NATIONAL DEMONSTRATION OF FULL REACTOR COOLANT SYSTEM (RCS) CHEMICAL DECONTAMINATION AT INDIAN POINT 2

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ABSTRACT

Key to the safe and efficient operation of the nation's civilian nuclear power plants is the performance of maintenance activities within regulations and guidelines for personnel radiation exposure. However, maintenance activities, often performed in areas of relatively high radiation fields, will increase as the nation's plants age. With the Nuclear Regulatory Commission (NRC) lowering the allowable radiation exposure to plant workers in 1994 and considering further reductions and regulations in the future, it is imperative that new techniques be developed and applied to reduce personnel exposure. Full primary system chemical decontamination technology offers the potential to be the single most effective method of maintaining workers' exposure "as low as reasonably achievable" (ALARA) while greatly reducing plant operation and maintenance (O&M) costs.

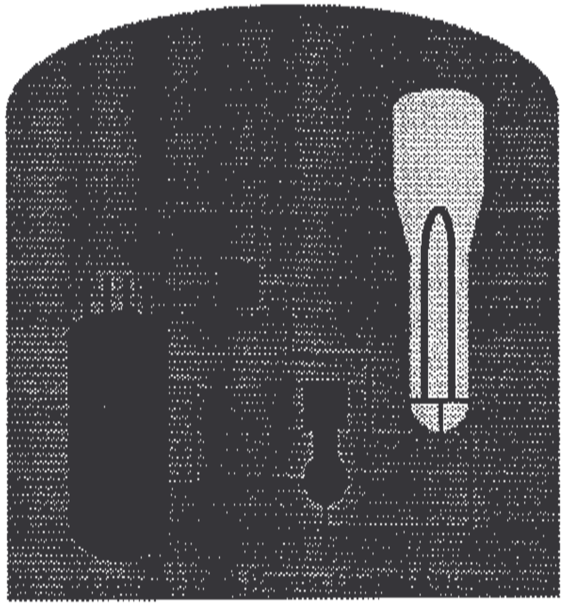
A three-phase program underway since 1987, has as its goal to demonstrate that full RCS decontamination is a viable technology to reduce general plant radiation levels without threatening the long term reliability and operability of a plant. This paper discusses research leading to and plans for a National Demonstration of Full RCS Chemical Decontamination at Indian Point 2 nuclear generating station in 1995.

BACKGROUND

The continued cost-effective operation of the 108 operating civilian nuclear power plants in the United States is an important part of our national energy strategy. To help implement this strategy, nuclear plant owners will need to reduce personnel exposure to radiation to the lowest level possible. In so doing, plant owners will improve the productivity of their work force and lower O&M costs for their plants. Thus far, the industry's aggressive radiation management programs have kept personnel exposure levels well within safe limits and, until recently, steadily reduced the average total exposure per plant, but, as nuclear plants age, maintenance and major equipment replacements can increase and contribute to increased collective exposure. Also, new governmental regulations have been issued that will reduce the allowable limits for an individual worker's annual exposure. The combination of the two factors could impair the cost-effectiveness of nuclear energy. Under these anticipated changes to the nuclear energy market, new methods to reduce personnel radiation exposure will likely be needed to maintain nuclear power as a commercially competitive option for the nation's current and future energy supply.

To deal with the twin problems of lower limits and increasing demand for personnel presence in radiation areas, the sources of radiation that contribute to personnel exposure must be reduced to the greatest extent practicable. While many approaches and technologies are being developed and implemented to address the problem, the decontamination of the entire primary system of a nuclear plant is the only method that offers the potential to reduce industry radiation exposure by an order of magnitude. Since 1975, Con Edison has been a leader in radiation management research and has had as a long-term goal the decontamination of the entire primary system at Indian Point 2, a pressurized water reactor (PWR) located in Buchanan, New York.

SOURCES OF PLANT RADIATION



Corrosion and wear products are found throughout the primary system of any nuclear power plant. In a PWR, the primary system is a separate loop called the reactor coolant system (RCS) (see Figure 1). These products circulate with the primary coolant, water, through the reactor vessel, where a small fraction become radioactive. A variety of radioisotopes are formed in this manner, but, for the most part, they are removed by filtration and demineralization in the chemical and volume control system (CVCS).

An oxide layer containing these activated products does form, however, on the surfaces of the RCS, including the fuel elements, CVCS, and other primary support systems.

