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Use of on-line ion chromatography in controlling water quality in nuclear power plants

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Abstract

Electric utilities that operate nuclear power plants must adhere to a tighter range of water coolant specifications that are commonly required in steam systems powered by other means such as coal, oil or natural gas. The reason for this situation is the higher negative impact of a failure in the coolant and steam piping relative to non-nuclear heat sources. This negative impact arises from the unique need of a nuclear reactor core to require cooling after shutdown of the chain reaction—due to the heat from undecayed radioactive fission products in the uranium fuel rods. Also, the cost of down time for repairs of corrosion damage in such stations is greater than for fossil fired plants because these nuclear plants are base loaded (running at *ca.* 100% power for several hundreds of days) and the replacement power required during their shutdown time must be provided by sources more costly by factors up to *ca.* 2. Since corrosion damage in nuclear plants usually occurs under crevice conditions in components such as steam generators where boiling occurs, even very small (parts per billion, ppb) initial feedwater concentrations of corrosive impurity salts such as sodium, chloride and sulfate may concentrate to corrosive brines—leading to breaches of the pressure boundaries from localized cracking or intergranular attack. This attack penetrates even the more corrosion-resistant alloys such as Inconel 600, Incoloy 800 and the stainless steels. Ion chromatography is the only technology able to readily measure ppb concentrations of such corrosive ions on a near real time basis, and to differentiate among different oxidation states of ions such as nitrate, nitrite, sulfate, thiosulfate, etc. These oxidation states respond to the general oxidizing tendency of the coolant—another variable that controls localized corrosion. A number of examples of the use of on-line ion chromatography in troubleshooting corrosion problems in light-water reactors will be given.

1. Introduction

Why would nuclear power stations need on-line ion chromatography (IC)? The answer: “to signal the onset of transient corrosive conditions from intrusions of ionic or ion-producing species into the water coolants”. In the mid-1970s, it became apparent that expensive components in nuclear power stations were undergoing corrosion damage of a localized nature from concentrations of only a few parts per billion (ppb,

w/w) of ions such as sulfate, sodium and chloride into the steam-producing water cycle. These ions were often associated with transient events which seldom coincided with the customary times for the “once a shift” or less frequent grabbing of a water sample for laboratory analysis. The on-line instruments in place such as conductivity meters did respond to such intrusions, but they seldom contained the information desired for fixing the trouble in a timely fashion. Significant damage sometimes occurred because the operators’ de-

layed action until the instrument's readings were corroborated by laboratory analyses delivered hours to days later.

Into this situation in the late 1970s entered the laboratory ion chromatograph, able to reliably measure almost any positive or negative ionic species in water at ppb levels. But could a laboratory instrument be configured for the rugged conditions of on-line use at several different sample locations around the steam loop? It appeared likely, since large beds of ion-exchange resins had been widely used in a plant environment for many years for water treatment. After all, were not these devices just miniaturized versions of the reliable ion-exchange beds?

An Electric Power Research Institute (EPRI) research project was approved with the objective of three plant demonstrations of on-line IC [1,2]. Those three demonstrations have since led to installations at almost half of all USA nuclear stations. Further penetration of the power industry market for on-line IC can be expected as designs become less demanding of operator attention.

Applications of the on-line IC in the USA nuclear power industry are organized below based upon the separate coolant loops to emphasize the unique nature of the water impurities and additives commonly found in each.

2. Pressurized water reactors (PWRs)

2.1. Secondary side coolant

The secondary side coolant in PWRs was the first to be considered for application of on-line IC for two main reasons: (1) Corrosion damage of the steam generator was a very expensive problem that needed solution, and (2) the coolant impurities were suspected as possible causes of some of the damage mechanisms. Analysis of the sulfate ion, one of the most significant of these impurities, was the key to convincing many PWR operators to install an on-line IC. Why sulfate? Sodium and chloride already had a number of procedures capable of ppb sensitivity, sodium more than chloride. Sulfate was a far

more difficult problem analytically. Furthermore, sulfate was in many steam systems far more abundant than chloride. Not only did it enter from cooling water in-leakage at the turbine condenser from both brackish and non-brackish waters, but internal sources such as the sulfonated cation resin of condensate polishers and sulfuric acid cation resin regenerant leachate were often dominant. Worse yet, as the anion resin of a mixed bed condensate polishing system gradually degraded its kinetics due to fouling by organics and other species, the first ion to show reduced kinetics for removal was the sulfate ion—due to its slower diffusivity arising from its two negative charges. It almost became, in many stations, a sulfate ion-dominated world!

