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EVALUATION OF LEAK SEAL ADDITIVES – COOLING WATER PIPE IN NUCLEAR WASTES

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ABSTRACT

Pre-deployment and degradation testing of commercial leak seal products were performed to evaluate the potential for remote, short-term repair of leaks in waste storage tank cooling coils. A liquid glass metallic product was identified for extensive testing after initial screening of four candidates. Testing was performed with manufactured holes and slits in an immersed pipe operated at nominal coil pressure (~50 psig). The maximum leak sizes that sealed under simulated field conditions were a slit, 0.016 × 0.291 in. (leak rate, 1.34 gpm) and a 0.046 inch diameter hole (leak rate, 0.63 gpm).

Degradation of seals and of the constituent fiber samples was studied for radiation and for immersion in water and simulated waste. Seals withstood doses up 1.66E7 R, equivalent to 2 years in a nuclear waste tank. A seal functioned for 50 days when immersed in simulated waste at 75-80 °C, low-pressure cooling water at 27-35 °C, and several salt/desalt cycles. A small leak occurred at 23 days, but self-healed.

The limited test results provided confidence that small leaks in the evaporator cooling coils could be repaired. Visual sighting of the leaks in situ was unsuccessful, so geometry and locations were unknown. A simple deployment system was designed to introduce the sealant to the coil assemblies. The coils have successfully operated for three years with only one reapplication necessary.

INTRODUCTION

At the Savannah River Site (SRS) and other nuclear facilities for the Department of Energy, waste from the processing of nuclear material is stored in large carbon steel tanks. Some of these tanks have closed-loop cooling coils for temperature control. At SRS, a receipt tank for evaporator concentrate developed leaks in its cooling loops. Commercial leak seal products were evaluated as a short-term repair to recover some of the cooling coil capacity.

The waste tanks require cooling to remove the radioactive decay heat and other sources of heat (i.e. steam heat loads, ventilation heat loads, or mechanical heat loads from pumping/mixing operations). Cooling at SRS is provided to the waste tanks by a closed loop chromate cooling water (CCW) system. This system has centrally located supply and return headers on the top of the waste tank, which can be individually isolated from the main distribution system. Cooling coil inlet and outlet valves are connected to the supply and return headers, respectively.

The receipt tank contained five cylindrical deployable-type cooling coil assemblies. Chromate-inhibited water was used as the coolant. These coils are 2-in, sch 40 carbon steel pipe. They were successfully operated without incident for about 21 years until five assemblies developed leaks into the tank. Leak rates varied from less than 1 gpm to greater than 20 gpm. Visual inspection was not successful in locating the leak sites. The nature of the failure, which was sudden following a drop in tank liquid level, suggested mechanical tearing or cracking rather than corrosion. Coil leaks in other tanks have been associated with both. The loss of this tank would cause shutdown and loss of the evaporator, which was untenable due to large new waste inflow into the waste storage area.

Several commercial products were evaluated in a set of screening tests with a prime candidate being chosen for further evaluation. The commercial leak sealant was characterized chemically and morphologically. Degradation testing was performed on formed seals, using simulated coil leak conditions. Additionally, a deployment system was designed for introducing the sealant into the coolant system at the coils. The details of this leak repair method are discussed herein.

CHARACTERIZATION OF SEALANT MATERIAL

The candidate leak sealant chosen for further study after the initial screening tests was Seal-Up® by Blue-Magic® (Houston, TX). Prior to use in the waste tank, the sealant had to be well characterized to assure no adverse reactions. The sealant was investigated in the as-received fluid form and as an as-formed seal. The chemical and morphological analyses techniques included Ion-Coupled Plasma Emission Spectroscopy (ICPES), Ion Chromatography (IC), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), and Scanning Electron Microscopy (SEM) with Electron Dispersive X-ray Spectroscopy (EDS).

Chemical Analysis

The compositional information given in manufacturer's Material Safety Data Sheet (MSDS) showed that sodium silicate ("liquid glass") and copper fines (10 wt % max) were the principal components. Other constituents include oxidizers and corrosion inhibitors [1]. Analytical results of the as-received material verified the MSDS information.

ICPES analyses were performed on as-received fluid and on the filtered liquid, Table 1. Principal constituents were sodium, silicon, copper, aluminum and iron. The aluminum may be the oxidizer [1]. The filtered liquid contained smaller quantities of the metallic elements and higher concentrations of sodium and silicon. This suggests that Fe, Cr and Al are solids in the as-received mix. IC results indicated the principal anion is nitrite (1900 ppm), which may be associated with the corrosion inhibitor. The liquid was alkaline, pH = 11.7.

