

## Advances in Chemical Decontamination Processes for Nuclear Power Plants

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### Abstract

Reactor structural materials at high temperatures and pressures in prolonged contact with the coolant will produce corrosion products, which are deposited on the surface of the equipment metals and can cause adverse effects such as reduced heat transfer efficiency, axial power migration and locally high radiation fields. The main in-service chemical decontamination processes currently used in engineering are HP/CORD, CANDEREM™, CITROX, LOMI, EMMAC, SP-HyBRID and Ce(IV), and decommissioning decontamination processes are DfD, ASDOC\_D and MEDOC. This paper provides an overview of the current research status and engineering applications of several typical in-service and decommissioning chemical decontamination processes, and provides indicative suggestions for subsequent research on decontamination technologies.

### Keywords

Chemical Decontamination Method; CRUD; In-service Chemical Decontamination; Decommissioning Decontamination.

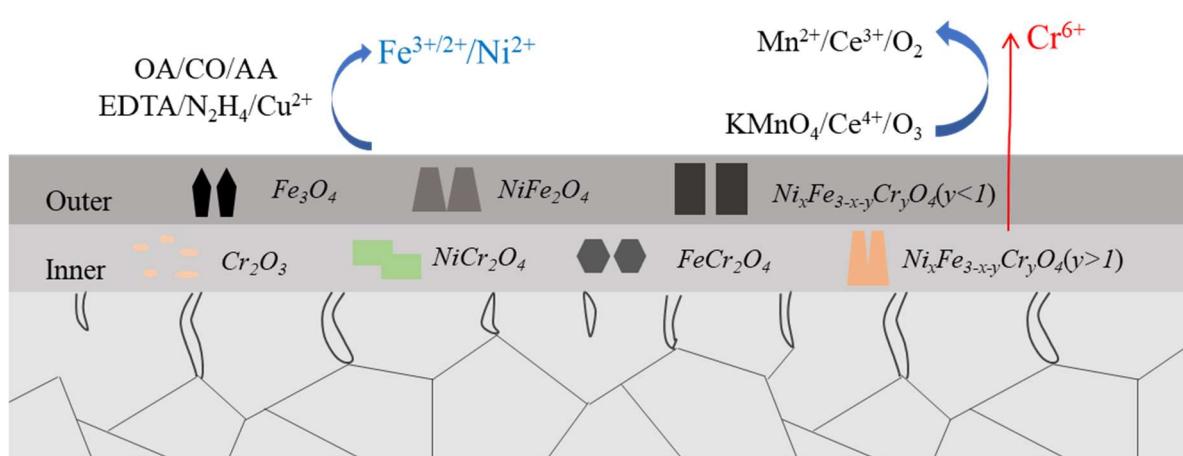


Fig. 1 Chemical decontamination mechanism

### 1. Introduction

During the operation of a nuclear power plant, the reactor structural material and the coolant will corrode in direct contact, forming a corrosion product, namely CRUD. These corrosion products accumulate for a long time and deposit in the steam generator heat transfer tubes, fuel cladding, and primary circuit pipelines, which will reduce the heat transfer efficiency of the equipment, increase

the flow resistance of the core, and may even cause partial flow channel blockage, causing serious accidents. When the corrosion products flow through the core, they may be activated by neutrons. The activated corrosion products pose a radiation threat to system maintenance and repair personnel and the surrounding environment. Decontamination of corrosion products is an important part of the safe operation of nuclear power plants, and it is also an indispensable first step during major maintenance[1]. Most nuclear power plants use chemical decontamination methods, which use the dissolution of chemical reagents to remove surface pollution. After decontamination, not only the amount of contamination on the surface of the equipment is greatly reduced, but also the accumulation of corrosion products in the equipment or system is reduced, the heat transfer efficiency of the equipment is improved, and the safety and stability of the operation of nuclear power plants are guaranteed.

The currently developed in-service chemical decontamination processes include HP/CORD UV process, CAN-DEREM™ process, CITROX process, etc. and decommissioning decontamination processes include DfD process, ASDOC\_D process and MEDOC process. These decontamination methods have high decontamination coefficients and are easy to operate, but they also generally have disadvantages such as long time-consuming and large amount of secondary waste liquid. For example, using the HP/CORD UV method to decontaminate 1 million kilowatt pressurized water reactor nuclear power plant produces approximately 900,000 gallons of waste water at a time, and the cost of treating these waste water accounts for more than half of the total decontamination cost. In the CANDU whole-system decontamination process, the secondary waste liquid produced by Picking 3/89 reactor is processed, and the volume of ion exchange resin used reaches 51 m<sup>3</sup>[2]. Therefore, various countries have recently developed new decontamination methods such as foam method, gel method, peelable film method and chemical decontamination reagent combined decontamination method. It is expected that while obtaining good decontamination effects, it can simplify the decontamination process and reduce secondary waste liquid produced. This article summarizes, contrasts and analyzes several representative decontamination processes of in-service and decommissioned chemical decontamination processes, and provides reference opinions on the further development and optimization of each decontamination process.

