**THEORY OF CORROSION PRODUCT
GENERATION, DISPERSION,
AND ACTIVATION PROCESSES**

J. W. BARTLETT

MAY 1968

**AEC RESEARCH &
DEVELOPMENT REPORT**

BATTELLE

NORTHWEST

BATTELLE MEMORIAL INSTITUTE

PACIFIC NORTHWEST LABORATORY

BATTELLE BOULEVARD, P. O. BOX 999, RICHLAND, WASHINGTON 99352

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

BNWL-676
UC-80, Reactor Technology

THEORY OF CORROSION PRODUCT GENERATION,
DISPERSION, AND ACTIVATION PROCESSES

By

J. W. Bartlett*

Surface and Coolant Chemistry Section
Chemistry and Chemical Engineering Department

May 1968

FIRST UNCLASSIFIED
DISTRIBUTION

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

* *Currently Associate Professor, Chemical Engineering
Department, University of Rochester, Rochester, New York*

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

THEORY OF CORROSION PRODUCT GENERATION,
DISPERSION, AND ACTIVATION PROCESSES

J. W. Bartlett

ABSTRACT

A theoretical discussion of transport phenomena for corrosion products in water cooled nuclear reactors is presented. Processes and mechanisms of corrosion product transport are defined, and a system of equations to describe corrosion product mass and activity dispersion is developed. Theoretical and experimental work required to advance understanding is described.

TABLE OF CONTENTS

ABSTRACT	iii
INTRODUCTION	1
BACKGROUND	2
SUMMARY	4
CORROSION PRODUCT DISPERSION AND ACTIVATION	6
I. Corrosion Product Inventories	7
A. Formation of Corrosion Products.	7
B. Corrosion Product Species	9
II. Theory of Dispersion of Species.	13
Summary.	24
III. Transport Processes and Physical Characteristics of Coolant Crud	25
IV. Core Crud Deposits	46
Deposition Processes	47
Release Processes	49
Net Release and Deposition Rates	49
Mechanisms of Deposition and Release	50
A Model for Deposition, Release, and Deposit Buildup Processes	52
Factors Important to Deposit Release	55
A Formulation of the Release Rate	58
Formulation of the Deposition Rate	64
Combination of Deposition and Release Expressions	65
V. Corrosion Product Films on Structural Surfaces.	66
Corrosion Film Transport Processes and Mechanisms	67
Significance of Transport Processes at Crud-Source Surface	69
Closing Remarks on Corrosion Product Film	70
VI. Dynamics of Corrosion Product Activity Dispersion Processes.	71

Activity Buildup Phenomena--	
General Discussion	72
Past and Present Methods	
for Predicting Activity Buildup	74
Activity Production in Core Deposits.	75
Release of Activity from Core Deposits	77
Activity in the Coolant	80
Activity Accumulation	
in Corrosion Films	84
VII. Summary of Quantitative Relationships.	90
VIII. Summary of Requirements for Future Work	93
A. Theoretical and Experimental Studies	
of the Properties of Coolant Crud.	93
B. Theoretical and Experimental Studies	
of the Mechanism(s)	
of Crud Deposition.	93
C. Theoretical and Experimental Studies	
of Release from Deposits	93
D. Activity Accumulation	
in Corrosion Product Films	94
Acknowledgements	94
REFERENCES	95
DISTRIBUTION	Distr-1

THEORY OF CORROSION PRODUCT GENERATION,
DISPERSION, AND ACTIVATION PROCESSES

J. W. Bartlett*

INTRODUCTION

This report is a presentation of some factors of importance to corrosion products in water cooled nuclear reactors. Emphasis is placed on phenomena of corrosion product transport, for purposes of describing their influence on the two major problem areas: deposition on core surfaces and corrosion product activation.

The discussion is at once general and detailed. A descriptive treatment of transport processes and mechanisms is given, but detailed quantitative relationships are also developed. The primary purpose for this presentation of a system of equations to describe the transport processes is to show how they define weaknesses in current knowledge and theory and at the same time predict requirements for future theoretical and experimental effort.

This paper is not primarily a report of new developments to practitioners of the art. The major intent is to indicate to those with interest in the subject something of its enormous complexity and the reasons why significant advances have been so hard to achieve.

Some ideas which appear to be new are presented, particularly in the areas of description of coolant crud and corrosion product deposits. It is hoped that these thoughts may provide some stimulus for future work.

* *Currently Associate Professor, Chemical Engineering Department, University of Rochester, Rochester, New York.*

BACKGROUND

Corrosion of materials of construction used in water cooled nuclear reactors is negligible in terms of base metal attack. However, the corrosion products produced (at a total rate on the order of kilograms per month) are to a large degree highly mobile and transport freely throughout the system via the reactor coolant.

