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Research Progress of Chemical Decontamination Technology in the Decommissioning of Nuclear Facilities

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Abstract

Nuclear facility decommissioning is a comprehensive project, including source investigation, decontamination, demolition, waste management, radiation detection, radiation protection, site decontamination, etc. Decontamination is an important activity for decommissioning of Nuclear facilities. After decades of research and development, nuclear facilities decontamination technology is divided into chemical decontamination, mechanical decontamination, electrochemical decontamination and biological decontamination. This paper reviews the methods and research situation of chemical decontamination technology in decommissioning of nuclear facilities.

Keywords

Nuclear facility; Decontamination; Chemical decontamination technology.

1. Introduction

Nuclear equipment decommissioning workers may be exposed to excessive doses during the disassembly, cutting, lifting and other construction processes in the facility, and may also cause radioactive contamination of the construction site and the environment. Although a series of radiation anti-skid measures have been taken to reduce the exposure to It is reasonable to reach a level, but it is still impossible to eliminate radioactive contamination on the surface of the facility, so it is necessary to attach great importance to decontamination treatment.

2. Purpose of decontamination

Decontamination means cleaning, heating, chemical or electrochemical action, mechanical action or other methods to remove radioactive contaminants on the surface of nuclear facilities or equipment. The research of nuclear equipment decontamination technology has a history of nearly 70 years. The United States, Canada, Japan, the European Union, India and other countries have conducted a lot of research work [1,2], covering a wide range, and comparing the research of related decontamination technology Go deep. my country has also carried out a large number of exploratory studies in the field of radiochemical decontamination [3,4]. In the nuclear industry, the purpose of decontamination is to reduce the amount of radioactive exposure, to recycle old equipment and materials, to reduce the waste level of materials, equipment and facilities contaminated by radionuclides or to turn radioactive waste into non-radioactive waste to reduce The quality and volume of waste reduce the difficulty and cost of storage, transportation and disposal, restore the site and facilities or parts of it to an unrestricted use state, remove loose radioactive pollutants and fix residual pollutants in place, so as to Make preparations for surveillance storage or permanent disposal activities, and reduce the number of residual radioactive sources in surveillance storage for the health and safety of the public or shorten the surveillance storage period. It also reduces the requirements for shielding and remote operation, which facilitates the maintenance and disassembly of equipment and facilities by operators, and facilitates the handling of accidents.

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3. Chemical decontamination method

Chemical decontamination [5] is a decontamination technology that uses specific detergents and dissolves radionuclides through a certain technological process, which is mainly used to remove fixed pollution. It is currently a decontamination technology with strong versatility and more research. Its main advantages are that it has more experience in industrial application of detergents, has better decontamination effects, and produces little or no airborne pollutants. Chemical decontamination can be divided into dilute chemical decontamination (DCD, soft decontamination) and concentrated decontamination (CCD, hard decontamination). The advantages and disadvantages of the two are compared as shown in Table 1. Among them, the dilute chemical decontamination is particularly It is suitable for reactor system decontamination.

Table 1. Chemical decontamination classification

	DCD	CCD
Characteristic	DF=2~10; Partially remove the oxide film layer without corroding the base metal	DF=10~100; Remove all oxide film layer and corrode base metal
Advantage	Low corrosion; Detergent is easy to regenerate; Recycle; Minimal waste	High decontamination rate; Short decontamination time; Remove deep fixed pollution
Disadvantage	DF＜10; Long decontamination time	Corrosive; Destroy the matrix; Most secondary waste;Difficulty in secondary waste disposal

Chemical decontamination is widely used to remove fixed radioactive contaminants on the surfaces of pipelines, components, equipment and facilities. The removal effect of radioactive contamination is usually measured by the decontamination coefficient DF and the decontamination rate DE. The decontamination coefficient DF is the ratio of the activity (or exposure) of the radioactive contaminants before and after decontamination. The research and development and utilization of chemical decontamination technology in my country are relatively early, and the most commonly used decontamination agents are AP ($NaOH+KMnO_4$), NP ($HNO+KMnO_4$) and EDTA.

