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Study on the leaching toxicity and performance of manganese slag-based cementitious materials

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Abstract

With the rapid development of electrolytic manganese industry, the environmental problems caused by the storage of electrolytic manganese slag are particularly prominent. It not only occupies land resources, but also easily causes heavy metal pollution in soil, surface water and groundwater. Therefore, it is necessary to treat electrolytic manganese slag safely and effectively. The paper mainly studies the solidification/stabilization of electrolytic manganese slag and its environmental safety for road filling, in order to open up a new way of harmless and resource utilization of electrolytic manganese slag. In this paper, lime and fly ash were used as stabilizers and cement was used as curing agent to stabilize manganese slag, and the stabilization effect of Mn and Pb in manganese slag was studied. The stabilization effect of manganese (Mn) and lead (Pb) in manganese slag was studied. The results show that the dosage of stabilizer quicklime is 2.5%, fly ash is 3%, and the dosage of solidifying agent cement is 12%, the solidification/stabilization effect is the best compared with other ratios, then the leaching concentrations of Mn and Pb meets the requirements of China’s surface water environmental quality standards for category III water sources, which can be used as domestic water after treatment. Under the optimal ratio of stabilization effect, the compressive strength and slump are 13.8 MPa and 50 mm, respectively. The research results of the paper can provide a new way for the harmless treatment of manganese slag and the resource utilization of new materials.

1. Introduction

With the rapid development of the electrolytic manganese industry, the environmental problems caused by the accumulation of electrolytic manganese slag are particularly prominent, which not only occupy land resources, but also easily cause heavy metal pollution in soil, surface water, and groundwater [1]. Therefore, safe and effective treatment of electrolytic manganese slag is necessary [2]. Tan et al [3] found that both red mud and electrolytic manganese slag in the mixture of steel slag, red mud and electrolytic manganese slag can stimulate the activity of steel and promote the formation of early strength of mixture. Ji et al [4] used electrolytic manganese residue instead of quartz powder or slag powder on the strength, shrinkage and heavy metal leaching toxicity of reactive powder concrete (RPC) were studied. The results show that using electrolytic manganese residue to partially replace quartz powder or slag powder, the compressive strength of RPC is generally improved. Zhou et al [5] studied the preparation of cement from electrolytic manganese slag-calcium hydroxide-blast furnace slag. The electrolytic manganese slag, calcium hydroxide, and slag are mixed in a mass ratio of 30:3:5, and the cement strength can reach C50 level. The initial and final setting time are 180 and 330 min respectively. Dong et al [6] studied results show that the replacement of silica sand with fly ash, vitrified beads and aerated concrete fine sand can not only reduce the dry density of aerated concrete with manganese slag, but also greatly reduce its compressive strength. Zheng et al [7] used electrolytic manganese slag and cementitious materials to prepare non-fired bricks. When the amount of electrolytic manganese slag was 30%, the best molding pressure was 25 MPa. After 1.2 MPa steam curing for 8 h, the performance of the bricks met MU25...
level. You et al [8] used electrolytic manganese slag and naphthalenesulfonic acid formaldehyde water reducer to prepare C40 marine concrete with better performance, and the electrolytic manganese slag content could reach 20%. Li et al [9] studied showed that kaolinite could be used as a supporting material for biogenic FeS during the formation process, which efficiently decreased the aggregation of FeS.

Although domestic and foreign researchers have carried out a lot of research on the resource utilization of electrolytic manganese slag as building materials, the comprehensive utilization of electrolytic manganese slag is small and the utilization rate is low, but the success of popularization and application have not yet been successful case. The main reason is that the high water content electrolytic manganese slag contains high ammonia nitrogen and sulfate content. The current deamination and desulfurization processes are immature and the pretreatment cost is high. The harmful substances in the electrolytic manganese slag are difficult to detoxify, and the products produced are easy to produce secondary pollution harms the ecological environment [10].

Therefore, based on the above literature, the curing experiment of electrolytic manganese slag was carried out, including the selection of curing agent and the optimal dosage. However, there are few studies on the leaching concentrations of Mn and Pb in electrolytic manganese slag and the treatment effect of these two heavy metals are rarely studied. Therefore, the paper adopts single factor experiment and orthogonal experiment to determine the optimal dosage of stabilizer quicklime and fly ash, and curing agent cement. On this basis, the
Physical properties of manganese slag-based cementitious materials are tested, which provides theoretical guidance for the realization of industrial production.

