CoSeq[™] Sequestration Resin Accelerates Cleanup of Nuclear Power Plant Coolant

Cobalt 60

Cobalt 60



o ensure worker safety during nuclear plant outages, access to the reactor containment building is delayed until processing equipment can reduce radiation to acceptable levels. Reducing this delay by a day could avoid as much as \$1 million in replacement power costs. Innovative work being conducted by EPRI may soon provide a solution enhancing the removal of cobalt-60 from plant water streams.

Cobalt-59 and nickel-58 are found naturally in nuclear power facilities in a variety of alloys that contain chromium, manganese, nickel, iron, and cobalt. With the corrosion of certain plant components, such as valves, piping, and reactor parts, the cobalt and nickel are released into the nuclear reactor's water streams and deposited in the fuel core. There they are exposed to radiation and are converted to the isotopes cobalt-60 and cobalt-58, which are the major contributors to outage occupational radiation exposure in both boiling water reactors (BWRs) and pressurized water reactors (PWRs).

Radioactive cobalt-60 and cobalt-58 are circulated from the fuel core surfaces through the reactor water to various parts of the containment area. Because of the gamma rays that accompany radioactive decay of cobalt-60 and cobalt-58, radiation in the containment area must be brought to predetermined levels by reactor water cleanup systems before workers are allowed to enter plant containment and begin outage activities, such as fuel moves and inspections. The more quickly those levels are brought down, the sooner work in the containment area can begin and the sooner the plant can return to service. Shorter outages can reduce worker exposure and potentially save millions of dollars in replacement electricity costs.

Traditionally, the ion-exchange process has been used in nuclear plants to remove corrosion products and radioactive isotopes from the plants' cooling water and to eliminate soluble chemical components that contribute to corrosion. In BWR

THE STORY IN BRIEF

EPRI's CoSeq[™] resin technology uses a novel sequestration chemistry to significantly increase the amount of cobalt that can be removed from water streams at nuclear power plants. That can possibly mean improved worker safety, reduced radiation exposure, and lower electricity costs due to shorter maintenance outages.

plants, for instance, ion exchange is used to treat makeup water, returned condensate, water in the spent fuel pool, reactor coolant, and radioactive waste (radwaste).

Today's ion-exchange resins are specialized polymer-based materials that attract ionic species using charged binding sites. Cobalt ions compete for the same exchange sites with zinc, iron, and other ionic species that are present at significantly higher concentrations but are less harmful from a radiation perspective. The ions are "exchangeable," however, meaning the attractions that take place can also be reversed. Over short periods, existing ion-exchange resins are 90%-99% effective in briefly controlling ionic corrosion products after being put into service, but their capacity to attract ions is quickly diminished. As a result, fresh resin must be used on a regular basis, and residual contaminants in the water that cannot be removed contribute to site radioactivity levels and occupational exposures. Ionexchange applications may take several days to reduce corrosion product concentrations to safe levels, so applications must be scheduled several days in advance of outages to ensure that contaminant levels are low enough to permit outage activities.

New Technology: Cobalt Sequestration Resin

EPRI began studying the possibility of sequestration, rather than ion exchange,

toward the end of 2009 through its Technology Innovation Program. Since then, EPRI researchers helped develop a resin that can sequester radioactive cobalt species. This new resin, which can be applied in powdered form to conventional demineralizer filters, captures and locks cobalt species through both physical and electronic interactions, avoiding the unwanted reversal of exchange that can occur with ion-exchange systems. Designed for use in reactor water cleanup systems, this new resin to reduce critical path downtime, replacement power costs, and site activity levels during outages by accelerating uptake of corrosion products responsible for most radiation exposure at plants. Dubbed $CoSeq^{TM}$, the resin preferentially targets elemental and activated cobalt.

