Preparation of Sintered Ceramsite from Leaching Residue in Electrolytic Manganese Production

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Keywords: Sintered ceramsite; Leaching slag; Electrolytic manganese; Shrinkage rate; Cylinder pressure strength

Abstract. Leach residue is the main raw material in the preparation process, and it is made from the leaching process with the Australian Mine and Yongzhou Mine by the ratio of 1:1. The sintered ceramsites are prepared by the leaching residue, 9% fly ash, a small amount of phosphogypsum, lime, silicon ore and other additives under certain condition. The result shows that, with the increasing of the residue and lime amount, the shrinkage rate and cylinder pressure strength of sintered ceramsite decrease, with the increasing of phosphogypsum and silicon ore amount, the shrinkage rate and cylinder pressure strength increase firstly and then decrease, with the increasing of roasting temperature and roasting time, the shrinkage rate and cylinder pressure strength increased. The optimal preparation condition of the sintered ceramsite is determined, 75% of the residue, 9% of the fly ash, 2% of phosphogypsum, 14% of the silicon ore, and the appropriate roasting temperature is 950 °C, the roasting time is 0.75h, under this condition, the shrinkage rate is 15.78%, and the cylinder pressure strength arrives at 4.08 MPa, they could meet the requirements of GBT17431.2-2010.

Introduction

Electrolytic manganese slag (EMS) is a kind of waste slag, which produced by the preparation of manganese electrolyte after leaching of manganese ore\textsuperscript{[1-3]}. The datum show that 7–9t of EMS is produced for every 1t of electrolytic manganese. At present, many enterprises treat manganese slag by the simple storage method, which will occupy a large amount of land resources, Long-term storage will cause water pollution, destroy the natural environment, and at the same time it will be a great waste of resources\textsuperscript{[4-10]}. Therefore, the comprehensive utilization of EMS has become a research hotspot for domestic and overseas metallurgical workers. Today, the domestic comprehensive utilization technology of EMS mainly includes the following, the recovery of valuable metals in slag, the production of fertilizers, the production of building materials and composite cementitious materials\textsuperscript{[11-17]}. Chousidis et al. studied the application of EMS in salt crystallized concrete, the results show that it does not have a negative impact on the performance of concrete immersed in chloride solution and has a certain anti-corrosion effect on steel bars\textsuperscript{[18]}. After a long period of exploration, the authors agree with some researchers that using EMS to make sintered ceramsite is one of effective ways to comprehensive utilization of manganese slag\textsuperscript{[19-23]}, on one hand, it add the utilization methods of EMS, on the other hand, the ceramsite can be used in building materials instead of gravel, which will reduce the use of gravel, as a result, the ecological damage to stone mountain will be avoided.

However, the use of EMS to make ceramsite has not achieved industrial production currently. The main reasons are as follows, the EMS was not pretreated before using for making ceramsite, the ammonium in the slag was not to be removed, when the service life was extended, the ammonium was gradually released, thereby the performance of the ceramsite would be decreased greatly. In addition, the manganese ions in the slag were not subjected to harmless treatment, so the leaching toxicity
results of the ceramsite was not met standard. Therefore, the authors pretreated the EMS before making the ceramiste to recover the ammonium and manganese in the early stages [24].

In this paper, leach residue is the main raw material in the preparation process, and it is made from the leaching process with the the Australian Mine and Yongzhou Mine by the ratio of 1:1. The effects of slag amount, phosphogypsum, silicon ore, lime, roasting temperature and roasting time on shrinkage rate and cycle pressure strength of sintered ceramsite will be studied, and the optimum process conditions will be determined to provide a theoretical basis for the future research.

**Experiment**

1. **Experimental material**

   The manganese slag used in the experiment is made from the leaching process with the the Australian Mine and Yongzhou Mine by the ratio of 1:1. After several times of washing, drying and crushing, 80% of the particle size is 80μm. The main element content is shown in Table 1. The phase analysis is shown in Fig. 1. The manganese slag mainly contains calcined gypsum, jarosite and so on.