Some of the early on-line data obtained in PWRs were dominated by sulfate ion spikes, more from resin intrusions than from condenser in-leakage. Figs. 1 and 2 show the first sulfate spikes seen by on-line IC in the EPRI program, observed at the Rancho Seco PWR right after a turbine trip (a sudden drop to near zero power) at points upstream and downstream of the deep bed condensate polisher beds. All the three ions, chloride, sodium and sulfate were observed in the upstream (hot well) sample, but sulfate was dominant in both up and down stream samples. Notice that the polisher was removing both the singly ionized sodium and chloride ions, but less than 25% of the doubly charged sulfate ion. All

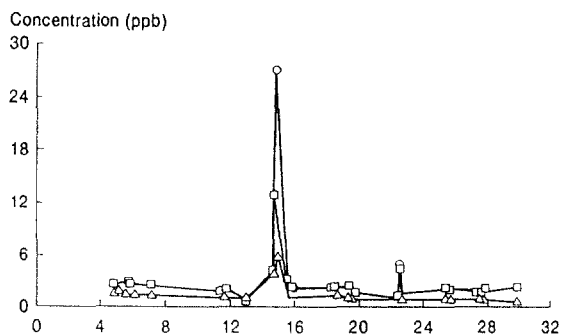


Fig. 1. Sulfate (○), chloride (□) and sodium (△) ion concentrations measured with on-line IC in the condenser hotwell of a PWR during a 22-day period in January 1982 within which a turbine trip occurred (x-axis: days).

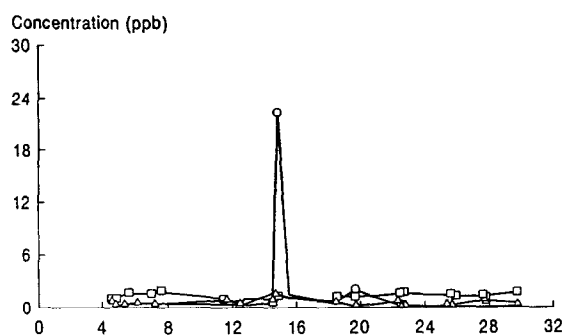


Fig. 2. Sulfate (○), chloride (□) and sodium (Δ) ion concentrations measured with on-line IC downstream of the condensate polisher ion-exchange bed during the same period as in Fig. 1 (x-axis: days).

three undoubtedly were entering the system water from deposits on dry, turbine cycle surfaces wetted during the sudden reduction of power. Conventional wisdom of that time would have expected all three to be removed by the polisher. It is probable that the polisher resin was kinetically fouled so it became a virtual separator for two negative ions! The point not to be missed in this story is the value of on-line data to see this transient and to learn from it the probable remedy—in this case to replace or refurbish the fouled anion resin.

It quickly became apparent that the on-line IC was proving an effective tool for quality assurance of the effluent from condensate polishers installed in many plants, and for troubleshooting their operation. Other ions, mostly anions, were found to be present but none of them were as significant corrosive agents as sulfate. However, the second most interesting anion class found were the weak carboxylic acids acetate, glycolate and formate, chief of which was acetate.

Acetate is even more ubiquitous than sulfate in PWR steam cycles. Eventually its source was discovered—tramp organics enter the cycle through the makeup water system or as lubricants left from maintenance on internal surfaces. All are thermally degraded partially to acetate. Before the time of the on-line IC, it was widely believed that all organics degraded all the way to carbonates (carbon dioxide) in the steam cycle.

Apparently, acetate is an extremely stable species in these nuclear steam cycles with peak temperatures of generally less than 320°C.

Acetate could be quantified for the first time at ppb levels with the on-line IC and its fractional contribution to the cation conductivity (CC) determined. (CC is actually the conductivity of water measured downstream of a hydrogen form cation-exchange column—thus making acids of all anions present—and hence is a measure of the totality of anions present in the water. It is used to remove the conductivity effect of ammonium or amine cations, the pH control additives present at levels far higher than all the anions other than hydroxide). High levels of acetate (tens of ppb), while essentially benign from a corrosion standpoint, would often increase operator concerns because of their effect on increasing CC. The on-line IC was able to distinguish when the CC was due to really corrosive anions and when it was merely reflecting the acetate from an organic intrusion. Fig. 3 shows the acetate (and formate) ion concentration measured during the morpholine ON-OFF-ON test at Beaver Valley Unit 1 [3].

