Advances in High Temperature Water Chemistry and Future Issues

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Abstract---*This paper traces the development of advances in high temperature water chemistry with emphasis in the field of nuclear power. Many of the water chemistry technologies used in plants throughout the world today would not have been possible without the underlying scientific advances made in this field. In recent years, optimization of water chemistry has been accomplished by the availability of high temperature water chemistry codes such as MULTEQ. These tools have made the science of high temperature chemistry readily accessible for engineering purposes. The paper closes with a discussion of what additional scientific data and insights must be pursued in order to support the further development of water chemistry technologies for the nuclear industry.*

INTRODUCTION

The title of this paper is somewhat misleading as the reader may expect a detailed review of the advances in high temperature water chemistry in recent years. The scope of this paper however is much more limited. The reader is referred to the review article by Chen, Izatt and Oscarson[1] and the ASME Handbook on Water Technology[2] for a compilation of high temperature data and background. This paper is written from a technologist's perspective as the author has not been a contributor to the science of high temperature water chemistry but hopefully as a user. I've attempted to provide a very brief historical outline of the parallel development of the underlying science and the technology that has been made possible with emphasis in the field of nuclear water chemistry.

In the development of this paper, I am indebted to William T. Lindsay, Jr. who did author a more complete picture of the development of the field of high temperature chemistry titled, "Coming of Age in Hot Water, A Personal View.[3]" Lindsay had the unique perspective of both a scientist and a technologist having made major contributions to the field on both accounts. His paper was the invited keynote at the last EPRI sponsored scientific conference focused on high temperature water chemistry. In the intervening thirteen years, EPRI has sponsored many water chemistry conferences and workshops, but the 1991 conference was the last truly large scale scientific conference arranged by EPRI that emphasized this subject matter. The current conference is more focused on the technology of water chemistry of nuclear reactors following the highly successful conferences of the same name held bi-annually by the national nuclear societies in the U.K., Japan and most recently in France.

Lindsay's paper traced the history of the development of the field of high temperature water chemistry from its introduction in around 1900 to about 1990. He pointed out that in high temperature water chemistry like most scientific fields; the science has followed very orderly the needs of the technologies requiring the knowledge. The science often goes in spurts to meet the then pressing issues faced by the technologists. Once the science fills the gaps, the technology spurts ahead with the new knowledge, and then the cycle continues. In this paper, I aim to continue this theme and pick up from where Lindsay left off until the present. The emphasis will be on the technology because this has been where the developments for the nuclear industry have been in recent years. For most of the period since 1990, I was the manager of water chemistry technology at EPRI or have been close to the developments.

I will close this paper with a brief discussion of some of the needs and issues for the near future. Hopefully, this will serve to stimulate discussion among the technologists, the scientists and the funding agencies jointly responsible for continuing to move the ball forward.

1900-1991

As stated earlier, the job of summarizing the first 90 plus years of scientific and technological progress in the field of high temperature water chemistry was already accomplished by Dr. Lindsay. Rather than simply point the reader to Lindsay's paper, I would like to highlight a couple of the ideas that he presented in his paper that will help to explain what has occurred during the last nearly 15 years. It is also interesting to review some of the open questions that Lindsay identified in 1991 based on the then current issues facing the industry.

The title of Lindsay's paper, Coming of Age stems from the idea that all specialized fields display a characteristic behavior regarding the accumulation of knowledge in that field over time. Figure 1 has been redrawn from reference 3.

