Leaching resistance study on immobilization of MnO$_2$/HMSS with sorbed simulated nuclide strontium by metakaolin-based geopolymers

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Abstract: Radioactive waste generated in nuclear energy utilization poses great environmental risks, and the safe disposal technology has become a hot research topic in the field of nuclear environmental security. Immobilization is a common radioactive waste disposal technique, and the leaching resistance of the solidified body is the key to safe disposal. In the study, metakaolin was used as a raw material to solidify strontium, a common nuclide in radioactive waste streams, and then conducted leaching resistance tests. Using control variables, the experiments were used to investigate the effects of adsorption pretreatment prior to solidifying, solidifying with and without the addition of adsorbent on the effect of immobilization. The leaching resistance of the solidified bodies were investigated in three leaching environments: 25°C deionized water, pH=1 sulfuric acid solution, and 5%wt magnesium sulfate solution during the 42d test cycle. The results showed that both leaching rate and cumulative leaching fraction of the 42d samples for the leaching resistance of radioactive waste immobilization under the environment of deionized water at 25°C. For the three leaching conditions, the adsorption pretreatment with (4:1)MnO$_2$/HMSS before solidifying or the addition of (4:1)MnO$_2$/HMSS while solidifying could effectively improve the leaching resistance of solidified body, and the former was more effective. The results of this study can provide reference for the disposal of strontium-containing radioactive waste.

1. Introduction

Nuclear energy is an energy source with many advantages, but its use produces radioactive waste streams containing $^{235}$U and $^{239}$Pu, and further nuclear fission to produce radioactive strontium ($^{90}$Sr and $^{89}$Sr)$^{1}$. Hazardous nuclides with long half-lives, high fission yields and high heat release, such as $^{90}$Sr, contribute a significant portion of the radiation and heat in highly radioactive waste streams$^{2}$.Currently, geological burial and solidification are commonly used worldwide to treat radioactive wastes, the radioactive wastes are first pretreated and then solidified into various types of solidified bodies, using multiple barriers to prevent the transfer of radioactive wastes to the biosphere and cause nuclear contamination. The selection of the solidifying body and the pretreatment process of the radioactive waste solution before solidifying are particularly important and will directly affect the stability of the radioactive waste solution in the solidifying body.

Cement-based materials are widely used to solidify low and intermediate level radioactive waste$^{3,4}$. However, hardened cement is a porous material with poor corrosion resistance and thermal stability$^{4,5}$. Therefore, cement is not the best choice for solidifying radioactive waste. In recent years geopolymers have gradually become a material for solidifying radioactive waste, which have good mechanical strength$^{4}$, leaching resistance$^{6,8}$, thermal stability$^{9}$, Van Deventer$^{10}$, John L. Provis$^{11}$, Yunsheng Zhang$^{12}$, Yao Xiao$^{13}$ et al. proposed that geopolymerization reaction is a complex multi-step reaction process, in which metakaolin-based polymers undergo three steps of silica-alumina source dissolution, monomer reconfiguration, and condensation under alkaline environment to produce silica-aluminate analogs$^{14}$, which are three-dimensional mesh structures of [SiO$_4$] tetrahedra and [AlO$_4$] tetrahedra cross-linked to each other. The many advantages indicate that metakaolin-based polymers can stabilize heavy metal ions and other substances in them.

Pre-treatment with a new adsorbent material (4:1) MnO$_2$/HMSS developed by our group before solidifying. The material adsorbs the nuclear strontium best at pH=7. When the strontium ion solution was 100 mg/L, the adsorbent was added at a ratio of 1 g/L, and the adsorption capacity could be as high as 91.08 mg/g in...
two hours, with a removal rate of 91.08%, so that the strontium ion solution concentration was increased to 1 g/L with the same injection ratio for saturation adsorption, and the adsorption capacity could reach 144 mg/g. Based on the saturated adsorption capacity of the material, this study prepared metakaolin solidified body containing the following three component combinations: (1) material with strontium already adsorbed, (2) a mixture of strontium nitrate and adsorbed material, and (3) strontium nitrate, respectively; and investigated the resistance to leaching of the solidifying bodies under different conditions such as deionized water, strong acid, and high salt, to reveal the effect of using (4:1)MnO₂/HMSS adsorption as a pretreatment process on the leachability of solidifying bodies. This ratio designed three groups of polymers aggregates is 1.2 water glass modulus and 0.6 strength ratio of the purchased partial metakaolin-based after preliminary experiments, the highest compressive body 2.2 Preparation of geopolymer nuclide solidified body