This mobility and transport results in deposition of corrosion products on all surfaces exposed to reactor coolant. Deposition on surfaces in the reactor core is of particular concern; deposits on these surfaces have produced operational problems which are at least a nuisance and at worst a severe limitation on the operability and habitability of the system.

The operational problems caused by the deposits are of three basic types: (1) increased hydraulic resistance, leading to reduced coolant flow; (2) increased thermal resistance to core heat transfer, resulting in higher fuel and cladding temperatures; and (3) accumulation of radioactive corrosion products on surfaces external to the core. The radioactive material is produced by release from core deposits.

The radioactive corrosion products can restrict accessibility to the system for maintenance; the deposits may produce fuel melting, burnout, boiling in cores designed not to boil, and steam-film blanketing of heat transfer surfaces in boiling cores.

To date, corrosion product deposits have not been identified as a specific cause of fuel element failure. However, decontamination to reduce radiation dose rates and core deposit inventories has been required in many reactor systems. At present, decontamination is the only method for attempting to control corrosion product problems. It is expensive, time-consuming,

hazardous, and of uncertain long-term effectiveness. Consequently, it must be accepted that effective methods for controlling corrosion product problems do not currently exist.

All indicators predict more severe corrosion product problems in the future. The possible ultimate magnitude of these problems is not predictable, however. Current understanding of phenomena responsible for observed corrosion product mass and activity dispersions is not sufficient to permit reliable predictions. Control of these dispersions is therefore also not possible today.

Improved understanding of the fundamental physical and chemical phenomena pertinent to corrosion products is essential to achieve predictive and control capacity for corrosion product mass and activity dispersions. Many attempts have been made to predict and control corrosion product behavior, but their effectiveness has been seriously limited by lack of knowledge of the fundamental factors that need to be considered.

Insufficient knowledge of the fundamentals is largely the result of the complexity of the corrosion product environment. Chemical and physical conditions are extreme by normal standards, and the transport processes available to the corrosion products are numerous and complicated. Many of these factors are obviously important to corrosion product behavior; therefore, predictive relationships which ignore them are unsuccessful.

Many relationships that attempt to describe corrosion product behavior have been developed in the past. These range from the extremely simple to the extremely complex, and from the largely empirical to the largely theoretical.

The complex, largely theoretical models have proven to be most successful, although none has been severely tested or proven adequate for all water cooled reactors. However, even the

most sophisticated models available today ignore many possibly important factors or describe them in terms of empirical coefficients whose values are derived from data. To a large extent, this practice is essential; requisite experimental observations and data have not been obtained.

But today's sophisticated models, no matter how detailed and penetrating, may not be sufficient. In particular, none seems to describe in sufficient detail the types and properties of crud in the coolant. This is probably a serious shortcoming, since it is the coolant-borne species that are the source of the deposits and the radioactivity. The writer believes major theoretical and experimental attention should be directed at coolant crud.

There is no reason to limit the degree of detail used to describe coolant crud or the attendant transport processes and mechanisms. Today's computers can handle virtually any level of complexity required. Consequently, the models used should reflect as faithfully as possible the fundamentals and complexity of corrosion product behavior. Such an approach will have the added virtue of pinpointing specific needs for experiment and improved models.

This paper presents a rather detailed description of phenomena, processes, and mechanisms believed important to corrosion product mass and activity dispersion.

SUMMARY

A discussion of phenomena pertinent to dispersion and activation of corrosion products in nuclear reactors is presented. Detailed quantitative relationships that describe transport processes and physical mechanisms are developed for purposes of demonstrating the complexity of the dispersion processes and the variables of significance.

The corrosion product inventory is shown to develop from the ions formed initially in the corrosion reaction to an array of many species which coexist in the coolant and transport freely throughout the system. The species are described in terms of a matrix of quantum-species; the physicochemical properties of the individual quantum-species and their influence on the properties of coolant crud are considered.

Possible mechanisms of deposition and release are described. A model for deposit buildup involving transport-controlled deposition and erosion-controlled release is developed to illustrate formulation of relationships which explain variation of amount of deposit with time and position. The model itself suggests methods for testing it experimentally.

Production and dispersion of corrosion product radioactivity is described in terms of detailed formulations; the coupling between these equations and those for mass dispersion is discussed. The need to determine the distribution of corrosion product radioactivity among the various coolant species is noted, and factors that impose severe limitations on current capacity to predict activity accumulation in corrosion films are made obvious with quantitative methods.

This probing of weaknesses in current knowledge and theory leads to clear definition of future work required to advance our capacity to predict and control corrosion product problems in water cooled nuclear reactors. Those subjects found most urgently to require fundamental research include:

1. Physical and chemical properties of coolant crud.
2. Mechanisms of corrosion product deposition.
3. Mechanisms of corrosion product release from deposits.
4. Theoretical parametric and scoping studies of activity accumulation in corrosion product films.

