Preparation and property of unfired brick using electrolytic manganese residue

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Abstract. The feasibility of making unfired brick from the EMR with some additives in laboratory experiments was investigated in this paper. The results show that the EMR can be used to produce unfired bricks meeting JC/T 422-2007 for Mu 25 non-fired rubbish gangue brick. XRD and SEM analyses indicated that C-S-H, calcite, gypsum were newly generated phases in the unfired brick and there are almost no large capillary holes in the unfired brick, which can increase the compressive strength of the brick. The leaching toxicity test demonstrated that the unfired EMR bricks samples showed significant reduction in leach ability of heavy metals compared to raw EMR.

1. Introduction
At present, the construction industry generally requires the use of environmentally friendly, low-cost and energy-saving building materials. Therefore, there is a great need to propose the advanced building materials, which not only can protect the environment, but also stand in line with national standards [1-2].

Different wastes have been investigated to produce building bricks [3-5]. Walker et al. [6] investigated on curing process for soil using cement and the effect of cement content on the properties of stabilized samples. Chen et al. [7-8] studied the possibility of applying hematite tailings, clay and fly ash to produce brick. And the obtained bricks are in accordance with bricks standard in China (GB/T5101-2003). Morchhale et al. [9] developed a novel production process for copper tailing bricks from copper mine tailings. Liu et al. [10] explored the feasibility of producing brick with dyestuff-making sludge and typical cements. The prepared bricks solidified with alumina cement and sludge can be used for road construction. Roy et al. [11] examined the possibility of taking gold mine tailings as a partial substitute during the preparation process of concrete. Results indicated that 30% replacement of gold mine tailings would not cause great decrease in strength performance. However, in the current research on unfired bricks, there are still some obvious shortcomings, such as high cost and mass application of cement.

Electrolytic manganese residue (EMR) is a by-product during the process of producing electrolytic metal manganese (EMM). Nowadays in China, almost all EMR are piled up into nearby landfill sites with no treatment except for a small proportion being used as building material. Although there are some studies on the utilization of EMR [12-14], new recycling techniques for EMR have to be developed to achieve environmental protection.

The main purpose of this study is to explore the feasibility of using EMR to prepare unfired EMR bricks. Meanwhile, the performance of unfired EMR bricks, such as compressive strength, mobility of heavy metals, water absorption and density, were systematically determined.
2. Experimental

2.1. Material.
EMR from an EMM plant (Xiangxi, China), river sand from the Xiangjiang River (Changsha, China), OPC (P.O. 42.5) from Changsha new star cement plant is used for production of unfired brick. The major chemical composition of those materials was listed in Table 1. Meanwhile, the additive used in the experiments is the samples of polycarboxylate manufactured by Huateng chemical Co. Ltd in Shanxi province. And quartz and gypsum are the main mineral phases of EMR.

| Oxides (wt. %) | SiO₂ | SO₃ | CaO | Al₂O₃ | Fe₂O₃ | MnO | MgO | K₂O | Na₂O |
|---------------|------|-----|-----|-------|-------|-----|-----|-----|------|
| EMR           | 24.6 | 37.8| 8.6 | 12.2  | 7.9   | 4.6 | 1.7 | 2.4 | 2.7  |
| river sand    | 67.21| 0.10| 3.45| 8.97  | 4.05  | -   | 2.68| 1.30| 0.12 |
| OPC           | 19.65| 2.01| 64.06| 7.36  | 2.01  | -   | 1.68| 0.02| 0.51 |

2.2. Preparation of brick samples.
The bricks were made at EMR: OPC: river sand ratios of 60: 20: 20, polycarboxylate dosage 1.8% (percentage of the OPC used in the experiment), water content 15% and forming pressure 20MPa. After 28 days of curing in an open air, compressive strength and water absorption of the prepared samples were tested according to GB/T 4111-1997. And all the determinations were carried out in triplicate. Moreover, the leaching toxicity was tested according to GB 5085.3-2007.

