

Laboratory Evaluation of Corrosion Mitigation Strategies for Large, Once-Through Heat Exchangers

D.G. ENOS, B.L. LEVIN, AND T.E. HINKEBEIN, *Sandia National Laboratories*

Corrosion in large oil coolers at U.S. Strategic Petroleum Reserve sites led to fouling and perforation of carbon steel cooling water tubes. Two mitigation strategies were studied in a laboratory simulation—the use of corrosion-resistant alloys (CRAs) for the tubing and the application of a corrosion inhibitor and anti-fouling package in the water. Data indicated the CRA alternative was more viable. This article describes the field conditions, laboratory simulation, data analysis, and conclusions drawn from the study.

The U.S. Strategic Petroleum Reserve (SPR) is a large stockpile of crude oil maintained by the Department of Energy to provide an emergency supply of oil for the country, should the need arise. At each of the SPR sites, oil is stored in massive underground caverns located within natural salt domes. Oil is extracted from the caverns as needed by pumping in water, which then displaces the oil, forcing it out of the cavern. Because of the depth of the caverns, the oil stored therein increases in temperature over time. This temperature increase causes a commensurate increase in the vapor pressure of low molecular weight species within the oil to unacceptably high levels. As a result, the oil must be cooled prior to being delivered to its final destination/storage container.

The cooling of the oil is accomplished through the use of large tube-shell heat exchangers known as oil coolers (Figure 1). The tubing within these heat exchangers is constructed largely of carbon steel (CS), conforming to ASTM A214A¹ or A179.² The cooling media used in these exchangers is the same water that is used to extract the oil from the caverns. This cooling water passes through the inner tubes in the oil cooler, and the oil is passed through the outer shell of the oil cooler. The water source for the majority of the SPR sites is an inter-coastal waterway. The water is high in chloride, sulfate, and calcium, with a pH at or slightly above neutral. This combination of CS and a high-chloride water source has caused severe corrosion, leading to tube fouling and failure within the oil coolers.

Two strategies were proposed to address this corrosion and fouling issue. The first is the replacement of the CS with a material intrinsically resistant to corrosion and fouling in SPR service environments. The particular material selected was a superferritic stainless steel (SS). The second potential solution, which is less expensive but poses higher risk, is to leave the existing CS tubing in place, and chemically moderate the corrosion and fouling pro-

FIGURE 1



Oil coolers located at the various SPR sites.

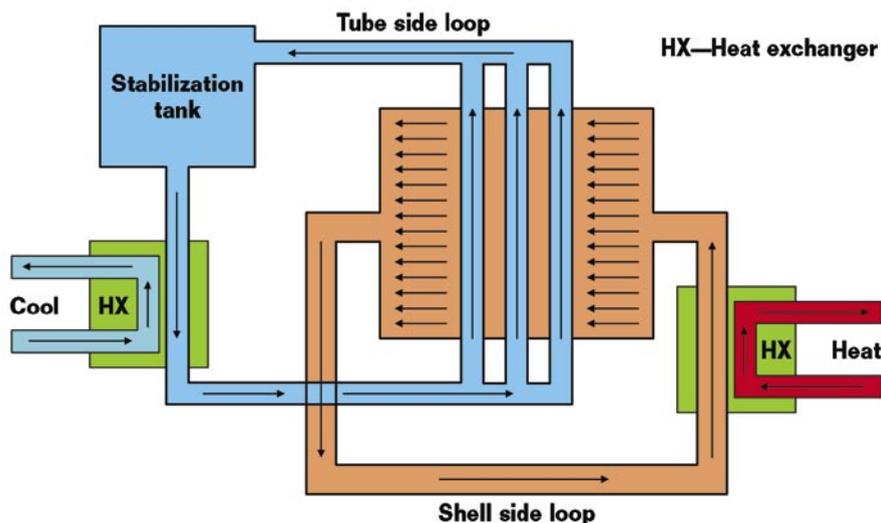
cesses using a corrosion inhibitor and deposit control agent.

The goal of this study was to compare the performance of these two proposed corrosion mitigation strategies in terms of their ability to address corrosion and fouling issues under SPR service conditions. A series of flow loops was constructed to simulate the conditions present within typical oil coolers in use at selected SPR sites, allowing assessment of the performance of each corrosion-mitigation strategy, as well as the baseline performance of the existing systems.