CORROSION PRODUCT DISPERSION AND ACTIVATION

The several kinds of operational problems caused by corrosion products in water cooled reactors may develop from a multiplicity of physical processes. To eliminate or minimize these problems through control of corrosion product behavior requires detailed, quantitative knowledge of the physical processes. This section describes current understanding of what these processes are and indicates some of the inevitable mathematical formulations necessary to describe them.

This discussion has five major objectives:

1. To show that the processes involved are in fact quite complex and require highly sophisticated analytical and experimental effort;
2. To demonstrate the power of a theoretical approach in providing working relationships capable of predicting corrosion product behavior;
3. To demonstrate the capacity of theoretical relationships for predicting data requirements and selecting variables to be measured;
4. to point out deficiencies in current theories; and
5. As a result of all the above, to demonstrate that an adequate, well-founded theoretical base is required to complete successfully a program designed to provide information needed to control crud problems.

The discussion considers detailed physical mechanisms involved in the three major areas that require quantitative treatment: (1) corrosion product inventory; (2) inventory distribution, and (3) generation and dispersion of corrosion product radioactivity.

I. CORROSION PRODUCT INVENTORIES

A. Formation of Corrosion Products

The corrosion products of concern are generated by corrosion and wear of structural materials exposed to reactor coolant. The significant elemental constituents include iron, nickel, chromium, cobalt, manganese, and in some systems, copper. Zirconium corrosion is not significant in the present discussion.

All atoms whose chemical and thermodynamic state changes from that characteristic of the base metal are potential contributors to the corrosion product inventory. This change in state inevitably first involves formation of ions, a process which may be immediate (oxidation at the metal-oxide interface) or delayed as in the case of wear particles released as pieces of metal that eventually dissolve. Parenthetically, it may be noted at this point that the contribution of wear products to the crud inventory should not be overlooked; wear of Stellites has been estimated in some systems to contribute ten times as much elemental cobalt (the only practical source of the major problem radionuclide, ^{60}Co) as base metal corrosion.

The rate of formation of corrosion product inventory (i.e., the ions of each elemental constituent) is usually assumed to be represented by the prevailing corrosion rates for materials exposed to the coolant. A tacit assumption always made is that ions are formed for each elemental constituent of an alloy at a rate proportional to mass concentration in the alloy, i.e., selective corrosion does not exist. If this assumption is accepted, reference to experimental data on corrosion rates should provide appropriate estimates of the rate of formation of corrosion product inventories for each species.

Numerous data on gross corrosion of reactor materials are available. In general, these data indicate that instantaneous corrosion rates are initially high and eventually decrease;

thus, the rate of formation of corrosion product inventory is not constant in time. In addition, close examination of available corrosion data shows that corrosion rates differ for various commonly used reactor materials, and for a given material the rates are dependent on variables such as surface finish and water chemistry condition. Furthermore, as shown below, it is quite possible that corrosion rates for a given material will depend on the physical system in which it exists; thus, corrosion rates in a reactor system may not be the same as in the test loop where the experimental data were obtained.

It is therefore apparent that corrosion data obtained in the laboratory provide at best a first estimate of the rate of formation of corrosion product inventory. An accurate determination can be made only with detailed knowledge of in-service corrosion rates. Obviously, it is also necessary to know accurately the total area of each material exposed to reactor coolant. In some cases, such as elemental cobalt, it is also necessary to know the contribution of wear products to the inventory.

It is generally accepted that the rate of formation of corrosion product inventory is one of the best known factors in corrosion technology. However, careful review of the literature shows large differences in apparent corrosion rates for supposedly identical exposure conditions, and differences in corrosion for different chemistry conditions are well known and accepted. How, then, should crud inventory production rates be calculated for systems that have operated with a variety of coolant chemistry conditions or have been decontaminated? What should be the basis for calculation of inventory production rates in a new system? Such calculations are essential, for knowledge of crud formation rates is a key element in the material balances needed to describe crud transport and dispersion and the potential for operational problems. The accuracy of

such calculations, is, however, currently limited by the reliability of the assumptions made. There have never been sufficient data obtained from a reactor system to permit ex post facto construction of a material balance that would check the veracity of the assumptions.

At present, then, knowledge of this most fundamental quantity -- rate of formation of corrosion product inventory -- is somewhat suspect.

B. Corrosion Product Species

The ions formed in the initial stages of the corrosion process become rapidly transformed into other corrosion product species. This transformation is a result of fundamental thermodynamic requirements; basically, that the constituents of a system exist in a state of minimum free energy consistent with prevailing state conditions (e.g., temperature and pressure).

For present purposes, the key questions relevant to corrosion product species concern species mobility relative to the system as a whole, existence of species, rates of transformation from one species to another, and the physical properties of the species present.