2.3. Characterization.
The mineralogical and microstructure analysis of dried samples was respectively evaluated by XRD (D8 Discover, Bruker, Germany) and FE-SEM (Mira3, Tescan, Czech Republic).

3. Results and Discussion

3.1. Compressive strength.
The results of present study indicate that the bricks made at EMR: OPC: river sand ratios of 60: 20: 20, polycarboxylate dosage 1.8%, water content 15% and forming pressure 20MPa shows reasonably high strength of 42.6MPa. Under those conditions, the EMR can be used to produce unfired bricks meeting JC/T 422-2007 for Mu 25 non-fired rubbish gangue brick.

3.2. Water absorption of the unfired EMR bricks.
The specimens were prepared at EMR: OPC: river sand ratios of 60: 20: 20, polycarboxylate dosage 1.8%, water content 15% and it is soaked with water at room temperature for 4 days under 20MPa. Based on the test results, the water absorption of the prepared bricks was 6.5%. Namely, all stabilized specimens with EMR-OPC-river sand mixtures meet the masonry brick requirement stipulated in Chinese standard.

3.3. Density of the unfired EMR bricks.
The density tests were carried out on the specimens prepared at EMR: OPC: river sand ratios of 60: 20: 20, polycarboxylate dosage 1.8%, water content 15%, 20MPa forming pressure and cured in an open air for 28 days. The density of the unfired EMR brick was within the range of 1.9370~2.0239g/cm³, which is favorable for the building.

3.4. Mobility of heavy metals in the unfired EMR bricks.
In order to study the environmental impact, leaching toxicity according to HJ 557-2010 was carried out to investigate the heavy metal availability and releasing potential of EMR and unfired EMR bricks. And the data are shown in Table 2. As seen in Table 2, it is clearly shown that the unfired EMR bricks samples showed significant reduction in heavy metals leachability compared to raw EMR. This can be
contribute to the fact that the pozzolanic reaction products, namely C-S-H, can be generated during the unfired EMR bricks preparation process, which can solidify the heavy metals in EMR [15].

Table 2. Availability of heavy metals elements containing in the unfired EMR bricks and raw EMR powders.

| Elements       | Availability of heavy metals elements, mg/kg |
|---------------|---------------------------------------------|
|               | Mn  | Pb  | Zn  | Co  | Cu  | As  | Fe  |
| EMR           | 359.6 | 1.1 | 30.9 | 50.1 | 2.3 | 1.0 | 3.3 |
| unfired EMR bricks | 1.2 | <0.01 | 0.12 | 0.95 | 0.01 | 0.41 | 0.86 |

3.5. SEM and XRD analysis.
Compared with main mineral constituents of the EMR, some new mineral constituents have been found in the Figure 1. The most prominent constituents are CaCO₃ and C-S-H products. The formation of C-S-H and calcite is helpful to increase the strength of the bricks [16]. On the other hand, as it can be observed in Figure 2, the distribution of particles is uniform, with only tiny voids, resulting in a more stable microstructure and lower water absorption.

Figure 1. XRD pattern of unfired EMR bricks cured in the open air for 28 days.

Figure 2. SEM micrograph of unfired EMR bricks cured in the open air for 28 days.
4. Conclusions
The performance of unfired EMR bricks, such as compressive strength, mobility of heavy metals, water absorption and density, were systematically determined. The results of present study indicate that the bricks made at EMR: OPC: river sand ratios of 60: 20: 20, polycarboxylate dosage 1.8%, water content 15% and forming pressure 20MPa possess high strength of 42.6MPa and low water absorption of 6.5%. Bulk density of bricks is changed in scope of 1.9370–2.0239g/cm³. Moreover, the unfired EMR bricks samples showed significant reduction in heavy metals leach ability compared to raw EMR. And under appropriate preparation conditions, unfired EMR bricks can meet the requirement of the National Standards stipulated in the JC/T 422-2007 for Mu 25 non-fired rubbish gangue brick.

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