TABLE 1
ICPES Analysis for Metallic Ingredients of Sealant

Element	Concentration (ppm)	
	As-Received	Filtered
Na	57,000	71,000
Si	103,700	131,000
Al	800	500
Cu	1,500	500
Fe	300	100

The compositional analysis by FT-IR suggested that the filtrate or filtered liquid contained a mixture of liquid polymers. The spectrum was diffuse, with no well defined peaks associated with specific constituents. However, wide peaks corresponding to hydroxyl and carboxyl absorbance were identified. These liquid components are probably precursors for fibers that are formed during the sealing process. In the process, fibers become stacked at the leak site to initiate the seal. The fibers were analyzed by XRD and found to be cellulose. Aluminum and copper metal particles were trapped between the fibers, as verified with SEM/EDS analysis.

A compatibility analysis was performed to evaluate impact of the leak seal chemistry on the waste and waste processing. No adverse reactions were identified. Moreover, the amount of sealant that might escape or spill into the waste at leak sites would be insignificant as compared with total volume of the waste.

Morphology Of The Sealant

The sealant forms cellulose fibers, which appear to grow rapidly via a thermally assisted process. The polymer is initially in solution as a liquid component of the sealant. The fibers trace the flow pattern of the moving coolant and follow the changes in flow direction at a hole or leak site. Fibers tend to align and where the stream pattern compresses, the fiber ends or tails become entangled. A tangled mass develops on the upstream side of the hole. On the downstream side of the opening, the stream lines expand and there are no tangles. The metal particles and sodium silicate fill into the interstices of the massed haystack to complete the seal on the inside.

The fibers, shown in Figure 1, are thin wall tubes, transparent or translucent, and predominantly beige or light tan in color. The diameters ranged from 6-20 microns (0.00024-0.00080 inches), with most at 11-17 microns. Lengths were less than one inch. As indicated above, the cellulose fibers develop as the compound is applied. The fibers appeared to grow larger with time. The sodium and copper contents in the seals varied.

The sealant is designed for application in water-cooled internal combustion engines. Such seals are not exposed to an aggressive liquid, but may be exposed to hot pressurized gas environments or ambient air. In the waste tank cooling system, however, leaks are actually in piping immersed in radioactive alkaline solutions. Thus, exposures to water and to simulated wastes were required to demonstrate integrity of a seal for this application. The exposure was not expected to impact formation of the fibers and initial formation of the seal

Testing on formed seals consisted of exposure to air and water, exposure to simulated waste, and exposure to radiation. The exposure to air and water was performed at nominal pressure and flow conditions, with the exterior at the leak site exposed to air or water. The exposure to simulated waste was performed in a low pressure cooling loop with the pipe exterior immersed in a representative waste simulate. Radiation exposure was done under static conditions on sealed pipe sections.

SIMULATED COOLING COIL TESTING

The shape of the leak in the cooling coil was unknown so holes and slits were made in 6-inch lengths of 0.5-in. sch 40 carbon steel pipe. Leak rates of 0.63 to 1.44 gpm were used with scaled nominal cooling coil conditions. Tests were run with a solution made of the sealant and water flowing in the interior, the exterior exposed to either air or water. The same pipe samples with seals in place were later used in an environmental flow loop tests.

The test loop, Figure 2, consisted of a simple loop and a pump. The system was adjustable to provide a selected leak rate at the machined leak sites. The sample section was connected on the discharge side of the pump. Flow was maintained at ~6 gpm and the solution was collected at a reservoir. The water was heated at the reservoir and used to supply feed to the pump. A PVC pipe trough at the test pipe section captured and recycled any leaking water back to the reservoir. Pressure and temperature were monitored. Pressure was maintained at 50 psig (coil operating pressure). The temperature was ramped from 115 to 160°F (46-71°C) during testing. The total liquid volume for the test loop was 4 gallons.

With air outside, a seal formed in a 0.016 x 0.291 in. slit (standard slit) in 4 minutes and in a 0.046 in. diameter hole (standard hole) in 20 minutes. Time for seal formation was longer with the pipe immersed in water, 20 and 40 minutes, respectively. The seals held for the length of the test, up to 120 minutes. With water exposure, seals did not develop at all for large leak sites. For example, leak rates did not change for a 0.062-in diameter hole (0.72 gpm) or for a 0.046-in. x 0.101-in. slit (1.44 gpm). Visual observations during testing suggested that the seal formed by fibers filling and protruding through the leak site and then coalescing on the exterior, slowly occluding the flow as opposed to a rapid pile up on only the interior.

To evaluate the impact of two leaks next to one another, a sample section with a standard hole and slit 0.75 in. apart was tested. The slit sealed in 40 minutes at 70°C. The hole, however, did not seal. When the flow direction was reversed, the hole was sealed in 90 minutes. The normal flow pattern was disturbed by the nearness of the two leak sites, so that the downstream site apparently experienced some eddy effects which disturbed seal development.

