

# *Research Status of Wet Oxidation of Spent Resin and Cement Solidification of Oxidation Residue*

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**Abstract:** Radioactive spent resin is a key low and intermediate level organic solid radioactive waste from nuclear facilities. Wet oxidation serves as an important approach for its efficient degradation, and the solidification of its oxidation residue has become a core issue for the engineering application of this technology. This paper reviews the technical principle, advantages and research progress of wet oxidation for radioactive spent resin at home and abroad. Relevant domestic engineering prototypes have achieved a resin degradation rate of over 99%, laying a foundation for industrial application. Meanwhile, the characteristics of four solidification technologies for radioactive liquid waste (cement, glass, asphalt and plastic solidification) are analyzed and compared. It is clarified that cement solidification is the optimal engineering solution for treating wet oxidation residue of spent resin due to its remarkable advantages in economy, process, safety and application scope. Aiming at the lack of systematic research on cement solidification of oxidation residue, this study verifies the feasibility of the wet oxidation + cement solidification technology combination, providing technical support and reference for the whole-process treatment of radioactive spent resin and the engineering application of low and intermediate level radioactive waste treatment technologies.

## 1. Introduction

Radioactive spent resin refers to the waste generated by ion exchange resins used for purifying radioactive liquid waste and adsorbing radionuclides in nuclear facilities such as nuclear power plants, nuclear fuel cycle facilities, nuclear medicine and research reactors. These resins become waste after being saturated with adsorption, exhausted in exchange capacity, degraded in performance or unable to be regenerated and reused, belonging to low and intermediate level organic solid radioactive waste.[1] The main radionuclides in radioactive spent resin include <sup>60</sup>Co, <sup>90</sup>Sr, <sup>137</sup>Cs, <sup>14</sup>C, <sup>63</sup>Ni, <sup>131</sup>I, etc.[2] Its radioactivity accounts for about 80% of the total radioactivity of nuclear waste,[3] with a volume ratio of 23%–43%. [4]Therefore, the safe and effective treatment of radioactive spent resin is of great significance for the treatment and disposal of radioactive waste.

Radioactive spent resin has the following characteristics:[5-7]

(1) Radioactivity: Spent resin adsorbs radionuclides generated during the operation of nuclear power plants and nuclear equipment, such as <sup>60</sup>Co, <sup>137</sup>Cs, <sup>90</sup>Sr, <sup>131</sup>I, etc.

(2) Poor chemical stability: Spent resin is usually an organic polymer compound with low chemical stability, which is easy to degrade under high temperature and high irradiation, potentially releasing the adsorbed radionuclides.

(3) High water content: Resin generally exists in a wet state with a high water content (usually about 50%–70%), which increases the total volume and weight of spent resin.

(4) Attenuated adsorption capacity: The used spent resin has almost exhausted its adsorption capacity due to the adsorption of a large number of ions and has no practical use value.

(5) Difficult to treat directly: It is difficult to separate or remove radionuclides from spent resin through simple mechanical or physical methods.

(6) Potential harmful gas emission: Organic spent resin may decompose and release toxic gases or volatile radionuclides (such as methane, benzene, formaldehyde and radioactive iodine) during high-temperature or wet oxidation treatment.

(7) Diversified sources: The composition and pollutant types of spent resin may vary greatly due to different nuclear power plants, operating conditions and water chemistry system treatment methods.

Cement solidification is mostly adopted for radioactive spent resin in domestic nuclear power plants. Cement solidification is widely used in the treatment of low and intermediate level waste such as spent resin, sludge and evaporated residue due to its advantages of simple process, mature technology, readily available raw materials and low cost. However, cement solidification also has some limitations. It is a waste volume-increasing treatment technology, and the volume of treated waste usually increases several times. Due to the swelling property of resin, cement solidified products may have the risk of cracking after a certain number of dry-wet cycles. As an organic substance, resin may undergo radiation degradation during long-term storage, leading to the loss of mechanical properties of cement solidified products and the generation of harmful gases.[8]

In addition to cement solidification, China is also researching and exploring other treatment methods for radioactive spent resin, such as high-integrity containers, hot supercompaction technology, plasma/pyrolysis incineration, steam reforming, supercritical water oxidation, catalytic electrochemical oxidation and Fenton oxidation. [9-11]These methods aim to overcome the limitations of cement solidification and realize the reduction and harmless treatment of radioactive waste.

## 2. Wet Oxidation Technology for Radioactive Spent Resin

Wet oxidation technology shows unique advantages in the field of radioactive spent resin treatment. Its basic principle is that under acidic conditions, hydrogen peroxide is catalyzed by iron ions to decompose and produce hydroxyl radicals ( $\text{OH}$ ) with strong oxidizing properties. These hydroxyl radicals have high reactivity, can efficiently attack and degrade the organic components in radioactive spent resin, and finally convert them into carbon dioxide ( $\text{CO}_2$ ), water ( $\text{H}_2\text{O}$ ) and inorganic salts.[12]

Wet oxidation technology for radioactive spent resin has the following advantages:[12-14]

(1) Efficient degradation: Using the strong oxidizing property of hydroxyl radicals, wet oxidation can efficiently degrade organic components in radioactive spent resin into carbon dioxide, water and inorganic salts with high degradation efficiency and fast treatment speed.

