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IN POWER PLANT WATERS

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WHY CORROSION PRODUCTS MUST BE CONTROLLED IN POWER PLANT WATERS

T. F. Demmitt - A. B. Johnson, Jr.

There are three fundamental reasons why corrosion processes must be controlled in power plant coolant systems.

- To minimize the operational problems that can occur if adequate control is not achieved and maintained.
- To facilitate operation of the systems at conditions which permit the most efficient conversion of heat to electrical energy.
- To facilitate the use of the least expensive materials and methods for system construction and maintenance.

In the simplest possible terms this means that corrosion processes must be controlled to avoid certain types of undesirable problems, and to achieve certain types of desirable benefits. Although these statements seem axiomatic, it is necessary to state them clearly at this point since they form the basis for all of the discussion which follows.

For the purposes of this discussion corrosion will be defined as follows.

"The processes whereby the environment in contact with the surface of a material interacts with the surface to cause deterioration of the chemical and/or physical characteristics of the surface."

Note that within the context of this definition some environment/surface interactions sometimes characterized as "wear" are included as corrosion processes. Examples include erosion, spallation, cavitation, fretting, cracking, etc. The definition also obviously includes the electrochemical processes which result in oxidation or reduction of the various materials comprising the surface and the environment.

It is important to realize that complete prevention of corrosion processes in power plant cooling systems simply is not possible! The reason is that the thermodynamically stable forms of all of the metals that are commonly employed as construction materials for these systems are oxides for the conditions under

which they operate. The alloy materials used are blends of individual metals which exist as chemical compounds (ores) in their natural state--that is, their lowest free energy state. These individual metals are extracted from their naturally occurring compounds for use in alloying operations only at the expense of expenditure of energy. The metallic materials thus formed and used for system construction are thermodynamically unstable due to their increased free energy. Thus they can and do react spontaneously with the coolant stream to form compounds with lower free energy. These reactions result in an increase in the oxidation state of the metallic elements. The reaction products formed initially--for example, metal ions or hydrous oxides--undergo further reactions which eventually result in formation of those compounds which are thermodynamically stable for the particular coolant system operating conditions.

Since the reaction products formed generally have properties--strength, ductility, thermal conductivity, etc.,--which are less desirable than the metal surfaces from which they were formed, the surfaces may properly be said to have "deteriorated" as the result of these reactions. Furthermore, since the reactions occurred as the result of interaction between the metal surface and the coolant system environment, we are justified in classifying them as "corrosion processes."

Similarly it is obvious that the "wear"-type reactions which result in removal of corrosion product films, and/or discrete particles of metal from the system surfaces, also represent deterioration of the surfaces. Cracking of surfaces is a further mechanism by which deterioration can and does occur. To the extent that processes of this type occur as the result of interactions with the coolant environment, they can and should be considered as "corrosion processes."

The products formed as the result of corrosion processes are called "corrosion products." The nature of these materials--that is, their chemical and physical properties--are dependent on a number of factors.

1. The type of corrosion process that resulted in their formation.
2. The composition and condition of the material surface from which they were formed.
3. The length of time that they have been exposed to the coolant system environment after initial formation.
4. The coolant environmental conditions including temperature, purity, pH, phase (liquid or vapor), velocity, etc.
5. External factors such as the presence of ionizing radiation in nuclear power plants.

6. Recent history of the system such as wet or dry layup, exposure to chemical cleaning solutions, etc.

Since the nature of the corrosion products is dependent upon such a large number of such diverse influences, it is not surprising that their properties and their behavior are complex. At any point in time the corrosion products present in a power plant system span the gamut from ions, colloids, and hydrous oxides; through the spectrum of thermodynamically-possible intermediates; to the stable oxides--including both pure and mixed-metal oxides. Some of these corrosion products are retained at their point of origin on the surface of coolant system components, others are present in the fluid coolant stream, while still others have been transported via the coolant from their point of origin to some other point within the system where they have been removed from the coolant, either by extraction in a purification system or by deposition on some other system surface.

It is control and manipulation of this complex corrosion product inventory that is crucial to achievement of optimum performance of modern, water-cooled, power plant systems. When properly conceived and executed, it is the corrosion product control program that, (1) results in surface films which provide inherent reduction of corrosion rates to acceptably low values, and (2) minimizes scale buildup on critical system surfaces. In the case of nuclear power plants it is also the corrosion product control program which is primarily responsible for minimizing the radiation buildup rate on coolant system surfaces external to the reactor core.