After preliminary experiments, the highest compressive strength ratio of the purchased partial metakaolin-based polymers aggregates is 1.2 water glass modulus and 0.6 liquid to solid ratio. This ratio design three groups of solidified body into A, B, C group, strict control of the solidified body in the Sr²⁺ content consistent, the Sr²⁺ content of group A as the basis for calculating the amount, group A for solidifying has adsorbed Sr²⁺ (4:1) MnO₂/HMSS, group B solidifying (4:1)MnO₂/HMSS and Sr(NO₃)₂, group C solidifying Sr(NO₃)₂, the specific solidified amount as shown in Table 2. The three groups of metakaolin-based polymers solidified body need to be placed in the standard maintenance room for 28 days.

<table>
<thead>
<tr>
<th>Group</th>
<th>Metakaolin</th>
<th>Sr²⁺(4:1) MnO₂/HMSS</th>
<th>(4:1) MnO₂/HMSS</th>
<th>Sr(NO₃)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>100g</td>
<td>5g</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B</td>
<td>100g</td>
<td>0</td>
<td>4.37g</td>
<td>1.52g</td>
</tr>
<tr>
<td>C</td>
<td>100g</td>
<td>0</td>
<td>0</td>
<td>1.52g</td>
</tr>
</tbody>
</table>

2.3 Leaching test

According to the requirements of GB7023-2011, the leaching agent is selected from deionized water, sulfuric acid solution with pH=1 and magnesium sulfate solution (5wt%), and the process of solidified body leaching test is as follows:

The three groups of A, B, C have been well-cared for metakaolin-based nucleophile solidifying body suspended in 500ml polyethylene bottles with chemically inert nylon rope, all three groups were added to deionized water, pH=1 sulfuric acid solution, magnesium sulfate solution (5wt%) three different leaching agent volume of 300ml, the sample geometric surface area of 24cm², and after adding the leaching agent to make the ground polymer solidified body in all directions at least 1cm thick leaching agent, do not allow the solution to be stirred during leaching, the temperature is 25°C.

The leaches were replaced after 1, 3, 7, 10, 14, 21, 28, 35, and 42 days. and the replacement of the leaching agent required immediate transfer of the sample to another container with a new leaching agent, and the transfer process required weighing, but no drying process. After each leaching cycle, the leachate was measured by atomic absorption spectrophotometer for Sr²⁺ concentration and cumulative leaching fraction (Pₜ) of each component were expressed as:

\[ R_n = \frac{a_n V}{A S} \]

where Rₙ is the leaching rate of Sr²⁺ in the n-th leaching cycle (cm/d); aₙ is the mass of Sr²⁺ leached in the n-th leaching cycle (g); V is the volume of sample (cm³); A is the initial mass of Sr²⁺ in the leaching test sample (g); S is the geometric surface area of the sample in contact with the leachate (cm²); tᵢ is the number of days in the n-th leaching cycle; and Pₜ is the cumulative leaching fraction of Sr²⁺ at time t (cm).

3 Results

3.1 Leaching test under deionized water

Using deionized water as the leaching agent, Figure 1 shows the leaching rates and cumulative leaching fractions of the simulated nuclides in the three groups of geopolymer solidified bodies. It can be seen from the figure that the leaching rate of the simulated nuclide Sr²⁺ in the three groups of solidified bodies is relatively similar with time, and the leaching rate generally decreases with time, especially at 7d, and then tends to level off[14,16-17]. According to the provisions of GB14569.1-2011, the solidified body in deionized water at 25°C to do anti-leaching test, ⁹⁰Sr 42nd d leaching rate and cumulative leaching fraction need to meet R≤1×10⁻³cm/d; P<0.17cm, three groups of solidified body at 42d leaching rate and cumulative leaching...
MnO2/HMSS has a good adsorption effect on Sr2+, and solidified Sr2+. The results indicate that the material (4:1) reduced the cumulative leaching fraction of Sr2+ by 65.86% of the values shown in Table 3.

Further hindering effect on the leaching of Sr2+.

Leaching test under acidic condition

General environmental water may contain acidic substances, so that the water is acidic, if the radioactive waste solidified body long-term contact with acidic substances, the solidified body will be damaged by acid corrosion, resulting in the leakage of radionuclides in the solidified body, and subsequently into the environmental water to cause radioactive contamination. Therefore, it is very important to study the leaching rate of solidified simulated nuclides under acidic environment. In this test, pH=1 sulfuric acid solution was selected as the leaching solution to study the leaching performance of the solidified body under acidic conditions.