(2) Environmentally friendly: This technology avoids the excessive use of high temperature, high pressure or chemical reagents, reduces the emission of harmful substances and has little impact on the environment. Meanwhile, the degradation products are mainly inorganic substances, which are easy for subsequent treatment and disposal.

(3) Simple equipment: The equipment required for wet oxidation is relatively simple and easy to operate, reducing equipment investment and maintenance costs.

(4) Mild conditions: Compared with high-temperature incineration or chemical treatment, wet

oxidation is carried out under relatively mild conditions, reducing energy consumption and safety risks.

(5) Reduced radionuclide carrying: The organic components in radioactive spent resin are effectively degraded by wet oxidation, reducing the carrying amount of radionuclides in the waste and lowering the difficulty and risk of subsequent treatment and disposal.

(6) Strong adaptability: Wet oxidation is suitable for treating various types of radioactive spent resin, including different types of ion exchange resins and organic adsorbents.

In 1976, Bibler et al.[15] applied wet oxidation to the treatment of radioactive spent resin, which subsequently triggered a research boom in wet oxidation treatment of spent resin at home and abroad. Gunale et al.[16] from the Institute of Chemical Technology, Mumbai, India treated INDION-223H resin with 20 mmol/L  $\text{Cu}^{2+}$  and 10 mol/L  $\text{H}_2\text{O}_2$  at 95 °C, and only residue remained without solid residue after the reaction. M. Aamir Hafeez et al.[17] from Pohang University of Science and Technology, South Korea studied the quasi-wet oxidation treatment of IRN-150 resin with  $\text{Cu}^{2+}$  as catalyst. Under the conditions of catalyst concentration 0.35 mol/L, initial pH 2, temperature 90 °C, catalyst flow rate 0.125 mL/min and 30%  $\text{H}_2\text{O}_2$  flow rate 0.375 mL/min, the resin degradation rate was 91.26% and TOC removal rate was 85.47%. Huang Chunping et al.[18] from National Cheng Kung University studied the improvement of wet oxidation technology using fluidized bed process. Cation exchange resin beads were ion-exchanged with  $\text{Fe}^{2+}$  to saturation, and then oxidation was initiated by injecting  $\text{H}_2\text{O}_2$  into the fluidized bed reactor. Under the conditions of solid loading 117.6 g/L, 25 mL  $\text{H}_2\text{O}_2$  (50 wt%) and 10 mmol/L  $\text{FeSO}_4$  at 75 °C, the conversion rate of resin to gas and soluble substances reached 91.6%. Li Jiangbo et al.[19] from Southwest University of Science and Technology combined microwave and wet oxidation to degrade cation exchange resin. The optimal degradation conditions were determined as pH 1.0,  $\text{Fe}^{2+}$  dosage 20 mmol/L, 30%  $\text{H}_2\text{O}_2$  dosage 100 mL, microwave power 120.0 W and irradiation time 60 min. The removal rate of cation resin by this method was 98.55%. Jia Shaoqing et al.[20] from China Institute for Radiation Protection conducted a preliminary study on the oxidative degradation of nuclear-grade IRN78 anion exchange resin using wet oxidation technology. The results showed that when the molar ratio of mixed catalyst  $\text{Fe}^{2+}/\text{Cu}^{2+}$  was 1:2, the catalytic effect of wet oxidation on IRN78 anion exchange resin was excellent, the oxidative degradation rate reached 99.7%, and the utilization rate of  $\text{H}_2\text{O}_2$  reached 92.7%. Feng Wendong et al.[21] from China Institute for Radiation Protection and Xi'an Jiaotong University conducted experimental research on  $\text{O}_3$  synergistic wet oxidation degradation of resin. Under the conditions of  $\text{O}_3$  concentration 106.1 mg/L, total  $\text{H}_2\text{O}_2$  144 mL, initial pH 2 and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  catalyst dosage 0.64 g, the resin degradation rate was 97.8%. Xu Lejin et al.[22] from Tsinghua University and Huazhong University of Science and Technology studied the wet oxidation of nuclear-grade cation exchange resin and found that  $\text{Fe}^{2+}$  had higher catalytic ability than  $\text{Cu}^{2+}$  in activating resin decomposition with  $\text{H}_2\text{O}_2$ . The weight loss was 73% under the conditions of initial temperature 75 °C,  $\text{H}_2\text{O}_2$  dosage 200 mL,  $\text{Fe}^{2+}$  concentration 0.3 mol/L and initial pH 0.01. Shen Huiyi et al.[23] prepared nano FeO and CuO to degrade nuclear-grade anion/cation mixed resin by quasi-wet oxidation method. The optimal reaction temperature was 90 °C,  $\text{H}_2\text{O}_2$  concentration 30 wt%, catalyst 0.06 g FeO/CuO (FeO:CuO=1:1), and the degradation rate of mixed resin was 82%. Jian Xingchao et al.[24] from Tsinghua University studied the wet oxidation treatment of spent resin and pointed out that  $\text{Fe}^{2+}$  was an effective catalyst for cation resin decomposition,  $\text{Cu}^{2+}$  was effective for anion resin decomposition, and the  $\text{H}_2\text{O}_2$ - $\text{Fe}^{2+}/\text{Cu}^{2+}$  system had the best decomposition effect in mixed resin. Wan Zhong et al.[25] studied Amberlite IRN77 resin at pH>1,  $\text{Fe}^{2+}$  catalyst concentration 0.2 mol/L and temperature (97±2) °C, the COD removal rate of residue reached 99%. Meng Xiang et al.[26] from Huazhong University of Science and Technology used wet oxidation to degrade nuclear-grade anion ZGANR170 and cation ZGCNR50 mixed resin. When the resin mixing ratio was 1:1, initial temperature (96±1) °C,  $\text{H}_2\text{O}_2$  dosage 200 mL and  $\text{H}^+/\text{Fe}^{2+}$  concentration 1/0.1 mmol/L, the resin

