

The Art of Electrochemistry in an Autoclave

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Introduction

A. Acknowledgments

When I sit down to write about tricks of the trade and lessons learned in the practice of performing electrochemistry in autoclaves, my first thought is of all of those who preceded me in the adventure. This is only a partial and personal list: They are the researchers, facility engineers, supervisors, and technicians at Bettis and Knolls who paved the way. Some names that come to mind are Rick Garstka, Ted Druga, Bert Setterberg, Rudy Majcher, Jack Carr, Bob Rubino, Doug Thompson, Ken Granger, Rosemary Janik, Bill Archer, Garry Lynch, Irene Rosati, Mike Ochap, Dave Kedzierski, Keith Eklund, George Halbfinger, Mike Danielson, Yinfang Wang. Chief among those in other organizations who shared their stories was Digby Macdonald, who broke ground for many of us and was always eager to share his experiences.

B. Scope and Intent

This note will cover many topics that have only hot water in common. To fit within the space limitations of an application note, it will be a collection of lessons learned. As such, none of this is purely my own. There will be a stream of consciousness or memory and no part will be comprehensive. There may be future, detailed application notes to cover particular situations in depth, but they will await the questions that we hope this note will stimulate.

I. Safety

A. Importance

Safety is paramount when working with autoclaves. Because of the amount of energy stored in water at high pressure and temperature, the consequences of an accident can be enormous. Many who have worked in the field can tell of jets of steam, or metallic objects ringing off a high bay roof thirty feet above. Some can tell of a two hundred pound autoclave head that came to rest on the grounds of a plant a quarter mile away. This list of safety measures is meant to encourage further

study and the development of a local set of requirements. A search in the library or on the internet on the subject of autoclave safety will produce many documents to guide the development of a local document. It is vital that the document be developed with the participation of all of the experts in the affected equipment, procedures, and personnel. An outside expert should be consulted to assure that nothing important has been overlooked and the requirements should be reviewed and updated annually and whenever there is an accident of any degree of severity. All personnel working with or around pressurized equipment should be trained in the requirements and the facility should be posted to alert visitors to the dangers and to recommend means of protection.

B. Administrative and Insurance Requirements

Besides the general guidance suggested above and any requirements developed locally, there are regulatory requirements and requirements imposed by insurers. These lead many large organizations to establish internal committees to develop and impose regulations. It is a good practice to inform the owner and the insurer of the facility of any plans to operate an autoclave on the premises. Besides requirements, some organizations and insurers have specialized inspectors and an industrial safety division to assist divisions and clients. Any jurisdiction, from local to national, can impose regulations for certifying, inspecting, or operating an autoclave and the operator of the facility should determine the relevant jurisdictions and regulations.

C. Good Practices

Here are some things good to do, even when the requirements are not enforced. The order is arbitrary and the list is not comprehensive.

1. Use the smallest pressure vessel consistent with the requirements of the experiment.
2. Monitor the temperature and pressure continuously to prevent accidents and minimize their severity.
3. Install overtemperature alarms and cutouts.

4. Monitor and limit heater temperatures to protect vessel materials.
5. Install pressure relief devices and pipe their exhaust safely.
6. Use appropriate tethers to prevent ejecting components. Thermocouples, and electrodes are prime examples.
7. Be sure that any sampling ports are properly protected and effluents delivered to safe disposal. This is especially important for toxic or corrosive materials. Anything that requires special handling in the laboratory is a greater risk in an autoclave.
8. Glass components are to be avoided in general. A sudden force can break glass and many solutions attack glass at high temperature. If a specialized component like a glass or diamond window or sight tube is required, shielding should be arranged as if failure is expected.

II. Autoclaves and Structural Materials

Autoclaves come in many sizes and shapes, from 1 ml to a meter in diameter and several meters high. They can operate from a few kPa to tens of MPa above ambient pressure. As such the design and selection materials are properly performed by specialists. Likewise, anyone attempting to construct or use an autoclave is well advised to consult the ASME boiler and pressure vessel code or to obtain certificates that any pressure vessel they use is constructed and maintained in conformance with that code and local requirements. Autoclave Engineers and Parr Engineering are two companies that design and build standard autoclave packages and custom autoclaves for which they provide design and certification services. Other providers of autoclaves and corrosion testing services can also manufacture autoclaves and testing systems. It is wise to consult with workers experienced in the kind of testing that you plan on doing before investing in the expense of specifying, buying, and operating an autoclave.