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>S</th>
<th>Si</th>
<th>Ca</th>
<th>Fe</th>
<th>Al</th>
<th>Mn</th>
<th>K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/wt%</td>
<td>48.18</td>
<td>12.83</td>
<td>11.73</td>
<td>9.77</td>
<td>5.81</td>
<td>3.72</td>
<td>3.36</td>
<td>1.35</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Mg</th>
<th>Na</th>
<th>Ni</th>
<th>Ti</th>
<th>Cr</th>
<th>Cd</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/wt%</td>
<td>1.21</td>
<td>0.83</td>
<td>0.58</td>
<td>0.54</td>
<td>0.05</td>
<td>0.02</td>
<td>0.01</td>
<td>0.0098</td>
</tr>
</tbody>
</table>

   ![Fig.1 XRD diffraction figure of EMS](image)

   Phosphogypsum is taken from Guizhou Kailin Group, whose main component is calcium sulfate. Lime is collected from a lime sintering plant in Guizhou. The effective calcium oxide content is 85%. The silicon ore is taken from a silicon mining company in Guizhou, its silica content is of about 85%. Fly ash was taken from a coal-fired power plant in Guizhou, the main oxide composition is shown in Table 2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>FeO</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>TiO$_2$</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content/%</td>
<td>43.6</td>
<td>30.2</td>
<td>7.5</td>
<td>7.4</td>
<td>4.2</td>
<td>4.8</td>
<td>2.3</td>
</tr>
</tbody>
</table>

2. **Experimental method**

   9% of fly ash is fixed, a certain amount of the EMS, phosphogypsum, lime and silicon ore are weighted firstly, then they are mixed with water in a certain proportion well, making green ceramasite by granulation process, the sintered ceramsite are produced after natural curing, roasting, cooling and other process. Each time, 5L sintered ceramsite were prepared. Finally, the shrinkage rate and cylinder pressure strength are tested according density grade of 800 in GBT17431.2-2010.
Results and Discussion

(1) Effect of phosphogypsum addition

The EMS amount is of 70%, the amount of silica ore is of 15%, the amount of lime is 6%, the roasting temperature is controlled at 1000°C, and the roasting time is 1h. The effect of phosphogypsum amount on the shrinkage rate and the cylinder pressure strength is shown in Fig. 2 and Fig. 3.

![Graph of phosphogypsum addition vs shrinkage rate](image1)

![Graph of phosphogypsum addition vs cylinder pressure strength](image2)

It can be seen from Fig. 2 and Fig. 3, the shrinkage rate and the cylinder pressure strength of the ceramsite increase firstly and then decrease with the increasing of the phosphogypsum amount. When the phosphogypsum addition was 4%, the shrinkage rate and cylinder pressure strength reach the maximum, they are 21.14% and 5.76Mpa respectively. According to the GBT17431.2-2010, when the cylinder pressure strength of 800 density grade ceramsite is greater than 4Mpa, it can meet the requirements. When the phosphogypsum addition is 2%, the cylinder pressure strength is 5.33Mpa, which not only satisfies the strength requirement but also saves the raw materials, so the optimum phosphogypsum addition is 2%.

(2) Effect of lime addition

The EMS amount is of 70%, the amount of silica ore is of 15%, the amount of phosphogypsum is 2%, the roasting temperature is controlled at 1000°C, and the roasting time is 1h. The effect of the lime addition on the shrinkage rate and the cylinder pressure strength is shown in Fig. 4 and Fig. 5.