weight loss rate was 79%. In 2021, China Institute for Radiation Protection successfully conducted a thermal test verification of its independently developed engineering prototype at a nuclear power plant site. The prototype has excellent performance, can treat 10 kg of resin at a single time, and efficiently oxidize and decompose more than 99% of different types of resin. This achievement is of far-reaching significance for solving the challenges encountered in the treatment of radioactive spent resin in China and improving the overall governance capacity of radioactive waste.

### 3. Solidification Technologies for Radioactive Liquid Waste

#### 3.1. Cement Solidification

Cement solidification is a method of stabilizing and solidifying waste by encapsulating it with cement materials, which is widely used in the treatment of radioactive waste, heavy metal waste and industrial waste. The core goal of cement solidification is to reduce the mobility, toxicity and environmental hazard of waste through solidification, and improve the mechanical strength and chemical stability of solidified products.[9,27]

Cement solidification usually involves mixing radioactive waste, cement base material, external water and other solidification additives into a uniform cement slurry, and forming a hard waste solidified product after curing for no less than 28 days under appropriate curing conditions. Commonly used engineering cement solidification technologies can be divided into out-of-drum mixing and in-drum mixing. At present, all domestic operating nuclear power plants adopt in-drum mixing technology. [28]The process flow of cement solidification is shown in Figure 1. It can be seen that the main processes of cement solidification include metering, feeding and mixing of waste and various solidification materials, and setting and curing of cement slurry.

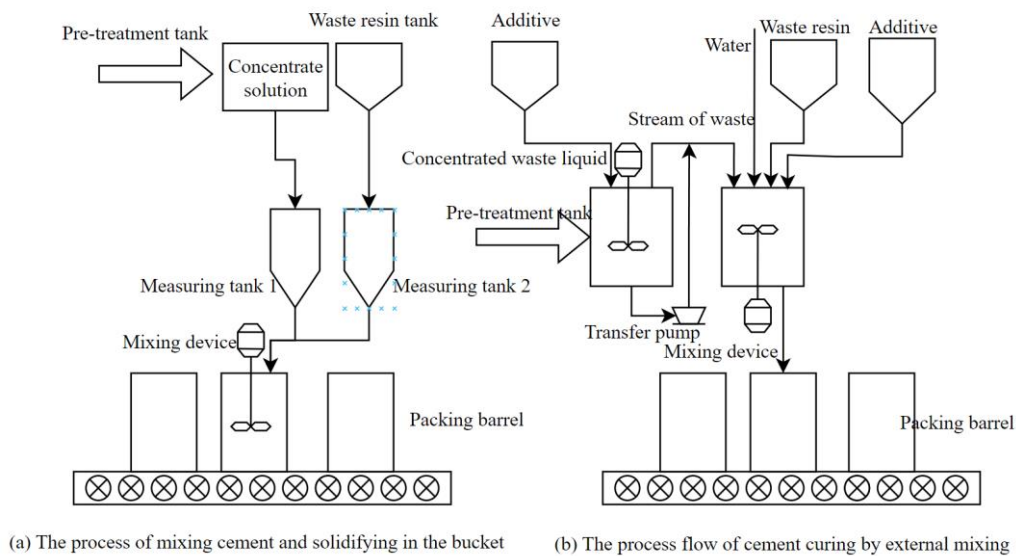


Figure 1: Process flow of cement solidification

China began to pay attention to and explore the cement solidification treatment technology of radioactive waste in the 1980s, and gradually promoted it based on foreign practical experience and combined with domestic actual demand. During this period, Wang Xilin and others collected 18 relevant literatures including those from the United States and Japan, translated and compiled them into a book, providing comprehensive technical data on cement solidification of radioactive waste for China. [29]These translations introduced the basic method of cement solidification and the

application of waste solidified products in packaging, transportation and disposal, laying a theoretical foundation for research.

In the early 1980s, the focus of domestic research included the development of solidification formulas at the laboratory stage, solidification process tests and the research and development of simple solidification devices. For example, China Institute of Atomic Energy built a medium-scale in-drum mixing cement solidification experimental device in 1982, accumulating practical experience for the large-scale application of solidification process. [30]The objects of solidification treatment cover various radioactive wastes, such as boron-containing liquid waste, decontamination solution, waste sludge, tritium-containing liquid waste and organic liquid waste.[31]

For the mass pouring of intermediate level liquid waste, domestic research on mass pouring cement solidification has been carried out for intermediate level evaporated residue, sodium metaaluminate liquid waste and other organic liquid waste generated from reprocessing plants, aiming to develop suitable formulas and improve the performance of solidified products. Studies have shown that reasonable adjustment of water-cement ratio and additives can significantly improve the compressive strength and durability of solidified products.[32-33]

On the basis of 1980s research, domestic radioactive waste solidification technology became mature and gradually standardized in the mid-1990s. The research focus shifted to the development of sand-free solidification formulas for boron-containing waste, optimization of accelerating technology and improvement of solidified product performance. [34-37]For example, CNNC Sichuan Environmental Protection Company built an asphalt solidification production line for low-level liquid waste and carried out thermal test feeding operation. Qinshan Nuclear Power Plant and Daya Bay Nuclear Power Plant also built supporting cement solidification treatment systems for low and intermediate level liquid waste and spent resin.