Most of the coolant system operational problems that occur due to the presence of corrosion products are the direct result of mass transport processes. These processes involve migration of a portion of the corrosion product inventory from the point of origin to other parts of the system via the coolant stream. These coolant-borne corrosion products can subsequently deposit on system surfaces where local conditions differ from those existing at the point where they were released from the coolant system surfaces.

Typically deposits form in areas where the fluid hydrodynamics change--for example, at orifices, valves, and low-velocity regions--or where variations occur in coolant temperature. Another obvious area where extensive deposition can occur is on surfaces where coolant boiling occurs, particularly if the phase change to steam is complete. Frequently the deposition behavior is anomalous from one system to another. Examples include the Dresden I and Garigliano nuclear power plants where a large amount of deposit formed on inlet orifices

while deposition on the fuel surfaces was tolerable,^(1,2) as contrasted with the Big Rock Point and Steam Generating Heavy Water nuclear plants where severe deposition occurred on fuel surfaces while only trivial amounts of deposition occurred on orifice assemblies.^(3,4) In the former case it was actually necessary to develop cleaning methods to permit maintenance of required flow rates. In the latter case numerous fuel failures occurred as the result of the corrosion product deposits.

In general, corrosion product deposits can impair plant performance in a number of ways including

- reduction of heat transfer capacity
- reduction of flow capacity
- fouling of process sensor equipment
- accelerated localized corrosion
- fouling of flow control equipment

If problems of the type mentioned do occur, the only effective method currently available to restore the system capabilities is to chemically remove the objectionable deposits. This imposes additional time and cost penalties on the utility organization. It also introduces the potential for accelerated corrosion of certain materials or components by the cleaning solutions. Finally, but by no means necessarily of least importance, is the problem of disposal of the wastes generated during the cleaning process. It is certainly reasonable to expect that this latter problem will become progressively more troublesome as more restrictive requirements are imposed to minimize the ecological effects of waste disposal.

An additional problem specific to nuclear power plants results from transmutation of the metallic corrosion products into radioactive nuclides. When these radioactive materials accumulate in coolant system locations external to the shielded core, they increase the radiation level in the access areas where maintenance and operations activities must be performed. This hinders the effectiveness of the personnel who perform these necessary functions, and can increase the overall operating cost for the system.

Thus it is clear that there is a significant incentive for maintaining a vigorous corrosion product control program to avoid unnecessary operational problems. Failure to maintain the required degree of control can impair operating

efficiency, and in some cases can cause unscheduled plant shutdowns with potentially drastic economic effects for the operating utility organization.

It was, however, stated at the outset of this paper that avoidance of unnecessary operating problems is only one of the justifications for pursuing effective corrosion control programs. The other primary objective must be to obtain as many beneficial effects as possible without incurring extravagant expenditures of time and effort. Clearly there are economic as well as technical considerations involved in obtaining the optimum benefit-to-cost ratio. For this reason what is possible may not always be practical. In other cases it may be necessary to take action to comply with certain regulations regardless of the benefit-to-cost ratio. Notable examples of this type include actions necessary to promote (1) employee and public safety, and (2) protection of the environment.

Most of the questions regarding corrosion and corrosion product control procedures for power plant systems can be resolved primarily on the basis of their benefit-to-cost ratio. Obvious exceptions include radiation exposure control in the case of nuclear plants, which impacts on the employee safety question, and disposal of wastes from cleaning operations from both nuclear and fossil-fueled power plants, which impacts on the environmental protection question.

It is possible to formulate a list of generally desirable properties for corrosion product films which, if achieved in practice, would result in significant operational advantages for water-cooled power plant systems. Such a listing would certainly include the following characteristics.

<u>Film Property</u>	<u>Advantages</u>
1. Adheres rigidly to surface where formed.	Minimizes mass transport within the system and resultant accumulation in selected areas.
2. Low coefficient of friction.	Minimizes frictional pressure loss and forces which tend to dislodge film from metal.
3. High thermal conductivity	Minimizes heat transfer capacity losses due to increased effective thickness of barrier.
4. Thermal expansion coefficient near that of base metal.	Minimizes forces which tend to cause fracture of the film and separation at the film-metal interface.

5. Minimum solubility
in coolant for all
exposure conditions.	Minimizes degradation of film by dissolution
and resultant release of dissolution products.
6. Minimum porosity	Increases thermal conductivity and reduces
transport of corrosion products and reactants
through the film.
7. Causes diffusion-
limited corrosion
kinetics	Minimizes corrosion rate compared to reaction
rate-limited kinetics.