In assessing the requirements for seal formation, flow and heat in the pressurized flow loop were found to be necessary for formation of fibers to occur. Fibers did not form in a static situation or even with stirring in a laboratory beaker. At low temperatures (30-40°C), the solution clouded; at higher temperatures (60-70°C) cotton-like clumps formed in the beakers.

ENVIRONMENTAL TESTING

Before running in the environmental flow loop, sealed pipe samples were exposed to simulated waste under non-flowing conditions. The pipe sections had standard-sized leaks first sealed with air or water on the pipe exterior. The pieces were then immersed in simulated supernate at 80°C for 7-10 days, after which they were removed and checked for leakage under a static head. The sealed pieces showed no leakage from the hole or slit. The pieces were then tested in the pressurized flow loop with water outside. A minor weep was observed at the hole, but the slit was leaking at one end. After about one minute, the leak stopped with only an occasional drip or weep thereafter.

Chemical exposure tests were also performed on fibers collected from the reservoir of the pressurized flow loop. These were centrifuged, filtered, rinsed, dried and weighed prior to testing. Samples were then exposed to the simulated waste or to chromated water (Table 2), at both 80 and 90°C. Fibers were then reweighed each week, using the following procedure: A) Centrifuge the tubes to push fibers to bottom, B) Decant the solution, C) Rinse with distilled water, D) Centrifuge, E) Decant rinse water, F) Dry the solids in an oven at test temperature, and G) Weigh samples.

TABLE 2
Simulant Chemistries for Seal Degradation Testing

Component	Concentrations (M)	
	Waste	Chromate Water
NaOH	5.0	0.0001
$NaNO_3$	3.0	--
$NaNO_2$	1.7	--
Na_2CrO_4	--	0.0043

Weight change results from these tests are shown in Figure 3. Weight losses occurred in all the test solutions. A seal degrades to a greater extent with waste exposure (no salt layer) than with exposure to chromated water. The water and simulated waste exposures resulted in dissolution and removal of some of the water glass/sodium silicate component in the seal, Figure 4. Attack of the seal by waste appeared to be more rapid than attack in plain water. In both cases, haystacked fibers remained after the exposure, though they were matted or pressed together. Individual tubular fibers were collapsed and the loose piles were compressed and closed down.

The environmental flow loop was used to test seal integrity with extended time exposures approximating real waste conditions. Coolant water was controlled at 27 - 35°C using a recirculating water bath. The waste simulant was also recirculated and the temperatures maintained between 68 and 75°C. A reflux condenser was used on the heated vessel to reduce evaporation of the simulated waste. The test setup is shown in Figure 5.

The first test was conducted in several phases. During the first eight-day phase, sodium nitrate was added until a salt layer began to form on the pipe. The second phase was conducted for four days to allow formation of a complete salt layer. Figure 6 shows sequential photographs taken during salt deposition. In the third phase, desalting was performed by shutting off coolant flow. In absence of cooling, the bath temperature spiked to 100°C and the sample pipe leaked. The circulating coolant with sealant was turned back on, but the leak sites did not reseal.

For the second test, a new sealed pipe section was placed into the loop with a fresh batch of supersaturated simulated waste. Exposure sequence and test results are summarized in Table 3. The test was operated for 23 days until a small leak was detected. Three salt/desalt cycles were performed during the first ten days with no leaking or occurrence of temperature spikes. During the subsequent thirteen days, the salt layer was maintained continuously on the pipe until a small leak was detected (~0.01 gpm). Some salt dissolution occurred during four more days, perhaps due to dilution of the supernate.

At this point, the sample section was removed and placed in the pressurized flow loop with fresh water to evaluate the degree of leaking and the self-repairing capability of the seal. Slight weeping was observed at the hole and leaks were seen at both ends of the slit. The total leak rate from the failed seals at nominal pressure was ~0.03 gpm.

TABLE 3
Long-Term Environmental Flow Loop Results

Test Period (days)	Salt Layer Condition	Solution Temp. (°C)	Comments
10	3 salt/desalt cycles	<80	No leaking
13	Continuously maintained	75	No leaking
1.5	Continuously maintained	75	<0.01 gpm leak
2.5	Slowly dissolved	75	No coolant flow Pipe removed
8*	Water immersion. Seals reestablished in pressurized flow loop	Water exposure only	Pipe tested in nominal pressure flow loop with water; 0.03 gpm leak at slit, leak healed; pipe maintained wet in Water/Seal-Up® solution before and after nominal pressure testing
23	Continuously maintained	70-75	No leaking

* Pipe section was transported between test loops in water containing some sealant material.