Entering the 20th century, with the rapid development of domestic nuclear power industry, most nuclear power plants have built radioactive waste cement solidification production facilities. These facilities mainly treat low and intermediate level radioactive concentrated liquid and spent resin, and also fix and dispose of waste filter cores and compressible/incompressible waste. The progress of solidification technology not only improves the safety of waste treatment, but also enhances environmental adaptability and long-term stability.

There have been some relevant studies on cement solidification of oxidation residue at home and abroad, but systematic research is still lacking. At present, the research on cement solidification of radioactive waste mainly focuses on the following aspects:

(1) Cement-based materials for radioactive waste packaging: used to fix radioactive waste into solid form to improve the safety of its storage and disposal.

(2) Backfill materials and waste containers: research on cement-based products suitable for backfill materials and durable waste containers to enhance the protection capacity of waste storage system.

(3) Emerging and alternative cement systems: explore new cement materials and their alternatives to improve the performance and environmental adaptability of cement solidified products.

(4) Physicochemical changes of cement-based materials during hydration and aging: in-depth analysis of the impact of these changes on the quality and long-term stability of cement matrix.

(5) Impact of disposal environment on the performance of cement-based materials: study the long-term effects of physical and chemical conditions, temperature changes, groundwater and radiation fields on the performance of cement-based materials.

(6) Quality inspection and non-destructive monitoring technology of cement solidified products: develop reliable technical means for real-time evaluation of the integrity and quality of cement solidified products.

(7) Long-term behavior simulation of cement solidified products: especially simulate the long-

term stability and behavior evolution of cement solidified products after the closure of disposal facilities.

### 3.2. Glass Solidification

Glass solidification is an important technology for the treatment of high-level radioactive waste. It forms solidified products by integrating waste into glass matrix to achieve long-term stability and reduce environmental impact. Glass solidification uses melting technology to combine high-level radioactive waste with glass-forming materials, and forms stable solidified products after cooling. The glass matrix effectively encapsulates radionuclides in waste through its chemical stability and leaching resistance. The core of this technology is the solubility of waste in glass matrix and the long-term safety of solidified products. It is mainly used for high-level liquid waste generated from spent fuel reprocessing. In recent years, attempts have been made to apply it to the stabilization of low and intermediate level waste.

China began to explore glass solidification technology in the 1980s, and gradually promoted it for the technical direction of high-level radioactive waste treatment, mainly focusing on experimental research, process development and pilot plant construction:[38-47]

(1) Laboratory research and technology exploration: Tsinghua University, China Institute of Atomic Energy and other units took the lead in carrying out research on glass matrix selection, radionuclide inclusion characteristics and solidified product performance. For example, a large number of experiments have been carried out on the radionuclide dissolution capacity and leaching resistance of borosilicate glass. Domestic research shows that the introduction of zirconium, phosphate and other components into the glass matrix can significantly improve the waste inclusion efficiency and long-term stability of solidified products.

(2) Pilot plant construction: A pilot-scale glass solidification facility was built at a nuclear reprocessing base in Lanzhou to verify the technical feasibility and stability. The solidification process verification focuses on the compatibility between liquid waste and glass raw materials, and the optimization of operating parameters (such as melting temperature and uniformity) during melting.

(3) Preparation for industrial application: To cooperate with the development of nuclear power industry, China has increased investment in nuclear waste treatment technology, including adding glass solidification facilities in the planning of nuclear fuel reprocessing plants.

Domestic research also attempts to adopt glass solidification technology in the treatment of low and intermediate level waste to explore the expansion of its application scope.

Internationally, glass solidification technology started early and has been industrialized in many countries. The research and development focus includes improving the treatment capacity of high-level radioactive waste, improving process equipment, and ensuring the long-term safety of solidified products.[42-47]

France applies borosilicate glass solidification technology at La Hague nuclear waste treatment plant, with extremely low leaching rate of treated waste and excellent performance of solidified products. With more than 40 years of operating experience, France has accumulated rich experience in glass formula optimization and process improvement, and established a complete system of waste classification and disposal.

Hanford Site is one of the largest glass solidification projects in the United States, carrying out large-scale industrial experiments on high-level liquid waste generated from spent fuel reprocessing. The focus of U.S. research is to develop more efficient melting equipment, such as electric furnace technology, to reduce energy consumption and improve solidification efficiency.

Japan takes the high-level waste treatment facility in Ibaraki Prefecture as the core, adopts French technology to treat domestic spent fuel reprocessing liquid waste. Japan has made some progress in

glass matrix optimization and low-temperature melting process development to reduce gas emissions during melting.

Russia has developed a variety of glass matrices, including borosilicate and aluminosilicate, for the solidification treatment of different types of waste. Its process focuses on improving the high-temperature performance and radiation resistance stability of solidified products.