The morpholine story brings out another chapter in the on-line ion chromatograph's contribution to improvement of PWR secondary water chemistry. Morpholine is an organic amine base

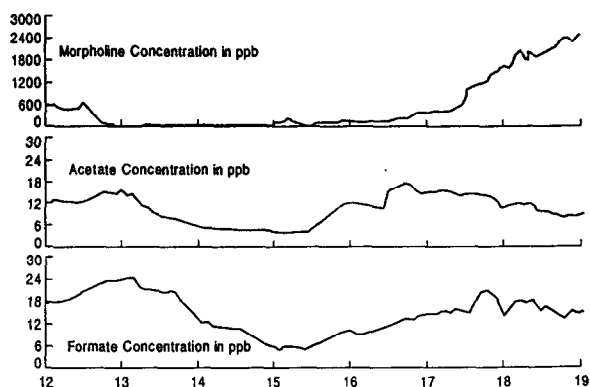


Fig. 3. Acetate and formate concentrations measured by on-line IC for water from the heater drain receiver tank of the Beaver Valley Unit 1 PWR during the 7-day ON-OFF-ON morpholine test (x-axis: days; y-axis: ppb).

less volatile than the commonly used ammonia under all volatile treatment (AVT). Its lower volatility allowed the pH of condensate in the wet steam region of the turbine cycle to be raised by amounts that significantly reduced the flow-assisted corrosion of carbon steel surfaces in that part of the loop. While that effect reduced the frequency of piping replacements, it had a much more significant effect. The iron oxide corrosion product particulate input to the steam generator was correspondingly reduced. This reduction in iron oxide deposits in the steam generator had a beneficial effect in reducing the rate of localized corrosion in that component, because the sludge deposits had enhanced the concentration of corrosive ions produced when boiling occurs within their porous structure.

How is all this related to the role of the on-line IC? In at least two ways: (1) acetate was always produced as a thermal degradation byproduct of morpholine addition and therefore the increase in CC had to be shown to be due to the benign acetate and not to the aggressive sulfate or chloride ions and (2) morpholine itself needed to be monitored in the presence of ammonia (ammonia is still present under morpholine-based AVT from morpholine thermal decomposition as well as from decomposition of the hydrazine added for oxygen control). The anion IC column measured the acetate ion and the cation IC column quantified morpholine.

Later other amines such as ethanolamine less volatile and with a higher base strength were found as improved replacements for morpholine. The on-line IC was up to the challenge—the new amine was just another peak on the cation chromatogram! Fig. 4 is a chromatogram showing separation of the ammonium and ethanolammonium ions from the work of Shenberger *et al.* [4]. Again, the on-line IC provided the assurance needed to overcome objections to a new PWR secondary side water chemistry, without which the changeover might have been significantly delayed.

Another area where the on-line IC has proven essential is in measuring the ions present in so-called “hideout return” (HR). Many ionic substances in water precipitate or adsorb on heat

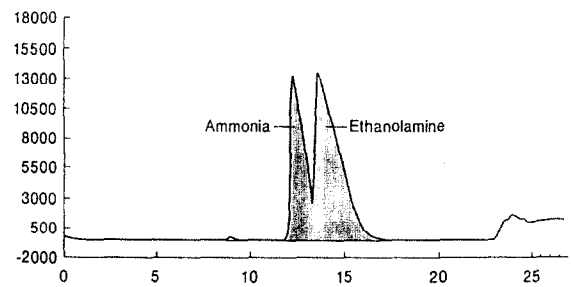


Fig. 4. On-line IC cation column chromatogram for ammonium and ethanolammonium ions, two species which had required significant adjustment in eluent conditions for adequate separation. Ammonia 500 ppb, ethanolamine 3 ppm (x-axis: time in min; y-axis: $\mu\text{S}/\text{cm}$).

transfer surfaces such as steam generator tubes and in the crevices between those tubes and their support plates. The HR studies occur during a cooldown in preparation for a refueling outage of some 40 to 80 days, so they must be conducted with little impact on the shutdown schedule. By noting the time of return, the puzzle of what solids constitute the chief storage mechanisms for both corrosive and benign ions can be better understood. Figs. 5 and 6 illustrate the pattern of HR reported by Bostic and Burns [5] using on-line IC. In this case the manganous ion dominates the positive ions returning from hideout, a discovery made possible by on-line IC. The full significance of manganese ions to crevice corrosion remains to be understood.