## 2. Decontamination Object

### 2.1 Activation Corrosion Products

The primary circuit activation corrosion products of nuclear power plants originate from the feed water of the primary circuit coolant and corrosion products introduced by boron, impurities introduced by chemical additives and corrosion of system structural materials[3]. With the increase in the life of nuclear power plants, compared with the former two, the corrosion contribution of primary circuit structural materials is relatively large. In the primary circuit system, the fuel cladding material is mainly zirconium alloy, which produces relatively few corrosion products. Corrosion products come from stainless steel and nickel-based alloys in the pipelines outside the core and steam generators[4]. The main activated corrosion products include  $^{58}\text{Co}$ ,  $^{60}\text{Co}$ ,  $^{51}\text{Cr}$ ,  $^{110}\text{mAg}$ , etc. Among them,  $^{58}\text{Co}$  and  $^{60}\text{Co}$  are the two nuclides with the largest contribution to the surface dose rate of the primary circuit system, and the dose rate contribution of the two nuclides accounts for 90%[5].

### 2.2 Chemical form

Primary circuit pipelines, pressure vessels, steam generator heat transfer tubes and other structural materials undergo processes such as dissolution, migration, activation and deposition after erosion and corrosion, forming activated corrosion products. The corrosion products mainly include nickel, iron, and chromium oxides, and a small amount of manganese. And trace amounts of cobalt. The activated corrosion products flow with the coolant in the primary circuit and deposit on the surface of the primary circuit system outside the cladding and core of the fuel element. In the high temperature, high pressure, low dissolved oxygen environment, the surface of stainless steel and nickel-based alloy

in the primary circuit system will form a double-layer structure of oxide film. The inner oxide film has a relatively high chromium content, is thinner and has a continuous spinel structure. The main components are  $\text{Ni}_{x}\text{Fe}_{3-x}\text{y}\text{Cr}_{\text{y}}\text{O}_4$  ( $y > 1$ ),  $\text{FeCr}_2\text{O}_4$ ,  $\text{NiCr}_2\text{O}_4$  and  $\text{Cr}_2\text{O}_3$ , the outer oxide film has a higher content of nickel and iron. It is composed of larger grains and looser structure. The main components are  $\text{Fe}_3\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$  and  $\text{Ni}_{x}\text{Fe}_{3-x}\text{y}\text{Cr}_{\text{y}}\text{O}_4$  ( $y < 1$ ) [6-7]. Due to the different generation rates of crystal grains, the outer oxide film presents an irregular shape. The inner oxide film contains  $\text{Cr}^{3+}$ , and the dissolution rate is relatively slow. In the chemical decontamination process, oxidants such as  $\text{KMnO}_4$ ,  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  are usually used to oxidize  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ , which destroys the structure of the inner oxide film, and then use organic acids such as oxalic acid, citric acid, EDTA and ascorbic acid and chelating agents to form water-soluble Sex chelate [8].

### 2.3 The Impact of Corrosion Products on the Operation of Nuclear Power Plants

The main effects of corrosion products on the operation of nuclear power plants include Axial offset anomaly, Acceleration of Localized Corrosion and Out-of-Core Radiation Fields [9]. Abnormal axial power deviation is a phenomenon that occurs due to the evaporation and deposition of materials on the fuel cladding. Since the sediment can incorporate boron into the structure, the neutron flux of the fuel and the output of the fuel rod at the position of the sediment are suppressed, which leads to a reduction in the overall power output of the power plant. The loose structure formed by the corrosion products provides conditions for the accumulation of corrosive substances such as lithium hydroxide and boric acid, which can corrode the alloy under high concentration and high temperature conditions, leading to accelerated local corrosion.  $^{60}\text{Co}$  is the main contributor to the dose rate of nuclear power plant workers. It can accumulate in the loose structure of the outer layer of corrosion products to form a local radiation field, which poses a radiation threat to the maintenance and repair personnel of the nuclear power plant system and the surrounding environment.

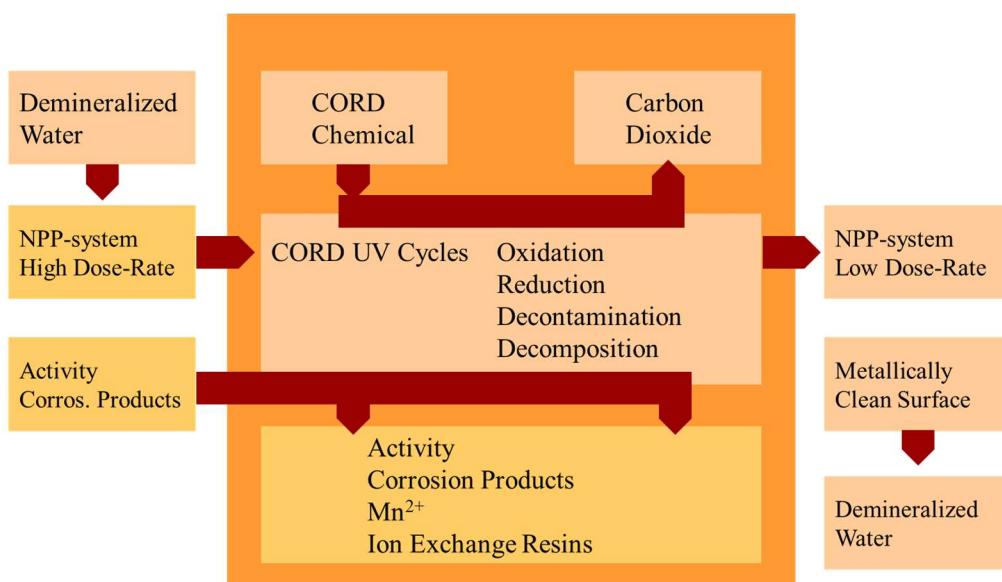
## 3. In-service Chemical Decontamination Process