A systematic progression of laboratory and field studies was necessary to test different resin formulations and to scale up production. "These tests help ensure, first and foremost, that we will do no harm when we introduce new cleanup technologies into a nuclear plant," said project manager Susan Garcia. "We are working with complex chemistries that involve difficult reactions, and we don't want to have a negative impact in any way—for instance, by introducing any impurities into the water."

No new equipment is needed for testing the $CoSeq^{TM}$ resin, since it can be used in existing water treatment systems. The resin can be used throughout a nuclear plant's operating cycle, as well as during plant outages.

Exelon Generation, in an effort to take dose reduction to the next level, hosted testing and development of this novel technology at its LaSalle County and Peach Bottom generating stations. The first tests involved plant reactor water and fuel pool water at LaSalle, where benchtop tests showed that CoSeq[™] outperformed the site's current resins for cobalt removal. EPRI then increased production of the powdered CoSeq[™] resin to provide enough for a plant demonstration in BWR reactor water cleanup systems. The resin was tested for physical properties important for a filter demineralizer demonstration, such as ease of removal from the system after use, impacts on differential pressure, and settling behavior.

Testing with plant water in actual plant treatment systems is necessary to prove that these resins outperform traditional ion-exchange resins. "The original benchtop studies were critical to our work, but we couldn't be absolutely sure of this resin's capabilities until we actually went into the plant itself," Garcia said. "We rely heavily on the industry to try new technologies, and the utilities that have stepped up to do this have been instrumental in the success of the project."

BWR in-plant demonstrations began in April 2012 at Exclon's LaSalle 1. The $CoSeq^{TM}$ powdered resin operated for 36 days with high removal efficiencies and no negative impacts on plant operation. The comparison test bed, which used LaSalle's normal resins, had to be backwashed twice during the 36-day test period because of high conductivity associated with a mechanical issue.

In a subsequent demonstration later in 2012, the $CoSeq^{TM}$ resin again outperformed the standard resin when tested side by side during and after an on-line chemical application that is known to be associated with higher cobalt-60 levels in the reactor water.

Last fall, powdered CoSeq[™] resin was

evaluated in a side-by-side demonstration during a plant shutdown at Exelon's Peach Bottom 2 BWR. The testing took place during a period when cobalt-60 levels were elevated, requiring added outage time for cleanup. Again, CoSeq[™] outperformed the standard resin for efficient removal. Additional BWR demonstrations and side-byside tests followed in February 2013 during a shutdown at Exelon's LaSalle 2.

"We were very pleased to be chosen to conduct the CoSeq[™] pilot testing at LaSalle and Peach Bottom," said Peter Orphanos, Exelon's vice president for fleet support. "We are currently pursuing an aggressive dose-reduction initiative that involves improvements in processes, shielding technology, worker behavior, and source term reduction. We believe resin optimization is a strategy that can make a big difference in reducing source term and improving worker safety."

Effective Results

The original goals for the new resin were as follows:

- Increase cobalt removal using existing plant water cleanup systems.
- Reduce outage time and replacement power costs required for water cleanup.
- Decrease worker exposure and waste management costs while supporting safe and economical long-term operations.

In-plant tests conducted so far have confirmed the laboratory results: A single $CoSeq^{TM}$ active resin site does the work of at least two ion-exchange sites while improving cobalt uptake rates and increasing overall effectiveness.

CoSeq[™] provides faster, higher-capacity uptake of those corrosion products responsible for most of the radiation dose in BWR applications. As a "plug-in" treatment solution for existing and new nuclear plants, this sequestration resin promises at least a threefold increase in longer-term uptake for key cobalt species, as well as higher overall removal capacity. Applying these resins in primary coolant treatment systems could reduce the time delay before the reactor vessel can be opened during outages (potentially by as much as 24 to 48 hours), leading to replacement power savings of \$500,000 to \$1 million per day.

Most important, whether the plant is operating or in an outage, this technology can decrease worker radiation exposure, extend resin lifetime, and help control radioactive waste production and associated management and disposal costs.