The future development direction of glass solidification technology mainly focuses on three fields: material optimization, process improvement and safety evaluation.[48]

In terms of material optimization, researchers are committed to developing new glass matrices, such as phosphate-based glass and composite glass matrix, to improve radionuclide inclusion capacity, radiation resistance and long-term thermal stability. These materials can better adapt to the complex components of high-level radioactive waste and ensure the stability of solidified products under extreme conditions. In terms of process improvement, the focus is on low-energy consumption and high-efficiency melting technology, such as low-temperature melting technology and intelligent electric melting furnace, and the introduction of automatic control system to realize the green and sustainable development of the process. In addition, researchers are committed to improving the waste loading rate to reduce the total volume of solidified products and further optimize the economy of waste disposal.

Safety evaluation is the core link of the development of glass solidification technology. In the future, it is necessary to comprehensively evaluate the physicochemical behavior of solidified products under long-term storage conditions through deep geological storage simulation tests, including radionuclide leaching rate, microcrack generation risk and compatibility with underground environment. These studies aim to ensure the stability of solidified products for thousands of years in deep geological repositories and provide a reliable guarantee for the safe disposal of high-level radioactive waste. Through the collaborative promotion of the above aspects, glass solidification technology will achieve further breakthroughs in the fields of material science, engineering technology and environmental safety, providing a more efficient and sustainable solution for global high-level radioactive waste management.

### 3.3. Asphalt Solidification

Asphalt solidification is a method of treating waste containing harmful components (such as industrial wastewater, sludge, hazardous chemicals, etc.) by combining with asphalt. It belongs to a stabilization technology in waste treatment, and its main purpose is to reduce the mobility and release of waste through solidification, thereby reducing the risk of environmental pollution.

Asphalt solidification forms solid bulk materials by mixing waste with asphalt. During the solidification process, asphalt not only provides a coating layer for waste, but also reduces the dissolution of harmful substances through reaction with chemical substances in waste. This method is commonly used to treat liquid waste, sludge or other materials difficult to solidify.

The traditional asphalt solidification method for spent resin is to grind spent resin into slurry first, then send it together with evaporated residue into a scraper film evaporator or other evaporation equipment to mix with hot asphalt and evaporate water. The evaporated residue is put into a waste container, and cooled and solidified to form asphalt solidified products.[49]

In 1960, Belgium first proposed the use of asphalt solidification for radioactive waste, and then the United States, Germany and France also carried out relevant research.[50] Relevant reports on asphalt solidification were mostly seen in the late 20th century, and many asphalt solidification devices were built, mainly for the treatment of low and intermediate level radioactive waste. The asphalt solidification treatment method applied in the waste treatment centers of Jaslovské Bohunice Nuclear Power Plant and Mochovce Nuclear Power Plant in Slovakia is to dry the spent resin first,

mix the dried residue with hot asphalt, and cool the mixture to form asphalt solidified products.[51] This treatment method has the advantages of simple process, easy operation, large volume reduction coefficient, good waste performance, strong safety and obvious economic benefits. According to relevant information, the asphalt solidification device for treating spent resin in this waste treatment center is still in normal operation. In recent years, the research enthusiasm for asphalt solidification is low, and basically no new devices have been built.

### 3.4. Plastic Solidification

Plastic solidification of radioactive waste is a treatment technology that encapsulates radioactive substances in plastic matrix to improve stability and isolation effect, suitable for low-level waste (LLW) and some intermediate level waste (ILW). Common plastic solidification methods include thermoplastic plastic solidification, thermosetting plastic solidification and polyurethane solidification. Thermoplastics such as polyethylene (PE) and polypropylene (PP) can be mixed with waste after melting and then cooled to form. The solidified products have good mechanical properties, but attention should be paid to the release of volatile radioactive substances at high temperatures; thermosetting plastics such as epoxy resin and phenolic resin form a stable structure through chemical cross-linking, suitable for treating liquid waste but with slightly higher cost; polyurethane can fill irregular waste shapes through foaming process to form dense solidified products.[52-53]

From 1969 to 1971, Oak Ridge National Laboratory in the United States published five articles successively. The main work was to solidify organic waste, sodium borate waste and intermediate level liquid waste (evaporated residue containing sodium and potassium nitrate and nitrite) generated by power reactors with polyethylene and asphalt. Harwell Atomic Energy Research Institute in the United Kingdom used waste plastics (half polyethylene and half polyvinyl chloride) to solidify radioactive sludge. Germany solidified suspended solids and solid substances in radioactive liquid waste with film-forming agents and adhesives, and also used thermoplastic monomers to solidify radioactive liquid waste and organic liquid waste. The characteristic of this solidification method is polymerization at room temperature or low temperature, and safe operation.[54]

The key problems of plastic solidification include the impact of radiation on plastic degradation, compatibility between waste and plastic, gas release during solidification, long-term stability and leakage risk. To address these challenges, it is necessary to select plastic materials with strong radiation resistance (such as modified polyethylene or high cross-linked polymers), optimize the mixing ratio of waste and plastic and add stabilizers, and conduct accelerated aging and irradiation tests on solidified products to evaluate long-term performance. In addition, plastic solidification can be combined with cement solidification to form a double barrier, thereby improving the crack resistance, water resistance and durability of solidified products. Plastic solidification of radioactive waste has the advantages of simple process and low cost, but it needs to overcome long-term performance problems such as plastic degradation. The future development direction includes developing new plastic materials with high radiation resistance, optimizing the process and introducing adsorbents to enhance the stability and safety of waste.[55-56]

### 3.5. Analysis and Comparison of Solidification Technologies

Table 1 summarizes the main technical contents, advantages and disadvantages of various solidification treatment technologies, and conducts a comprehensive analysis.