The materials of construction of an autoclave for corrosion testing are particularly important. The choice of material should include the assumption that the vessel will corrode to some extent. Even noble metals like gold and platinum can corrode and they are quite soft, so that they can deform or be damaged to expose the underlying base metal. This can lead to worse corrosion problems than using an ordinary, corrosion-resistant alloy with suitable structural strength. Of course, the vessel should be sufficiently corrosion-resistant and inspected often to minimize the risk of failure. Another

consideration is that the nature of the corrosion process of the vessel should not compromise the planned experiment. Some corrosion-resistant alloys produce a corrosion product film that can be dissolved in the test solution. Even if the net result is a protected vessel, the resulting contamination may change the test solution to make it less or more corrosive or it may deposit on test specimens and change their behavior. Stainless steels and nickel-based alloys are usually good choices, but must be considered thoroughly. The same is true for materials used for supporting and retaining specimens.

Stress corrosion cracking of pressure vessels and structural materials is a very serious concern that is beyond the scope of this note. The structures require considerable strength and can undergo stress corrosion cracking if the materials are susceptible and corrosion and stress are present. Most designs avoid the need for high strength materials wherever possible. Threads present a particular problem, so most designs avoid immersed threads.

Plastics

Because of the risk of degradation by overheating, plastics are very rarely used in autoclave applications. Because electrical insulation is sometimes required, some exceptions are made. The material of choice is generally polytetrafluoroethylene (PTFE) Teflon™. This material is used for sleeving electrical leads, isolating specimens, and sometimes for seamless autoclave liners. It has very little structural strength and the strength declines drastically above 150°C. It also has a high coefficient of expansion, so it often deforms when confined by metallic fittings. Conversely, properly designed fittings can sometimes retain a PTFE insulator in place and assure better hermeticity than might be expected. Unfortunately, there is no guarantee of hermeticity, so crevice corrosion must always be considered in designing experiments and interpreting results. With care to support the PTFE insulators and not deform them, such insulators have been used successfully up to 350°C. Monitoring of product lots and vendors is very important for such extreme applications because slight variations in degree of polymerization or contaminants can reduce the effective softening temperature. Similarly, care must be taken by the manufacturer to minimize the amount of free fluorine-containing materials in the PTFE. It is wise to test a lot of new material to avoid contamination in critical applications.

At present, no other material approaches the performance of PTFE in aqueous systems from reliable manufacturers. Perfluoroalkyl (PFA) Teflon[®] is preferred in some applications because it has a higher softening temperature, so it retains some structural strength up to 280°C. However, it softens much more abruptly above its useful range and many accidental temperature excursions have resulted in the complete collapse of an PFA insulator. Polyimide and epoxy materials have much higher melting points than Teflon[®] materials. However, they hydrolyze at temperatures as low as 150°C, leading to disintegration of the insulator and contamination of the test solution.

Ceramics and Diamond

Many of the concerns about plastics have parallels in the use of other materials as insulators for electrochemistry in autoclaves. Most glasses and ceramics that we take for granted at room temperature and in air are attacked by water at elevated temperature and even modestly elevated pH. Glass corrodes by forming silicates and sapphire and alumina corrode by forming aluminates. Sapphire and alumina serve in some applications, but many researchers have been disappointed by a bad batch of ceramic or by pushing an experiment to a higher pH or temperature. Yttria fully stabilized zirconia (YSZ) is the only widely used ceramic that resists attack in water above 150°C and solutions to 1 M NaOH and beyond. As with other materials, manufacturers must be chosen carefully. Partially stabilized zirconias are widely used in mechanical applications for their better strength and toughness, but they are susceptible to attack by hot water. Sometimes lots from the same manufacturer are more subject to softening in hot water. YSZ has semiconducting properties which can be useful in electrochemistry at high temperature and which can vary from lot to lot.

Diamond would seem like the perfect material for structural materials in autoclave testing. Natural and synthetic diamonds have been used for windows at tremendous cost. It has good insulating properties, but no flexibility and cannot be formed. Diamond-like carbon coatings formed by chemical deposition show some promise, but are still being developed and are very expensive.

III. Oxygen

The amount of oxygen in a sealed autoclave is almost never what was planned. If one is preparing an oxygen-free test, air will be trapped in cracks, even after the

vessel is evacuated and the solutions purged with inert gas. On heating, adsorbed gases and corrosion films can decompose to release oxygen. If one planned a fixed amount of oxygen, an unknowable amount will form oxides on exposed metal surfaces. Using an oxygen scavenger will sometimes suffice to eliminate it from the system, provided the products of scavenging do not affect the test. Maintaining a fixed gas composition in the vapor space at the top of the vessel may control the solution composition by Henry's law, but only if the system is adequately mixed and the rate of oxygen consumption by corrosion in the vessel does not overwhelm mass transfer. This whole picture is further complicated by the fact that air can diffuse in through a leak, establishing a steady, low level of oxygen. The most reliable means of controlling oxygen is by sampling from the vessel. This usually requires replenishing the test solution, so a circulating system is required. That complicates the design and operation of the test system considerably, but oxygen is a critical parameter in electrochemistry. A makeup system also allows for the monitoring and maintenance of other reagents and system parameters.