Figure 2 shows that the leaching rate and cumulative leaching fraction of Sr2+ in sulfuric acid solution at pH=1 for the three groups of geopolymer solidified bodies varied with time similar to the trend in deionized water, but it can be found that the leaching rate and cumulative leaching fraction of Sr2+ increased significantly at each time period.

### Table 3. Values of leaching rate and cumulative leaching fraction of solidified bodies in deionized water at 42d

<table>
<thead>
<tr>
<th>Group Number</th>
<th>Solidified Object</th>
<th>Leaching rate</th>
<th>Cumulative leaching fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Sr2+(4:1)MnO2/HMSS</td>
<td>0.057·10⁻⁶ cm·d⁻¹</td>
<td>39.478·10⁻⁶ cm</td>
</tr>
<tr>
<td>B</td>
<td>(4:1)MnO2/HMSS</td>
<td>1.547·10⁻⁶ cm·d⁻¹</td>
<td>176.016·10⁻⁶ cm</td>
</tr>
<tr>
<td>C</td>
<td>Sr(NO3)2</td>
<td>2.724·10⁻⁶ cm·d⁻¹</td>
<td>267.269·10⁻⁶ cm</td>
</tr>
</tbody>
</table>

Comparing the leaching rates of the three groups of solidified bodies (Figure 1(a)), the leaching rate of group A was always the lowest and the leaching rate of group C was basically the highest. At 42d, the leaching rate of group A was 3.68% of the leaching rate of group B and 2.09% of the leaching rate of group C. Comparing the cumulative leaching fractions of the three groups, those of group A remained the lowest and those of group C were likewise still the highest. At 42 d, the cumulative leaching fraction of group A was 22.43% of that of group B, and group A was 14.77% of that of group C.

The above results showed that the pretreatment of Sr2+ adsorption using (4:1) MnO2/HMSS followed by solidifying was the most effective, which could result in an 85.23% reduction in the cumulative leaching fraction at room temperature and at 42d of deionized water leaching. Simultaneous solidifying of (4:1) MnO2/HMSS and Sr(NO3)2 resulted in 56.79% of the leaching rate and 65.86% of the cumulative leaching fraction of directly solidified Sr2+. The results indicate that the material (4:1) MnO2/HMSS has a good adsorption effect on Sr2+, and the use of its adsorption pretreatment of Sr2+ and then solidifying it into the metakaolin geopolymer is more effective in preventing the transfer of nucleophiles to the environment. Even without pre-adsorption, the addition of (4:1) MnO2/HMSS while solidifying has a certain hindering effect on the leaching of Sr2+.

3.2 Leaching test under acidic condition

General environmental water may contain acidic substances, so that the water is acidic, if the radioactive waste solidified body long-term contact with acidic substances, the solidified body will be damaged by acid corrosion, resulting in the leakage of radionuclides in the solidified body, and subsequently into the environmental water to cause radioactive contamination. Therefore, it is very important to study the leaching rate of solidified...
in Figure 3, after 3d of leaching in an acidic environment at pH = 1, the groundpolymer solidified bodies lost an average of 33.33% of their mass after 42d of leaching. This occurred because under acidic conditions, the Si-O-Si, Si-O-Al structural blocks in the metakaolin skeletal structure began to dissolve and then reorganize into generating zeolites[21], at which time the metakaolin-base aggregates dissolved and had flake exfoliation, the structure became loose, and the densities decreased[22]. The destruction of the structure and the increase in porosity inevitably lead to the fact that the Sr²⁺ solidified in it cannot be better continued to be blocked, so the leaching rate and cumulative leaching fraction keep increasing. Therefore, the three solidified bodies are particularly poor in blocking Sr²⁺ under acidic conditions, especially under strong acidic environments.

Fig. 3. Appearance and morphology of the three groups of solidified bodies after 42d leaching in sulfuric acid solution at pH=1

3.3 Leaching test under sulfate condition

Groundwater is not only acidic environment affects the solidifying effect, but also may contain SO₄²⁻ will cause erosion to the solidified body, and among many sulfates, magnesium sulfate has the greatest effect on the erosion of the solidified body[23].

