

A Portable Remote Chemical Analyzer for Identification of Deposits and Leak Characterization at Nuclear Power Plants.

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Abstract-- *Reactor coolant pressure boundary leakage in pressurized water reactors leaves a white boric acid residue that is corrosive to reactor components. However, not every white deposit found in a PWR is boric acid, and identification of unknown deposits can be crucial in determining if an active leak exists. Current methods for identifying the source of unidentified deposits require a sample to be removed and analyzed using radiometric techniques. This approach is time-consuming, requires potential exposure of personnel to radiation, suffers from false positives, and may not be possible in locations that are inaccessible or where only small amounts of deposits exist. A new technique based on Raman spectroscopy allows in-situ analysis and positive identification of boric acid residue. This technique can also determine the state of hydration of the boric acid which will help understand the nature of the source of the residue. The spectroscopic analyses of other common materials that may be mistaken for boric acid are also presented*

I. INTRODUCTION.

Nuclear power plants, especially pressurized water reactor plants (PWRs) have identified a need for a field test to determine unequivocally if an unidentified deposit is boric acid, either from a reactor coolant solution (RCS) pressure boundary leak or a spill. Formerly, potential pressure boundary leaks were identified by visual identification of white deposits, followed by laboratory

confirmation using radiometric techniques. Radiometric techniques, however, do not determine that a white deposit is RCS, which is predominantly boric acid, and such techniques are subject to false positives and errors in interpretation. Also, there is significant cost associated with removal of a sample from the suspected leak site and laboratory analysis, both in time and increased radiation exposure to personnel.

PNVGS and Symphotic TII have developed a technique for *in-situ* analysis that gives positive identification of boric acid deposits without requiring removal of a sample for laboratory analysis.

II. OVERVIEW OF POTENTIAL BORIC ACID DEPOSITS AND FALSE POSITIVES.

Figure 1 shows a typical leak with an associated boric acid deposit. In this case, the leak is easily identified visually, and is readily accessible, with a large enough quantity of deposit for sampling and laboratory confirmation.



Figure 1. Hot leg instrumentation nozzle with boric acid deposit.

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Figure 2. Reactor vessel bottom mounted instrumentation nozzle.

Figure 2 shows a reactor vessel bottom mounted instrumentation (BMI) nozzle, courtesy of South Texas Project. This deposit is smaller and more inaccessible than that shown in figure 1, but has been identified as a leak. In contrast, figure 3 shows white paint on BMI penetrations. Without prior knowledge of the application of paint, these white deposits might be mistaken for a serious set of leaks.



Figure 3. White paint on BMI penetrations



Figure 4. Duct tape residue

Figure 4 shows white duct tape residue below BMI penetrations that might also be mistaken for boric acid residue.

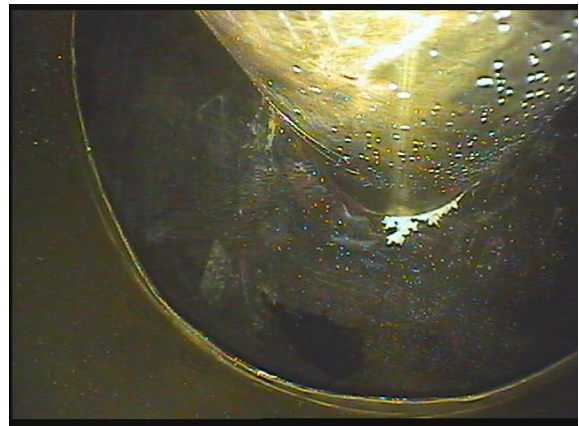


Figure 5. "Popcorn" deposit

Figure 5 shows a small deposit in a location that is inaccessible for easy sample removal.

All these deposits may require analysis to either verify a leak or to demonstrate conclusively that a deposit is not a leak.

III. PROBLEMS WITH PREVIOUS METHODS OF DEPOSIT IDENTIFICATION.

Previous methods for identification of deposits require a visual assessment and judgment, sampling, removal of the sample from containment to the laboratory,

and radiometric and chemical analysis. These steps are all subject to false positives or incorrect interpretations. For example, cross contamination during the sampling and removal process may lead to a false positive that could lead to an unnecessary reporting and repair. In addition, small, inaccessible locations present difficult challenges for sampling.

The ideal identification technique would allow *in-situ* analysis with no potential for cross contamination or false positives, the ability to test small, difficult to reach deposits, and would give unequivocal results.