![Graph of lime addition vs shrinkage rate](image3)

![Graph of lime addition vs cylinder pressure strength](image4)

It can be seen from Fig. 4 and Fig. 5, the shrinkage rate and the cylinder pressure strength of the ceramsite decrease with the increasing of the lime addition, the maximum is obtained without adding lime, they are 23.63% and 7.02 MPa respectively. The reason for this is that, the melting point of calcium oxide is 2572°C, the high melting point of calcium oxide will reduce the possibility of liquid
phase, so increasing lime addition will lead to decreasing of the shrinkage rate and cylinder pressure strength, when it is 0%, the cylinder pressure strength is greater than the national standard, so the optimum amount of lime is 0%, that is to say the addition of lime has a negative effect.

(3) Effect of silicon ore addition

The EMS amount is of 70%, the amount of phosphogypsum is 2%, the roasting temperature is controlled at 1000°C, and the roasting time is 1h. The effect of silicon ore addition on the shrinkage rate and the cylinder pressure strength of the ceramsite is shown in Fig. 6 and Fig. 7.

Fig.6 Effect of silicon ore addition on the shrinkage rate

It can be seen from Fig. 6 and Fig. 7, the shrinkage rate and the cylinder pressure strength of the ceramsite increase firstly and then decrease with the increasing of silicon ore addition. When the silicon ore addition is 14%, the maximum is obtained. At this time, the shrinkage rate is 17.99%, and the cylinder pressure strength is 6.46MPa. The possible reasons are as follows, silicate is an important component of the ceramsite skeleton. The SiO$_2$ content affects the stability of the ceramsite skeleton directly, Si$^{4+}$ and oxygen can form a stable regular tetrahedral structure during high temperature roasting. When the silicon ore addition is small, the content of Si$^{4+}$ is small, the silicate skeleton could not be formed stably to a large degree, and the sintered ceramsite has a low shrinkage rate and low cylinder pressure strength. When the silicon ore addition is moderate, the chemical reaction of each phase in the ceramsite reaches equilibrium, and the phenomenon of micro-glass appears, and the ceramsite development is relatively complete, so the sintered ceramsite has high shrinkage rate and high cylinder pressure strength. When the SiO$_2$ content is too high, the eutectic point of the raw material component is raised, and a higher roasting temperature is required, at the low temperature, the ceramsite is roasted incompletely, as a result, which will decrease the shrinkage rate of the ceramsite, and there will be a small cylinder pressure strength. The results show that, when silicon ore addition is 14%, the shrinkage rate is the largest and the cylinder pressure strength is the largest also, so the optimum silicon ore addition is 14%.

(4) Effect of EMS addition

The silicon ore addition is of 14%, the amount of phosphogypsum is 2%, the roasting temperature is controlled at 1000°C, and the roasting time is 1h. The effect of the amount of EMS on the shrinkage rate and cylinder pressure strength of the ceramsite is shown in Fig. 8 and Fig. 9.

It can be seen from Fig. 8 and Fig. 9, the shrinkage rate and the cylinder pressure strength decrease with the increasing of the EMS addition. When the EMS addition is 60%, the maximum is obtained. At this time, the shrinkage rate is 18.05%, and the cylinder pressure strength is 5.01MPa. The EMS contains a large amount of calcium, when the EMS addition is increased, the ceramsite contains more calcium, this is the same as the effect of the preceding lime. In order to guarantee the consumption of EMS, the pressure strength of the ceramsite is 4.07Mpa when the slag amount is 75%, which is higher
than the 4Mpa specified by the national standard, so the optimum slag amount is 75%. After the above research, the appropriate ratio of raw materials can be obtained, 75% of EMS, 9% of fly ash addition, 14% of silicon ore addition, 0% of lime addition and 2% of phosphogypsum addition.

![Fig.8 Effect of EMS addition on the shrinkage rate](image8)

![Fig.9 Effect of EMS addition on the cylinder pressure strength](image9)

(5) Effect of roasting temperature

The EMS addition is of 75%, The silicon ore addition is of 14%, the amount of phosphogypsum is 2%, and the roasting time is 1h. The effect of the roasting temperature on the shrinkage rate and cylinder pressure strength is shown in Fig. 10 and Fig. 11.

