

NPOX DECONTAMINATION SYSTEM

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ABSTRACT

The nitric acid/potassium permanganate/oxalic acid (NPOx) Phase II system is being prepared for remote operation at the Idaho National Engineering and Environmental Laboratory (INEEL). Several tests have been conducted to prepare the system for remote operation. This system performs very well with high decontamination efficiencies and very low quantities of waste generated during decontamination.

INTRODUCTION

The NPOx Phase II system is a remotely operated decontamination process that uses small amounts of chemicals in conjunction with an ultrasonic bath to decontaminate metal items. The NPOx system is an INEEL adaptation of the Siemens' permanganic acid (HP)/ complexing organic reduction decontamination (CORD) system; which is a novel, low waste, highly efficient system for decontamination. The NPOx system uses more common chemicals in a combination of decontamination processes to affect decontamination. After decontamination is complete, the chemicals are treated, and the contaminants are transferred to an ion exchange resin, leaving low level radioactive water that is ready to be used again in another decontamination cycle. Tests of the computer control, ultrasonic and chemical, and the ultraviolet (UV) oxidation systems have been performed to demonstrate their operability for deployment into radioactive service. A previous process, the NPOx phase I system, was deployed in 2001, with very good decontamination results.

NPOx System Development

The NPOx decontamination process is similar to the Siemens' HP/CORD UV process and combines several non-proprietary processes that use multiple steps and chemicals to remove radionuclides from metal surfaces. The process involves multiple steps that accomplish the surface decontamination through the successive oxidation, complexation, solubilization, and separation of the radionuclides, along with other ancillary steps to make the process continual and destroy or otherwise treat the waste solutions. This process is a hybrid of many decontamination processes that use nitric acid, potassium permanganate, oxalic acid, ion-exchange resins, and ultraviolet light with hydrogen peroxide to achieve the desired decontamination, removal of the radionuclides from solution, and destruction of the remaining solution components.

The process begins by exposing a contaminated stainless steel (SS) surface to an aqueous nitric acid/potassium permanganate solution. The nitric acid and potassium permanganate are mixed in equal molar concentrations and introduced into the cleaning system in sufficient quantity to result in a nominal 200 ppm KMnO_4 solution with a resulting pH of approximately 2. This solution rapidly oxidizes the surface of the SS part to be decontaminated. Ultrasound and/or heating are desirable to increase the rate of surface oxidation. At this point in the process, the surface metals are oxidized and many are soluble to some extent. The oxidized metals are dissolved and removed by the addition of oxalic acid to the solution. The oxalic acid complexes the low

solubility metal hydroxy-oxides and makes them soluble. After the metals are dissolved, they are swept through the system and captured on a cation-exchange column.

There are numerous reactions that oxalic acid participates in, so it is necessary to control its concentration to achieve the desired result. Excess permanganate in the system without excess oxalic acid will result in the formation of MnO_2 precipitate that will potentially absorb other metal species, plug system hardware, and deplete the solution of oxalic acid needed to solubilize the scale on the parts to be decontaminated. With excess oxalic acid, the MnO_2 dissolves alleviating some of the aforementioned problems; however, the metal solubility increases making it more difficult to remove them in the cation-exchange columns. Alternatively, the oxalic acid is destroyed *in situ* by one of two methods. Permanganate may be added to destroy the oxalic acid after the oxalic acid has had sufficient time to dissolve the scale. Another method for the oxidization of oxalic acid is the use of ultraviolet. This operation uses peroxide, or peroxide and an iron catalyst, to destroy the oxalic acid.

After understanding the nature of the process and the different steps, it becomes clear that many hybrid or similar processes can be considered. For example, the oxidation step can be conducted using any of several strong oxidizing compounds, mixtures of strong oxidizing compounds, or electrochemical methods. Nitric acid/potassium permanganate solutions were used in this process; however, perchloric acid, nitric acid/potassium periodate, or permanganic acid solutions could just as easily have been used. The Siemens' process uses permanganic acid, which avoids the introduction of potassium or other non-essential metal ions into the system. Permanganic acid was not used in the INEEL system because of economic and safety concerns. Similarly, oxalic acid is only one of several organic acids that could be used. Tartaric acid and citric acid are two others that could work well.