The in-service chemical decontamination process requires a high decontamination factor, little impact on matrix metal corrosion damage, easy disposal of secondary waste liquid waste, low dose of decontamination personnel, and low secondary radioactive waste.

### 3.1 HP/CORD Process

The HP/CORD (Permanganic Acid/Chemical Oxidation Reduction Decontamination) process was developed by Siemens in Germany in the mid-1980s. It uses permanganic acid and oxalic acid for in-service decontamination of pressurized water reactors. Due to the corrosion of the base metal during the decontamination process, countries such as France, South Korea, and Japan have improved the process. The French company Areva Framatome developed the HP/CORD UV process [10]. The schematic diagram of the process is shown in Fig. 2. It includes four processes of oxidation, reduction, decontamination and decomposition. First, 200 mg/L  $\text{HMnO}_4$  is used to oxidize  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ , then use 2000 mg/L oxalic acid to reduce the excess  $\text{HMnO}_4$  to  $\text{Mn}^{2+}$  reduction, and dissolve the corrosion products, and then use ultraviolet light and  $\text{H}_2\text{O}_2$  to decompose the excess oxalic acid into  $\text{H}_2\text{O}$  and  $\text{CO}_2$ . South Korea [11] adopted 0.05%  $\text{KMnO}_4$  + 0.025% phosphoric acid as the oxidation formula, replaced oxalic acid with hydrogen peroxide and activated carbon as the reduction formula, and added 0.5% EDTA and 0.2% oxalic acid during the dissolution process. The decontamination formula used in Japan [12] is 500 mg/L  $\text{KMnO}_4$ , 200 mg/L oxalic acid and hydrazine. In addition to improving the HP/CORD decontamination process, the main decontamination components in the process, such as AP (alkaline permanganate), NP (nitric acid and potassium permanganate, acid potassium permanganate), and oxalic acid, are used to improve the metal. The damage of the matrix has also been extensively studied. For example, Cui [13] carried out AP (0.25%  $\text{NaOH}$  + 0.25%  $\text{KMnO}_4$ ) + 0.25% oxalic acid and 0.25% citric acid decontamination experiments on stainless steel. The damage is within the relevant standards. Tian [14] used AP (0.4 g/L  $\text{NaOH}$  + 1 g/L  $\text{KMnO}_4$ ) to carry out a cyclic decontamination study on the oxidized 304L stainless steel test piece, and the results showed that the oxide on the surface of the stainless steel can be removed after two cycles. And there

is no obvious damage to the base metal. Liu[15] used NP (1.5 g/L HNO<sub>3</sub>+1.5 g/L KMnO<sub>4</sub>)+1.5 g/L oxalic acid and 1.5 g/L citric acid to conduct corrosion tests on stainless steel 1Cr8Ni9Ti and Inconel-690 alloys, and the results showed that the formula The oxide layer on the metal surface can be removed without causing structural damage to the substrate, but there is pitting corrosion. Wu[16] used the combined ultrasonic and chemical decontamination process to decontaminate the complex components of the PWR nuclear power plant and found that the decontamination coefficient can reach 1750. Other studies have shown that the corrosion depth of ultrasonic + chemical decontamination on the surface of stainless steel workpieces is 46.1 nm, which meets the corrosion depth requirements of nuclear power plant decontamination processes[17]. Because the HP/CORD process has a high decontamination ability, in recent years, its improvement has also focused on reducing the damage of chemical decontamination reagents to the metal matrix, by changing the concentration of chemical decontamination reagents or using methods such as ultrasound. Combined use and achieve a higher decontamination factor while reducing damage to the base metal.