The seals healed within approximately one minute, to one drop every 20 seconds. Recurrence of the leak and rehealing for short durations was observed at the slit several times during two hours of testing. At the end, the leak rate was approximately 1 drop/min. After removal from the flow loop, the interior of the pipe was inspected and found to have 50% less deposit at the slit than before starting the test. The hole had little apparent loss of deposit. The test piece was returned to the environmental flow loop with conditions set the same as before. The salt layer formed immediately and was maintained for an additional 23 days.

The agglomeration of salt on the cooling pipes is common. Desalting is performed to eliminate thermal insulation caused by the salt and to recover cooling ability of the coils. Desalting had not been addressed when the tank liquid level was dropped. It is believed that the leaks developed due to salt overloading the umbrella-like structure of the deployable coils, causing tearing at rib connections in the steel pipe.

RADIATION TESTING

Radiation testing was performed to evaluate its effect on degradation of the seal and to determine the capability of the product to self-repair after exposure. A sealed pipe section immersed in tank simulant was irradiated in a cobalt-60 gamma source at 1.04 E6 rad/hr and 50°C. The inside of the pipe contained a sealant and water solution. The pipe was given four consecutive 4-

hour exposures for a total dose of 1.66E7 Rads, equivalent to 2 years irradiation in the waste tank. The pipe section was inspected, tested under static head pressure, and then tested in the pressurized flow loop after each 4-hour period. Table 4 summarizes the results. The seal showed no leakage for 6-months equivalent exposure. A small drip was observed in subsequent exposures up to 2 equivalent years.

Another sealed pipe was subjected to a higher total dose of 1.0 E8 Rad, equivalent to about 12 years service. There was no leak under static head pressure after 5.0E7 Rad, but a leak did occur after the full dose. Resealing was attempted in the pressurized flow loop, but a small leak remained at both the slit and hole.

TABLE 4
Leak Detection after Radiation Exposure

Order	Dose (Rad)	Cumulative Total Dose (Rad)	Static Leak? (Yes, No)	Dynamic Leak (drop/min)
1	4.16 E6	4.1 E6	No	No
2	4.16 E6	8.3 E6	No	Slit – 1 Hole – 0.25
3	4.12 E6	12.4 E6	No	Slit – 0.67 Hole – 0.0
4	4.12 E6	16.6 E6	No	Slit – 0.25 Hole – 0.0

SEALANT DEPLOYMENT SYSTEM FOR FIELD APPLICATION

A sealant deployment system (SDS) was designed to tie into spare branch connections of the CCW supply and return headers located on the tank top. The deployment system, Figure 7, consists of a charge funnel for loading the sealant into a small holding tank prior to mixing, an interim mixing tank with internal heater for blending coolant water and sealant, and a circulation pump for introducing the blend into the pipe loop. A diagram of the SDS configuration is shown in Figure 8.

The deployment strategy for sealant application involved: 1) Close all cooling coil inlet and outlet valves to isolate the coils from the CCW supply and return headers, 2) Isolate the waste tank CCW supply and return headers from the distribution system, 3) Connect the SDS to spare branch connections on the tank top supply and return headers. With these actions implemented, the sealant blend can be introduced and recirculated in the tank top distribution piping. Sealant would flow from the SDS skid to the CCW supply header, through a cross-tie line connecting the supply header to the return header, and then back to the skid. This strategy permitted treatment of the individual coils by isolating the cross-tie line circulation and then opening the coiling coil inlet and outlet valves to establish flow in the coil.

Sealant was circulated through one coil at a time for approximately one hour, and then the treated coil was isolated. To determine the efficacy of the sealant application, an in-service leak check was performed on the affected cooling coil.

DISCUSSION

Testing of an *in situ* leak seal product demonstrated that under simulated waste tank conditions there was reasonable chance of success for this application. Upon addition to a circulating water system, cellulose fibers started to form. As they circulated, the fibers were drawn to leak sites. The complete mechanism of sealing is unknown; however, copper particles became entrapped between the fibers and sodium silicate, the major component of the sealant, was also incorporated. Where the leak site was exposed to air, the silicate typically formed a crystallized shell at the air-side exit. This shell contributes to the overall seal. The silicate may also act as a corrosion inhibitor within the coolant system.

Testing showed the seal was susceptible to degradation under tank conditions. However, the seal was maintained for a period up to 50 days. Direct fiber immersion testing indicated significant dissolution can occur in a relatively short time. However, salt deposition and normal coolant, both serve to mitigate degradation of the seal. When leaking does occur, tests showed that the seal may heal by shifting the buildup of product located outside the leak site.

