Environmental Stability of High Temperature Molten Vitreous Residue of Hazardous Waste

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Abstract. Vitrification technology is one of the harmless treatment methods for hazardous waste containing heavy metals and other harmful substances, converting solid waste into vitreous residue with amorphous structure by high temperature melting. In this paper, we propose the acid dissolution rate in acidic environment to characterize the environmental stability of molten vitreous residues. We have tested six high temperature melting residues from different enterprises. The results of our experiments show that the higher the degree of vitrification, the lower the acid dissolution rate, and most of them are similar to basalt, quartz and architectural glass. This work demonstrate that the vitreous residue produced by high temperature melting has high stability and low leaching toxicity. Vitrification technology can solidify heavy metals and other harmful substances in the dense three-dimensional structure of glass state.

1. Introduction

A large amount of solid wastes are produced in China every year, which causes serious environmental and geological hazards, making the problem very serious for human and environmental being. The treatment, disposal and utilization of solid waste, especially hazardous waste, has always been the key problem restricting the construction of ecological civilization in China, and has become the focus of attention of the society, the public and the government departments. [1]At present, the widely used incineration treatment cannot solve the environment problem at one time. Vitrification technology is a harmless treatment method for solid waste, especially for hazardous waste containing heavy metals and other harmful substances. It uses high-temperature means such as plasma to convert solid waste into glass with amorphous structure.

Compared with usual incineration technology (temperature lower than 900 ℃), vitrification treatment technology can dispose various types and forms of hazardous wastes including POPs. It has a wide range of applications, large disposal capacity, high incineration efficiency and high degree of flue gas purification. At the same time, the residue produced by high temperature melting is vitreous residue, which has high stability and low leaching toxicity. It is usually used to landfill as a general solid waste in developed countries [1], or as building and paving materials for comprehensive utilization. It is conducive to reduce the volume of hazardous waste, improve the environmental and economic benefits of hazardous waste for high temperature heat treatment facilities, realizing the reduction, harmlessness and recycling of hazardous waste. [2]
Vitrification technology can solidify heavy metals and other harmful substances in the dense three-dimensional structure of glass state, so as to form general solid waste which is not easy to release to the environment and has low environmental risk. Due to the different raw materials and processes in the vitrification process, the contents of heavy metals in the vitrification products are different. As the actual industrialized vitrification process may have certain fluctuations, the vitrification residue may not be perfect homogeneous glass phase material, so heavy metals and other harmful substances may bring potential environmental risks when the vitrification products are used in natural environment. The environmental stability of high temperature molten vitreous residues largely depends on whether it can be dissolved from the residues in natural environment.[3,4] In Poland, researchers have studied the physico-chemical stabilization method of electrical power plant fly ash of the Province of Lodz. [5] The ashes were vitrified in a thermal plasma process and their chemical stability was tested to determine whether the ashes can be disposed safely into the environment, specifically onto surface soil. The heavy metal leachability tests proved that the products after vitrification were more stable than non-vitrified waste, making it more suitable for disposal into the environment. And the low leachability of heavy metals from vitrificates qualifies this physico-chemical method of stabilization to the one of the most effective process of waste utilization. The vitrificates could be stored on a land without any harmful effects to the soil.

In this paper, we simulate the dissolution of residue under acid rain, and use the mass loss rate of the residue in acidic environment, $R_a$, as the index to characterize its environmental stability. We have tested six high temperature melting residues from different enterprises. The results of our experiments show that the higher the degree of vitrification, the lower the acid dissolution rate, and most of them are similar to basalt, quartz and architectural glass.

2. Experimental

Vitreous residue is an amorphous state in which there is no long-range order or translational symmetry of the constituent atoms. Since the amorphous structure does not contain long-range three-dimensional periodicity and cannot give sharp diffraction peaks, the glass state properties of solid materials can be studied by X-ray diffraction spectroscopy.

Put the vitreous residues into the buffer solution of acetic acid and sodium acetate, and stir for 6 hours. Then weigh accurately the weight of the sample before and after the dissolution process. And the vitrification degree of the sample was judged by the acid dissolution rate ($R_a$).

2.1. Reagents and materials

The reagents, including glacial acetic acid, sodium acetate and sodium hydroxide, in this study came from China Alfa Aesar Company and China Akzo Nobel Company. They were analytical reagents and could be used without further purification.

The buffer solution: Take 1.0 mol/L sodium acetate and 1.0 mol/L acetic acid respectively, mix with 49:51 by volume ratio, and the pH value of buffer solution after mixing is 4.6.

2.2. Testing steps

2.2.1. Crushing

The sample needs to be dried before it is broken. For the particles with large size, the sample is treated by jaw crusher, hammer or grinder, so as to ensure that at least 95% of the sample particle mass can pass through a 1.0 mm aperture sieve. If the mass of the sample exceeding the particle size is greater than 5%, the whole part larger than 1.0 mm shall be separated and broken again to reduce the particle size to a value less than 1.0 mm. The sample shall not be finely ground.