**Fig. 2** HP/CORD UV decontamination process[10]

### 3.2 CAN-DEREM™ Process

In the 1960s, Atomic Energy of Canada Ltd. (AECL) in Canada developed the CAN-DECON™ (CANadian DECONTamination) decontamination process for CANDU piles. The formula is 2:1:1 ratio of EDTA, oxalic acid and citric acid, and the concentration is It is 0.1% ~ 0.2%[18]. In the mid-1980s, the CAN-DECON™ process was improved to CAN-DEREM™(CANadian Decontamination and REMediation). The detergent does not contain oxalic acid. The decontamination temperature is 85~120°C, and the pH value is 2.1 ~ 2.3. The time is 24 ~36 h[19]. The Point 2 pressurized water reactor in India used this process to carry out the whole system decontamination. Subsequently, AECL developed the CAN-DEREM Plus™ process. The decontamination formula is similar to CAN-DEREM™, but the concentration is much higher. It can be used to decontaminate the surface of a large area system. It has been used for the decontamination of the steam generator of the Pickering 1 reactor[18]. Different from HP/CORD decontamination process, CAN-DECON™, CAN-DEREM™ and CAN-DEREM Plus™ are reduction decontamination processes, which have poor removal effect on chromium-containing oxides, and the stainless steel surface is observed during the decontamination process Localized corrosion occurred, such as intergranular corrosion during the decontamination of the Peach Bottom 2 reactor[20]. In recent years, further improvements have been made to the CAN-DECON™ series of decontamination processes. The main improvement measures include removing the oxides in the steam generator by mechanical methods, adding ascorbic acid to

reduce Fe<sup>3+</sup> to reduce corrosion to the base metal, and decontamination with AP. Decontamination process combined with decontamination.

### 3.3 CITROX Process

The CITROX (CITRic and OXalic acids) process was developed by EPRI in the United States in the 1960s. It is used in the decontamination of Hanford and Shippingport reactors, and after improvement, it is used in the regeneration process of boiling water reactors and pressurized water reactors[21]. The process formula is 2.5% oxalic acid + 5% diammonium citrate + 2% iron nitrate or 0.1% diethyl thiourea, of which iron nitrate or diethyl thiourea acts as a corrosion inhibitor[22]. Due to the presence of chromium oxides in the corrosion products, AP or NP formulations need to be pre-oxidized[23]. The presence of oxalic acid in the CITROX process can induce intergranular corrosion of stainless steel. Therefore, some scholars have improved the decontamination formula. For example, Varga[24] used 10 g/L NaOH+5 g/L KMnO<sub>4</sub> as the oxidation formula, and 10 g/L oxalic acid and citric acid as the reduction formula. They found that the oxide layer can be removed after three cycles without damage to the metal substrate. Song[25] used 0.2 g/L HNO<sub>3</sub>+1.25 g/L KMnO<sub>4</sub> as the oxidizing formula and 2 g/L oxalic acid as the reducing formula. They carried out a cyclic decontamination study at 80°C and found that after 5 cycles of decontamination 304 stainless steel has no intergranular corrosion.

For the treatment methods of oxalic acid and citric acid in the secondary waste liquid, there are mainly chemical methods, physical methods and biological methods. The chemical method is to use Ca(OH)<sub>2</sub> as a neutralizer to pretreat oxalic acid and citric acid, and at the same time, it can also precipitate some radioactive metal ions in the solution[26]. The physical method is to use gamma rays to accelerate the degradation of citric acid and oxalic acid[27]. The biological method is to use anaerobic microorganisms to decompose citric acid under alkaline conditions. Studies have found that citrate can be completely degraded and removed from the solution under pH=10~11.7[28].

### 3.4 LOMI Process

The LOMI (Low Oxidation Metallic Ion) process is a decontamination process developed by the British Central Electricity Generating Board (CEBG) in the 1980s, and has been awarded by the Electric Power Research Institute (EPRI)[29]. The composition of the process formula is 2 ~ 4×10<sup>-3</sup> mol/L tris (picolinic acid) vanadium or vanadium picolinate, 1 ~ 2×10<sup>-3</sup> mol/L picolinic acid, 1 ~ 2×10<sup>-3</sup> mol/L formate[30]. V<sup>2+</sup> in vanadium picolinate can reduce Fe<sup>3+</sup> to Fe<sup>2+</sup>. Under low pH conditions, picolinic acid and Fe<sup>2+</sup> form a stable complex. The V<sup>2+</sup> in the detergent can also be regenerated. Lamaan[31] found that the V<sup>2+</sup> can be regenerated in a solution of vanadium sulfate, picolinic acid, and formate containing supersaturated N<sub>2</sub>O within the range of pH=4.2 ~ 6.3 . During the decontamination process of the Hungarian Paks reactor using the LOMI process, it was found that the corrosion products containing chromium were difficult to remove. Therefore, similar to the CITROX decontamination process, it is also necessary to use AP or NP formulations to remove the chromium-rich corrosion products through pre-oxidation. Perform LOMI decontamination[32]. Manjanna[33] found that AP+V(II)/picolinic acid and AP+V(II)/citric acid have better dissolution effects on chromium-containing oxides than AP+citric acid/oxalic acid.