The phase I system was manually controlled and did not make use of the UV oxidation technology during its deployment. The deployment of this system was conducted in the New Waste Calcination Facility Decontamination Cubicle. The NPOx system itself consists of a 5-L ultrasonic bath, an anion and cation exchange column on a movable cart. An average decontamination factor of 22 (95%) was achieved during its short deployment on radioactively contaminated items. This system is small and does not have nearly as powerful an ultrasonic bath as next year's deployment system. It is expected that even better results may be achieved with the phase II system. This system also achieved 97% less waste loading (compared to standard INEEL decontamination procedures) during the deployment, which used a potassium permanganate oxidation of oxalic acid. The phase II system should exceed this because of the better UV oxidation technology.

NPOx System

The NPOx phase II system is remotely operated to shorten the time personnel spend in a radioactive environment to decontaminate items. The system is constructed of stainless steel tubing, a diaphragm pump, an ultrasonic bath, electric heaters, a UV light, resin columns, chemical metering pumps, and an on-line monitoring instrumentation for temperature, thermal conductivity, flow rate and pH. It uses approximately 17 gallons of demineralized water and small amounts of nitric acid / potassium permanganate / oxalic acid and hydrogen peroxide. It is a closed, recirculating process that uses resin columns and a UV light to clean the liquid stream after the decontamination process is complete. The resin columns collect the metals and radioisotopes that are in the liquid stream. The UV light, in combination with hydrogen peroxide, oxidizes the organics that are present in the liquid stream. When the process is complete,

relatively clean water remains in the system, which is reused. The resin columns may be used until the radiation levels are too high or the resins have reached a calculated lifespan.

NPOx Hardware

The NPOx phase II system is a mobile system consisting of three 5 feet L x 3 feet H x 2 feet W metal carts. A diagram of this system is shown in Figure 1. The separate pieces of the system are connected with stainless steel tubing. The equipment that is attached to these carts is as follows:

- 2- Cimarec Hot Plates
- 3- Pulsatron Series MP Electronic Metering Pumps
- 2-Worcester Series 75 electric valve actuators
- 1-ThermoOrion 4 cell conductivity electrode
- 8-Worcester Series 36 electric valve actuators
- 1-ThermoOrion Ross Combination pH electrode with BNC connection
- 1-ARO 35 gpm Diaphragm Pump
- 1-Hanovia 2.5 kW UV light
- 2-Semetrics in-line flow meters
- 1-2 feet L x 1 feet H x 1.5 feet W stainless steel bath
- 2-Resin Columns