Table 1: Summary of various solidification treatment technologies

Solidification Technology	Applicable Objects	Advantages	Disadvantages
Cement Solidification	Evaporated residue; waste ion exchange resin; sludge; incineration ash	Mature technology, readily available solidification raw materials; wide applicability, low cost; no high-temperature operation, no secondary waste and tail gas problems, safe process; good self-shielding ability and mechanical properties	Some waste components affect the fluidity of cement slurry; waste needs pretreatment such as pH adjustment and evaporation concentration; some solidified products may expand or crack when exposed to water; overheating occurs during cement hydration
Glass Solidification	High-level liquid waste; low and intermediate level concentrated liquid; spent resin; incineration ash	Realize solid volume reduction; good compatibility with waste; extremely low radionuclide leaching; good thermal stability; good chemical stability	High-temperature operation; expensive equipment and devices; complex equipment and process conditions; poor mechanical properties of waste
Asphalt Solidification	Evaporated residue; waste ion exchange resin; sludge; incineration ash	Realize waste volume reduction for liquid waste; no free liquid, no chemical reaction involved, low radionuclide leaching rate; low price of solidification base material	Asphalt is easy to melt and flammable when heated, and solidification has temperature requirements; limited salt capacity of asphalt; generation of radioactive gas
Plastic Solidification	Organic liquid waste; evaporated concentrated liquid; waste ion exchange resin; filter residue; chemical sludge	Suitable for various types of waste; high waste loading capacity; no chemical reaction involved; low radionuclide leaching	High-temperature melting operation; may expand when exposed to water; generation of radioactive gas; high device cost

After analysis and comparison, cement solidification is the optimal engineering solution for the fixed treatment of wet oxidation residue of spent resin. The rapid engineering application of cement solidification in the stabilization treatment of wet oxidation residue of resin is mainly attributed to its material characteristics, process advantages and economic adaptability. Compared with glass solidification, asphalt solidification and plastic solidification, it has the following advantages:

(1) Significant economic advantage (core): Extremely low equipment investment, only requiring conventional mixing and forming equipment, without high-temperature melting furnace and tail gas treatment system for glass solidification, or heating and polymerization reaction device for asphalt/plastic solidification; raw materials (cement) are cheap and readily available, low operating energy consumption (normal/low temperature curing), low labor cost, and the overall disposal cost is much lower than the other three technologies; although the volume increase ratio is slightly higher, the low basic cost offsets the additional expenditure caused by volume increase.

(2) Simple and easy process and operation: Extremely simple process flow, no complex pretreatment, waste with high water content can be directly treated, only completing the steps of "cement + waste + water + additives → mixing → forming → curing → hardened block"; low operation threshold, ordinary workers can get started after simple training, easy to realize automatic control and remote operation; loose curing conditions, curing can be completed at room temperature, no special temperature control equipment, suitable for on-site rapid treatment; high technical maturity, longest application history, rich engineering cases, low failure risk.

(3) Outstanding safety and stability: Non-flammable solidified products, no flammable volatiles, no combustion and explosion risk, safer compared with flammable asphalt solidified products and easy aging decomposition of plastic solidified products; excellent mechanical strength (compressive strength up to 10–20 MPa), can be directly landfilled or used as roadbed and building foundation materials, no additional container packaging, reducing leakage risk, better than asphalt and plastic solidified products which need container disposal due to low strength; strong heat and radiation resistance, can withstand hundreds of degrees Celsius high temperature, suitable for treating radioactive waste, more advantageous compared with poor heat resistance of plastic solidified

products and easy melting and flowing of asphalt solidified products at high temperature; the alkaline environment (pH 12–13) formed by cement hydration products can inhibit heavy metal leaching and neutralize acidic waste, good environmental compatibility, safer compared with glass solidification which is easy to produce secondary pollution when treating volatile heavy metals.

(4) Wide and comprehensive application scope: Can treat various inorganic hazardous wastes such as heavy metal sludge, electroplating wastewater, radioactive waste, waste acid and oxides, with far more adaptation types than the other three; low requirements for waste pretreatment, no complex dehydration, neutralization and other steps, strong adaptability to waste component fluctuations; flexible treatment scale, applicable from laboratory small-batch treatment to industrial large-scale disposal, adapting to different project needs, while glass solidification is mainly suitable for high-level radioactive waste, and asphalt and plastic solidification have strict restrictions on waste types and components.

(5) Outstanding and practical additional advantages: Reliable long-term stability of solidified products, stable for decades or even hundreds of years in natural environment without obvious aging; great resource utilization potential, can be used as building materials and roadbed materials to realize resource utilization with high strength, reducing final disposal volume; good environmental protection, no harmful gas emission during production (unless treating waste containing volatile substances), minimal impact on the environment.