2. Solidification test design

The electrolytic manganese slag yard of a manganese product company in Guizhou Province covers an area of about 7000 m². 8 sampling points are randomly arranged in the yard, the sampling hole diameter is 10 cm, and the depth is 4 m. After mixing, two diagonal samples were taken according to the quartile method, each weight was 200 kg, and saved in double-layer woven bags. The leaching toxicity analysis of manganese slag was carried out. As shown in the results in table 1, the concentration of Mn and Pb in the manganese slag exceeded the specified limit of the ‘Integrated Wastewater Discharge Standard’ and belonged to Class II general industrial solid waste. Four groups of single factor experiments were designed. The materials used were manganese slag, lime, fly ash and cement, as shown in figure 1. The single-factor experimental scheme is shown in table 2. A total of 20 g manganese slag was placed in a 200 ml wide-mouth flask, and the moisture content was controlled at 25%. The raw lime was added in different proportions, and the mixture was stirred evenly and then maintained for 1d under indoor natural conditions. The leaching concentrations of Mn and Pb were detected. The single factor experiment operation method of fly ash and cement is consistent with the single factor experiment of quicklime. Instruments for measuring leaching concentrations of Mn and Pb are shown in table 3.

3. Solidifying effect analysis

According to the different proportions of quicklime, fly ash and cement as shown in table 2, the single factor leaching toxicity and curing effect test are carried out to analyze the influence degree of three materials under different contents.
As can be seen from figure 2, when the content of quicklime increases from 1% to 2%, the leaching concentration of Mn and Pb decreases significantly, and then Mn tends to be flat. At 2%, the curing rate of Mn and Pb is more than 99%. At 2%, the leaching concentration of Mn and Pb are 0.138 mg l\(^{-1}\) and 0.084 mg l\(^{-1}\), respectively. The leaching concentration of Pb still exceeds the standard of Class IV, indicating that quick lime has a good stabilization effect on Mn. Quicklime can undergo a hydration reaction with water to form an alkaline environment, the hydration product can package and adsorb heavy metals. Quicklime can package and fix the Mn\(^{2+}\) in the manganese slag and undergo a chemical reaction to convert it into a stable form of insoluble substance MnO\(_2\) through oxidation, which is stabilized in the manganese slag\(^{[11]}\).

As shown in figure 3, when the fly ash content increases from 1% to 5%, the leaching concentration of Mn and Pb decreases significantly, and then tends to level off. When the fly ash content is 5%, the solidification rates of Mn and Pb are 99.99% and 99.98%, respectively. The leaching concentration of Pb still exceeds the standard of Class IV, indicating that fly ash contains Al, Si, Fe, Ca and other oxides, it has exclusive adsorption of heavy metals. Fly ash can package and fix the Mn\(^{2+}\) in the manganese slag and undergo a chemical reaction to convert it into a stable form of insoluble substance MnO\(_2\) through oxidation, which is stabilized in the manganese slag\(^{[11]}\).

As shown in figure 4, when the cement is added from 1% to 5%, the leaching concentration of Mn and Pb decreases significantly when the cement is added from 1% to 5%, and then tends to be flat. When 5% cement is added, the solidification rates of Mn and Pb are 99.99% and 99.98%, respectively. At 5%, the leaching concentration of Mn and Pb is 0.188 mg l\(^{-1}\) and 0.049 mg l\(^{-1}\), respectively, and the leaching concentration of Mn and Pb meets the standard requirements. Cement is a kind of cementitious material that can undergo hydration reaction with water. The hydration product can wrap and adsorb the heavy metals in manganese slag, and convert toxic and harmful heavy metals

### Table 4. Orthogonal experiment scheme and test results.

| NO. | Fly ash A(%) | Cement B(%) | Quicklime C(%) | Mn leaching concentration (mg l\(^{-1}\)) | Pb leaching concentration (mg l\(^{-1}\)) | Compressive strength/MPa | Slump mm\(^{-1}\) |
|-----|-------------|-------------|----------------|------------------------------------------|------------------------------------------|-------------------------|----------------|
| 1   | 3           | 3           | 1              | 0.026                                    | 0.063                                    | 12.3                    | 72             |
| 2   | 3           | 6           | 1.5            | 0.024                                    | 0.046                                    | 13.8                    | 80             |
| 3   | 3           | 9           | 2              | 0.034                                    | 0.044                                    | 16.4                    | 61             |
| 4   | 3           | 12          | 2.5            | 0.023                                    | 0.022                                    | 13.8                    | 50             |
| 5   | 5           | 3           | 1.5            | 0.023                                    | 0.042                                    | 13.7                    | 134            |
| 6   | 5           | 6           | 1              | 0.033                                    | 0.062                                    | 10.4                    | 150            |
| 7   | 5           | 9           | 2.5            | 0.027                                    | 0.037                                    | 20                      | 110            |
| 8   | 5           | 12          | 2              | 0.033                                    | 0.039                                    | 16.1                    | 83             |
| 9   | 7           | 3           | 2              | 0.034                                    | 0.058                                    | 8.9                     | 186            |
| 10  | 7           | 6           | 2.5            | 0.024                                    | 0.041                                    | 10.5                    | 203            |
| 11  | 7           | 9           | 1              | 0.037                                    | 0.056                                    | 8.7                     | 186            |
| 12  | 7           | 12          | 1.5            | 0.024                                    | 0.035                                    | 8.8                     | 221            |
| 13  | 9           | 3           | 2.5            | 0.022                                    | 0.046                                    | 7.8                     | 194            |
| 14  | 9           | 6           | 2              | 0.031                                    | 0.056                                    | 7.2                     | 189            |
| 15  | 9           | 9           | 1.5            | 0.026                                    | 0.051                                    | 7                       | 211            |
| 16  | 9           | 12          | 1              | 0.034                                    | 0.037                                    | 6.8                     | 178            |