The oxide layer of a PWR is a black spinel of primarily iron, chromium and nickel, formed in a slightly reducing chemistry with a pH less than 7.0. An analysis of the Indian Point 2 oxide layer shows that its composition is essentially:

$$(Ni_{1-x}Fe_x)\ (Cr_{1-y}Fe_y)_2O_4$$

with roughly 50% iron, 30% chromium and 20% nickel, although these may vary. Many radioisotopes of elements such as cobalt, manganese, zinc and antimony replace the iron, nickel and chrome, or otherwise become trapped, in the oxide layer matrix in small quantities. Two of the radioisotopes of cobalt (58 and 60) are typically the main contributors to the radiation fields in a PWR nuclear plant. The amount of radioactive material deposited on the different surfaces varies and depends primarily on the corrosion rate of the various plant materials, the chemistry of the primary water used as coolant, and the number of sources of cobalt. In a PWR plant, the oxide layer is rather tenacious, thereby making it difficult to remove the trapped radioisotopes from plant systems. As can be seen from table 1, it takes only a small degree of corrosion of base plant materials to create a significant radiation source on plant systems for long periods of time.

Table 1. Effect of Small Amounts of Radioactive Material

Average Cobalt in PWR	
Steam Generator Tubes	0.040%
1 Ounce	28.4 Grams
1 Gram of Cobalt 60	1,100 Curies
1 Curie of Cobalt 60	11 Rem/Hour at 3 Feet
Half-Life of Cobalt 60	5.2 Years
Personnel Exposure Limit	5 Rem/Year

As maintenance is performed on plant systems, personnel are exposed to radiation, primarily gamma, emitted from the radioactive material in the oxide layer. Radiation fields from the oxide layer increase with time from initial plant start up and level off after several years of plant operation.

Personnel exposure to radiation is highest during refueling outages, when routine maintenance is performed on such major plant components as steam generators and reactor coolant pumps. In fact, radiation fields from the steam generators are usually the largest single contributor to PWR personnel radiation exposure. The reason for this is that steam generators can require extensive maintenance and inspection, and the radiation fields inside the steam generator where this maintenance must be performed can be as high as 40 rem per hour.

DECONTAMINATION RESEARCH HISTORY

Because the PWR oxide layer is tenacious, mechanical methods are relatively ineffective at removing the oxide and trapped radioisotopes. Research has therefore focused on chemical decontamination processes that are effective at dissolving the oxide layer. When the oxide layer is dissolved, the radioisotopes are again returned to solution in the reactor coolant, where they can now be removed by filtration and demineralization. In the mid-1970s, with the support of the Department of Energy, Con Edison began research on ways to remove the radioactive material by dissolving the cobalt-containing primary system oxide layer.[1] This research effort is important from a historical basis in that it had a different objective than much of the chemical decontamination research, done prior to that time, which had focused on decommissioning. Unlike decontamination methods for decommissioning, where the post-decontamination plant equipment condition is a relatively minor concern, methods for operating reactors must not impact the life of the decontaminated equipment. The project identified some of the more important issues of PWR decontamination, while a the same time laying some of the ground work for future research programs. The issues identified include:

- The first plan of how to perform a chemical decontamination of a PWR primary system and be able to restart the plant,
- A comparison of various chemical techniques to perform an effective decontamination, and
- A screening study to conduct some limited material/chemical tests.

Concentrated chemical solvents, typically 1-10% in concentration, referred to as "hard" decontaminations, are often used for decommissioning. This early work led to a focus by researchers on dilute chemical solvents typically less than 0.5% in concentration, referred to as "soft" decontaminations, for operating reactors. Soft decontamination solvents are weak acids such as citric acid.

During the late 1970s and early 1980s, Con Edison and many organizations, including the Empire State Electric Energy Research Corp. (ESEERCO), conducted extensive research programs to investigate the compatibility of dilute chemical solvents with the materials used in nuclear plant systems. Con Edison's and ESEERCO's efforts[2,3] centered around the AP/Can-Derem[a] process, a modified version of a process originally developed by Atomic Energy of Canada, Limited (AECL) of Chalk River, Canada, for the heavy water CANDU reactors. The process, which will be used for the first full primary system decontamination, has been used many times for component decontaminations, which are characterized by the small volume of equipment to be cleaned. The reactor coolant system of a PWR is much larger in volume and scope than the typical component decontamination. The AP/Can-Derem process was selected because it has several advantages over other decontamination processes in that it produces less waste, can be easily controlled on a system as large as a reactor coolant system, is benign with regard to material corrosion and yet achieves high decontamination factors. Decontamination factor, the ratio of radiation fields before to after a decontamination, is the measure used in the industry to assess results. At the present time Vectra Technologies, Richland, Washington and Westinghouse Electric Corporation, Pittsburgh, Pennsylvania are two vendors licensed in the United States by AECL to provide the AP/Can-Derem process.