Chemical decontamination methods can be divided into chemical foam method, chemical gel method, organic acid treatment method, fluoroboric acid treatment method, inorganic acid treatment method, detergent treatment method, redox treatment method, complexation treatment method, gas phase decontamination Method, ultraviolet/ozone/ultraviolet light activation method, volatilization/low temperature thermal desorption method. Usually the decontamination effect is related to many factors such as the type and concentration of the decontamination agent, the time of action, the temperature, and the stirring condition. At the same time, it should also be based on the nature of the pollutant, the matrix condition, the budget, the allowable degree of corrosion of the material, the safety design, the cost and subsequent waste For specific conditions such as disposal methods, chemical decontamination methods should be reasonably selected or used in combination with several other methods to improve decontamination effects. Several commonly used chemical decontamination methods are now introduced.

3.1 Chemical foam method

The foam decontamination method sprays the detergent and wetting agent on the surface of the object to be decontaminated under pressure to form a foam layer, so that the detergent and the contaminated surface are in contact for a long time. After a certain period of time, use rinsing or spraying to remove foam to obtain surface decontamination. In 1960, Ayres first applied foam decontamination technology to radioactive decontamination [6]. Because this method can effectively reduce the amount of secondary waste generated, it is ideal for the decontamination effect of walls, ceilings and complex structural parts. Its unique advantages and easy-to-use characteristics have attracted the attention of various countries, such as the United States, Britain, France, Japan and other countries.

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A lot of research work has been carried out successively. After 50 years of research and development, the application of this method in engineering has become mature day by day. The most representative one is the two-step foam decontamination device jointly developed by Britain and France [7] .

The French Ministry of Energy[8] used the COMODIN foam system to decontaminate the two decommissioned valves of the air-cooled system. After 4 hours of operation, the average dissolved metal thickness was 10μm. After the reaction, the surface pollution was reduced to 0.1Bq/g, and the valves could be re-melted and re-melted. use. The foam system is used to clean 6 heat exchangers with an internal surface area of 1000m2 and a volume of 27m3. The results show that: for the removal of 106Ru, alkaline detergent is better than acid detergent; foam containing Ce(IV) The decontamination coefficient of the detergent on the surface with the initial emission level of 20GBq can reach 40~50; the decontamination coefficient of the foam detergent containing O3 can reach 160.Wu Qiang [9] used foam cleaning technology to carry out decontamination experiments on simulated pollution samples from post-treatment plants. The experimental results show that the two acid detergents have good decontamination effects on the stainless steel and painted carbon steel equipment contaminated by fission nuclides in the post-treatment plant. Among them, the decontamination coefficient of the cerium sulfate detergent on the stainless steel samples is From 12.39 to 24.08, it is 3.62 to 5.14 for the samples of painted carbon steel sheet; the decontamination coefficient of oxalic acid detergent for stainless steel samples is 8.87 to 14.34, and for the samples of painted carbon steel sheet it is 6.57 to 8.40. The decontamination effect of the two acid detergents on stainless steel is significantly higher than that of alkaline detergents such as EDTA, potassium permanganate and sodium citrate.

3.2 Chemical gel method

Chemical gel decontamination is to use chemical gel as the carrier of detergent, spray the gel on the surface of the object to be decontaminated, so that the detergent and the contaminated surface can be kept in contact for a long time. , Rinse with water or remove the gel by spraying, and the surface of the object will be decontaminated. Commonly used formulas are nitric acid-hydrofluoric acid-oxalic acid-nonionic surfactant-carboxymethylcellulose-aluminum nitrate system. This method can effectively remove the pollutants that can be wiped off the surface. The decontamination coefficient is high, and the secondary waste generated is less, but the technology is more complicated.

Oxidation gel has good corrosion effects on stainless steel, acid gel on carbon steel, and alkaline gel on aluminum. Liu Zhihui [10] used the spraying method to experimentally study the effect of gel dosage and action time on the corrosion effect. The results show that when the amount of oxidized gel is greater than 0.6kg/m and the action time is 3~4h, the surface layer of stainless steel contaminated metals can be corroded and removed more than 1μm; the amount of acid gel is greater than 0.4kg/m and the action time is At 30 minutes, the corrosion depth of carbon steel can be greater than 3.5 μm; when the amount of alkaline gel is controlled at 0.5 kg/m and the action time is 1 h, the maximum corrosion depth to aluminum can reach 35 μm, but the corrosion depth is more than 2 hours A negative value appears.