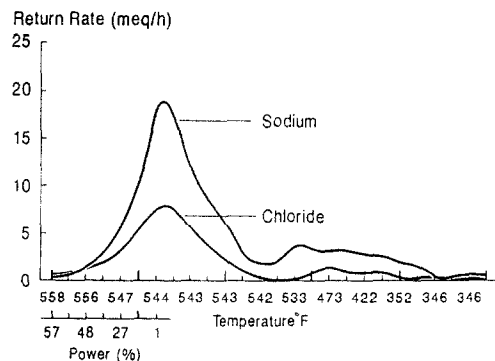


Fig. 5. Hideout return of sodium and chloride ions as a function of temperature and power level in a PWR steam generator measured by on-line IC during a gradual shutdown prior to refueling.

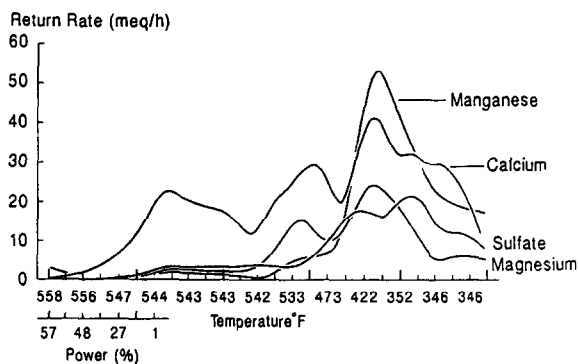


Fig. 6. Hideout return of calcium, magnesium, manganese and sulfate ions in steam generator water measured by on-line IC during the same shutdown of a PWR shown in Fig. 5.

The frequently more abundant ions such as silicate and borate can also now be quantified by on-line IC in spite of their being extremely weak acids [6]. The object is to find the likely pH of the crevices from which much of the HR comes, and plan water chemistry strategies to bring crevice pH into the more benign neutral range. The semi-volatile weak organic acids that are stable in these steam loops have a potential to neutralize the current predominantly caustic crevices. Again, on-line IC will be needed to keep such additives under constant control, should they be found useful in the future.

Finally, on-line IC has been used in at least one case for early warning of PWR primary-secondary leakage [7]. In this case, the extreme sensitivity of the IC cation column for lithium ions (low ppt levels) allowed detection of this leak before even the radiation monitors sensitive to radioactive species could detect it, as they did two weeks later when the leak had grown in size. Lithium-7 ions are present on the primary side at levels in the ppm range as natural products of the boron-10 (n, α) reaction, boron being present at the hundreds of ppm level as boric acid for reactivity control.

2.2. PWR primary side coolant

While, to my knowledge, on-line IC has not been applied to surveillance of PWR primary coolant, specific problems have been addressed

by various short-term campaigns on the primary water. These usually have revolved around sulfate intrusions, suspected to arise from the ion exchange resins in the chemical and volume control system (CVCS). The generally reducing chemistry of the primary PWR coolant arising from the use of dissolved hydrogen gas, has led to speculation that sulfate could be reduced to more aggressive reduced sulfur species such as sulfite, sulfide and thiosulfate. Some of these anionic species could be readily observed by on-line IC to either confirm or refute this conjecture, which is still unresolved.

2.3. Makeup water systems

Since makeup occurs at about 1% of total system flow in many power system coolant loops, it represents an opportunity for intrusions of corrosive impurities if the makeup output quality should degrade. On-line ion chromatographs for secondary water often have one sample line from the makeup system output as a check on this source of impurity intrusion. Such upsets usually occur during periods when the resin beds or membrane systems near the end of their use cycle due to exhaustion or fouling.

3. Boiling water reactors (BWRs)

Coolants in BWRs are less complex than PWRs because no ionic additives are used. This simplifies the analytical problem for IC. However, the fluids are measurably radioactive, making IC applications deal with the nuisance of small volumes of so-called mixed wastes—mildly toxic eluent chemicals combined with mildly radioactive waters. Water quality has traditionally been followed with on-line conductivity and pH meters plus measures of oxidizing tendency such as electrochemical potential (ECP) or measures of the main species that influence ECP, namely dissolved oxygen and hydrogen gases.

Recently, the reactor water (water that circulates through the reactor core), was found to have higher conductivity than the sum of known impurities commonly seen such as sodium, sul-

fate, nitrate and chloride. A major effort using both on-line and off-line IC resulted in the discovery of the culprit: the chromate ion. This ion arose from corrosion of the stainless-steel feedwater heater system piping during normal operation with spikes occurring whenever an abrupt increase in ECP occurred. Such abrupt changes were observed in many stations when a transition from hydrogen (reducing) water chemistry (HWC) to normal (oxidizing) water chemistry (NWC) was experienced. This phenomena has been interpreted as the release of chromate by sudden oxidation of a piping surface layer of solid chromium oxide in the +3 Cr oxidation state to dissolved chromate ion in the +6 Cr oxidation state. Fig. 7 shows one such chromate spike observed by on-line IC at the Nine Mile Point unit 1 BWR, while Fig. 8 gives the corresponding hydrogen gas concentration [2]. Note the timing of the chromate spike occurring just after hydrogen is shut off.