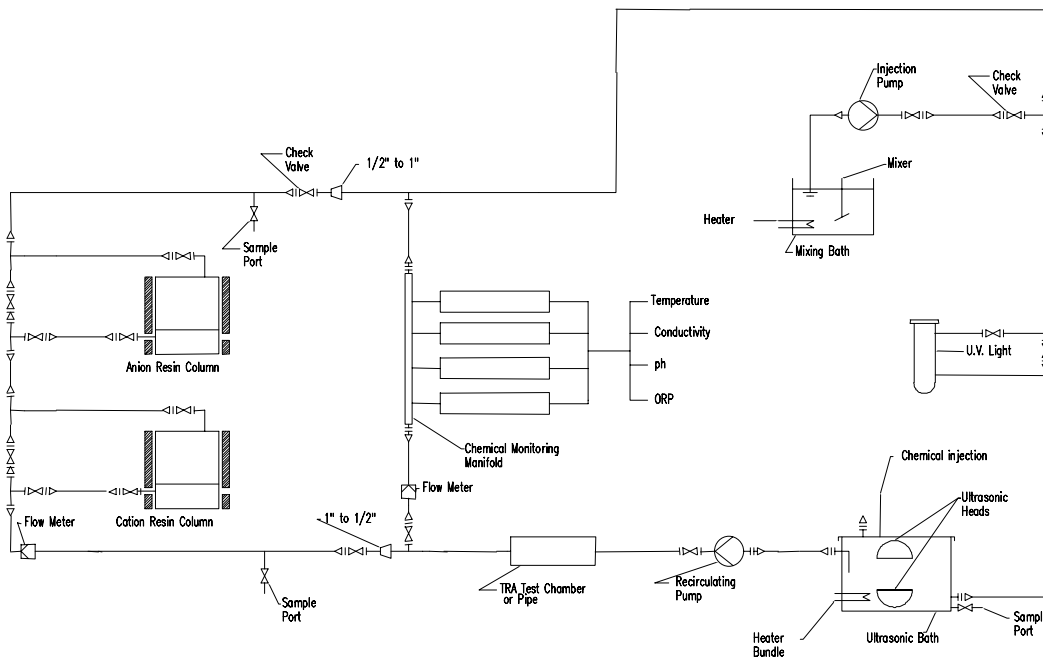


Fig. 1, Diagram of the NPOx Phase II Decontamination System

NPOx Control System

The NPOx control system utilizes a control program written with National Instruments "LabView 6I" software. The program is separated into two sections, continual monitoring and sequential operations. The continual monitoring section displays system parameters on the computer screen as long as the program is running. The sequential operations are a set of functions that run at specific times, for a specified duration, during the decontamination operation when triggered by

an event. The sequential operations are triggered when one of the monitored parameters reaches a specific setpoint or by initiating them manually with the computer.

The continual monitoring function graphs the process fluid temperature, pH, conductivity, flow rates, and measures the UV spectrometer intensity at a wavelength of 530 nm. These readings are taken continually during the process and interact with the sequential operation portion of the control program.

The sequential operation controls the equipment and includes the following cycles: 1) system set-up, 2) heating the system, 2) potassium permanganate cycle, 3) oxalic acid cycle, 4) UV destruction, and 5) solution clean up. Each of these cycles will be discussed in more detail below.

The first step in all the sequential cycles is to align the valves and set required flow rates. This allows for proper operation during any individual cycle. (i.e. prevents the system from over pressuring, ensures that no solution will flow through the ion exchange columns until after the potassium permanganate is destroyed to prevent the nitric acid/potassium permanganate solution from damaging the ion exchange resins, etc.).

The heating cycle heats the system to process temperature using two hot plates. The cycle will turn the heaters on while maintaining a flow rate of 10 gpm. When the process fluid reaches the desired temperature, the potassium permanganate cycle is initiated.

The potassium permanganate cycle oxidizes the metal surface of the decon article. A 0.25M potassium permanganate solution is injected into the system using a metering pump for 60 sec. at 0.04 gpm (2.53 ml/sec) to obtain a permanganate concentration of 200 mg/l. Potassium permanganate is injected into the system intermittently to maintain a 200 ± 50 mg/l permanganate concentration. The oxalic acid cycle starts when the system has been able to maintain the 200 ± 50 mg/l permanganate concentration for five minutes.

The oxalic acid cycle, accomplishes two things. First enough oxalic acid is added to terminate the oxidation step by conversion of the permanganate to manganese dioxide. Then, additional oxalic acid is added until the concentration reaches 2 g/l. The additional oxalic acid increases the dissolution of metal ions and enhances the removal of other, less soluble species and radionuclides from the surface. During this cycle, oxalic acid is injected into the system by running a metering pump for 5 min. at 0.04 gpm. The solution is allowed to circulate for five minutes to allow the oxalic acid to thoroughly mix. Then, the ultrasonic generator begins running in 15-min. intervals for two hours and a slipstream allowed to flow through the cation resin column. As the metal and radionuclide ions are transferred to the exchange resin, the oxalic acid is freed up to complex with other metal and radionuclide ions on the metal surface providing additional capacity for metal removal. After two hours, the UV destruction cycle begins.