These results collectively indicated that a seal could remain viable for an extended period, even when exposed to tank waste. Some uncertainty existed, however, as some factors had not been evaluated. These included turbidity in the chromate water, rusting on the pipe interior, varying pipe diameters, fatigue loading at coil supports on the framework, as well as the location, geometry, and actual sizes of the flaws. Operational parameters not investigated, that could affect seal formation and maintenance, included effect of preheating the water, sealant concentration, degree of agitation, and addition rate of the sealant.

The SDS was utilized to internally apply the sealant to the leaking waste tank cooling coils. Consequently, two of five coiling coils were returned to service, recovering 40 percent of the tank cooling capacity. The initial treatment remained leak tight for 39 days of normal cooling operations. Seal failure was attributed to depressurization and low flow during non-routine CCW system evolutions. Re-application of the sealant successfully returned the coils to service. The coils are routinely monitored for leakage, and periodic re-application of the sealant mixture using the deployment system is expected. However, the restored cooling capacity permitted continued waste tank and evaporator operations, while permanent cooling capacity modifications were undertaken.

CONCLUSIONS

Testing of commercial leak sealant provided confidence that a temporary seal could be made in leaking cooling coils of a HLW tank. The maximum leak that was successfully sealed with immersion in water was a slit, 0.016 inches wide by 0.291 inches long and 1.34 gpm loss at nominal operating pressure. The maximum hole that was successfully sealed was 0.046 in.

diameter and 0.63 gpm. Two actual leak rates in waste tank cooling coil assemblies were 0.9 and 0.07 gpm.

Seal degradation did occur with exposure to simulated tank conditions. The seal remained viable for 50 days with waste at 75-80°C, low-pressure cooling water at 27-35°C, and several salt/desalt cycles. A small leak (~0.03 gpm) was observed after 23 days. However, the leak self-healed suggesting that a seal would remain viable for >23 days. The seal also retained capability after 1.66 E7 Rad exposure, equivalent to roughly 2 years service. The impact of numerous other parameters that may affect seal formation and integrity were unknown at the time.

ACKNOWLEDGEMENTS

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REFERENCES

1. Personal communication: J. I. Mickalonis with Dr. David Bell of Cargo Chemical Corporation, February 13, 2001.

FIGURE 1. SEM photomicrograph of filtered fibers from sealant

FIGURE 2. Pressurized Flow Loop. The pipe sample with machined flaws is positioned in the trough in order to catch spills.