### 3.5 EMMAC Process

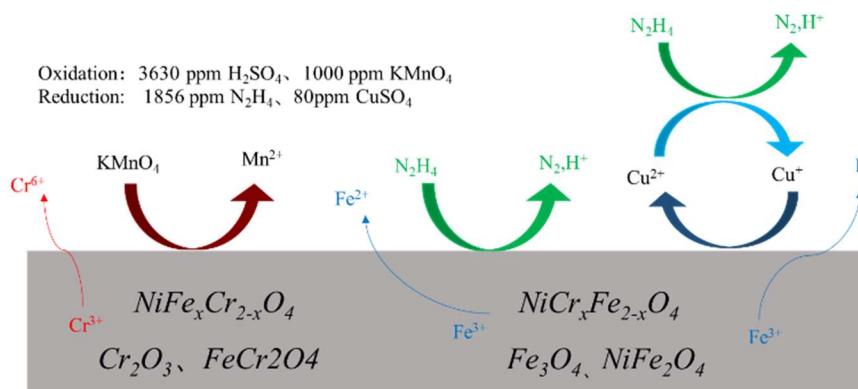
The EMMAC process was developed by the French Electric Power Company (EDF)[34], with 0.7 g/L ~ 1.0 g/L KMnO<sub>4</sub> and 0.8 g/L ~ 1.0 g/L HNO<sub>3</sub> as the oxidant formula, 0.7 g/L ~ 1.0 g/ L ascorbic acid and 0.8 g/L ~ 1.0 g/L HNO<sub>3</sub> are reducing agents. The EMMAC process affects the waste heat removal system of the Flamanville 1 nuclear power plant, the non-regenerative heat exchanger of the chemical capacity control system of the St Laurent des Eaux nuclear power plant, the waste heat removal system and chemical capacity control system of the Bugey 2 nuclear power plant, and two of the Westinghouse Belgian service center, see Table 1.

**Table 1.** EMMAg and EMMAC POA Decontamination process parameter[35]

Decontamination process	Process flow	Parameters	
	Oxidation process	1 g/L KMnO <sub>4</sub>	pH=2.5
		0.2 g/L HNO <sub>3</sub>	80°C, 1h
EMMAg	Nitric acid flushing	0.2 g/L HNO <sub>3</sub>	649
	Reduction process	1 g/L Ascorbic acid	pH=2.5
		0.2 g/L HNO <sub>3</sub>	80°C, 1h
	Deionized water		
	Oxidation process	1 g/L KMnO <sub>4</sub>	pH=12
		0.4 g/L NaOH	80°C, 8h
EMMAC POA	Reduction process	1 g/L Ascorbic acid	pH=1.8
		1 g/L HNO <sub>3</sub>	80°C, 4h
	Deionized water		

Since the loop contains equipment made of stainless steel, it cannot be decontaminated for a long time in a low pH environment. The EDF process was subsequently improved, and two processes, EMMAg and EMMAC POA, suitable for surface decontamination of stainless steel were developed. The concentration of nitric acid is reduced in the EMMAg process formula. The EMMAC POA process formula replaces nitric acid with sodium hydroxide. The specific process parameters are shown in Table 1. Since the detergent concentration is low, the amount of detergent needs to be increased to ensure a higher decontamination factor, which will greatly increase the amount of secondary waste liquid and waste resin.

### 3.6 SP-HyBIRD Process



**Fig. 3** SP-HyBIRD decontamination process[40]

The SP-HyBRID (Sulfuric acid Permanganate-Hydrazine Base Reductive metal Ion Decontamination) process was developed by the Korea Atomic Energy Research Institute. It is a two-step decontamination process with KMnO<sub>4</sub>+H<sub>2</sub>SO<sub>4</sub> as the oxidation formula and N<sub>2</sub>H<sub>4</sub>+CuSO<sub>4</sub> as the reduction formula[36]. The schematic diagram of its decontamination mechanism is shown in Fig. 3. KMnO<sub>4</sub> in sulfuric acid medium is used to remove chromium-containing oxides, hydrazine is used to decompose residual permanganate and dissolve corrosion products. Excess hydrazine, metal ions and sulfate are removed with hydrogen peroxide and barium hydroxide[37]. Experimental results show that the process has a good decontamination effect on samples obtained from the test loop of the HANARO research reactor in South Korea[38]. Compared with the HP/CORD-UV process, the

SP-HyBIRD process has the same decontamination effect, but the amount of waste can be reduced by 60%[39-40]. SP-HyBIRD process does not use ion exchange resin, but a solid-liquid separation device needs to be designed. The process is still in the stage of theoretical verification in the laboratory and has not been applied in practical engineering.

### 3.7 Ce(IV) Process

The in-service chemical decontamination process requires a high decontamination factor, little impact on matrix metal corrosion damage, easy disposal of secondary waste liquid waste, low dose of decontamination personnel, and low secondary radioactive waste.