AP/CAN-DEREM DILUTE CHEMICAL SOLVENT PROCESS

Dilute acids are used in most decontamination processes applied in the civilian reactor industry to dissolve

[a] Can-Derem is a trademark of AECL

the oxide layer. For example, a simple one-step acid dissolution approach is used for the CANDU reactors and U.S. boiling water reactors (BWR). Since a PWR oxide layer contains a high chromium content, dilute chemical solvent processes for such plants must contain two diverse steps. The high chromium content (20-40% Cr as Cr^{+3}) found in a PWR oxide layer acts as a barrier to dissolution of the iron and nickel. An oxidizing step is therefore used to dissolve the chromium portion of the layer. While the following is a simplification of the complex reactions associated with such processes, the basic steps are illustrated.

The Alkaline Permanganate (AP) oxidizing step (see Figure 2), often referred to as a pretreatment, is used to convert insoluble Cr^{+3} in the PWR oxide layer to its soluble valence state, Cr^{+6}. The Can-Derem dissolution step (see Figure 3) is then applied to dissolve the iron and nickel oxide portion and release the majority of the radioisototpes to solution. The reaction steps can be expressed as:

<u>Oxidation step</u> - chromium oxide plus an oxidizing agent form soluble chromium in the form of chromate, typically:

$$Cr_2O_3 + 2MnO_4^- + 2OH^- \dashrightarrow 2CrO_4^{-2} + 2MnO_2 + H_2O$$

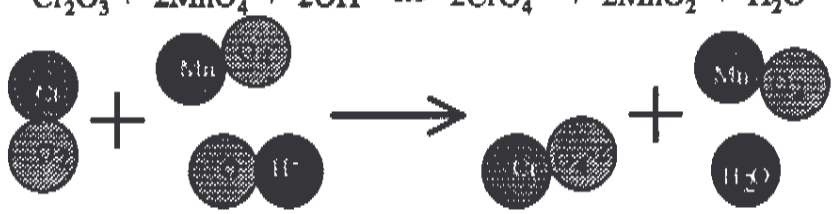


Figure 2. Alkaline Permanganate (AP)

<u>Dissolution step</u> - iron oxide plus a dilute acid form soluble iron and water, typically:

$$Fe_3O_4 + 8H^+ \dashrightarrow Fe^{+2} + 2Fe^{+3} + 4H_2O$$

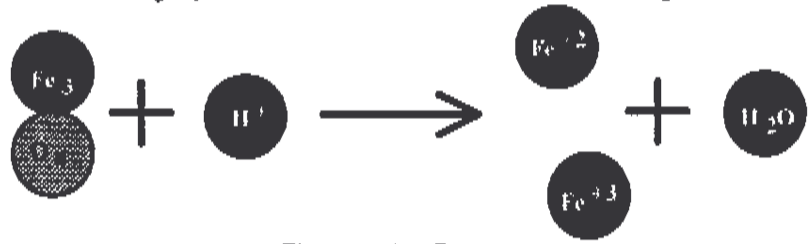


Figure 3. Can-Derem

The number of steps and their sequence of application depends on the composition of the deposit layer, the concentration of the chemicals, and the relative effectiveness of each step.

When applied to a plant component or system, the AP/Can-Derem is a multi-step dilute chemical decontamination process with alternating oxidizing and dissolution steps. Five steps are commonly used in PWR applications to dissolve alternately the chromium and iron/nickel. By alternating steps, the most effective dissolution of the oxide layer can be achieved in the shortest amount of time. For the oxidizing step, Alkaline Permanganate (AP), the process is a reagent solution of dilute (0.1%) potassium permanganate ($KMnO_4$) with 0.01% sodium hydroxide (NaOH) to adjust the pH to between 10 and 11.

AP pretreatment is very effective on inconel surfaces. Reagent additions are used to maintain the AP concentration and pH as the chemicals are circulated through the plant systems. No significant activity or oxide removal occurs during the AP pretreatment. At the conclusion of the pretreatment steps oxalic acid is added to decompose the remaining permanganate and acidify the solution prior to the dissolution step. Virtually no radioisotopes are released during the AP step clean-up.