The UV oxidation of the oxalic acid uses hydrogen peroxide and UV light to decompose the oxalic acid in the system. This cycle injects hydrogen peroxide into the system for 1 hour at a flow rate of 0.04 gpm. The solution is passed through a UV light where the combination of the hydrogen peroxide and the UV light energy decomposes the oxalic acid into carbon dioxide and water by photocatalytic wet oxidation. This cycle continues for 1 hour, after which the solution cleanup cycle will begin.

During the solution clean up cycle the solution passes through both cation and anion resin columns depositing the metal and radionuclide ions along with various anionic components. If the process solution is above 60 °C, the system will bypass the columns until the solution

temperature falls below 60 °C to prevent damage to the resin. The process solution will continue to flow through the columns at 0.4 gpm until the on-line conductivity reading falls below 10 us/cm. This ends the decontamination process.

NPOx Testing

Two separate tests were conducted with the NPOx process. The first test determined whether the available UV/H₂O₂ system would be effective in oxalic acid destruction. The second test actually used the system to decontaminate SIMCON II coupons. To demonstrate and verify the effectiveness of the UV/H₂O₂ process to decompose oxalic acid, a 2.5 KW medium pressure mercury UV reactor manufactured by Hanovia was installed in the NPOx system. The reactor volume is 14 liters and the total system volume (reactor plus ultrasonic bath and piping) is approximately 64 liters. In a typical run, the test unit was loaded with about 64 liters of DI water and oxalic acid added to a concentration of 2 g/l. The solution was then heated to 40°C and re-circulated through the UV reactor at 38 L/min. Optimization of the operating variables such as oxalic acid concentration, solution circulation rate, hydrogen peroxide feed rate was not performed. The pH was not adjusted during the test. The concentration of hydrogen peroxide in the solution was targeted for approximately 100 ppm. The UV lamp was turned on before H₂O₂ was added to the system. During this testing the system showed that the Total Organic Carbon (TOC) can be reduced from approximately 540 ppm to near zero concentration in 40 minutes when peroxide is used in conjunction with the UV light.

The SIMCON II coupons are stainless steel metal coupons with a coating of zirconium and cesium salts adhered to the metal surface through a high temperature baking process, which are used to simulate fixed contamination. The NPOx system was as effective or more effective at decontaminating SIMCON II coupons than other techniques that have been tested in the past as shown in Table 1. Test results also indicated that the use of heat and ultrasonics are needed to obtain optimal cleaning with ultrasonics being the primary factor. Use of the NPOx process without ultrasonics resulted in 95% removal of the cesium (Cs) and 80% removal of zirconium (Zr), which is much more effective than traditional decontamination methods employed in the decontamination of the INEEL reactor loops and the INTEC decontamination shop. Use of the NPOx system with ultrasonics resulted in 100% removal of both the Cs and Zr.

Table I. Decontamination comparisons.

Technique	Average % Removal	
	Cs	Zr
NPOx Tests 3 & 7 –w/ ultrasonic bath and heat	100%	100%
NPOx Test 5 – w/ heat, no ultrasonic bath	95%	80%
Hot Water	72%	17%
Abrasive Blasting	100 % ^a	100%
CO ₂ Pellet Blasting	81% ^a	100%
Alkaline Permanganate	60%	29%
Nitric/oxalic	50%	20%
Nitric Permanganate	60%	12%

a. (100 %) – Below Detectable Limits on Instrumentation

Conclusions

This NPOx phase II system will incorporate several improvements over the previous NPOx system. It is computer controlled for more accurate timing and more effective use of the chemicals. Its remote control system allows less operator exposure to chemical and radiological hazards. This larger system also has a more powerful ultrasonic bath for more effective decontamination. Lastly, this phase of the NPOx development incorporates the more efficient UV oxidation, rather than wet chemical oxidation with potassium permanganate. In addition to being a more effective decontamination system, it will generate less waste than the previous system.