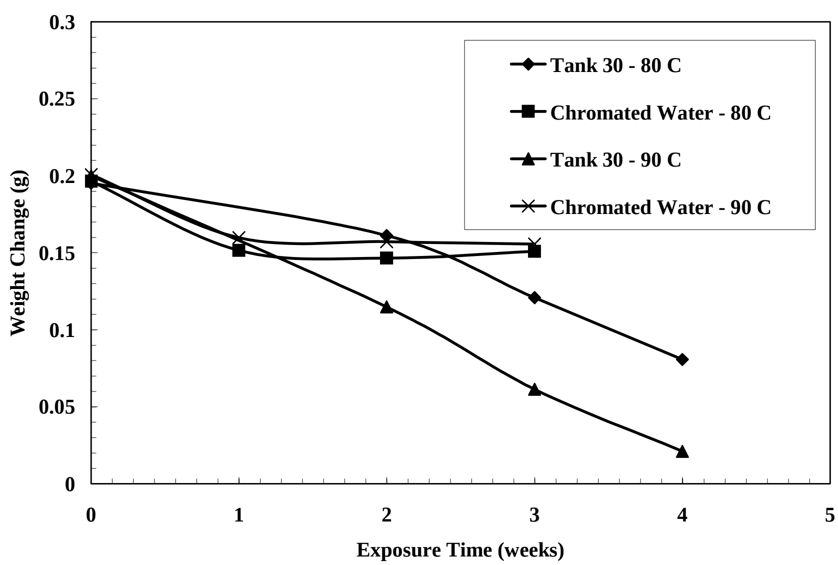
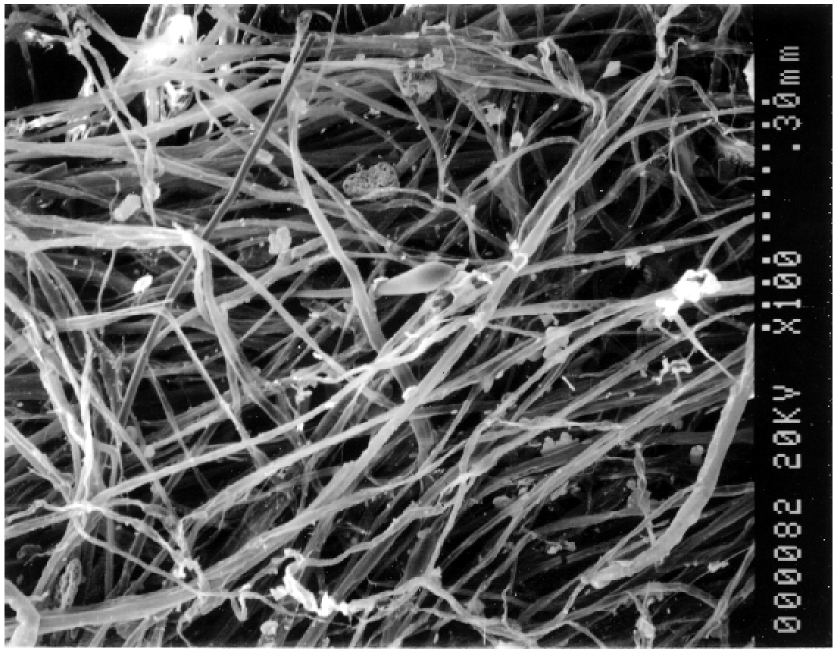
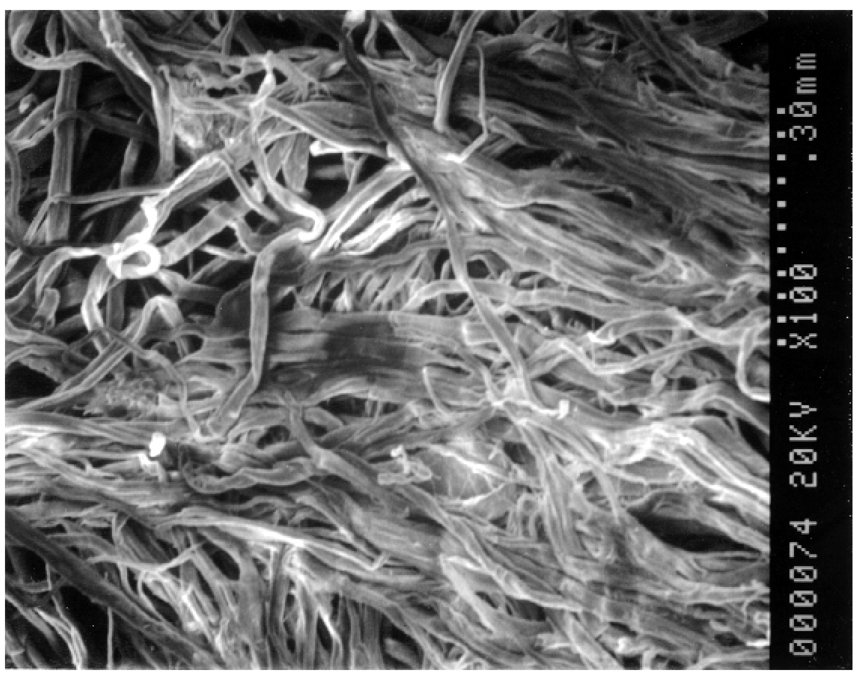


FIGURE 3. Weight Change of Fibers in chemical degradation tests



(A)



(B)

FIGURE 4. SEM photomicrographs of sealant fibers exposed to (A) water and (B) sodium hydroxide solution