The dissolution step is a 0.1% solution of Can-Derem, an organic acid/chelant mixture composed of citric acid and ethylenediaminetetraacetic acid (EDTA), at a resultant pH of 2.3-3. The dissolved oxygen concentration of the solution (reactor coolant for a full RCS decontamination) is adjusted to less than 0.2 ppm by the addition of hydrazine (N_2H_2) prior to the introduction of the Can-Derem reagent.

Table 2 is a set of conditions and steps shown to be a good sequence for effectively obtaining decontamination factors in excess of 5 on 304SS, Inconel 600 and other PWR primary system materials:

Table 2. Optimized AP/Can-Derem Process

Sequence: Can-Derem, AP, Can-Derem, AP, Can-Derem

Step	Reagent	Concentration	Time	Temperature
1:	Can-Derem	0.1%	24 hours	120C
2:	AP	0.1%	12 hours	95C
3:	Can-Derem	0.1%	24 hours	120C
4:	AP	0.1%	12 hours	95C
5:	Can- Derem	0.1%	24 hours	120C

In the AP/Can-Derem process, the acidic solution removes the vast majority of the surface oxides and radionuclides which are then subsequently captured by cation exchange resin. As the cation resin captures the dissolved metals, it regenerates the decontamination solution for reuse. Each Can-Derem step may be continued as long as contaminants are still being removed. Decontamination is terminated by isolating the cation demineralizers and using mixed cation and anion resin for system cleanup. The anion resin removes the chemical reagents themselves, and the cation resin removes any remaining dissolved metals.

The primary advantages of AP/Can-Derem with regard to ease of field application are its online process control, chemical stability, and regenerative nature, which reduces waste generation.

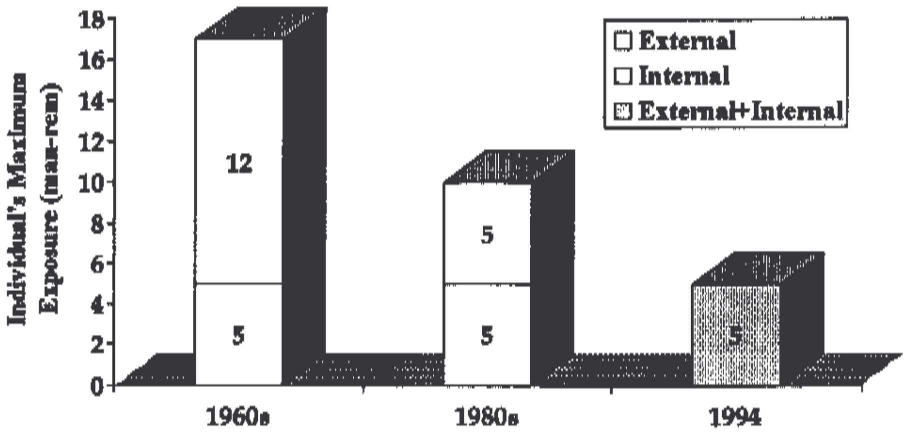
Laboratory research and more than a hundred decontaminations of components and systems in the field have shown that a variety of components and systems can be decontaminated with AP/Can-Derem without adverse impact on the long-term reliability of the equipment. Con Edison has already performed decontaminations at Indian Point 2 of its regenerative heat exchanger in 1989, CVCS in 1991, residual heat removal system (RHRS) in 1993 and retired Unit 1 steam generators in 1992, all with the AP/Can-Derem process.

NEED FOR FULL PRIMARY SYSTEM DECONTAMINATION

The International Committee on Radiation Protection and the National Committee on Radiation Protection have recommended personnel radiation exposure limits that are, on average, less than half current limits (see Figure 4). These recommendations will affect nuclear plant owners in several ways. Higher radiation exposure and lower limits on exposure will likely make it more difficult to obtain skilled labor as workers expend their yearly allotments. This would be particularly likely to arise if a refueling outage were to occur late in the calendar year, when annual radiation exposure allotments have been depleted. Such a situation would leave utilities with fewer resources to respond to unanticipated maintenance requirements.