Experimental System Design and Operating Conditions

Simulating a large, single-pass system in a laboratory environment introduces a number of significant experimental challenges. As an example, at the typical operating flow rate of 6 gpm, the system would require 8,640 gal (32,702 L) per tube segment per day—corresponding to 777,600 gal (2,943,216 L) per tube for the total 90-day operating time of the system. Clearly this is not feasible for even the most well-equipped laboratory. In addition to the chemical conditions of the system, an effective simulation must also encompass the temperature and flow conditions within the exchanger. As such, the availability of an appropriately sized heating/cooling apparatus is essential—this

FIGURE 2



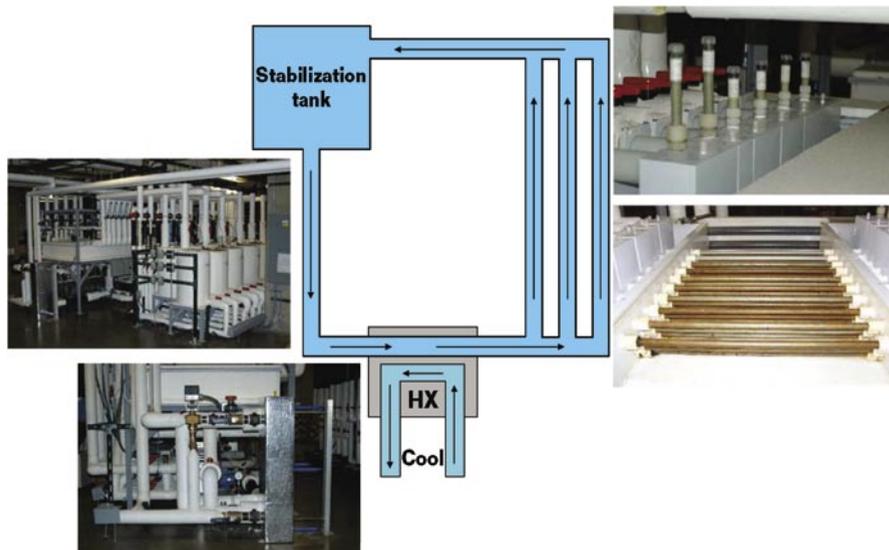
Schematic of the laboratory-scale closed loop recirculating flow loop system.

also becomes increasingly difficult and cost prohibitive to accomplish in a laboratory setting for large-scale, once-through systems.

To address these issues as completely as possible, a closed-loop, recirculating system was designed and constructed. To ensure that the water was as close as possible in composition to that utilized by the SPR, actual site water was used. A large quantity (600 gal [2,271 L]) of water was obtained from each of two SPR locations (West Hackberry and Bryan

Mound) prior to beginning the test. The water chemistry utilized in this test represents a snapshot in time; that is, while it is representative for the site at the time the sample was taken, it does not account for temporal variations in the solution chemistry from, for example, the action of the tides at the Bryan Mound site. As the experiment progressed, the solution chemistry was periodically monitored and adjustments made to maintain this similarity (e.g., chemical additions, filtering corrosion product particulates, etc.).

FIGURE 3



Schematic of a single tube side loop containing the water chemistry relevant to each SPR site.

The flow rates and internal (tube side) and external (shell side) temperatures were selected based upon the typical operating conditions within an actual system. Thermal conditions were selected to bracket those that exist at various positions within the actual oil coolers. Summer temperatures were selected (combination of tube and shell side temperatures) to capture the conditions at the hot side (oil inlet, water outlet) and cool side (water inlet, oil outlet) of the heat exchanger at a time when temperatures would be seasonally higher, thus exacerbating any corrosion processes taking place. The temperatures corresponding to the hot and cold side of the oil coolers consisted of a tube side temperature of 95°F (35°C) and a shell side temperature of 120°F (49°C) for the former, and a tube side temperature of 85°F (29°C) and shell side temperature of 95°F (35°C) for the latter.

Figure 2 shows an overall schematic of the closed-loop recirculating system. The system allowed pertinent environmental variables (temperature, water chemistry, and flow rate) to be controlled as a function of time. Instrumentation to monitor the corrosion performance of each tubing material was also incorporated into the system. The overall system consisted of 12 tube side loops (where a chemistry similar to the source water at the SPR sites was maintained) and two shell side loops

(which maintained inhibited deionized [DI] water at a temperature equivalent to a typical oil temperature in the actual oil coolers). Each shell side loop controlled the temperature of six tube side loops.