In-situ spectroscopic analysis closely approaches the ideal identification technique. Using fiber optics, a laser can be sent through a remote probe and directed to the unidentified deposit. Scattered light from the deposit is collected by optics and returned through fiber optics back to a spectrometer for spectral analysis. For determination of boric acid, the technique known as Raman spectroscopy provides positive analysis.

IV. RAMAN SPECTROSCOPY USING REMOTE PROBES.

Raman spectroscopy is named after Sir C.V. Raman, who was awarded the Nobel Prize in 1930 for the discovery of Raman scattering. Raman scattering is a change in the energy of light, also called “shifting”, when it interacts with molecules in such a way that some of the energy of the light is transferred from the photons to the molecule. Since different molecules interact with photons in different ways, the change in energy differs from one substance to another, and each substance that can produce Raman scattering will have a unique spectral “signature”. In order to see Raman scattering, a monochromatic light source, such as a laser, is required. Boric acid has a Raman spectrum that is unique to boric acid, and cannot be confused with other compounds that may be found in nuclear power plant deposits.

In principle, laser light scattering off the surface of a molecular compound can interact in three ways with the compound. These are elastic scattering (also known as Rayleigh scattering), Raman scattering, and Fluorescence. See figure 6: In elastic scattering the incident photon (yellow ray in the figure) strikes the surface and the electronic structure of the surface is excited to a “virtual state”. It then rebounds, sending off a new photon of the same wavelength as the incident photon, but in a random direction. Most photons are scattered in this way.

In Raman scattering, some of the energy of the photon remains in the electronic structure of the molecule, so when the surface rebounds, it does not return to the original state. Since some of the energy remains in the molecule, the new photon scattered will have a slightly longer wavelength, shown in red in the figure.

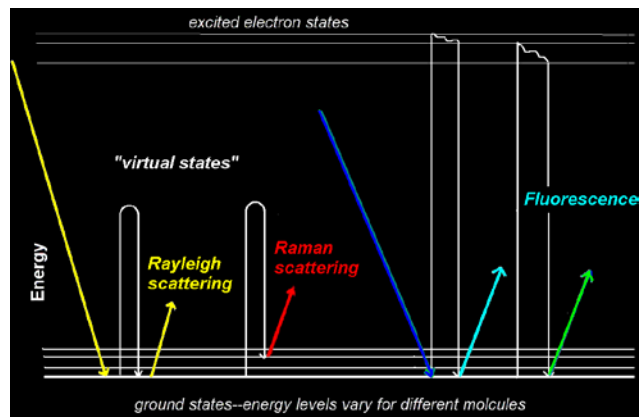


Figure 6. Photon interactions in Raman spectroscopy

The third effect is caused when the incident photon has enough energy to move the electrons to a stable excited state. The energy of these excited states varies also from substance to substance. These states lose some energy to low energy transfers, then give off the remaining energy as new photons over a broad band of wavelengths.

Boric acid has a strong Raman signal which can be detected using our equipment.

A remote Raman spectroscopy system consists of a laser source, a fiber optic to carry the light from the laser to the sample, a probe where the light is directed to the sample, collection optics and filters to reject the laser light that has not shifted in energy, a fiber optic cable to return the light, a spectrometer to measure the Raman shifts, and a readout system. It is also useful to have a computer program that can identify the Raman signature and compare it with those of known compounds to identify the substance being analyzed. Figure 7 shows the InSITE™ Analyzer. The main unit contains the computer, controls, laser, spectrograph, and interface, and can be placed in a convenient location inside or outside containment for analysis. On the right is a fiber optic cable, which can be made long enough to reach inside containment to the location of suspected deposits. The probe is at the end of the fiber optic cable. The tip of the probe is placed in or near contact with the deposit either manually or with a pole or robot.



Figure 7. The InSITE™ Analyzer

V. SPECTRA OF TYPICAL UNIDENTIFIED DEPOSITS.

Figure 8 shows a Raman spectrum of boric acid taken with the InSITE™ Analyzer.