Other interesting ionic changes occurring during changes from NWC to HWC and *vice versa* have been observed by on-line IC. The changes observed involved known species present at a concentration of a few ppb and they followed known and expected chemical changes. For example, nitrate ion [nitrogen (N) in the +5 state] present at 4 ppb under NWC was observed to be transformed successively to nitrite ion (N in +3 state) and ammonium ion (N in -3 state) on going from NWC to HWC at one plant. The

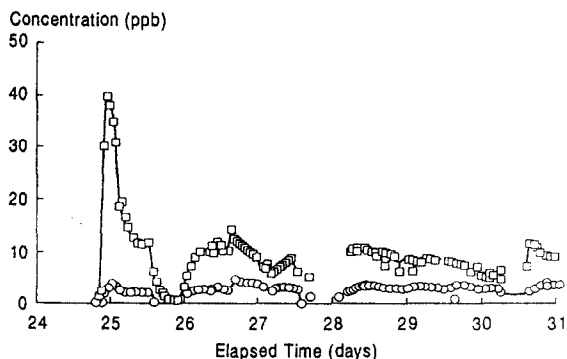


Fig. 7. Chromate (□) and nitrate (○) ion concentrations measured by on-line IC in the reactor water of a BWR following the transition from hydrogen (reducing) water chemistry to normal (oxidizing) water chemistry.

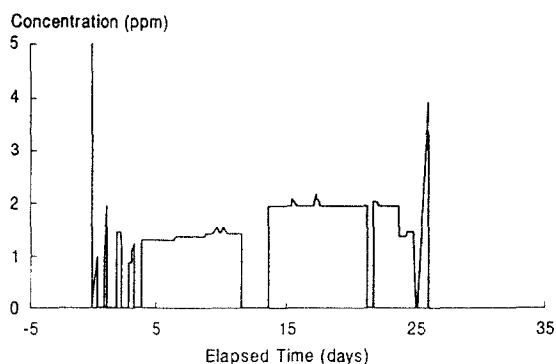


Fig. 8. Dissolved hydrogen gas concentration in the feedwater of a BWR prior to and during the chromate and nitrate ion measurements shown in Fig. 7.

nitrogen species were also detectable on a radiation detector using the 10-min radionuclide nitrogen-13 produced by the $N-14(n,2n)N-13$ reaction on a small fraction of the nitrogen atoms passing through the reactor core. Since the ratio of two species of differing oxidation state varies with ECP some indication of the latter can be acquired by on line IC.

Another area of concern to BWR operators is the quality of the water downstream of the condensate polishers and the reactor water cleanup system resin beds. Here again the on-line IC was equal to the task. Copper ion removal has been the focus of several campaigns in this arena. For as yet undetermined reasons, copper is an unusually aggressive species inducing several forms of localized corrosion on the zirconium alloy fuel rod cladding in the core. The on-line IC has been used to check polisher outlet concentrations of copper down to the 0.1 to 1 ppb levels commonly observed [8].

4. The future

I see no end in sight for the uses of on-line IC in the power industry. Particularly when extrapolating from the history of the past 15 years, one could with some confidence predict many more exciting discoveries to be made in the chemistry and transport of both corrosive and benign ionic substances in high-temperature

water and steam. Here are a few of my predictions: (1) using on-line IC for control, the role of the acetate and glycolate ions will be found to be significant in both crevice corrosion and in iron oxide deposit transport in PWR secondary side coolant and may eventually lead to the use of these ions as additives during frequent on-line episodes of chemical control of deposits; (2) on-line IC will be increasingly used in waste water processing within the power station with the objective of recycling an increasingly greater fraction of such water into makeup; (3) analogous to the discovery of the manganous ion as an indicator of erosion–corrosion of carbon steel piping, other trace element ions will be found which signal corrosion of other metals and alloys used in steam power systems. For example, the oxygenated anions molybdate, tungstate, niobate produced by oxidative corrosion of ferrous alloys containing molybdenum, tungsten and niobium are observable by an on-line IC anion column with modified eluent.

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