Oxygen analysis from a pressure vessel can be done by sampling or by continuous analysis. Sampling is most economical and Chemets[®], self-filling ampoules with colorimetric reagents^(x), are widely used for this purpose. The greatest drawback to sampling is lack of consistency: A skilled operator can consistently measure oxygen content to 20 ppb or less, but many experienced operators cannot measure less than 100 ppb. Once properly established and calibrated in a flowing system, fixed oxygen analyzers can measure oxygen to 1% of the measurement down to 1 ppb. Polarographic sensors are available economically for operation only up to 300 kPa, so they are usually used on a line flowing to drain or to a pumped makeup system. For pressures up to 30 MPa, Orbisphere makes highly accurate and sensitive analyzers at much higher prices. Oxygen analyzers based on quenching of fluorescence are approaching the sensitivity required to measure a few ppb of oxygen. Anyone with this requirement should consult InSitu Instruments, Orbisphere, and Ocean Optics to determine their current capabilities and ask the author about the most recent test results. (i), (ii), (iii)

Detailed description of makeup and recirculation systems for autoclave testing is beyond the scope of this

^xChemets: Self-filling ampoules for water analysis; See <http://www.chemetrics.com/Oxygen+%28dissolved%29>; The ASTM reference: ASTM 11.01, ASTM D 5543-94 (2005), Standard Test Methods for Low-Level Dissolved Oxygen in Water

note. Anyone with a particular design question or history of problems should contact the author for discussions. Suffice it to say that choice of designs and components is critical to success. For example, a piston pump can entrain air past the seal rings or by adsorption on the cylinder walls and subsequent dissolution.

IV. Monitoring

After pages of mechanical problems, we can get to applications of electrochemistry. The concept that will pervade the discussion of electrochemistry as observed in an autoclave is that corrosion is very different at high temperature in water than near room temperature. For example, the rates of the $\text{H}_2\text{O}-\text{H}_2/\text{O}_2$ exchange reactions are much faster. They approach RedOx equilibrium and can dominate many electrochemical measurements. High temperature also can lead to hydrogen produced by corrosion which affects the rate of corrosion reactions. Sometimes the rate of corrosion can be much different in a closed vessel from that measured in a circulating vessel with H_2 and O_2 stripped out of the solution. This discussion will be limited to a few of the most widely used techniques. Almost any known electrochemical technique can be applied in an autoclave, though the mechanics of some are prohibitive. A few techniques have been especially developed to take advantage of the temperatures and pressures that can be achieved in an autoclave. The autoclave, itself, drives some choices of instrumentation for electrochemistry because safety requires grounding it. Many of the familiar potentiostats that are used in glass vessels on an open benchtop cannot be used when grounding of the vessel constrains which electrodes can be grounded. The solution is a floating potentiostat that can measure and control independent of grounded electrodes or intermediate structures. In 1990, there were very few floating potentiostats, while there are now several offered. However, the user is advised to find a potentiostat that has been proven in systems like his. References and advice from experienced users are invaluable.

A. Polarization Resistance

Polarization resistance may be the most widely used electrochemical technique and this applies in autoclaves as well. The caveat is that the desired measurement of corrosion rate can be obscured in the results. At a minimum, it is necessary to compare polarization resistance measurements under identical conditions and take the difference as the change in corrosion rate. In this way, qualitative comparisons can be made and sometimes they can be made quantitative. However,

the exchange current of the $\text{H}_2\text{O}-\text{H}_2/\text{O}_2$ reaction may so dominate the measurements that only qualitative comparisons are possible. Sometimes a system can be calibrated by measuring corrosion rates by weight loss, but the correction is often greater than the measured value. This is particularly true in systems like high-purity water, where solution resistance dominates the measurements and varies with contamination.

B. Electrochemical Noise

Electrochemical noise monitoring has found wide use over the last twenty years for measuring corrosion rates and detecting corrosion problems in chemical processes. (ENM is one of several acronyms for this family of techniques.) It has found use in autoclaves, as well. However, the effects that decrease the resolution of polarization resistance, high exchange currents and high solution resistance, tend to overwhelm the ENM signal entirely. Users of ENM in autoclaves are left with the phenomena that led many researchers originally: Bursts that appear to be noise, but are caused by discrete electrochemical events. With statistical analysis, the origins of the signals can often be determined and the results can be used to identify events in the process or structure that cause corrosion. The introduction of corrodants with process additives is an example. Structural stress caused by temperature change or mechanical action is another.

