Effect of Aggregate Addition on The Properties of Unburned Brick of Electrolytic Manganese Slag

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Abstract. The study about the unburned brick of electrolytic manganese slag had become the research focus because of the large amount of manganese slag and the lower cost of making bricks. The effect of aggregate addition on the properties of unburned brick of electrolytic manganese slag as main material was studied. When the molding pressure was 2MPa, mixing water content was 25%, and the content of aggregate was 30%, the compressive strength and flexural strength of electrolytic manganese brick were 11.36MPa and 2.92Mpa after 7 days, and those were 16.40MPa and 3.19Mpa after 28 days, the volume density was 1.38g/cm³, the linear shrinkage rate was 0.938%, the water absorption rate was 30.52%, the saturation coefficient was 1.531, and there was no frost phenomenon.

1. Introduction
Electrolytic manganese slag was the acid residues when electrolytic manganese metal were produced, and they contained a large number of harmful substance. At present, one of the characteristics of electrolytic manganese slag was a large amount of emissions, and the comprehensive utilization rate was particularly low. In recent years, due to the indiscriminate digging of manganese resources, resulting in the decreasing of manganese ore grade, there would produce 8~9t manganese residue when 1t metal manganese was produced. A large amount of manganese slag was not only the waste of industrial raw materials, but also did harm to the environment. At present, China was the world's largest producer of electrolytic manganese, the production accounts of electrolytic manganese was about 98% of those of the world's. So far, there was no real industrial technology could solve the problem of electrolytic manganese residue in a short time. In order to solve this problem, domestic and foreign researchers [2-9] conducted a lot of research, hope for the recycling of electrolytic manganese dross[10-12], some researchers believed that making burning brick [13-15] could not only solve the storage problem, but also increase the utilization of manganese slag. There were many advantages in the technology of unburned brick, high consumption of electrolytic manganese residue, lower production cost, and replacing the clay. Harmless treatment of electrolytic manganese residue had been done, so this paper focuses on the influence of the aggregate addition on the performance of unburned brick, which would lay the foundation for the subsequent study.

2. Experimental

2.1. Experimental materials
The electrolytic manganese slag used in the experiment was derived from Zunyi Tiancai Manganese
Industry, and the particle size of <80μm was 80%. Cement was 42.5 ordinary Portland cement, produced in Guizhou Wujiang company. Lime was derived from the Shougang Guigang steel enterprises, the effective CaO content was of 87%. WJ additives was produced by the research team own, and they were complex mixtures. Aggregate was taken from the housing construction site, they were prepared after breaking and mixture building materials waste (brick, cement and stones), and their particle size was controlled between 0.1-2mm. The main chemical compositions of electrolytic manganese slag and cement were shown in Table 1 and Table 2.

| Component | Percentage of mass/\% |
|-----------|-----------------------|
| O         | 46.28                 |
| S         | 13.88                 |
| Si        | 10.74                 |
| Ca        | 10.05                 |
| Fe        | 5.66                  |
| Mn        | 4.88                  |
| Al        | 3.32                  |
| K         | 1.87                  |
| Mg        | 1.42                  |
| Na        | 0.66                  |
| Ni        | 0.43                  |
| Ti        | 0.28                  |
| Cr        | 0.05                  |
| Cd        | 0.01                  |
| Pb        | 0.01                  |
| Zn        | 0.0098                |

| Component | Percentage of mass/\% |
|-----------|-----------------------|
| CaO       | 60.15                 |
| SiO₂      | 21.3                  |
| Al₂O₃     | 5.79                  |
| Fe₂O₃     | 2.53                  |
| MgO       | 2.35                  |
| MgO       | 2.54                  |
| SO₃       | 0.72                  |
| Total alkalinity/ % | 3.66 |

2.2. Experimental process
The raw materials were mixed in accordance with a certain proportion, and they were added the appropriate amount of water and were aged for 1-2 days. The compression moulding was adopted, and the steel mold had a size of 79.0mm×39.0mm×40.0mm, molding pressure was of 2 MPa, and the rate of water content was of 20-25%. In the experiment, the manganese slag was used as the main raw material, the cement adding amount was 20%, and the aggregate addition amount was 20%, 25%, 30%, 35% and 40%. After compression moulding, the green bodies was taken out, the natural curing was carried out, at last, the properties of bricks were studied respectively.

3. Results and discussion
3.1 Effect of aggregate addition on compressive strength and flexural strength
The effect of aggregate addition on compressive strength and flexural strength were shown in Fig.1 and Fig.2. Compressive strength reflected the internal structure of the brick, the flexural strength reflected the bending ability of brick, they were the main detection indicators of brick. The results showed that with the increasing of aggregate, the compressive strength and flexural strength increased gradually. When the aggregate addition was 30%, they all reached the maximum value, the aggregate amount was been increased unceasingly, they all were decreased. When the aggregate amount was about 20%, the strength was lower because of too much addition of the manganese slag cementing material, which would lead to much particles in the bricks and relatively little aggregate content, and bring about the lack of aggregates that acted as skeletons, so the compressive strength and flexural strength were lower. When the aggregate addition exceeded 30%, the aggregate content was too much, the relative content of the cementitious material was small. The cementitious material were produced after hydration of the cementitious material were not sufficient to cement the aggregate well. The structure of bricks was loosed and the density was reduced, which would result in the decreasing in compressive strength. And the aggregate addition of 30% could satisfy the best gradation principle between the materials, so that the cementing function of the cementitious material and the skeleton function of the aggregate could achieve the best balance.
3.2 Effect of aggregate addition on bulk density and line shrinkage