Each shell side loop consisted of three primary components—the main exposure tank, a heat exchanger, and a circulation pump. Water was pumped through the heat exchanger, where its temperature was adjusted appropriately. After passing through the heat exchanger, the water passed through the main exposure tank, across the tube side loops, and was then pumped back through the heat exchanger. Each shell side loop contained ~48 gal (182 L) of DI water with 200 ppm of a phosphate corrosion inhibitor (to minimize external attack of the tube segments).

The tube side loops (Figure 3) contained the SPR source water. Each tube side loop consisted of a stabilization tank, a pump, a heat exchanger, and a manifold, which contained the metal tubing being evaluated in each loop. The stabilization tank was used to maintain a large volume of solution, and was where all solution sampling and augmentation took place. In addition, a gas dispersion tube was present in each tank, and air was continuously bubbled through the tank to ensure that the oxygen concentration (~6 ppm) was not depleted over time. Water was pumped

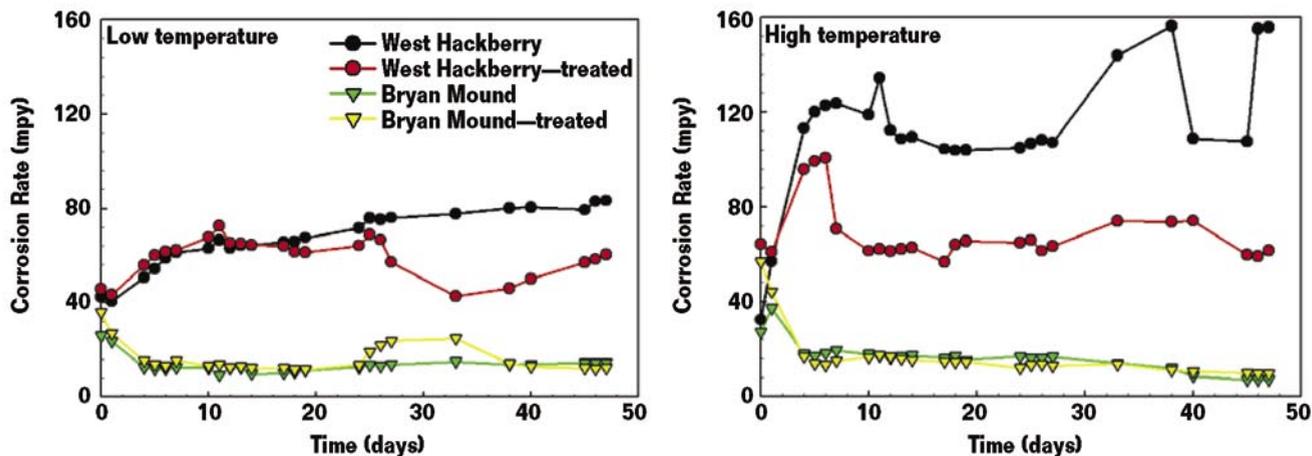
from the stabilization tank, through a heat exchanger, to set the desired tube side temperature. Once brought to temperature, the water was pumped through a manifold containing tubes of the desired metallurgy, and then returned to the stabilization tank. In addition to the tube segments being evaluated, each manifold contained a corrosion sensor and ports for thermocouples. The water temperature, chemistry, and flow rate were monitored and maintained throughout the test. Each tube side loop contained ~32 gal (121 L) of solution, which was either used as-received or with the addition of an inhibitor and antifoulant chemistry.

Three different materials were evaluated in this study—ASTM A214A electric-resistance-welded (ERW) CS tube, ASTM A179 seamless cold-drawn low-carbon steel tube, and UNS S44660 superferritic SS. The two CS materials represented the current composition of the heat exchangers, and the SS represented the proposed replacement. All of the materials were evaluated in raw (untreated) source water from each of the two SPR sites evaluated. In addition, the CS samples were evaluated in source water treated with a phosphate-based corrosion inhibitor combined with an anionic polymer deposit control agent.

Results and Discussion

A primary concern in the operation of the heat exchangers is the remaining wall thickness in each tube section, as well as the thickness of any deposits, which form along the inner diameter of the tubes over time. Corrosion sensors made of either CS or the superferritic SS were placed into the exit manifold of each of the 12 tube side flow loops. The corrosion sensors were monitored over time using a commercially available linear polarization resistance (LPR) meter. Figure 4 shows the results from the corrosion sensors, expressed as an effective corrosion rate, showing the effects of source water, inhibitor, and temperature. As can be seen in the figure, the samples exposed to West Hackberry source water had an initial corrosion rate of 40 to 60 mpy (1 to 1.5

FIGURE 4



Corrosion sensor data for CS in each solution chemistry.

mm/y) in all environments. Untreated West Hackberry source water had the highest overall corrosion rates, which reached 80 and 150 mpy (2 and 3.8 mm/y) for the low and high temperatures, respectively. For the treated West Hackberry water there is little effect of temperature on the corrosion rate, though the rates were lower compared to the untreated condition. The exposure to Bryan Mound source water yielded much lower corrosion rates, with a similar 30 mpy (0.8 mm/y) initial rate in all environments, which stabilized after a week or so to 15 mpy (0.4 mm/y), both with and without the presence of the inhibitor. The corrosion rate of the SS material was effectively zero in all cases.