3.3 Peelable film decontamination method

Decontamination is carried out using a polymer film with various functional groups made of chemical detergents and film formers. Because of the addition of various complexing agents, emulsifiers, and wetting agents, the peelable film has strong decontamination and film-forming properties. Before film formation, it is a polymer solution or aqueous dispersion emulsion, which can be sprayed or brushed Method to apply it to the surface of the object to be decontaminated and dry to form a film. In the film formation process, the functional groups on the polymer chain and the complexing agent in it interact with the contaminating nuclides, the contaminating nuclides are extracted into the film, and the coating film is stripped to achieve the purpose of decontamination. At present, the most commonly used peelable films are polyethylene or polyvinyl chloride series, polyvinyl acetate and its modified series and polyacrylate series. The amount of secondary waste decontaminated by the peelable membrane is reduced by two-thirds compared with the general chemical method, which saves half of

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the working hours and one-third of the cost. Peelable membrane decontamination has a good decontamination effect on objects with smooth surfaces, and has a poor decontamination effect on porous, rough objects, complex structural components and deep radioactive contamination.

Wang Zhentao et al. [11] studied an ethylene polymer peelable film used for the removal of radioactive contamination on the surface of stainless steel equipment, and discussed the concentration of ethylene polymer as the main agent of the film, the complexing agent EDTA-Na-Ca, and the thickening agent CMC-Na, plasticizer PEG-200, surfactant nm$CaCO_3$, and HCl doping amount affect the main performance parameters such as the physical and chemical properties and decontamination efficiency of the peelable film. The film forming drying time of the peelable film is 8h, which is pollution to 90Sr The surface decontamination efficiency of 0.02-0.20 Bq/cm2 is over 80%.

3.4 Redox method

Many metals or their compounds are easy to fragment or dissolve in the high oxidation state. Therefore, potassium permanganate, potassium dichromate, hydrogen peroxide and other oxidants are often used to treat oxides on metal surfaces, dissolve fission products and Various chemical substances, oxidation treatment on the metal surface [12]. At present, the internationally developed redox treatment system is the potassium permanganate decontamination system, including alkaline potassium permanganate decontamination system and acid potassium permanganate decontamination system.

The American Hanford Radiochemical Laboratory uses redox treatment to use 57% (mass fraction, the same below) HNO_3+1%H_3BO_3 and 57%HNO_3+6%AlF_3+1%H_3BO_3 to decontaminate or use alkaline Two-step decontamination of potassium permanganate and HNO_3, washing with water during reagent exchange, the decontamination coefficient reaches 104. The Ag(II)/HNO_3 decontamination technology used in the redox treatment method in France is developed for the decontamination of waste and the recovery of Pu, and has been used for the decontamination of stainless steel and plastics. This technology uses the strong oxidizing properties of Ag(II) to dissolve Pu, and the actual measured decontamination efficiency is 80%-95% [13].

4. Research status of chemical decontamination

In recent years, domestic and foreign countries have gradually paid attention to the research of chemical decontamination technology. There have been a large number of literature reports on the research of chemical decontamination technology, and nearly 20 chemical decontamination methods have been successfully applied to the decontamination of nuclear facilities.

Zhang Taoge [14] used hydrogen peroxide reduction method to treat Ce(IV)/nitric acid simulated decontamination waste liquid residual Ce^{4+} ions; used distillation to remove ammonium; and determined the nickel content in the simulated decontamination waste liquid. The nickel content in the liquid is estimated to simulate the corrosion amount of stainless steel. The test results show that adding hydrogen peroxide to the waste liquid according to the ratio of the amount of hydrogen peroxide to Ce^{4+} is 1:2, and all the remaining Ce^{4+} ions can be reduced. Adjust the pH value of the waste liquid to 11.5-12, heat and distill for 30 minutes, and the ammonium removal rate in the waste liquid reaches more than 99%.

Based on the traditional chemical removal of radioactive pollutants, Wu Qiang et al. [15] proposed a new technology that combines ultrasonic and chemical decontamination. After laboratory simulation and nuclear power plant decontamination practice test, its radioactive decontamination effect Excellent. After the contaminated workpiece is decontaminated, the radioactive decontamination coefficient on the surface is more than 1750, and the surface contact dose rate is also reduced to less than 0.5‰. Bertholdt et al. [16] applied a method to purify the surface of a nuclear device component or system containing an oxide layer. An acidic water film is generated on the surface of the device, the water film is brought into contact with gaseous acid anhydride, and the oxide layer is treated with gaseous ozone as an oxidant.