The effect of aggregate addition on bulk density and line shrinkage were shown in Fig. 3 and Fig. 4. Bulk density reflected the light-heavy of the brick, the transport cost of lighter bricks were lower, the amount of labor could be reduced, the construction efficiency of site would be increased effectively. Line shrinkage reflected shrinkage and deformation of the bricks in the process of natural conservation. Fig. 3 showed that, with the increasing of aggregate, the bulk density increased first and then decreased. When the aggregate addition was 30%, the volume density was the biggest, it was 1.38g/cm³, but still lower than the volume density of ordinary clay brick. When the aggregate addition was of 30%, the compressive and flexural strength was the largest, the hydration reaction was the best inside the bricks, a large number of gelled substances was generated, increased the weight of the brick, and the aggregate particles and density were larger, so the volume density of bricks was higher under same volume of the case. And the highest strength could indicated their internal structure was close and the interior gap is smaller, so the bulk density was higher relatively. Fig. 4 showed that the shrinkage rate of the unburned bricks was decreasing, and the linear shrinkage decreased obviously at the addition of 20-30%, which was due to the optimization of the ratio, the hydration reaction inside the bricks increased, and the compaction degree of internal structure was increased gradually, the internal structure became strong, as a result, the larger line shrinkage was difficult to be occurred.
3.3 Effect of aggregate addition on water absorption and saturation coefficient
The effect of aggregate addition on water absorption and saturation coefficient of unburned brick of electrolytic manganese slag was shown in Fig.5 and Fig.6. The water absorption of the brick was mainly related to the internal gap of the bricks, which reflected the tightness of their internal structure. The saturation coefficient mainly reflected the anti-weathering performance of the bricks. When the water absorption of the brick was high, it indicated that the internal materials had strong water absorption, or they were not enough to cohere. When the saturation coefficient of brick was high, their anti-weathering performance was poor. Fig.5 showed that the water absorption decreased with the increasing of the aggregate addition firstly. When the aggregate addition was 30%, the water absorption was the lowest, it was 30.52%. But when the aggregate addition increased from 30% to 40%, the water absorption would increased from 30.52% to 35.41%. Fig.6 showed that the change trend of saturation coefficient was similar to that of water absorption with the increasing of aggregate addition. When the aggregate amount was 30%, the saturation coefficient was the smallest, it was 1.531. Therefore, the aggregate addition of 30 could make the internal structure of the bricks to be filled more densely.

![Figure 5. Effect of aggregate addition on water absorption](image1)

![Figure 6. Effect of aggregate addition on efficient saturation](image2)

3.4 Effect of aggregate addition on frost
The effect of aggregate addition on frost of unburned bricks was shown in Fig.7. The frost was the salt out phenomenon that the soluble salts in bricks body were produced on the surface of bricks with the evaporation of water in the bricks. Fig.7 showed that the frost situation of five bricks was not much difference, they are relatively minor. When the aggregate addition was 25%, 35% and 40%, a small part of the surface only had small layer of frost film, some frosts emerged in edges and corners. When the aggregate added at 20% and 30%, there were no frost or frost spots on the surface, but a small amount of frost point, and the blurred cream layer was in the edges and corners. According to GB/T2542-2012, the aggregate addition was 25%, 35% and 40%, the bricks belong to a slight frost, when aggregate addition was 20% and 30%, the brick was no frost.
4. Conclusion

With the increasing of the aggregate addition, the compressive strength and flexural strength of unburned bricks were increased first and then decreased. When the aggregate addition was 30%, the maximum value was achieved. With the increasing of aggregate addition, the bulk density increased first and then decreased, while the shrinkage rate of unburned bricks decreased as a whole, and the linear shrinkage decreased obviously when the aggregate addition was 20-30%. When the aggregate addition was 30%, the bulk density was of the largest, it was 1.38g/cm³, but it still was lower than the bulk density of ordinary clay brick.

With the increasing of the aggregate addition, the water absorption and saturation coefficient of unburned brick of electrolytic manganese slag showed a tendency of decreased first and then increased. When the aggregate addition was 30%, the water absorption and saturation coefficient were the lowest, at this time, the internal bonding of unburned bricks was tight relatively, the anti-weathering performance was better, and the frost phenomenon was relatively minor.

It was considered comprehensively, when the aggregate addition was 30%, the amount of cement was 20%, the mixing water content was 20%~25%, and the molding pressure was 2 MPa, the performance of unburned brick made from electrolytic manganese slag was the best. The compressive strength and flexural strength of electrolytic manganese bricks were 11.36MPa and 2.92Mpa after 7 days, and those were 16.40MPa and 3.19Mpa after 28 days. The volume density was 1.38g/cm³, the linear shrinkage rate was 0.938%, the water absorption rate was 30.52%, the saturation coefficient was 1.531, and there was no frost phenomenon, the performance met the requirements of GB/T2542-2012.

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