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As shown in figure 4, the leaching concentration of Mn and Pb decreases significantly when the cement is added from 1% to 5%, and then tends to be flat. When 5% cement is added, the solidification rates of Mn and Pb are 99.99% and 99.98%, respectively. At 5%, the leaching concentration of Mn and Pb is 0.188 mg l\(^{-1}\) and 0.049 mg l\(^{-1}\), respectively, and the leaching concentration of Mn and Pb meets the standard requirements. Cement is a kind of cementitious material that can undergo hydration reaction with water. The hydration product can wrap and adsorb the heavy metals in manganese slag, and convert toxic and harmful heavy metals
into low solubility, low mobility and low toxicity substance. The hydration products produced by cement solidification include Ca(OH)$_2$, hydrated calcium silicate gel and other substances. These substances have low permeability, small voids, and large specific surface areas. They can wrap and adsorb Mn and Pb in manganese slag.

4. Multi-factor orthogonal experiment analysis

4.1. Leaching concentration analysis

Through orthogonal experiments, select quicklime, fly ash, cement as experimental factors, fix the amount of manganese slag in each batch of experiments, control the moisture content of about 25%, and use the 3-factor 4-level orthogonal experiment table L$_{16}(4^3)$ to carry out the experiment and test the leaching concentration of Mn and Pb. As shown in table 4.

The multi-factor anova analysis of leaching test results based on SPSS software shows that, quicklime has significant influence on leaching concentration of Mn, while fly ash and cement have no significant influence. And quicklime and cement have significant influence on Pb leaching concentration, but fly ash has no significant influence, as shown in table 5. The leaching concentration values were averaged at 4 levels for analysis. As shown

![Figure 5](image)
in figure 5, when the fly ash content is 3%, the cement content is 12%, and the quicklime content is 2.5%, the leaching concentration of Mn and Pb reaches the lowest. And the leaching concentrations of Mn and Pb meet the standard requirements, so the optimal combination can be determined as A1B4C4.

4.2. Physical performance analysis

In order to ensure that the manganese slag cementitious material has certain strength characteristics when used as a building material and good fluidity during transportation, orthogonal experiments are carried out on the cementitious material under different fly ash, cement and quicklime contents, and the resistance is analyzed. The changes in compressive strength and slump are shown in figure 6.

Based on SPSS software, the mechanical properties of the specimens were analyzed by multi-factor anova analysis. The results show that fly ash and cement have no significant effect on compressive strength, but lime...
has significant effect. And cement and lime have no significant effect on slump, but fly ash has significant effect, as shown in table 6.

As figure 6 shows that with the gradual increase of fly ash content, both the compressive strength and slump show a trend of first increasing and then decreasing, but the compressive strength reaches the maximum value of 15.3 MPa when the content is 5%, and The slump reaches the maximum value of 119.25 mm when the content is 7%; at the same time, the compressive strength and slump show a trend of first increasing and then decreasing under different cement contents, and the maximum values appear at 6% and 9% respectively. ; But the compressive strength under different content of quicklime showed a gradually increasing trend, reaching the maximum at 2.5%, while the slump showed a trend of first increasing, then decreasing and then increasing, reaching the maximum at 1.5%. Under the optimal ratio of stabilization effect (A1B4C4), the compressive strength and slump are 13.8 MPa and 50 mm, respectively.

5. Results and discussion

In this experiment, lime and fly ash were used as stabilizer and cement was used as curing agent to complete the single factor and orthogonal test of manganese slag material curing treatment. The leaching concentration of Mn and Pb was mainly determined, and the physical properties of compressive strength and slump of the material were analyzed. The results show that through orthogonal test analysis, when the optimal ratio of fly ash content is 3%, cement content is 12%, and quicklime content is 2.5%, the leaching concentration of Mn and Pb reaches the minimum. And the leaching concentration are 0.023 mg l⁻¹ and 0.022 mg l⁻¹, respectively, which meets the Class III water standard of ‘Surface Water Environmental Quality Standard’. At the same time, under this optimal ratio, the compressive strength and slump are 13.8 MPa and 50 mm, respectively.

The paper opens up a new way for harmless treatment and resource utilization of electrolytic manganese residue, and provides a reliable theoretical basis for practical engineering construction. But there are still shortcomings to be improved, in the process of exploring the optimal dosage of curing/stabilizing agent for electrolytic manganese slag, the influence of the dosage of curing/stabilizing agent on the leaching results was only considered, focusing on providing a theoretical basis for practical engineering construction. Therefore, the phase analysis and morphology determination of the solidified/stabilizing manganese slag before and after leaching were not carried out.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Data availability

The data that support the findings of this study are available on request from the corresponding author.

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Notes

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