C. Electrical Potential Drop / Electrical Resistance

Another technique that has seen application in specialized laboratories and infrastructure is that of electrical resistance or electrical potential drop monitoring. (EPD and ER are common acronyms.) This is distinct from other *in situ* monitoring techniques in that no electrochemistry is used at all. Loss of metal from a test piece is detected by measuring the resulting loss in electrical conductance, which appears as an increase in electrical resistance. Extraordinarily sensitive and accurate instruments are required to measure the associated currents and voltages, but this has become commonplace over the past thirty years. What has generally not been appreciated is that ER is incidentally an electrochemical technique. In air, where the technique was originally used to measure deformation and cracking of tensile test specimens, electrochemistry does not occur. However, in water, applying a current, even longitudinally, to a specimen results in a potential, however small. At 200° to 400°C , the small potentials (a few millivolts, typically) can affect the high exchange currents in corroding systems. The results can be transients that affect the ER measurements and changes

in corrosion rates. There can also be insulating or conducting layers generated by the corrosion process that can have dramatic effects on the ER measurements, especially in cracks. As with many other techniques in autoclaves, the experienced, alert user can often identify the effects, assign them to causes, and extract meaningful results from the data. Without this interpretation, the data can be misleading.

V. Reference Electrodes

As in other electrochemical environments, reference electrodes are essential to making electrochemical measurements in autoclaves. The difference is that the reference electrodes have often been improvised, due to a dearth of economical, proven designs with ample supporting data.

A. Secondary Reference

Most improvised references are secondary reference electrodes and it is helpful to present some examples here because the concepts are widely used. Platinum wires and non-polarized test specimens have often been used very effectively. These have been called pseudo-references, secondary references, or just reference electrodes, depending on the rigor of the experimenter. For valid interpretation, it is essential to know what variables affect the potential of the reference. Platinum is sometimes more useful than other pseudo-references because its potential at high temperature is dominated by the $\text{H}_2\text{O}-\text{H}_2/\text{O}_2$ exchange reactions. Thus it is seldom influenced by effects other than hydrogen concentration and pH. If these are known and constant and $\text{H}_2\text{O}-\text{H}_2/\text{O}_2$ equilibrium can be demonstrated, platinum potential can be calculated from thermodynamic data and termed a "secondary reference electrode". More often, pH and $[\text{H}_2]$ are unknown and assumed to be constant, so the potential is assumed constant. For some experiments, this is a useful approximation, but corrosion can affect both pH and $[\text{H}_2]$, with dramatic results for electrochemical measurements. Most of the same statements apply to the use of non-polarized test specimens as pseudo-references, except that corrosion processes also influence the potential. This can sometimes be an advantage in that this balances out some uncontrolled variables and clearly shows the effect of applied phenomena like coatings or mechanical stress.

B. Primary Reference

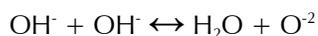
Experienced electrochemists have long adapted conventional reference electrodes for use in autoclaves, but the increased solubility of precipitates like silver

chloride and the increased rate of diffusion at high temperature made most of them difficult to use and inaccurate. This changed when Digby Macdonald introduced the pressure-balanced reference electrode. (PBRE, ^{iv}) Instead of a fixed container, the PBRE contained the components of a salt bridge in a flexible, impermeable membrane, usually Teflon[®]. As a result, changes in pressure that would have extruded the control solution from the reference cell or introduced contaminants to affect the potential were balanced by equivalent pressure in the reference cell. The composition of the reference cell was maintained and the reference potential could be calculated as accurately as available thermodynamic data allowed.

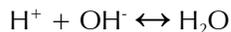
Since Macdonald's insight, many workers have developed embodiments of the PBRE to fit their own apparatus or experimental constraints. (^v) Discussion of the advantages and disadvantages of each design is beyond the scope of this note and the interested reader is encouraged to contact the author for further discussion. However, one warning is important: Even the PBRE experiences some contamination. Pressures are not perfectly balanced and some permeability is required in the liquid junction. In hours or days, reagents from the salt bridge diffuse out to contaminate the test solution and contaminants from the test solution diffuse into the reference junction and affect the potential. Most of the membrane materials are slightly permeable to gas at elevated temperature, but this can usually be tolerated. By careful choice of the reference junction solution and understanding of the requirements of the particular test, these problems can usually be managed.