The CoSeq[™] resin can be used with conventional water cleanup systems.





Photograph courtesy of Korea Hydro & Nuclear Power | Kori Nuclear Power Plant

Based on the successful laboratory and plant testing, EPRI began exploring mechanisms for making the resin commercially available to the industry. In April, EPRI licensed the technology to a commercial resin vendor, who will then supply the material to nuclear power plants. Production of commercial-scale batches may begin this Fall.

"Typical ion exchange resins are not designed to go after cobalt specifically," Exelon's Orphanos pointed out. "CoSeq[™] is the first resin developed with cobalt removal as the primary focus. We are very excited about the potential to commercialize this new technology, which will clearly help Exelon and the industry reduce exposure of our workforce."

The Studies Continue: Additional Uses for CoSeq™

At most BWR plants, water streams pass through demineralizer filters, which can be coated with a powdered form of the CoSeq[™] resin. In PWR plants, some BWR plants, and radwaste treatment systems, the streams to be decontaminated are passed through deep-bed demineralizers—large containers that hold hundreds of kilograms of resin beads stacked like loose marbles. These applications will require a bead form of the CoSeq[™] resin, which EPRI is also pursuing.

CoSeq[™] bead-type resins have been generated successfully at bench scale with a variety of substrates, and several utilities have volunteered their PWR plants as demonstration sites. Radwaste testing is scheduled for this spring at a plant owned by Korea Hydro & Nuclear Power. The four-column testing of various resins will include evaluation of colloidal cobalt removal, as well as removal from multiple waste streams. Radwaste testing is also in progress at NextEra Energy's Seabrook Station. Macroporous and gel-form bead resins with and without a sequestration ligand will be screened with the radwaste water.

Another use for powdered CoSeq[™] resin is in submersible filter applications. Submersible filters are used during outages to quickly clean up a plant's cooling water. If successful, the technology could be tailored to specific needs, such as cavity cleanup and fuel pool cleanup. Already, powdered CoSeq[™] has been embedded in a submersible filter, and a combination of filter and submerged deep-bed demineralizer could constitute a viable test configuration as well. Demonstrations at a plant slated for an outage this fall will help quantify the value and use of submersible units.

EPRI will continue to study sequestration of other elements to determine whether this technology could be used with other radioisotopes and in other applications. Applying sequestration chemistry for lead, mercury, or antimony removal at fossil plants, for example, could enhance water treatment options across the electric power industry.

This article was written by Debra Murphy. Background information was provided by Susan Garcia, sgarcia@epri.com, 650.855.2239; Daniel Wells, dwells@epri.com, 650.855.8630; and Keith Fruzzetti, kfruzzet@epri.com, 650.855.2211.



Susan Garcia is a senior project manager specializing in BWR chemistry, with particular focus on optimized chemistry treatment, mitigation and monitoring of

stress corrosion cracking, fuel performance, and dose reduction. Before joining EPRI in 1999, she was a technical project manager at GE Nuclear Energy. Garcia has a B.S. in nuclear chemistry from San Jose State University.



Daniel Wells is a senior project manager specializing in corrosion mitigation and chemistry regimes as they relate to radiation fields and activity transport.

Before joining EPRI in 2010, he worked as a project engineer at Radiological Solutions, Inc., and earlier at ExxonMobile Process Research. Wells received a B.S. in chemical engineering from Auburn University and a Ph.D. in chemistry from Northwestern University.



Keith Fruzzetti is a technical executive in the Nuclear Fuels and Chemistry Division, focusing on optimizing chemistry for corrosion mitigation, fuel performance,

and radiation management. Before joining EPRI in 2001, he worked at NVVT Corporation as a senior consultant involved in PVVR primary and secondary water chemistry issues. Fruzzetti received a B.S. in chemical engineering from San Jose University and M.S. and Ph.D. degrees in the same field from the University of California, Davis.