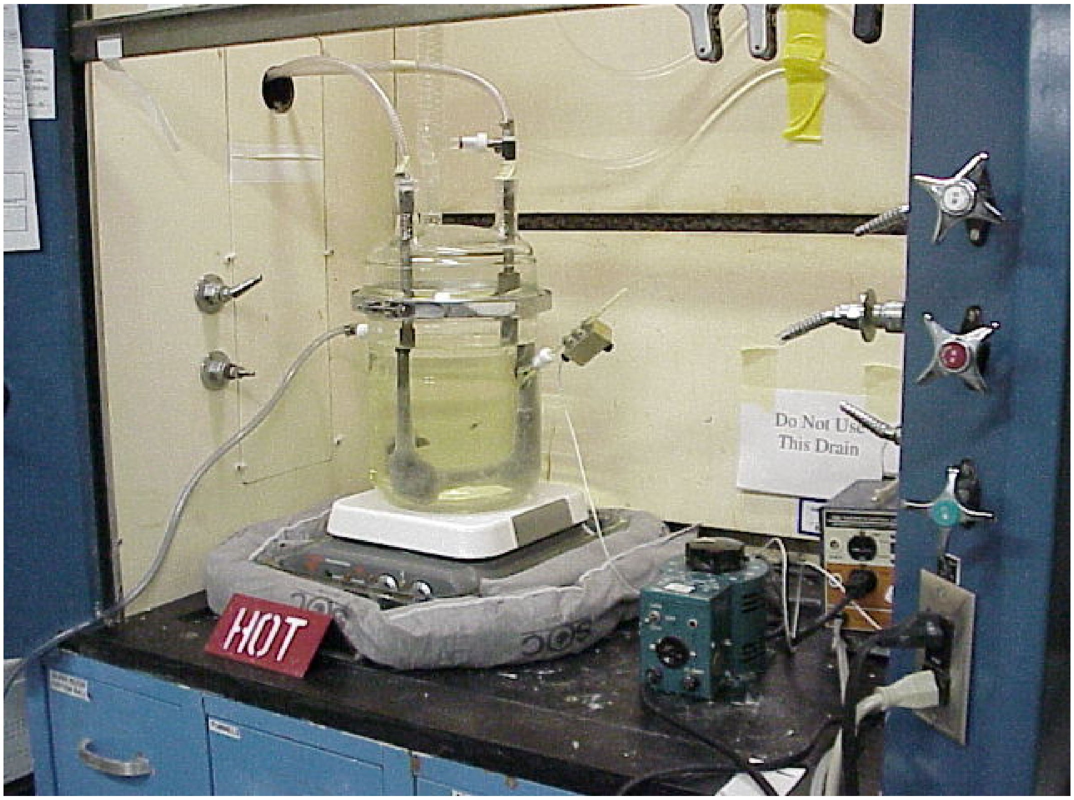


FIGURE 5. Environmental Flow Loop Test set up

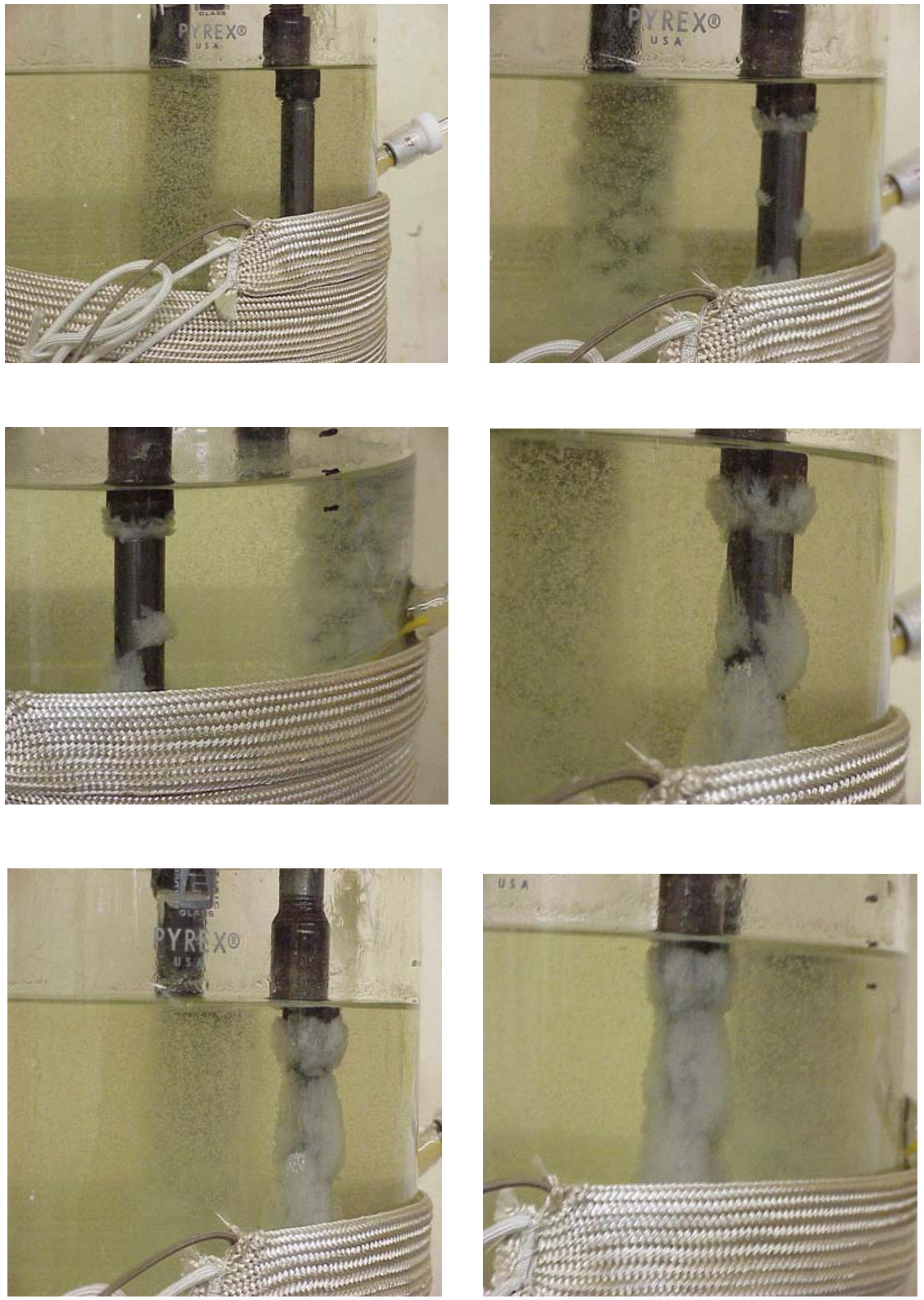


FIGURE 6. Salt layer formation on cooling pipe