**Table 2.** Research status of Ce(IV) Ozone Regeneration and Electrochemical Regeneration

Regener- ation	Experimental parameters					Ref
	T °C	C <sub>(Ce<sup>3+</sup>)</sub> mol/L	C <sub>(H<sup>+</sup>)</sub> mol/L	Ozone flow rate g/h or mL/min	Ce conversion rate%	
ozone regenerat ion	25	1.0	3.0	1000 mL/min	80	[47]
	25	0.05	1.0	1000 mL/min	90	[48]
	25	0.4	4.0	5 g/h	100	[49]
	25	0.1	8.0	1 g/h	>95	[50]
Electro- chemical regenerat ion	T °C	C <sub>(Ce<sup>3+</sup>)</sub> mol/L	C <sub>(H<sup>+</sup>)</sub> mol/L	Current density A/cm <sup>2</sup>	Ce conversion rate %	Ref
	23	0.51	2.0	0.11	99.7	[50]
	50	0.0092~0.2 6	0.5~4.0	5	92~97	[51]
	80	1.0	3.0	10	95	[52]
	25	0.2	4.0	0.05	64	[53]
	70	0.2	4.0	0.89	94	[54]
	40	0.39	4.0	0.89	81.4	[55]
	60	0.2	2.0	—	>80	[56-57]

Westinghouse began to conduct research on the decontamination process of cerium acid in the 1980s[41]. The decontamination formula used 0.3% ~ 5% cerium sulfate tetrahydrate, cerium hexasulfamate, cerium perchlorate hexahydrate or their mixtures. And 1% ~ 5% of inorganic acid. Ce(IV) can be recycled through electrolysis or ozone to reduce the generation of secondary waste. The decontamination process can be widely used in radioactive decontamination of metal surfaces, decontamination of reactor loops, decontamination of nuclear facilities before decommissioning, and decontamination of radioactive waste water[42]. The Swiss company Studsvik RadWaste has developed the SODP (Strong Ozone Decontamination Process) decontamination process. The detergent formula is nitric acid, cerium nitrate and ozone, and the nitric acid concentration and cerium ions used are relatively high. Studies have found that this process has a good decontamination effect on Inconel-600 and stainless steel test pieces in the Swiss Ringhals 3 reactor, the American Keewaunee reactor and the French Cruas 1 and Gravelines 1 reactor[43]. Compared with other decontamination processes, the solidified waste produced by the SODP process is small in size, and the treatment of secondary waste is more efficient, fast and simple[44]. Japan has developed the REDOX (REduction-Oxidation) decontamination process, and the decontamination agent is formulated with cerium sulfate and sulfuric acid. Ce<sup>4+</sup> is used as an oxidant to oxidize some of the

corrosion products, and Ce<sup>3+</sup> can be oxidized to Ce<sup>4+</sup> by electrolysis, thereby achieving the regeneration of Ce<sup>4+</sup> and greatly reducing the amount of secondary waste generated[45]. The REDOX decontamination process is similar to SODP, but its working temperature is higher, ranging from 60°C to 80°C, and the regeneration of Ce<sup>4+</sup> is achieved through a more efficient electrochemical method[46].

At present, the proposed regeneration methods of tetravalent cerium mainly include ozone regeneration and electrochemical regeneration. Table 2 lists some experimental results on Ce(IV) regeneration in recent years, see Table 2.

The main factors affecting ozone regeneration are Ce<sup>3+</sup> concentration, ozone flow rate, acidity and temperature. The results of Chung[47] showed that at 25°C, the ozone flow rate was 1000 mL/min, the Ce<sup>3+</sup> concentration was 0.05 mol/L, the acidity was 1.0 mol/L, and the conversion rate of tetravalent cerium reached 90%. Pan[58] used a batch bubbling reactor to explore the effect of temperature on ozone regeneration Ce(IV), established a reaction kinetic model, and fitted the relationship between the reaction rate constant and temperature  $k=733585.9\exp(-39257.1/RT)$ . Xie[59] used the CFD simulation method to optimize the conversion rate of ozone regeneration Ce(IV) in the SK and SMV static mixers. The results showed that the Ce<sup>3+</sup> concentration was 0.04 mol/L ~ 0.12 mol/ L, the conversion rate reaches 100%.

The tetravalent cerium electrochemical regeneration device is more complex than the ozone regeneration device. The anode electrode material in the device mainly includes the mesh titanium electrode[51-52] and platinum electrode[53-54] plated with IrO<sub>2</sub>. The cathode material mainly includes Stainless steel[51], mesh titanium electrode[52], Ag/AgCl electrode[53] platinum electrode[54]. Guo[56] found out. The surface of titanium electrode is plated with elements such as iridium and tantalum to improve the life of the electrode. The area ratio of cathode to anode can be 1:1, 1:2.25 or 1:20, and it needs to be designed according to specific requirements. The main types of ionic membranes are Nafion-324 series[51], Nafion-117, Nafion-212[54], perfluorosulfonic acid cation membrane Nepem-117, reinforced perfluorosulfonic acid cation membrane Nepem-417, high temperature resistance selectivity Anion membrane AHO and electrodialysis anion membrane CJ-EDA200[57]. Guo[57] found that the enhanced perfluorosulfonic acid ion membrane has excellent performance and is suitable for electrochemical regeneration of tetravalent cerium. Raju[51] studied the regeneration of tetravalent cerium using titanium mesh electrode as anode, stainless steel as cathode, an area ratio of anode to anode of 1:1, and Nafion324 as an ion-exchange membrane electrochemical device. The results showed that the temperature was 50°C, the Ce<sup>3+</sup> concentration was 0.0092 mol/L ~ 0.26 mol/L, the nitric acid concentration was 0.5 mol/L ~ 4.0 mol/L, and the conversion rate of tetravalent cerium reached 92% ~ 97%. The electrochemical regeneration efficiency is high, and the regeneration efficiency of tetravalent cerium is high, but it is still in the laboratory research stage and has not yet been applied in engineering.