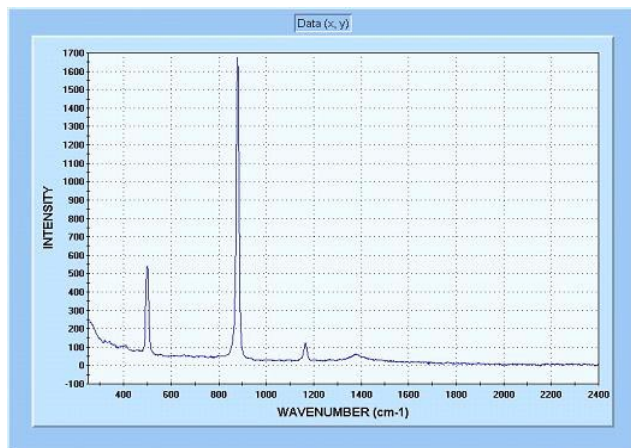


Figure 8. Raman spectrum of boric acid

Boric acid shows clear Raman scattering and no fluorescence. The conventional units for measuring the change in energy is inverse centimeters, (cm^{-1}), also known as wave numbers. Higher wave numbers mean a greater shift to the red end of the spectrum and more energy lost in the photon interaction. Boric acid hydrate will always show peaks at 500 cm^{-1} and 875 cm^{-1} with a weaker peak at 1170 cm^{-1} . In its pure, hydrated form, there is no fluorescence.

Figure 9 shows white paint used in figure 3. This material shows strong fluorescence and some peaks possibly from optical brighteners used in the paint. Its spectrum clearly differs from that of boric acid.



Figure 9. Paint used in BMI application.

Figure 10 shows duct tape residue of the same type as that shown in Figure 4. This substance shows significant differences from both white paint and boric acid, and is also characterized by strong fluorescence.



Figure 10. Duct tape residue.

VI. ANHYDROUS BORIC ACID

Boric acid deposits in a PWR can take one of two forms: orthoboric acid, H_3BO_3 , which is formed by drying boric acid or solutions, or RCS at low temperatures, less than $169 \text{ }^\circ\text{C}$. When orthoboric acid is superheated, it loses water and decomposes to metaboric acid, HBO_2 . The molecular structure of metaboric acid is quite different from orthoboric acid, and shows strong fluorescence rather than the Raman effect when analyzed with the InSITE™ system. See figure 11.

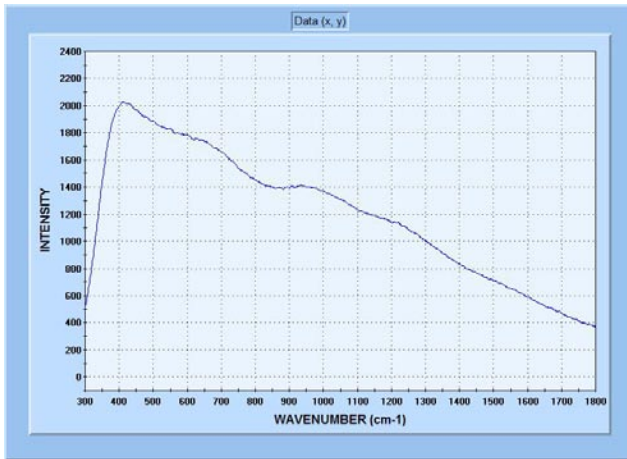


Figure 11. Metaboric acid Raman spectrum (superheated RCS)

A small amount of water from a mister or sponge applied to a superheated RCS sample will immediately convert the metaboric acid back to orthoboric acid as shown in Figure 12. Using this technique, it is not only possible to positively identify boric acid, but to determine the temperature history of the deposit.

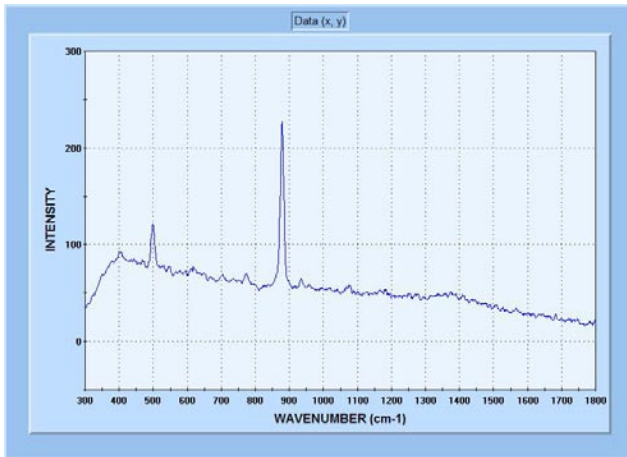


Figure 12. Superheated RCS after partial rehydration.

VII. SUMMARY

This new technique for identification of deposits at PVNGS has proven especially useful for identifying and characterizing boric acid deposits. The system can identify the form of the boric acid, and thereby provide an indication of the heating and moisture environment in which the deposit was stored. This system is now in use by the In Service Inspection Group and PVNGS to conclusively identify boric acid deposits and eliminate the need and risk involved with sample removal from in containment.

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