, 0.0403 mg/l, 0.2885 mg/l and 0.0020 mg/l and met the requirement of MCL limitations of drinking water. In fact, rainwater filtered and harvested through PPC will mostly be reused as ground water, which would have a lower requirements than drinking water. Therefore, the PPC prepared from steel slag and tailings is safe when it is put into practices.

As discussed in Figs. 10 and 11, because CC was granulated with steel slag as a core and tailings in an outer-layer, it had different composition and crystals even it was sintered. Harmful elements mostly derived from steel slags (shown in Table 1) were accordingly existed in the core with higher contents than that in the outer layer. Therefore, the outer layer of CC played a role of protective layer to block diffusion and dissolution of harmful elements. Bulk sample, PPC-5mm kept most of CC in its own shapes, and thereby had a significant lower leaching concentration than powder samples, PPC-75μm (with size of less than 75 μm).

Elements of Mn, V and Pb in PPC-75μm had the lower concentrations than in Green body-75μm except Cr. It meant that during sintering process, formation of new crystals in PPC, esseneite, anorthite, and augite had a stronger solidification ability for Mn, V and Pb but a weaker solidification ability for Cr than mineral phases in steel slag, because most of the four elements came from steel slag.

4. Discussion

PPC and mixture ceramics had the same compositions, but PPC composed of CC had a different structure than the mixture ceramics. When PPC green bodies were molded from the initial unfired CC, slag in the core of unfired CC played the role of aggregates, and this was important for the molding process because aggregates in unfired bricks provide strength for an unfired ceramsite and also decrease deformation of tailings to ensure initial porosity of the PPC green bodies. Meanwhile, tailings in the outer layer of each ceramsite are bonded to each other to ensure overall strength of the unfired PPC. Therefore, PPC green bodies with initial porosity was hard to mold from a mixture of raw materials.

During a lower temperature sintering process from 1 000–1 170°C, PPC had little reaction between tailings and slag with low bending strength (Figs. 3 and 10). Reactions in this stage mainly occurred separately in tailings layers and in slag areas. In tailings layers, mullite was generated following decomposition and reaction of raw materials (Figs. 8 and 10). Meanwhile, in slags areas, oxidation of FeO in RO phase and dehydration of calcium silicate hydrate resulted in an increase in hematite.

During the full reaction range of 1 180–1 190°C, ceramics and PPC changed from an orange color and became brown (Figs. 2 and 10), and the inner reaction areas became yellow (Fig. 10). Diffusion of cations in slag to the tailings layer results in formation of new crystals, pyroxene and anorthite. Such reactions provided an effective method for eliminating the instability of steel slag by transforming lime (free CaO) into stable pyroxene or anorthite.

In this stage, mullite and quartz were derived from tailings in the ceramsite (Fig. 12), and hematite from slag, pyroxene and anorthite from reaction of steel slag and tailings become the main crystals to ensure overall strength of PPC.

With sintering at 1 180°C, mixture ceramics had significantly different crystals than PPC (Fig. 12). Because of

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Table 3. Leaching concentration of PPC and green body, and MCL limitations (mg/l).

| Elements    | Mn   | Cr   | V    | Pb   |
|-------------|------|------|------|------|
| PPC-5mm     | 0.0342 | 0.0403 | 0.2885 | 0.0020 |
| PPC-75μm    | 0.0435 | 0.0601 | 0.5168 | 0.0036 |
| Green body-75μm | 0.0676 | 0.0543 | 0.5304 | 0.0039 |
| MCL         | 0.05  | 0.1   | –    | 0.015 |

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Fig. 12. XRD Patterns of PPC, tailings ceramics, and mixture ceramics sintered at 1 180°C. (Online version in color.)
complete mixture, slag and tailings reacted sufficiently, and resulted in a notable decrease in peaks of quartz and mullite and an increase in peaks of esesseneite, anorthite, and augite. Meanwhile, because of the special composite structure in PPC, reactions between the outer tailings layer and inner slag core were gradually limited by their diffusion process. Therefore, the special composite structure in CC ensured enough bonding among ceramsites by the outer tailings layer and maintained steady sintering via the gradual diffusion of components from slag to tailings.

5. Conclusions

In this study, PPC (porous permeable ceramics) were prepared from bauxite tailings and steel slag by a novel granulation processes. Composite ceramsites (CC) were granulated with steel slag as a core and bauxite tailings in an outer-layer. Green bodies of PPC molded from CC under pressure of 2 MPa from unfired ceramsites were sintered via a single firing process.

PPC had a wider distribution of pores from 0–300 μm sintered at 1 160°C. With an increase in sintering temperature, ceramics were densified with disappearance of 27.5% and medium pore diameter of 92.7 μm at 1 180°C to 70 μm at 1 190°C. Big pores larger than the threshold values would enlarged due to shrinkage of CC during the densification process. The decreasing amounts of pores with reduced porosity and an increasing medium pore diameter respectively had negative and positive effect on its permeable properties.

In the experiment, PPC sintered at 1 180°C with porosity of 27.5% and medium pore diameter of 92.7 μm had the best properties with bending strength of 10.92 MPa and water permeability of 0.039 cm/s, which were significantly above the Chinese national standard bending strength of 4.5 MPa and permeability coefficient of 0.02 cm/s.

The outer layer of CC played a role of protective layer to block diffusion and dissolution of harmful elements. PPC sintered at 1 180°C had the low Mn, Cr, V and Pb leaching concentration of 0.0342 mg/l, 0.040 mg/l, 0.2885 mg/l and 0.0020 mg/l and met the requirement of MCL limitations of drinking water.

During sintering process, the composite structure in CC ensured enough bonding among ceramsites by the outer tailings layer and maintained steady sintering reaction via gradual diffusion of components from slag to tailings. The diffusion resulted in formation of new crystals, anorthite and pyroxene minerals in the reaction areas. Such reactions provided an effective method for eliminating the instability of steel slag by transforming lime (free CaO) into stable pyroxene or anorthite.

This study would promote a more feasible and economic method for producing porous permeable ceramics and improving added value of steel slag and tailings.

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