An important piece of information to note for the corrosion sensors is that as the corrosion progressed, the effective surface area of the probes themselves was changed because of a thinning of the probes coupled with the nonuniformity of the corroded surface. As such, the accuracy of the reported data will decrease as the electrodes are attacked (i.e., the calculation of corrosion rate from the LPR instrument assumes a specific sample geometry and surface finish—deviations from that can yield inaccuracies in the reported corrosion rate). The periodic replacement of the electrodes—while it would alleviate the surface area change issues—would cause a metal/solution interface that differed radically from that of

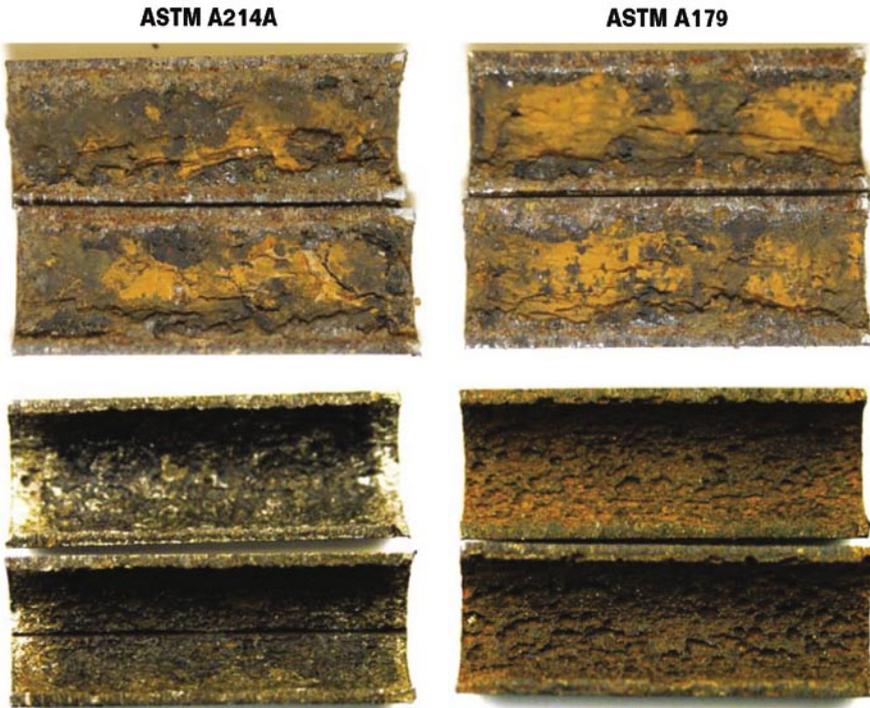
the tube segments (i.e., clean metal to solution vs being covered with a voluminous corrosion product layer, the interior pH and composition of which will deviate greatly from the bulk solution).

While the information obtained from the corrosion sensors is very useful, it cannot simply be assumed that the measured value is in fact representative of the actual tube segments without performing a physical inspection of the tube walls themselves. As such, tube samples were extracted for each of the CS materials in all of the environments evaluated in this study. Once removed from the test system, a 2-in. (51-mm) segment was cut from the center of each tube and then split longitudinally. The exposed surfaces were then photo documented, after which the copious corrosion product deposits were removed, and the base metal surface again photo documented. Figure 5 shows a series of representative pictures. A visual examination of the tube walls revealed that the corrosion in the West Hackberry solution was highly localized in nature, with numerous pits visible across the surface. The resulting corrosion product deposit was similarly rough and nonuniform, the high and low temperature samples were similar in appearance, and in both cases the number of localized corrosion sites was reduced somewhat by the presence of inhibitor. For the Bryan Mound water, the surface appeared similar in both the treated and untreated solu-

tions at low and high temperature. The resulting corrosion product was smoother and more uniform in appearance than that observed on samples exposed to West Hackberry water. The observed attack was also relatively uniform over much of the metal surface, although there were still a number of deep pits present. In both environments, the electric resistance welded (ERW) material exhibited significant localized attack along the entire weld line (Figure 5).