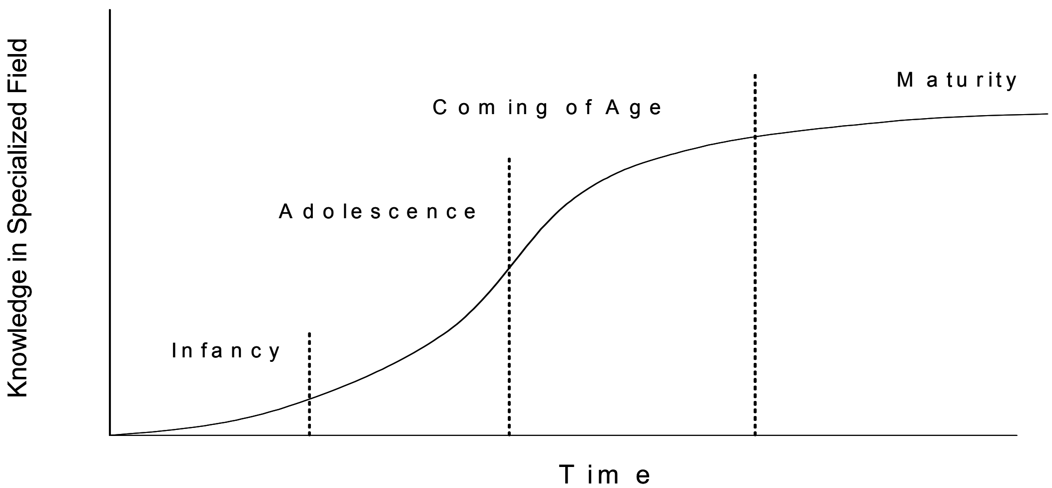

Figure 1- Knowledge in High Temperature Water Chemistry

Lindsay argued that the field of high temperature water chemistry was in the process of , "Come of Age" by the time of the conference. The first fifty years to about 1950 were driven by the technologies of hydrothermal geology followed by boiler chemistry and steam turbines. Nuclear power came towards the end of the first 50 years. The scientific advances began with the first high temperature conductance measurements of Noyes in 1900, followed by high temperature solubility and vapor pressure measurements of saturated solutions by the time steam turbine deposits were becoming a problem in the power industry.

It seems that the push for scientific progress occurred with the introduction of nuclear power. Lindsay included this quote from the 1957 edition of the Corrosion and Wear Handbook,[4] where Rickover wrote the following foreword:

"….In spite of this work, our basic understanding of water technology is weak. We do not fully understand, for example, the process by which metals become dissolved or suspended in the reactor cooling water, how the radioactivity is transported to the external system, and how it is deposited on surfaces…"

The inflection point in Figure 1 perhaps corresponds with this prognosis. The 1960's through the 1980's was a period of major advances in the scientific understanding of high temperature water chemistry. Much of the science in the U.S. came out of the high temperature laboratories at Oak Ridge and it continues today. During the earlier part of this time period, measurements were made of ionization equilibria, solubility and hydrolysis of cations. Batch calorimetry was used to accurately measure heats of solution by Cobble and others. Later on, flow calorimetry became widely used as well as direct raman spectroscopic observations; high temperature pH measurements and other techniques were used to study electrolyte systems. In parallel and made possible by the accurate measurements made during this period were the development of fundamental methods of correlating data and theoretical predictions of the properties of high temperature aqueous solutions. These included the widely used Criss-Cobble Principle, as well as the activity coefficient models of Pitzer and co-workers.

For at least the commercial nuclear industry and the technologists in particular, this period perhaps culminated in the development of the MULTEQ code by EPRI. Although it had its roots in the laboratories of Bawden at CERL, MULTEQ really was enabled by the advances made during the 1960's through the 1980's just described. It was of course widely disseminated because it was created during the birth of the personal computer. MULTEQ is somewhat unique in that it is not only a tool for scientists to use to predict what occurs in high temperature solutions but rather a tool for engineers and plant chemists to use. This computational tool is so valuable for those users because the thermodynamic data underpinning the calculations are carefully screened and re-fit if necessary for use in the code by the MULTEQ Database Committee. The membership of this group has included three of the most influential leaders in this field, Lindsay, Baes and Cobble since it's inception in the late 1980's. Thermodynamic concepts not invented for MULTEQ but made practical and widely useful in the code, include the extrapolation techniques of balanced like charges or isocoloumbic equilibria and the model substance approach for activity coefficients. The use of these approaches makes MULTEQ a good tool for engineering purposes.

MULTEQ has truly enabled the rapid expansion of water chemistry technologies used in the nuclear industry beginning in the late 1980's and continuing today. In the way that Rickover's comments may have spurred the scientific community in the early 1960's, MULTEQ and similar computational tools have had the same effect on many of the technologists in the industry.

This section would not be complete without a review of the needs of the power industry, circa 1991 as articulated by Lindsay. This is not a complete list, but selected items that will serve as a snapshot of some of the issues facing the nuclear industry at the time. We will come back to this list later in the paper.

Some Open Questions Relating to Concerns in Nuclear Power Plants (Reference 2)

Table 1

1. Volatility of sodium hydroxide, sulfates and other substances for turbine deposits and corrosion.
2. Phase diagrams for sodium hydroxide/sulfuric acid on the acidic side for possible liquid-liquid immiscible phases.
3. Chemistry of boric acid/magnetite systems for denting and IGSCC control in PWR's.
4. Chemistry of lead for stress corrosion cracking of Inconel.
5. Solubility of ferrites and electrical properties of metal oxide suspension (e.g. zeta potentials) for radiation field control.
6. Diffusion coefficients, ionic mobilities and transference numbers in concentrated media for modeling of electrochemistry in cracks and crevices.