Many of these characteristics are interrelated both with respect to the properties described and the advantages obtained. There are other properties which could also be specified as desirable. An example in the case of nuclear plants is minimization of the presence of metals in the corrosion products which transmute to long-lived, γ -energy emitting radioisotopes after irradiation in the reactor core.

Much of the materials research work that has occurred in support of the power plant development program, both here and abroad, has included some consideration of the characteristics of the corrosion product films formed. Much useful information has been obtained from this work regarding the materials which should be used, and the coolant quality control methodology which should be employed, to achieve generally satisfactory performance. However, the results have not been conclusive in defining the exact mechanisms by which desirable properties are obtained, nor in adequately explaining observed behavior even from an engineering standpoint. Thus no completely definitive yardstick exists by which the potential benefits of materials changes, surface pretreatment variations, system prefilming operations, or coolant chemistry changes can be predicted with confidence. The result is that progress is being made primarily by the painfully slow process of trial-and-error.

The authors contend that the desirability--indeed the necessity--for establishing effective corrosion product control programs for water-cooled power plants is self-evident. We are also convinced that this fact is well recognized by virtually everyone concerned with the problem of achieving optimum performance of the coolant systems in these plants. It is therefore regrettable that more progress is not being made toward obtaining the fundamental base of information

required to define the basic mechanisms involved, and the specific effects of process parameters on these mechanisms.

A major change in emphasis will be required in most current research and development efforts to correct this situation. Considerably more attention must be directed toward defining the characteristics of the corrosion product films which form on material surfaces under various conditions. This must involve detailed examination of composition and structure, rather than simple determination of weight per unit area and elemental composition. Investigators must also determine quantitatively the differences between those films which have generally satisfactory properties and those with properties which are less satisfactory. Mechanisms must then be devised and demonstrated which define the reasons for this difference in behavior. Finally, the precise effect of the coolant environment on the individual properties of the corrosion products must be defined in a much more rigorous way than has ever been done before. This will require a commitment to this task which will probably not yield much in the way of immediate rewards, but which is the only approach in our judgment which holds promise for ultimately resulting in a major step forward in the area of materials development for the power industry. It is precisely in this area where we believe that corrosion scientists and engineers should concentrate their efforts, and where industry should concentrate its financial resources, to obtain the greatest possible benefit-to-cost ratio for both present and future generations of power plants. All other approaches seem to us to represent primarily treatment of the symptoms rather than attempts to cure the basic problems.

Admittedly there are other important problems related to corrosion product control which must also be considered. Most of these bear directly on the subject of mass transport processes involving corrosion products present in the coolant stream. These problems deserve careful attention, particularly for the near future, or until some giant strides are made in methodology for achieving reduction of the amount of corrosion product material released into the coolant stream.

Basically these problems relate to removal of the transported corrosion products from the coolant stream. Considerable work has been and continues to be performed in the areas of ion exchange and coolant filtration. Other work has evaluated techniques such as electrostatic, electromagnetic, and

centrifugal separation of the corrosion products from the coolant. Clearly the objective of this work is to define effective and economical methods for achieving this separation before the transported materials can form objectionable deposits in critical parts of the system. Encouraging results are being obtained from some of this work. We need to move in a timely and effective manner to capitalize on these developments.

Still other efforts are in progress to develop methods for quantitatively predicting whether, and to what extent, deposits will form in specific systems under certain specific operating conditions. Some of this work has reached the stage where instruments are becoming available which can provide operator alarms to call attention to the fact that conditions are conducive to deposit formation. We need to be aware of this work, and to apply both the results and the instruments in power plant systems to the maximum extent feasible.

In short we must utilize effectively the tools and techniques which are and/or are becoming available to achieve the best performance possible within the restraints imposed by the particular system designs and operational requirements. We must concentrate on obtaining immediate relief from some of the more pressing immediate problems; however, we must also be actively pursuing those longer-range types of research and development work which offer potentially great advances in the state-of-the-art of corrosion product control. It is the authors contention that these longer-range efforts should focus on developing methods for quantitative characterization of corrosion product properties, and on devising and demonstrating models which accurately relate these properties to the system operating conditions. The ultimate result of this effort should be a comprehensive theory or set of principles which will permit confidence in predictions concerning the relative advantages which should occur as the result of proposed changes in system materials or method of operation.

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