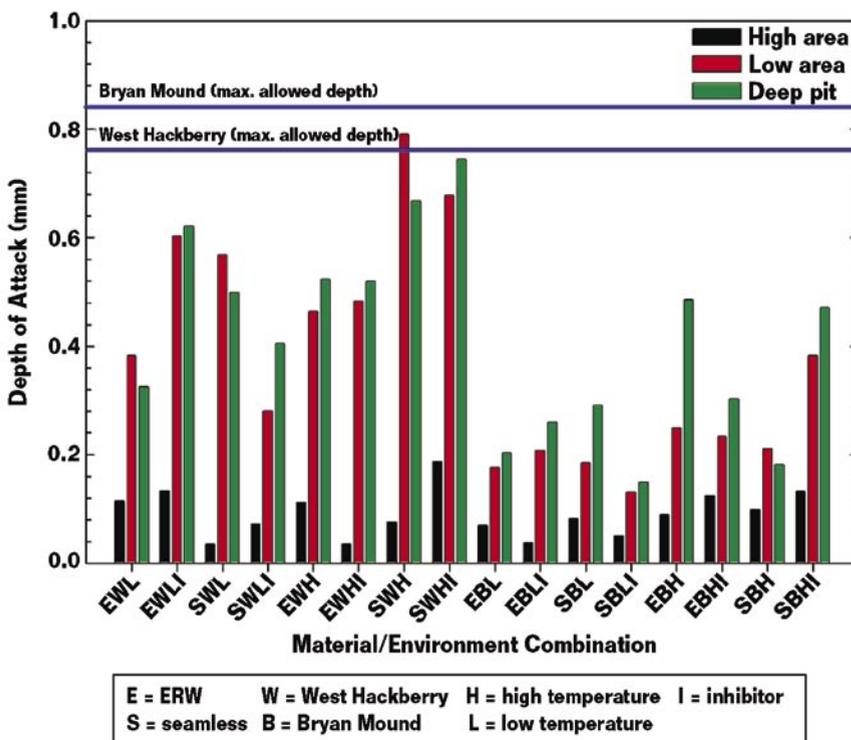
At this point, it should be stressed that the attack was nonuniform in nature—as such, measurements of the average reduction in cross section or overall weight-loss calculated from the corrosion sensor data are a poor representation of the true depth/severity of corrosion. To illustrate this effect further, the depth of localized attack was measured, and is shown in Figure 6. The corrosion that occurred along the tube can be grouped into three general categories—high areas (minimal attack), low areas (significant, general attack), and pits (significant, local attack). Also indicated on the figure is the maximum depth of attack allowed in order to ensure that the system will be able to contain the operating pressures for the Bryan Mound and West Hackberry sites (as calculated by the site engineer). As can be seen, there are situations where after only 60 days of operation, the depth of attack is sufficient to potentially cause failure of a tube section.

FIGURE 5



Representative images of the CS tubing after 90 days. (Samples shown are from the high-temperature, untreated West Hackberry loop.) Top pictures are before removal of corrosion product, and the lower pictures are cleaned surfaces.

FIGURE 6



Depth of attack as a function of environmental conditions (60-day data).

Although not shown in the figure, the SS samples appeared the same as they had when they were inserted into the system—no visual attack or discoloration had occurred.

Summary and Conclusions

From the data acquired thus far, a number of conclusions can be made in terms of the corrosion performance of the system.

1) A closed-loop system, which simulated the environmental conditions present within an SPR oil cooler, was constructed and utilized to evaluate the relative performance of two corrosion mitigation strategies. Pertinent environmental variables were monitored and maintained such that the conditions within the laboratory scale system mimicked as closely as possible those within the actual in-service system.

2) Evaluation requires physical observations. Because of the localized nature of the corrosion observed on the CS samples, the LPR data, while it did provide information on the relative severity of the attack, was not representative of the true depth of the observed localized corrosion.

3) No quantifiable corrosion was observed on the superferritic SS under any of the conditions explored in this study, and therefore it is a viable replacement material for the heat exchangers.

4) The inhibitor package did reduce the overall extent of corrosion on the CS, but the resulting magnitude and depth of localized attack that was observed still presented the potential for tubing perforation and substantial reductions in tubing strength.

5) The ERW steel exhibited significant localized attack along the entire weld root, in addition to pitting along the rest of the surface, as observed on the seamless tubing.