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The decontamination technology needs to have a high decontamination rate and decontamination factor to be suitable for irregularly formed metal waste and minimize the amount of secondary waste for component replacement and decommissioning. Fujita R[17] developed a new decontamination technology, using Ce^{4+} for decommissioning, which was named "REDOX decontamination technology". This paper studies the decontamination and regeneration conditions in non-radioactive basic experiments. Use different Ce^{4+} concentration, HNO_3 concentration, temperature and linear flow rate of purification solution to simulate samples in nitric acid solution to select decontamination conditions, that is, the dissolution conditions of stainless steel and carbon steel. Select the regeneration conditions of the decontamination reagent among various electrode materials, and change the electrode spacing, the ratio of anode area/cathode area, current density, Ce^{4+} concentration and HNO_3 concentration.

As new technologies for decontamination continue to emerge, traditional decontamination equipment is constantly improving. The ultimate goal of decontamination technology development is to maximize decontamination efficiency and minimize secondary waste. In order to meet the higher and better decommissioning needs of nuclear facilities, it is bound to put forward higher requirements for the development of traditional decontamination technologies.

References

[1] Editor-in-chief of the U.S. Department of Energy. "Nuclear Facilities Decommissioning Manual" [M]. 1994.

[2] Decontamination of water cooled reactors[R]. IAEA Technical Reports No365. IAEA. Vienna, 1994.

[3] W.H. Zhou, X.W. Zhang, et al. Field experiment study on decontamination effect of radioactively contaminated surface of a ship[J]. Journal of Nanjing University (Science and Technology Edition), 2003.

[4] 822/01 Preliminary feasibility study report on decommissioning plan of reprocessing plant[R]. The Second Research and Design Institute of Nuclear Industry, 1989.

[5] J.J. Jiao. Chemical cleaning technology of industrial equipment[M]. Petroleum Industry Press, 1995.

[6] Ayres J A, Demtmitt T F,Larrick A P, et al. Decontaminationstudies for HAPO Water-Cooled Reactor Systems[R].USAEC Hw-67937, 1960.

[7] Gauchon J P Saas A Decontamination of a large volume nuclear component using foams [J]. Contract CEE No.F12D-0035. CEE France.Third progress report, 1992.

[8] J R Costes. Foam decontamination of large nuclear components before dismantling[R]. Summary report of the first research coordination meeting on decontamination.IAEA, 1994.

[9] Q. Wu, X.W. Ren, et al. Foam decontamination technology for simulating contaminated samples in reprocessing plants[J]. Radiation Protection, 2001.

[10] Z.H. Liu, Y.X. Wang, et al. Gel decontamination experiment[J]. Nuclear and Radiochemistry, 2013.

[11] Z.T.Wang, Y.F. Yang, et al. Research on peelable membrane for radioactive decontamination of equipment surface[J]. Nuclear Technology, 2010.

[12] J.H. He, W.B. Zhong, et al. Decontamination technology for nuclear facilities[J]. Radiation Protection Newsletter, 2007.

[13] R.T. Zheng, S.K. Sun. Chemical cleaning and decontamination of nuclear facilities[J]. Chemical cleaning, 1998.

[14] T.G. Zhang, M.L. Wu. Preliminary study on Ce(IV)/nitric acid simulated decontamination waste liquid pretreatment[J]. Journal of Radiation Research and Radiation Proces, 2013.

[15] Q. Wu, H.L. Cui, et al. Application of Ultrasonic-Chemical Decontamination Process in Nuclear Power Plants[J]. Applied Chemical Industry, 2007.

[16] Bertholdt; Horst-Otto (Forchheim, DE), Maciel; Terezinha Claudete (Bamberg, DE), Strohmer; Franz (Ba. METHOD FOR THE DECONTAMINATION OF AN OXIDE LAYER-CONTAINING SURFACE OF A COMPONENT OR A SYSTEM OF A NUCLEAR FACILITY[J]. 2011.

[17] Fujita R, Enda M, Morisue T. REDOX Decontamination Technique Development, (I)[J]. Journal of Nuclear Science and Technology, 2012.