It can be seen from Fig. 10 and Fig. 11, the shrinkage rate and the cylinder pressure strength of the ceramsite increase with the increasing of the roasting temperature, and the maximum is obtained at 1000°C, they are 16.09% and 5.84 MPa respectively. When the roasting temperature is lower than 950°C, the ceramsite is calcined incompletely, the internal silicate skeleton is not formed completely, and the ceramsite is loose and porous, so the shrinkage rate is small and the cylinder pressure strength is poor. When the roasting temperature is higher than 950°C, the ceramsite roasting is relatively complete, the chemical reaction of the internal phases is balanced, the internal skeleton is formed well, the ceramsite structure is tight, the pores are few, and the micro-glass phenomenon occurs. As a result, the shrinkage rate is large and the cylinder pressure strength is high. Increasing roasting temperature will enhance energy consumption and production costs. When the roasting temperature is 950°C, the shrinkage rate of the ceramsite is 14.66%, and the cylinder pressure strength is 4.66 MPa, which is higher than the 4Mpa specified by the national standard. Therefore, the optimum roasting temperature is 950°C.

![Fig.10 Effect of roasting temperature on the shrinkage rate](image10)

![Fig.11 Effect of roasting temperature on the cylinder pressure strength](image11)
(6) Effect of roasting time

The EMS addition is of 75%, The silicon ore addition is of 14%, the amount of phosphogypsum is 2%, and the roasting temperature is 950°C. The effect of the roasting time on the shrinkage rate and cylinder pressure strength of the ceramsite is shown in Fig. 12 and Fig. 13.

It can be seen from Fig. 12 and Fig. 13, the shrinkage rate and the cylinder pressure strength of the ceramsite increase rapidly at the beginning and then increase slowly with the increasing of the roasting time. The maximum are reached when the roasting time is 1.5h, the shrinkage rate of the ceramsite is 16.23% and the cylinder pressure strength is 4.85 MPa. When the roasting time is short, the ceramsite appears to be under-burned, which makes the internal reaction of the ceramsite incomplete, the texture is loose, and the influence on the strength is large. Increasing the roasting time, the internal reaction of the ceramsite is relatively complete, part of it is molten, the shrinkage rate of ceramsite increases, the ceramsite texture is hard after cooling, and the cylinder pressure strength is better. When the roasting time is 0.75h, the ceramsite cylinder pressure strength is 4.08Mpa, which meets the 4Mpa specified by national standards. Therefore, from the perspective of energy saving and emission reduction, the optimal roasting time is determined to be 0.75h.

Conclusions

1. With the increasing of EMS and lime addition, the shrinkage rate and cylinder pressure strength of ceramsite show a decreasing trend. Considering the utilization rate of EMS, the optimum EMS addition is 75%, and lime addition does not to be added.

2. With the increasing of phosphogypsum and silicon ore addition, the shrinkage rate and the cylinder pressure strength of the ceramsite increase firstly and then decrease. When the phosphogypsum addition 2% and silicon ore addition is 14%, the ceramsite has better cylinder pressure strength.

3. With the increasing of roasting temperature and roasting time, the shrinkage rate and cylinder pressure strength of ceramsite increase. Considering the production cost and energy consumption, the optimum roasting temperature is 950°C and the optimum roasting time is 0.75h.

4. Comprehensive consideration, the appropriate ratio of raw materials is 75% of EMS, 9% of fly ash, 2% of phosphogypsum, and 14% of silicon mine, the roasting temperature is 950°C and the roasting time is 0.75h. under this condition, the shrinkage rate of ceramsite is 15.78%, and the cylinder pressure strength is 4.08MPa, which meets the national standard(GBT17431.2-2010)
Acknowledgements
This work was financially supported by the National Natural Science Fundation (51764006, 51864012).

References


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