1990-Present

Although scientific advances have continued through the last decade and one half, it has been at least in this author's opinion, the advances made possible by the science performed prior to this period that have occupied most of the attention of the industry. The reason for this is multi-faceted, having to do in part with the shift in business climate and trends in operation of the plants. It may have also been due to the fact that there was in effect pent up demand to develop and apply high temperature water chemistry technologies that used the new scientific tools available.

Beginning in the late 1980's and continuing today, a fundamental change in the way the owners of power plants have run their business has had a significant effect on the research and development activities of the industry. Up until that point, utilities essentially operated with the assurance of a monopoly in their geographic region. This encouraged large investments in infrastructure with little concern that a return on investment would be seen over time. Much of the basic science required to support the industry has been focused on the environmental degradation of materials of construction. The fact that the science took decades to develop was not a significant problem for an industry that operated with such a long term horizon.

De-regulation has among other things changed the time frame in which a return on investment is required. This has shifted the research budgets of most agencies towards short term projects with a high likelihood of success and a quicker return on investment. The water chemistry program at EPRI during the last fifteen years has reflected this fundamental change. As noted in the introduction to this paper, it has been nearly fourteen years since EPRI last sponsored a scientific conference on high temperature chemistry. There have been numerous workshops and meetings where the new technologies and applications were discussed among the users.

Because there was less demand for basic science, the industry focused its development resources on shorter term projects that would be cost effective to develop and implement. Finding new water chemistry operating regimes to slow down or eliminate the costly corrosion problems occurring in the field fit well with this strategy. The new and more importantly very accessible form of the advances in high temperature chemistry made this easier for the industry. A few examples of the science enabling the technology during this period follow.

One of the most widely promoted concepts in the nuclear industry during the 1990's was optimized water chemistry. It was made possible by the advances in high temperature water chemistry during the preceding 90 years. Considering PWR secondary systems as an example, the idea of molar ratio control came from the possibility of predicting the high temperature pH in crevice regions where local corrosion was occurring. Although the accuracy of such calculations is very low, the industry would not have recognized that molar ratio was a reasonable strategy if this calculation capability were not available. Amine based pH control of secondary systems is a more dramatic example. The industry recognized that the flow accelerated corrosion of low alloy steels could be effectively controlled by increasing the high temperature pH in two phase regions of the steam cycle. The industry was able to use the newly available chemical thermodynamic codes to calculate the high temperature pH that resulted from various amines. The wide variation of amines being used in nuclear plants world-wide today is at least partially due to this capability. These codes were made possible by the in-depth survey of the high temperature thermodynamic properties of amines conducted by Cobble and Turner.[5] That work was enabled by decades of pioneering work in the field of high temperature aqueous chemistry by Cobble.

At EPRI, we recognized that the widespread acceptance and understanding of optimization would be enhanced by providing the industry with a user-friendly set of computational tools for designing and troubleshooting water chemistry. ChemWorks[6] which uses the MULTEQ thermodynamic engine for calculating the solution chemistry was developed for this reason. Tools such as the plant chemistry simulator allow BWR and PWR owners to investigate the effect of changes in the water chemistry program. The simulator combines fundamental first principles with empiricism. Thermodynamics are used to calculate the solution chemistry and some processes that cannot be rigorously described because our knowledge is lacking are fit to plant data.

The benefits of high temperature chemistry are not limited to PWR secondary systems. The primary side of PWRs has benefited from the ability to calculate high temperature pH and an understanding of the solubility of ferrites. This has aided in the reduction of radiation fields and enabled a full understanding of the benefits of zinc addition in both BWRs and PWRs. The use of hydrogen water chemistry (HWC) in BWRs to reduce the electrochemical potential (ECP) in recirculation piping was made practical by the ability to directly measure the ECP of the piping. High temperature reference electrodes that were first developed and used for the purpose of making high temperature thermodynamic measurements in the laboratory were adapted for use in the plant. Noble metal chemistry (NMC) would likely not have been invented either if not for this capability. Without the ability to model the ECP throughout the reactor it would not have been possible to determine that HWC would not protect the entire core.