Along with lower exposure limits, federal regulations were revised to make the ALARA concept law. The concept means that personnel exposure to radiation must be kept "as low as reasonably achievable." This will

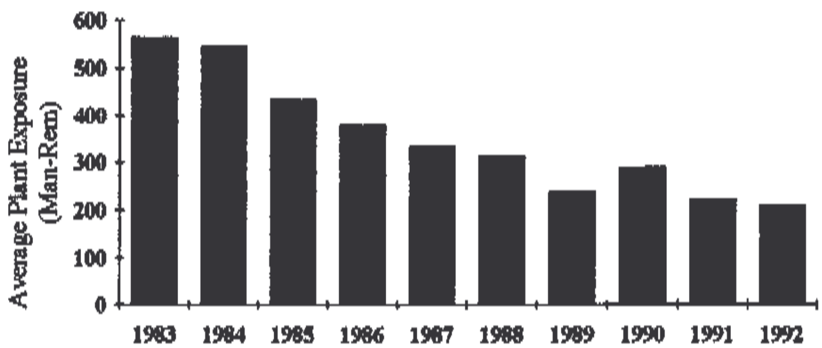
Figure 4. Exposure Limit Trend



enable the Nuclear Regulatory Commission (NRC) to set strict rules to ensure that utilities make personnel exposures ALARA.. Figure 5 shows that over the last few years average exposure for s (PWRs) has leveled off. This is because the prospects for new exposure reducing technology are limited.

Additionally, radiation exposure contributes to lost productivity. More and larger crews are needed and work is less productive in a radioactive environment. The time that crews can stay in the radioactive environment is shorter and set-up and clean-up requirements for manpower and materials are much higher than they would be for the same work in a clean environment. A study performed in 1992 indicated that a 10-50% increase in operation and maintenance costs will be incurred by utilities due to the above factors.[4]

Figure 5. PWR Exposure Trend



While new radiation field reduction techniques (such as high pH chemistry and specifying low cobalt alloys for replacement parts) have helped, a more substantial reduction in radiation fields is needed to help nuclear plant owners comply with new regulatory requirements, enhance worker productivity, and help keep nuclear power operating costs competitive. Full primary system decontamination is the only new technology with the potential to meet this need for a large industry-wide improvement.

The step from component to full primary system decontamination is, however, technologically a large one. The systems involved, the technical issues to be addressed, and the logistics for performing such a large-scale chemical decontamination are very complex.

QUALIFYING THE PROCESS

In 1987, Con Edison spearheaded a three phase program whose goal was demonstrating for the first time chemical decontamination on the entire primary system of a U.S. PWR plant. The first two phases, Feasibility and Qualification, are now complete. Phase 3, Demonstration, is in the engineering and fabrication stages.

ESEERCO, ten other utilities that own PWRs, and the Electric Power Research Institute have participated in the program thus far, along with Westinghouse and other decontamination service vendors.

The objective of the Feasibility phase was to determine the technical acceptability of dilute chemical solvent processes for primary system decontamination of a typical PWR plant. Studies of the Westinghouse PWR primary systems were conducted to establish the conditions, parameters, and criteria for a test program to qualify the solvents for the full RCS.[5] One important finding was that existing PWR plant systems can be used to control the solvent process on the full primary system. A temporary decontamination support system will be needed on site to feed the chemicals into the plant and receive and process the decontamination waste stream. Another important finding is that full primary system decontamination without fuel is highly cost beneficial, although leaving the fuel in place in the reactor would provide some additional savings. For the first demonstration of full primary system decontamination, fuel will be removed from the reactor vessel. Ultimately, once experience has been gained with full primary system decontaminations, fuel will likely be included. Extensive surveys were also conducted to establish a complete list of materials that would be exposed to the chemical solvents, and a series of tests was designed to address all possible issues for each material at the flow and chemistry conditions expected in the RCS.

In the Qualification phase, more than 250 specimens of more than 80 different materials were tested. Tests were also performed with the chemical concentrations and temperatures slightly increased. This results in a more corrosive test and demonstrates that the process could still be applied with a margin of safety under hypothetical fault conditions.

The tests were designed to establish a technical basis for performing at least three applications of the process during the remaining life of a plant. The tests were done in two test loops constructed at Westinghouse laboratories in Churchill, Pennsylvania. Engineers at Westinghouse, the original supplier of the reactor system at Indian Point 2, evaluated the test results. These evaluations were compiled, recommendations were made for application in the field, and a safety assessment was performed. Westinghouse prepared reports on the successful qualification for submittal to the NRC.[6,7] The NRC has reviewed the reports and issued a letter authorizing their use within an approved framework.