#### 4. Conclusions

This paper systematically studies the wet oxidation treatment of radioactive spent resin and the cement solidification of oxidation residue, aiming to provide technical reference for the safe and efficient disposal of low and intermediate level nuclear waste. As a typical low and intermediate level organic solid waste generated by nuclear facility operation, radioactive spent resin has become the focus of nuclear waste management due to its high radioactivity ratio and complex physical and chemical characteristics. Although the current mainstream cement solidification method is mature and economical, it has inherent limitations, and the exploration of various new treatment technologies is continuing.

With the advantages of efficient degradation, mild conditions and environmental friendliness, wet oxidation technology has become an effective technical approach for the degradation treatment of radioactive spent resin. After years of research by scholars at home and abroad, many breakthroughs have been made in catalyst ratio, reaction parameter optimization and process improvement. Improved processes such as microwave synergy and ozone synergy have greatly improved the degradation efficiency. The thermal test verification of domestic engineering prototypes at nuclear power plant sites has laid a solid foundation for the industrial application of this technology, realizing the efficient decomposition of organic components of spent resin and reducing the difficulty of subsequent liquid waste treatment.

For the solidification treatment of residue after wet oxidation, this paper systematically analyzes the principle, development history, application scenarios, advantages and disadvantages of four mainstream solidification technologies: cement, glass, asphalt and plastic. Through comprehensive comparison, it is found that cement solidification has become the optimal engineering solution for the fixed treatment of wet oxidation waste liquid of resin by virtue of its core advantages such as outstanding economy, simple process operation, excellent safety and stability, and wide application scope. Its solidified products also have additional characteristics such as long-term stability, great resource utilization potential and good environmental protection, adapting to the rapid treatment needs of engineering sites.

At present, there is still a lack of systematic research on cement solidification of oxidation residue

at home and abroad. In the future, in-depth research can be carried out around the optimization of cement-based materials, solidification formula design, and long-term stability monitoring of solidified products to further improve the performance of cement solidified products and adapt to the characteristics of wet oxidation waste liquid of resin. Through the comprehensive review and analysis of wet oxidation technology of radioactive spent resin and residue solidification technology, this study clarifies the feasibility and adaptability of the wet oxidation + cement solidification technology combination in the treatment of such nuclear waste liquid, provides technical support for the whole-process treatment and disposal of radioactive spent resin in nuclear facilities, and also provides a reference for the engineering application and optimization upgrading of low and intermediate level nuclear waste treatment technologies.

## References

- [1] Xia Lili. *Study on the Formula of Polymer Cement for Stabilizing Spent Radioactive Ion Exchange Resins*[D]. China Institute of Atomic Energy, 2006.
- [2] Guo Zhimin. *Treatment Technology for Radioactive Solid Waste*[M]. China Atomic Energy Press, 2007.
- [3] Zhang Lidong, Li Yonghong. *Investigation on Treatment Technology of Spent Radioactive Resins and Exploration of Route Selection*[J]. *Science Times*, 2015, 14: 73-74.
- [4] Hu Xiangmeng, Liu Hui. *Optimal Management of Nuclear Grade Resins in Ningde Nuclear Power Plant*[J]. *Radiation Protection Bulletin*, 2014, 34(5): 24-27.
- [5] You Xinfeng, Zhang Shengdong. *Progress in Treatment and Conditioning Technologies for Spent Radioactive Resins*[J]. *Environmental Engineering*, 2023, 41(4): 225-233.
- [6] Li Yuankui, Zhao Gang. *Research Progress in Treatment Technologies for Spent Radioactive Resins*[J]. *Chemical Engineer*, 2023, 37(12): 81-85.
- [7] Fu Yulong. *Study on Cement Solidification of Spent Radioactive Resins*[D]. Southwest University of Science and Technology, 2017.
- [8] Lu Xinhua, Zhang Hongjian, Wei Fangxin, et al. *Comparative Study on Treatment Technologies of Spent Radioactive Resins in Nuclear Power Plants*[J]. *Nuclear Safety*, 2017, 16(3): 55-61.
- [9] Liu Wenlei, Jia Zhanju, Ran Mingdong, et al. *Current Status and Prospect of Immobilization Technology for Radioactive Wet Waste*[J]. *Sichuan Environment*, 2023, 42(4): 351-359.
- [10] Fang Xianghong, Ma Ruoxia, Yang Bin, et al. *Study on Treatment Methods of Spent Radioactive Resins*[J]. *Guangzhou Chemical Industry*, 2015, 43(3): 6-7.
- [11] Xue Hailong, Yan Xiaojun, Feng Wendong, et al. *Inorganic Volume Reduction Treatment Technology for Spent Radioactive Resins*[J]. *Contemporary Chemical Industry*, 2020, 49(9): 1934-1940+2087.
- [12] Gao Shuai, Guo Xiliang, Gao Chao, et al. *Treatment Technologies for Spent Radioactive Resins*[J]. *Radiation Protection Bulletin*, 2014, 34(1): 28-33.
- [13] Li Jiangbo, Wang Lielin, Xie Hua, et al. *Wet Oxidation Treatment of Spent Radioactive Ion Exchange Resins*[J]. *Journal of Isotopes*, 2019, 32(1): 45-52.
- [14] Jia Shaoqing, Feng Wendong, Li Xiaolong, et al. *Preliminary Study on Hydrogen Peroxide Wet Oxidation of IRN78 Anion Exchange Resin*[J]. *Radiation Protection*, 2017, 37(3): 193-199.
- [15] Jian Xingchao, Yun Guichun. *Study on Hydrogen Peroxide Wet Catalytic Oxidation Technology for Spent Radioactive Ion Exchange Resins*[J]. *Radiation Protection*, 1993, 13(3): 203-210.
- [16] Chen Min, Lu Chunhai, Fang Xianghong. *Cement Solidification of Radioactive Waste and Its Research Progress*[C]//Chinese Nuclear Society. *Progress Report on China Nuclear Science and Technology (Vol.5)*, 2017.
- [17] Li Honghui, Fan Zhiwen. *Cement Solidification of Radioactive Waste from Nuclear Power Plants*[J]. *Radiation Protection Bulletin*, 2010, 30(3): 34-38.
- [18] Wang Xilin. *Translation Collection on Cement Solidification of Radioactive Waste*[G]. Beijing: Atomic Energy Press, 1982.
- [19] Xu Suzhen, Xu Guowen, Chen Zhuying. *Barrel Mixing Cement Solidification Experimental Facility*[J]. *Radiation Protection*, 1985, 5(2): 105-111.
- [20] Xu Suzhen, Chen Zhuying, Xu Guowen. *Study on Cement Solidification of Radioactive Chemical Precipitation Sludge*[J]. *Radiation Protection*, 1986, 6(2): 96-100.
- [21] Chen Baisong, Chen Zhuying, Zeng Jishu. *Study on the Formula of Mass Pouring Cement Solidification for Intermediate-Level Liquid Radioactive Waste*[J]. *Radiation Protection*, 1989, 9(2): 110-115.
- [22] Chen Zhuying, Chen Baisong, Zeng Jishu. *Feasibility Study on Mass Pouring Process for Cement Solidification of Intermediate-Level Liquid Waste*[J]. *Atomic Energy Science and Technology*, 1988, 22(6): 664-668.