C. pH

As one will infer from the discussion of the PBRE, above, the ideal reference electrode would have an impermeable junction to the test solution. The typical, glass pH electrode has this and makes an excellent secondary reference if the pH of the test solution is known and constant or measured continuously. Unfortunately, the glass in glass pH electrodes is like any other and is attacked by hot water. It is also very thin and brittle, making a poor choice for a pressure boundary. However, the same YSZ ceramic that serves as a structural and insulating material in some applications also has semiconducting properties and conducts oxide ions at elevated temperature. With an internal reference cell like Hg/HgCl or $\text{Fe}/\text{Fe}_2\text{O}_3$, a closed-end YSZ tube can serve as a pH electrode via the reactions:



(The oxide ion equilibrates through the membrane to control the potential inside the electrode.)



YSZ sensors with Fe/Fe₂O₃ or Cu/Cu₂O internal reference junctions are widely used in autoclave testing in solutions where the pH is known or constant. ^(vi, vii) By selecting for the required properties, YSZ pH sensors have been used as low as 90°C. ^(viii)

D. Other Electrodes

With the principles identified above in mind, many other reference electrodes can be imagined. The interested reader can contact the author for further discussion.

VI. SCC testing

Stress corrosion cracking is a very important problem that often requires autoclaves to produce the conditions for its occurrence and study. As such, it has an extensive literature of its own and this note will not explore the topic. Some considerations peculiar to autoclave testing warrant mention here:

A. Load/Displacement Control can be affected by changes in temperature, with surprising increases in sample fatigue.

B. Crack Monitoring techniques can have unintended, electrochemical consequences, as can be inferred from the paragraph on EPD. Displacement measurements, although nonintrusive in principle, require sensitive devices that can be affected by corrosion and electrochemistry.

VII. Summary and Conclusions

Electrochemistry is fun and exciting. This can be even more true in autoclaves. Take care in planning

experiments and consult organizations and individuals with experience in the particular techniques you want to apply. As a result, the work is expensive to undertake properly. Remember that safety is paramount.

VIII. References and Additional Reading

The reader is referred to the publications in the list of references. They, in turn, lead to other reading that will reveal a vast body of work by Digby Macdonald and others who pioneered this field. ^(ix) Contact the author for other suggestions on specific topics.

IX. About the Author

James Hardy is the principal of ChemCorr, LLC, a consulting firm working in chemistry, corrosion, electrochemistry, and chemical kinetics. He worked from 1987 to 2009 for Bettis Atomic Power Lab in water chemistry at high temperature and pressure, chemical instrumentation, and corrosion modeling and control. He worked for Exxon Research to control pollution in the development of difficult resources like coal and oil shale. He received his Ph.D. in physical chemistry from the University of Texas (1976). James is a member of NACE and ASTM and The Combustion Institute. He can be contacted at www.chemcorrllc.com/contact.

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734 Louis Drive • Warminster PA 18974 • Tel. 215 682 9330 Fax 215 682 9331 • www.gamry.com • info@gamry.com

i. <http://www.in-situ.com/>, In-Situ, Inc.
ii. <http://oceanoptics.com/>, Ocean Optics, Inc.
iii. <http://www.hach.com>, Hach Ultra Instruments, makers of Orbisphere electrochemical and fluorescent analyzers.
iv. D. D. Macdonald, "Reference Electrodes for High Temperature Aqueous Systems-A Review and Assessment," Corrosion, 34, (76-84), 1978.
v. M.J. Danielson, Corrosion, 35, (1979) p. 200; and Corrosion, 39, (1983) p. 202.
vi. Digby D. MacDonald; Ting Zhu; Xueyong Guan, "Current state-of-the-art in reference electrode technology for use in high subcritical and supercritical aqueous

systems" European Federation of Corrosion Publications (2007), 49(Electrochemistry in Light Water Reactors), 3-42. Publisher: Woodhead Publishing Ltd., CODEN: EFCPE4 ISSN: 1354-5116. Journal.
vii. Although the calomel electrode (Hg/HgCl) is a better reference than Cu/CuO or Fe/FeO because its potential is well defined, it is excluded from most applications by the use of mercury. Besides its toxicity, mercury can cause liquid metal embrittlement, which can destroy autoclaves. Good operating practices exclude all mercury from any autoclave facility.
viii. Private communications from Lietai Yang and Corr Instruments, <http://www.corrinstruments.com/>.
ix. Techniques for Corrosion Monitoring, (L. Yang, ed., Woodhead Publishing, Success, UK 2008).