in Environmental Flow Loop

FIGURE 7. Sealant Deployment System

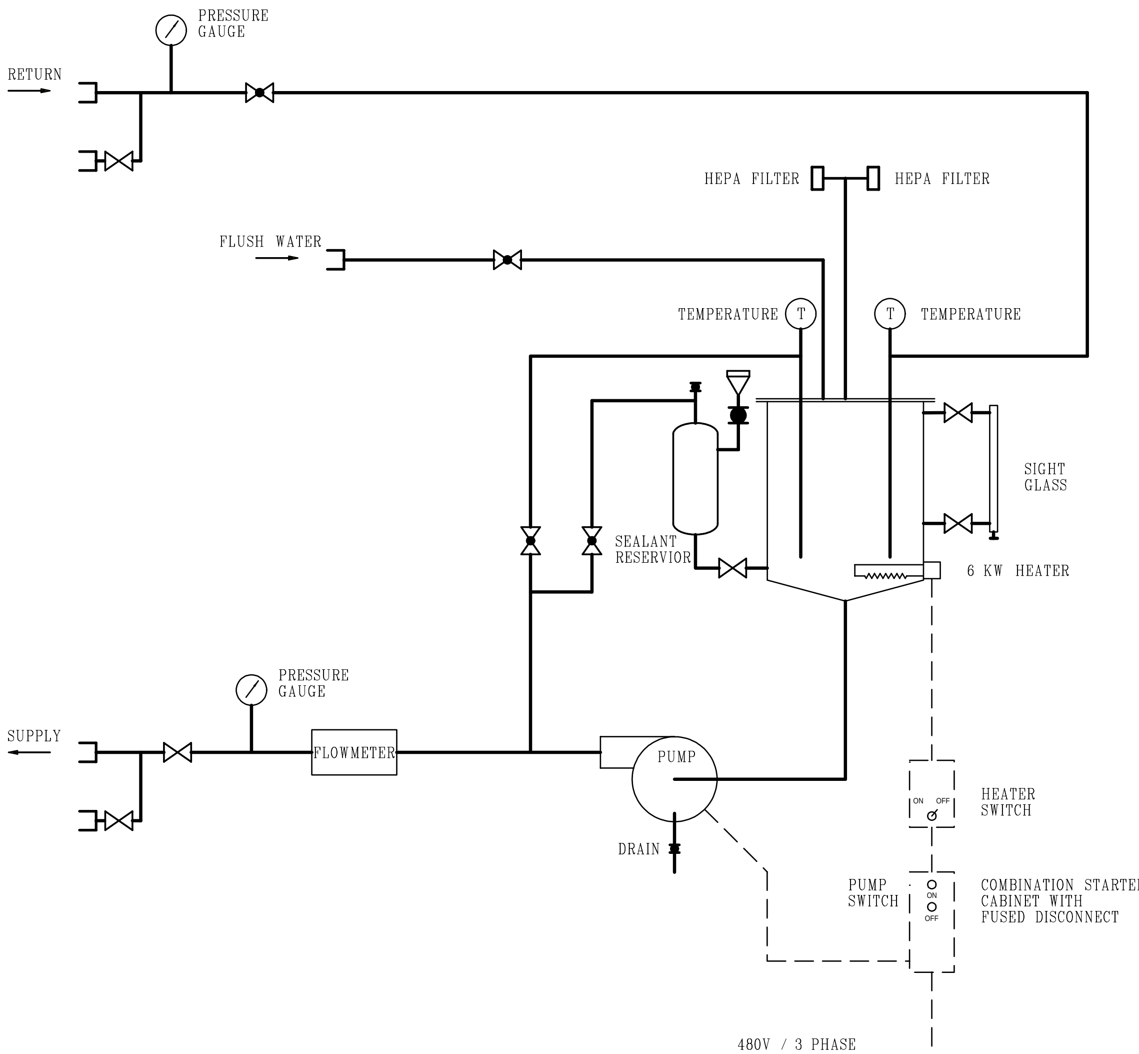


FIGURE 8. Sealant Deployment System process and instrumentation diagram