Although Ce(IV) can be regenerated after decontamination, a certain amount of secondary waste liquid will inevitably be produced. The waste liquid contains residual Ce<sup>4+</sup>, which will cause corrosion to the waste liquid storage system. In addition, the waste liquid also contains a certain amount of NH<sub>4</sub><sup>+</sup> ions. Zhang[60], Liu[61] and others proposed that H<sub>2</sub>O<sub>2</sub> can be added to the secondary waste liquid after Ce(IV) decontamination to reduce Ce<sup>4+</sup> to reduce corrosion of the equipment. NH<sub>3</sub> can be effectively removed by heating and boiling. The ozone oxidation treatment process effectively destroys the organic matter in the decomposed waste liquid. Li[62] studied the immersion corrosion experiment of Ce<sup>3+</sup> in the secondary waste liquid on materials such as brass, A3 steel and stainless steel. The results showed that the corrosion of cerium-containing waste liquid on stainless steel and carbon steel at high or normal temperature It is less resistant, but more corrosive to brass.

In recent years, in order to further reduce the generation of secondary waste liquid in the Ce(IV) decontamination process, and at the same time improve the decontamination efficiency of Ce(IV), researchers have proposed Ce(IV)+foam decontamination[63-66], Ce(IV)+gel decontamination [67-

70], Ce(IV)+ultrasonic decontamination[80] and other collaborative decontamination technologies. Compared with Ce(IV) decontamination, Ce(IV)+foam decontamination and Ce(IV)+gel decontamination can obtain a considerable decontamination coefficient while greatly reducing the amount of secondary waste. Ce(IV)+ultrasonic decontamination can not only increase the decontamination coefficient, but also shorten the decontamination time.

#### 4. Decommissioning Chemical Decontamination Technology

The service chemical decontamination process focuses on reducing the radioactive dose rate on the surface, reducing the amount of secondary waste liquid, and reducing the dose damage to maintenance and operators.

##### 4.1 DfD Process

DfD (Decontamination for Decommissioning) process is a decontamination process for decommissioning reactor coolant systems developed by EPRI and Bradtec in 1996[74]. The decontamination formula mainly uses a diluted solution of 0.088% fluoroboric acid, and KMnO<sub>4</sub> and oxalic acid are added during the decontamination process[75]. This process has been applied to the decontamination of the Big Rock Point and Maine Yankee reactors in the United States and the Zorita reactor in Spain. EPRI developed the DfDX process on the basis of the DfD process, which introduces an electrochemical ion exchange cell, which can greatly reduce the amount of secondary waste such as ion exchange resin[76].

##### 4.2 ASDOC\_D Process

The German Siempelkang NIS engineering company has developed a decommissioned chemical decontamination process, the ASDOC\_D cyclic decontamination process[77]. Using 100 mg/L or lower concentration of methanesulfonic acid, potassium permanganate and oxalic acid as the decontamination formula, the decontamination can be recycled 15 to 20 times. The schematic diagram of the process flow is shown in Fig. 4. The detergent enters the primary circuit system through the reactor feeding device. After the reactor operation system is started, the detergent circulates in the primary circuit, and the decontaminated ions are discharged through the reactor ion exchange purification system[78]. The decontamination process can be accurately detected and controlled to achieve the decontamination effect while reducing the generation of secondary waste. However, ion exchange resins are still needed in the process, and further research is needed for the disposal and regeneration of ion exchange resins.

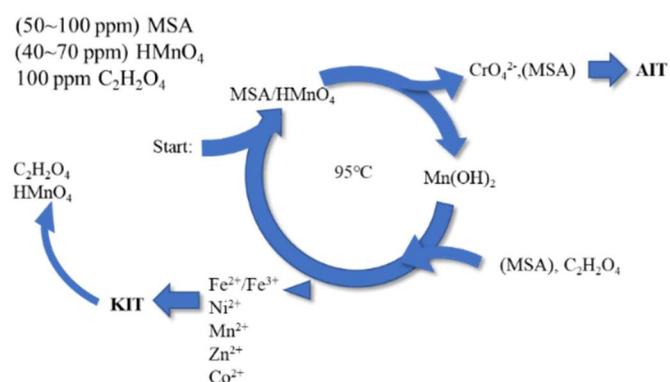
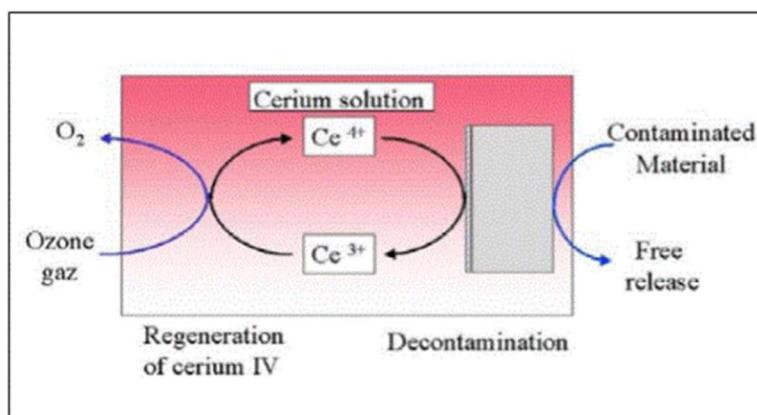