Figure 4 shows that the leaching rate and cumulative leaching fraction of Sr²⁺ in magnesium sulfate solution (5wt.%) for the three solidified bodies was found to be similar to the trend in deionized water. The leaching rate and cumulative leaching fraction of group A at 42d were the smallest for the same reason as the leaching agent was deionized water and sulfuric acid solution with pH=1. The leaching rate at 42d was 53.28% of the direct solidifying of Sr²⁺ and the cumulative leaching fraction was 48.76%, while the leaching rate at 42d for group A was 82.81% of the leaching rate for simultaneous solidifying of (4:1)MnO₂/HMSS and Sr(NO₃)₂ and the cumulative leaching fraction was 66.02%.

Fig. 4. Leaching rate and cumulative leaching fraction of Sr²⁺ in sulfate condition from ground aggregates of metakaolin solidified bodies. (a) Leaching rate of Sr²⁺ (b) Cumulative leaching fraction of Sr²⁺

The leaching rate and cumulative leaching fraction of solidified bodies in each group at 42d were higher than the leaching test results of deionized water in the corresponding test group, but lower than the results of sulfuric acid solution at pH=1 as leaching agent. The reason for this may be mainly related to the influence of metal ions. Under sulfate environment, the structure of metakaolin-base aggregates is more stable, but (4:1) MnO₂/HMSS will compete with other metal ions for adsorption sites when adsorbing Sr²⁺, Mg²⁺ and Sr²⁺ are the same 2-valent metal ions, which may lead to a shift in the adsorption equilibrium of Sr²⁺ due to competitive adsorption, thus affecting the anti-leaching properties of the solidified body.

3.4 Analysis of interaction

Adsorption pretreatment of Sr²⁺ using (4:1) MnO₂/HMSS in both deionized water, pH=1 sulfuric acid solution and magnesium sulfate solution (5wt.%), followed by solidifying into the metakaolin geopolymer, was found to be more effective in preventing the transfer of nucleophiles to the environment. Even without pre-adsorption, the addition of (4:1) MnO₂/HMSS while solidifying has some hindering effect on the leaching of Sr²⁺. These are the results obtained by making comparisons in the same environment, but the same treatment certainly has different effects on Sr²⁺ in different environments and will be influenced by the environment.

Taking group C as a reference, the effect of different environments on solidification without the interference of (4:1) MnO₂/HMSS was very high. The cumulative leaching fraction was nearly 1000 times higher in the sulfate solution at pH=1 than in the deionized water environment, mainly because the metakaolin skeletal structure was damaged under acidic conditions at pH=1, which led to a dramatic decrease in the solidification effect. The cumulative leaching fraction in the magnesium sulfate solution (5wt.%) was nearly 50 times higher than that in the deionized water environment. In the sulfate environment, the structure of the metakaolin-base aggregates was more stable, but SO₄²⁻ would react with Sr²⁺ on the surface of the solidified body to produce precipitation, resulting in a poor solidification effect. The solidifying effect was particularly improved in the deionized water environment after adsorption pretreatment, but not in the sulfuric acid environment at pH=1 and in the magnesium sulfate environment (5wt.%). Combined with the analysis, the effect of environmental changes on the solidification effect was more pronounced than the effect of advance pretreatment with (4:1) MnO₂/HMSS adsorption on the solidification effect.

4 Conclusion

The 42d leaching rate and cumulative leaching fraction of Sr²⁺ of the three groups of geomers solidified bodies at 25°C when the leaching agent was deionized water were well below the requirements of GB14569.1-2011. The use of (4:1) MnO₂/HMSS advance adsorption has the best solidification effect before solidifying the radioactive waste. And if the radioactive waste is not treated in time, adding (4:1) MnO₂/HMSS together with
solidifying can also improve the solidification effect. When the leaching agent was pH=1 sulfuric acid solution or 5 wt% magnesium sulfate solution, the anti-leaching performance of the solidified bodies decreased compared with the deionized water condition, but the overall trend was still that the performance of the solidified bodies with advance adsorption was the best, the performance of the adsorbent added during solidifying was the second best, and the solidifying of strontium salt solution alone was the worst. The results indicate that either pretreatment with (4:1) MnO₂/HMSS while solidifying can effectively improve the leaching resistance performance of the solidified bodies. Changes in environmental conditions have a significant impact on the solidified body's ability to resist leaching, and care should be taken to avoid strong acidic conditions when using metakaolin-based polymers to cure strontium.

References


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