2.2.2. Mixing and weighing

Mix the samples passing 1.0 mm sieve, then put the sample in the blower drying box, and set the temperature to $(110 \pm 5)$ °C for 2 hours. After drying, remove the sample and transfer it to the dryer to
cool to room temperature and weigh. Repeat the above steps, and heat for 30 min at a time until the weight remains constant. The drying process of the filter film is the same as that of the sample.

The weight of the test sample with constant weight is $(100 \pm 5)$ g, and the accuracy is 0.01 g. The dry mass of the test sample is recorded as $M_0$ and the dry mass of the filter film is recorded as $M_1$.

Note: constant weight refers to the difference between two consecutive weighing times not greater than 0.02 g.

2.2.3. Leaching steps
Clean and dry the sealed leaching bottle, place the test sample into the leaching bottle, add 1.0 L of the buffer solution with pH value between 4.6-4.8. Then, place the sealed leaching bottle on a flipped or swing agitator, stir for $(6 \pm 0.5)$ hours. During the experiment, the pH value of the solution should be checked regularly and recorded. It is recommended to check the pH value at 30 minutes, 60 minutes, 180 minutes after the beginning of the leaching stage and at the end of the test.

In order to make the dissolution effective, the pH value in the leaching stage should be controlled at 4.5-5.5. Adjust the pH by adding acetic acid solution or sodium hydroxide solution. If the pH value measured during the test is not 4.5-5.5, the test will be invalid.

2.2.4. Solid separation from liquid
The solid and liquid phases contained in the leaching bottle were separated by filtration through 0.45 μm microporous membrane by vacuum or pressure filtration. At the end of the filtration, the leach bottle and filter shall not be washed with water or any other solvent, and the residual solid in the bottle shall be flushed with buffer solution.

When the residual solid in the leaching bottle is recovered into the filter membrane, then the residual solid on the filter membrane is washed with pure water for more than 3 times. After washing, put the filter film containing residual solid into the air blower drying box, and set the temperature to $(110 \pm 5)$ °C, and take out the filter after drying, and then transfer it to the dryer for cooling to room temperature and weigh. Repeat the above steps for checking drying, and heat for 30 min each time until the weight measured remained constant. The dry mass of the filter film containing residual solid is recorded as $M_2$.

2.2.5. Calculation
Calculate the acid dissolution rate ($R_a$) of vitrified residues as follows.

$$ R_a = \frac{M_0 - (M_2 - M_1)}{M_0} \times 100 $$

Where:
- $R_a$ is the acid dissolution rate of the sample, %;
- $M_0$ is dry mass of the test sample, g;
- $M_1$ is the dry mass of the membrane before acid solution test, g;
- $M_2$ is the dry mass of the filter film and the sample after leaching process, g.

3. Results and Discussion
We collected six high temperature melting residues from different enterprises. We have studied the degree of vitrification of these six samples by X-ray diffraction spectroscopy. The detection spectrums are shown in Figure 1.
It can be seen from the above XRD patterns that there are no sharp peaks in the sample a), b), c) and f), indicating that they have a good degree of vitrification. However, sample d) and e) have sharp peaks, which indicate that there are a certain amount of crystal composition in them, and indicate that the degree of vitrification are not very good.

The acid dissolution rate of the six samples are shown in Table 1.

| Samples | pH at beginning | pH after 60 min | pH at the end | $M_0/g$ | $M_2-M_1/g$ | $R_a/%$ |
|---------|----------------|----------------|--------------|--------|-------------|--------|
| a)      | 4.67           | 4.67           | 4.67         | 50.004 | 49.969      | 0.07   |
| b)      | 4.66           | 4.66           | 4.67         | 50.006 | 49.925      | 0.16   |
| c)      | 4.66           | 4.67           | 4.70         | 50.006 | 49.982      | 0.05   |
| d)      | 4.72           | 4.72           | 4.73         | 8.002  | 7.961       | 0.51   |
| e)      | 4.72           | 4.72           | 4.73         | 50.009 | 49.821      | 0.38   |
| f)      | 4.70           | 4.70           | 4.68         | 25.002 | 24.943      | 0.24   |

It can be seen from Table 1 that the pH value of buffer solution has not changed greatly from the beginning of test to the end, well controlled from 4.5 to 5.5, which meets the requirements of the test. The acid dissolution rates of sample a), b), c) and f) are smaller, from 0.07% to 0.24%. However the acid dissolution rates of sample d) and e) are larger, from 0.38% to 0.51%. The acid dissolution rates of basalt, quartz and architectural glass are 0.44%, 0.06% and 0.02%. It can be seen that sample a) and c) are similar to quartz and architectural glass, but sample d) and e) are similar to basalt. This is also consistent with the vitrification degree of sample d) and e) shown in XRD, which may have some crystal components.
4. Conclusion
The residues of high temperature molten of hazardous waste with vitrification technologies are mainly vitreous state like glass. And in acidic solutions vitreous residues are very stable, and they hardly dissolve in acidic solutions, which is similar to quartz and building glass. This work also proves that vitrification technology can obtain products with very low environmental risk, which indicates a kind of very promising technology for hazardous waste treatment. The vitrification is an effective method of neutralizing hazardous wastes such as fly ashes from electrical power plants, which makes a possibility to obtain the environmentally harmless products with a significant reduction of volume.

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