Fig. 4 ASDOC\_D Circulating decontamination process[78]

##### 4.3 MEDOC Process

In the late 1990s, the Belgian SCK•CEN company developed the MEDOC (Metal Decontamination by Oxidation with Cerium) decontamination process. The schematic diagram of the process is shown in Fig. 5. It was applied to the decontamination of the Belgian Reactor 3 nuclear power plant in 1999. The decontamination formula is tetravalent cerium + sulfuric acid, which is the same as the SODP

decontamination process, and uses ozone to realize the regeneration of tetravalent cerium[79]. After decontamination by this process, the activity of the surface of the material is less than 0.1 Bq/g, and the decontamination factor for  $^{137}\text{Cs}$  can reach more than 10,000[47]. Through ozone oxidation, the regeneration and recycling of tetravalent cerium is realized, which improves the utilization rate of chemical decontamination reagents and reduces the generation of secondary waste.



**Fig. 5** MEDOC decontamination process[79]

**Table 3.** Three Scheme comparing

Chemical decontamination process	Reagent	Advantages	Disadvantages
In-service decontamination	HP/CORD-UV	HMnO <sub>4</sub> C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	High decontamination factor
	CAN-DEREM	AP+EDTA/ Citric acid	Weak matrix corrosion resin secondary waste
	AP-CITROX	HMnO <sub>4</sub> C <sub>2</sub> H <sub>2</sub> O <sub>4</sub> / Citric acid	High decontamination factor Intergranular corrosion secondary waste liquid
	AP-LOMI	AP+V <sup>2+</sup> Picolinic/Formic	High decontamination factor secondary waste liquid resin secondary waste
	EMMAC	AP/NP ascorbic acid	Secondary waste liquid can be processed Limited decontamination factor
	SP-HyBRID	H <sub>2</sub> SO <sub>4</sub> +KMnO <sub>4</sub> N <sub>2</sub> H <sub>4</sub> +CuSO <sub>4</sub>	Low ion exchange resin consumption Generate a lot of solid waste
	Ce(IV)	Ce(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O Ce(ClO <sub>4</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	Less secondary waste generated ozone or electrochemical methods to regenerate Ce <sup>4+</sup>
Decommissioning and decontamination	DfD	HBF <sub>4</sub> +KMnO <sub>4</sub> C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	High decontamination factor secondary waste liquid resin secondary waste
	ASDOC_D	MSA+KMnO <sub>4</sub> C <sub>2</sub> H <sub>2</sub> O <sub>4</sub>	Low concentration resin secondary waste
	MEDOC	Ce <sup>4+</sup> +HNO <sub>3</sub> O <sub>3</sub>	High decontamination factor ozone or electrochemical methods to regenerate Ce <sup>4+</sup>

Table 3 analyzes and compares a variety of typical chemical decontamination processes. It can be seen from the table that most processes use two steps of oxidation and reduction for decontamination. The oxidation formula is AP or NP, which is mainly used to oxidize Cr<sup>3+</sup> in corrosion products to

Cr<sup>6+</sup>, and the reduction formula is organic such as EDTA, oxalic acid and citric acid. The combination of chelate and organic acid mainly dissolves, complexes and removes corrosion products containing iron and nickel. The two-step method has a high decontamination coefficient, but sometimes it will corrode the base metal and produce a large amount of secondary waste liquid at the same time. Ce(IV) decontamination is one of the few one-step decontamination processes. Ce(IV) has a good decontamination effect as an oxidant. Since Ce(IV) can be regenerated by ozone or electrochemical methods, the secondary waste is greatly reduced. quantity. See Table 3.

## 5. Conclusions and Recommendations

This article summarizes and analyzes the in-service and decommissioned chemical decontamination processes, and compares and analyzes the decontamination processes. The in-service chemical decontamination process focuses on high decontamination factors, low metal matrix damage and low secondary waste, while the decommissioned chemical decontamination process focuses on reducing the surface radioactive dose rate and low secondary waste. As well as low personnel dose rate absorption, etc.

The two-step chemical decontamination process has a good decontamination effect and has accumulated many years of operating experience, but it produces a large amount of secondary waste liquid, which will also cause local corrosion to some metal substrates. Ce(IV) decontamination process is a one-step chemical decontamination process with good decontamination effect and low secondary waste liquid. It has potential application prospects in the field of nuclear power plant decontamination, such as foam decontamination, gel decontamination, and ultrasonic decontamination. Combine decontamination methods with Ce(IV) method to obtain better decontamination effect.

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