It is useful to go back to Lindsay's list of open questions to see what work has been done and has found application in the industry during the past 15 years. A major contribution has been made in a number of very detailed and accurate volatility measurements for compounds such as sodium hydroxide and sulfuric acid[7]. These data from Oak Ridge have found there way into the MULTEQ code as well as more detailed and accurate thermodynamics of zinc and lead chemistry. Although boric acid is still used in PWR secondary systems, no new knowledge with respect to the chemistry of boric acid/iron phase diagrams has been obtained. As most PWR SG's have been or will be replaced with more corrosion resistant tubing, boric acid treatment may soon no longer be deemed useful or at least there will be no need to optimize the treatment programs further. There has been some limited work on electrical properties of metal oxides, but no new knowledge or data in the area of transport properties of high temperature aqueous solutions. More will be said about that shortly.

FUTURE NEEDS/ISSUES

One way of assessing where the needs of the industry are is to look at what topics are being pursued today. The distribution of subject matter for this conference provides an opportunity to do this. A less than scientific analysis of the papers for this conference provides the following breakdown of topics:

Table 2
Distribution of Papers at this Conference

Basic or Applied Science	13% (33% if include Corrosion Science)		
Corrosion product properties		73%	
Electrochemical properties		~20%	
Miscellaneous		balance	
Technology Applications	67%		
Non-modeling		65%	
Modeling		35%	
Fouling/Deposition/Activity Transport			45%
Corrosion Modeling			20%
Miscellaneous			balance

As can be seen from Table 2, the emphasis in this conference is as expected technology. What is interesting to note from the paper topics is both the emphasis on corrosion products both from a need to obtain fundamental data and modeling their behavior and transport. This should not be surprising since corrosion products or crud are involved in several of the key problems facing the industry today including; BWR fuel corrosion, PWR axial offset anomaly (AOA), BWR and PWR activity transport and PWR steam generator tube fouling. There is a similar but less pronounced trend with respect to corrosion modeling, and there is some effort to obtain electrochemical properties to support fundamental models of the corrosion processes occurring in the plants.

The trends shown in Table 2 are consistent with Lindsay's assessment back in 1991 that fundamental data is needed for the electrical properties of metal oxides and transport properties in solution, although the work has not been accomplished yet. Further progress in modeling both corrosion product behavior and the electrochemistry of corrosion are dependent on this data. It is not surprising and it is appropriate that the emphasis is in the area of modeling. The most daunting problems facing the industry are complex and draw on multiple disciplines of science. To take thermally driven fuel corrosion in BWRs as an example, this problem requires knowledge of; high temperature crud chemistry, transport properties in solution, zirconium oxide kinetics and electrochemistry, heat transfer properties of crud and spinel formation. A complete understanding of the influence of all of the factors may not be tractable, but only through a complete model of the problem will you be able to understand how all of the variables interact with each other to produce the observed corrosion.

In addition to fundamental data to support modeling for corrosion, radiation field control and fouling, it is anticipated that the industry will continue to seek to discover new inhibitors to slow down or eliminate corrosion. It is hopeful that the models will shed some light on the desired properties of new chemistries. It will then be up to the industry to support some fundamental research programs to develop the high temperature chemistry data needed to identify and understand the role of inhibitors in the corrosion process. In parallel with this work, the industry should continue much of the fundamental work to understand the underlying materials degradation processes, some of which is presented at this conference.

Reflecting back to Figure 1, it might be easy to conclude that the slowdown of support of new science is simply due to the fact that the field has entered the maturity phase. It is more likely that we have reached a period where the technology has caught up to the science and further advance will require new science. It may be time for the industry to sit down again and work through a framework or roadmap to insure that the science needs of the industry can be met by the research community. An unfortunate side effect of the most recent emphasis on technology development during the last 15 or so years is that the capability to perform this science is disappearing. It would be advisable for the industry to take a look at this now rather than later.

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[2] "The ASME Handbook on Water Technology for Thermal Power Systems," P. Cohen, Ed., ASME, New York, (1989).
[3] W.T. LINDSAY, JR., "Coming of Age in Hot Water, A Personal View," Proceedings:1991 Symposium on Chemistry in High-Temperature Aqueous Solutions. EPRI TR-102706, (1993).
[4] "Corrosion and Wear Handbook," D.J. DePaul, ed. McGraw-Hill, New York, (1957).
[5] PWR Advanced All-Volatile-Treatment Additive, By-Products and Boric Acid, EPRI TR-100755, (1992).
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