THE NATIONAL DEMONSTRATION

A joint effort is needed to assure that the broadest benefit is achieved by the entire industry from the first full RCS decontamination of an operating commercial nuclear power plant in the United States. An R&D consortium of utilities and other organizations including EPRI and ESEERCO has been organized to sponsor a national demonstration of the technology at Con Edison's Indian Point 2 in 1995. Participants will gain direct experience through a technical advisory group and will be provided with detailed information such as process and material test results, specifications and safety evaluations. This information and the experience gained should lower substantially the cost of their own subsequent decontaminations. The cooperative effort will enhance technology transfer by assuring that input is received from experts throughout the industry and by promoting exchange and publication of the results. For more information about the program or the technical advisory group contact Stephen Trovato, (212) 460-2090, or John Parry, (914) 526-5038, of Con Edison.

The National Demonstration is currently on schedule for Indian Point 2 in February 1995. Vectra Technologies (formerly Pacific Nuclear) has been selected to conduct the decontontamination. A temporary process system has been designed that will have minimal impact on the existing plant. This majority of this system will be located in a small room of the Indian Point 2 primary auxiliary building (PAB) normal used for temporary waste storage. The process system will be controlled remotely from outside the PAB with communication to the plant central control room for coordination with plant operation. The PAB contains much of the equipment for the RCS support systems, such as the RHRS pumps and heat exchangers. The proximity of the room selected for placement of the temporary process system to the RHRS facilitates the plant to process system tie-in. Decontamination chemicals, clean demineralizer resins and clean water for sluicing resins will be supplied from equipment placed outside the PAB. Demineralizers will be placed inside the PAB to provide adequate shielding of removed radioactive material. Feed of chemicals to the primary system and removal of system water for cleanup will be through the RHRS. From the RHRS the solvents travel through the RCS and the CVCS. While only one reactor coolant pump is required to circulate the solvent, up to three may be operated to provide an even decontamination of the reactor coolant loops. The reactor coolant pumps generate more than enough heat to maintain the temperature required for the solvents to work. The RHRS heat exchangers, which provide cooling, are used to balance the primary system temperature. Once the decontamination has been completed the spent resins are sluiced to high integrity containers, and dewatered for eventual storage or burial.

Major components of the decontamination process system were procured in 1993 and fabrication and assembly are nearing completion. A five week factory acceptance test of the process system is scheduled for Spring 1994. The decontamination process system operating procedure has been drafted and plant operating procedures have been written. A test plan that defines the data to be captured, its form, frequency and accuracy has been developed. Design work on the low level waste cask storage modules has also been completed. Numerous supporting analyses were conducted to support the operation of the plant in "decon mode" and the preparation of a safety evaluation including:

- Required reactor vessel head closure studs
- Off-site radiation exposure levels
- Major component cladding cracks (if existing)

Plant system walk-downs have been completed and plant modification packages prepared. A program was put in place to identify all potential dead legs and methods to flush them after the decontamination. Outage task planning is now in progress.

To prepare for the demonstration in 1995, Con Edison performed many activities during the 1993 refueling outage of Indian Point 2. For example, the RHRS was modified to provide the connection points for the temporary decontamination support system. Another change was to test a new low pressure seal, to be used when the reactor in-core instrumentation is pulled out of the vessel, to upgrade the existing seals to the operating pressure anticipated during the decontamination. Several tests of plant equipment were conducted to very their ability to meet "decon mode" operating conditions including component cooling, charging flow and the reactor coolant pump seals. During the current plant operating cycle, other site preparations will be performed, such as clearing areas to accept the temporary decontamination support system, including a small room within the plant's primary auxiliary building that will hold the demineralizers.

BENEFITS TO BE GAINED

While benefits will vary depending on plant age, radiation fields, and maintenance and equipment-replacement activities, the broad benefit to the utility industry as a whole is estimated at a direct saving of roughly one billion dollars over the next 10 to 20 years. An estimated 3,500 man-rem could be saved at Indian Point 2 alone over a 5 cycle operating period.

There are many non-quantifiable benefits of the demonstration too. Full primary system chemical decontamination will provide the nuclear industry with a means to substantially reduce the collective radiation exposure of its workers in the future. As a direct result of lower radiation fields, worker productivity will improve thereby making nuclear energy more competitive. In the long term, full system decontamination should become a regularly applied technology. It will facilitate life extension of current plants because it will provide a way to maintain equipment without incurring large radiation exposure doses. For the next generation of light water reactors, routine full system decontaminations could help provide for sustainable lower maintenance costs. Finally, reducing the collective radiation exposure should improve the image of the nuclear industry at a time when public perception is an important factor affecting a utility's ability to extend the life of a nuclear power plant past the expiration of its original license.

In summary, full system decontamination should become a vital part of life extension and the future of nuclear energy in this country.

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Author Biography

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