- [23] Wang Xiande, Sun Mingsheng. *Research and Development of Treatment Technologies for Low and Intermediate-Level Liquid Radioactive Waste in the Past Decade*[J]. *Journal of Nuclear and Radiochemistry*, 1990, 12(2): 65-71.
- [24] Gong Li, Cheng Li, Zheng Junhua, et al. *Study on Cement Solidification of Boric Acid Waste and Concentrate from PWR Nuclear Power Plants*[J]. *Radiation Protection*, 1995, 15(1): 33-41.
- [25] Zheng Junhua, Gong Li, Cheng Li. *Preliminary Study on Boric Acid Waste Liquid Cement Solidification Formula and High Volume Reduction Technology*[J]. *Shanghai Environmental Sciences*, 1998, 17(2): 35-39.
- [26] Wei Baofan, Li Runshan. *Study on Solidification of Radioactive Boron-Containing Waste Liquid from Reactors*[J]. *Journal of Nankai University (Natural Science)*, 1995, 28(3): 71-75.
- [27] Liu Weiping, Gao Zhen, Fan Chengrong, et al. *Research Progress in Vitrification and Artificial Rock Solidification Technologies for High-Level Radioactive Waste*[J]. *Chinese Journal of Nuclear Science and Engineering*, 2023, 43(1): 225-232.
- [28] Qian Min, Fan Sijun, Xue Tianfeng, et al. *Research Progress in Borosilicate Glass Formulation for High-Level Liquid Waste Vitrification*[J]. *Journal of the Chinese Ceramic Society*, 2021, 49(10): 2251-2265.
- [29] Li Xiuying, Xiao Zhuohao, Tao Xinyue, et al. *Research Progress in Phosphate Glass for High-Level Radioactive Waste Immobilization*[J]. *Materials Review*, 2021, 35(5): 5032-5039.
- [30] Wang Yu, Xing Qingli, Meng Baojian, et al. *Research Progress in Vitrification Technology for High-Level Radioactive Waste*[J]. *China Building Materials Science & Technology*, 2020, 29(4): 26-28.
- [31] Liu Weiping, Gao Zhen, Fan Chengrong, et al. *Latest Progress in French High-Level Liquid Waste Vitrification Technology*[J]. *Radiation Protection*, 2014, 34(6): 404-406.
- [32] Yan Cangsheng. *A Method for Bitumen Solidification of Spent Radioactive Resins after Drying*[J]. *Southern Energy Construction*, 2017, 4(1): 102-104+108.
- [33] Luo Shangeng. *Plastic Solidification for Radioactive Waste Treatment*[J]. *Chemical World*, 1985, (11): 29-31.
- [34] Wang Zhiming. *Treatment Technologies for Low-Level Radioactive Solid Waste in Japan*[J]. *Radiation Protection Bulletin*, 1987, (1): 10-17+9.
- [35] Wang Fengxiang, Zhuo Zongliang, Feng Shengtao, et al. *Plastic Solidification Method for Intermediate and Low-Level Waste*[J]. *Nuclear Protection*, 1978, (3): 52-63.
- [36] Che Chunxia, Teng Yuancheng, Gui Qiang. *Research and Application Status of Radioactive Waste Solidification Treatment*[J]. *Materials Review*, 2006, (2): 94-97+101.
- [37] Du Dahai. *Introduction to Plastic Solidification Method for Intermediate and Low-Level Waste*[J]. *Radiation Protection Bulletin*, 1981, (4): 12-18+53.