Acknowledgments

Sandia is a multi-program laboratory operated by the Sandia Corp., a Lockheed Martin Co., for the U.S. Department of Energy's National Nuclear Security Ad-

ministration under contract DE-AC04-94AL85000.

The authors would like to thank Margie Lappin, Stacey Dalton, and Sam Wallace at Sandia as well as Charlie Deluca and Pat Mihalik from DynMcDermot for their technical assistance for this study.

References

1. ASTM A214/A214M-96, "Standard Specification for Electric-Resistance-Welded Carbon Steel Heat-Exchanger and Condenser Tubes," Annual Book of ASTM Standards (West Conshohocken, PA: ASTM International, 2001).

2. ASTM 179, "Standard Specification for Seamless Cold-Drawn Low-Carbon Steel Heat-Exchanger and Condenser Tubes," Annual Book of ASTM Standards (West Conshohocken, PA: ASTM International, 2001).

DAVID G. ENOS is a Principal Member, Technical Staff in the Corrosion and Electrochemical Science department, at Sandia National Laboratories, PO Box 5800, Albuquerque,

NM 87185-0888. He has worked in the area of corrosion and corrosion protection for 14 years. He has a Ph.D. in materials science and engineering from the University of Virginia, and is a member of NACE.

BRUCE L. LEVIN is a Member, Technical Staff, at Sandia National Laboratories. He has 23 years of experience designing and evaluating mechanical systems and performing heat transfer, fluid mechanics, and dissolution analysis for several departments at Sandia. He is a registered professional engineer in the State of New Mexico.

THOMAS E. HINKEBEIN is Manager of the Geochemistry department at Sandia National Laboratories. He is responsible for fundamental studies of water-solid interactions as well as applied programs in advanced water treatment technologies. He has a Ph.D. in chemical engineering from the University of Washington. *MP*



What's in your water?
Get the answers, ask us how.

Call us for information on how to receive a
6 Point Water Chemistry Analysis compliments of:

 **PLYMOUTH TUBE CO.**—USA®
EAST TROY

2061 Young Street
East Troy, WI 53120
PHF 262-642-8201
Fax # 262-642-8486

www.plymouth.com
www.seacuresolutions.com





PLYMOUTH TUBE CO.—USA®

29W150 Warrenville Rd.
Warrenville, Illinois 60555-0768
800.323.9506 Fax: 630.393.3551



PLYMOUTH TUBE CO. DELIVERS TO U.S. DEPARTMENT OF ENERGY

EAST TROY, WI (August 1, 2005) –

The East Troy CWA (Cold Work Anneal) Plant of Plymouth Tube is preparing to ship the final orders of SEA-CURE® heat exchanger tubing to the Department of Energy (DOE). Plymouth SEA-CURE® is being used to re-tube 33 heat exchanger units at the DOE's Strategic Petroleum Reserve (SPR). The tubing orders were placed through DynMcDermott and ASRC, the DOE's Management and Operating Contractors, beginning in 2002.



The SPR is stored at four sites along the Gulf of Mexico in a series of artificial caverns within salt domes below the surface. As the crude is stored at high temperature, it needs to be cooled prior to pumping into the pipeline. The 33 heat exchangers are used to do this. Originally installed with carbon tubing during the early-seventies, the heat exchangers at the Strategic Petroleum Reserve began to corrode and leak as a result of a combination of high chlorides and high microbiological activity in the brackish water used to cool the crude.

Following an extensive evaluation of a variety of materials at DynMcDermott, Los Alamos Laboratory, and Plymouth Tube Co. – East Troy, SEA-CURE was determined to be the most cost effective material to solve the problems. The high mechanical strength, high modulus of elasticity, and excellent corrosion resistance provided the combination of needed properties to solve the problems caused by the high pressures and aggressive cooling water.

With over 65 million feet of SEA-CURE® in service worldwide, Plymouth Tube takes pride in the SEA-CURE® tubing installed in the SPR.

About Plymouth Tube Co.

Plymouth Tube Company is a privately-held, family-owned global supplier of specialty carbon, alloy, stainless steel, and nickel alloy tubing. Additionally, Plymouth produces steel, nickel alloy and titanium extruded shapes and cold drawn shapes. Headquartered in Warrenville, Illinois with 8 plants in the U.S., all Plymouth mills are certified to ISO 9000/ISO 9002, QS-9000, or TS16949.

Check out our website at www.plymouth.com or www.seacuresolutions.com