The lifetime of a corrosion product atom as an ion is probably extremely short. If the ion is immediately incorporated into the lattice structure of the adherent oxide film on a surface it will probably never, in effect, escape the surface. Its mobility will be low (characterized by normal migration processes in crystal structures), and it will be an integral part of the species in the film. Species whose history is represented by such limited processes* are of negligible

* It is not certain that such a "minimum mobility" process really exists. All ions may actually escape the surface with some fraction of these redepositing immediately. If this is indeed the case, the process is of great significance to pickup of radioactivity as discussed below.

concern to corrosion product problems; it is important, however, to know what fraction of the total inventory suffers this fate, since the remainder is the material that transports and becomes radioactive.

The ions that actually escape the surface and its adherent oxide film are free to react with all species in the water and to be transported in and with the fluid by convective and diffusional processes. All released ions obviously have, therefore, potentially unlimited mobility within the system. A corollary of this observation is that all species in any parcel of fluid -- even those immediately adjacent to a surface -- have lost identity with respect to point of origin, since convective (i.e., mixing) effects in the fluid persist even to the wall where the fluid velocity is zero.^(1,2) This mixing of species is potentially of great importance in processes by which radioactive atoms become incorporated in corrosion products.

The released corrosion products will therefore be subjected simultaneously to fluid motion effects and the thermodynamic exigency for transformation via chemical reaction. The chemical reaction to form the stable oxide is not, however, immediate. The appropriate stable oxide is formed as an end product of a series of reactions, each of which is characterized by a kinetic rate constant and a particular species as the end product. Such a series might be represented by

where A is the first species in the series (the ion; N is the stable oxide); B, C, etc. are the intermediate species; and k_1 , k_2 ... are the appropriate reaction rate constants. Alternative reaction products B', C', etc. might also exist.

Thus, in a steady-state system, species A, B, C, ... N will all coexist, and for each of these species there will continually

be inputs and outputs. The input that starts the chain (formation of A) is corrosion; characteristic quantities of the other species are governed by this input and the reaction rate constants.* The existence of a variety of species for each elemental constituent of nuclear reactor corrosion products is well known.⁽⁵⁾ With iron, for example, the intermediate species include $\text{Fe}(\text{OH})_2$, FeOOH , and Fe_2O_3 . For most reactor operating conditions the stable oxide is Fe_3O_4 .

When all of the major elemental constituents of corrosion products are considered, it is clear that there are as many as 25 or 30 different species in the coolant, each with its own characteristic chemical and physical properties and each potentially significant with respect to crud problems. For each of these species it may be noted that:

1. The inventory is free to move with the coolant;
2. The inventory is free to interact and exchange with material on surfaces (note that the total inventory of a species is the sum of that in the coolant plus that on surfaces);
3. For all species (except possibly stable end-product oxides) the identity of the constituent atoms is continually changing as a result of chemical reaction (i.e., specific atoms enter and leave a species population by chemical reaction).
4. The inventory is free to interact with inventories of other species (e.g., a ferrous ion may attach to a particle of Fe_3O_4).

These broadly stated physical processes may be more quantitatively (although, for the moment, generally) stated in terms

* If all chemical reactions are first order, the process is exactly analogous to a radioactive decay series.⁽³⁾ Some experimental data on transformations of iron species are given by Kesten and Lasher.⁽⁴⁾

of the equation of continuity for each species, which may be written, for the mass inventory of the i -th species, M_i ,

$$\frac{\partial M_i}{\partial t} + \vec{v} \cdot \nabla M_i = D_i \nabla^2 M_i + \sum_{n=1}^n k_n M_n - \sum_{\substack{j=1 \\ n,j=i}}^j k_{i,j} M_i \quad (2)$$

where $\vec{v}$ = vector velocity components

D_i = diffusion coefficient*

k_n = characteristic rate constants for formation
of i from other species 1, 2, ... n

$k_{i,j}$ = characteristic rate constants for removal
of i by processes 1, 2, ... j .

Similar equations will exist for each of the species, and it is necessary to write such a relationship for a given species in each uniquely describable portion of the system. Altogether, a total of several hundred such equations and appropriate boundary conditions might be required to describe completely the behavior of corrosion products in a reactor system. Description of corrosion phenomena in terms of relationships such as Equation (2), although obviously formidable, is not outside the realm of possibility when the availability of modern computers is considered. Application of this approach to the relatively simple case of corrosion phenomena near a surface is demonstrated in a recent paper by Bartlett et al.⁽⁶⁾

In summary, a large number of corrosion product species, each with uniquely characteristic properties, will exist in the reactor. The population of any species will be in a dynamic state of exchange with other species and various portions of the system, and the constituent atoms of that population will change continually as a result of chemical reactions.

* This could be the turbulent diffusivity or the molecular ("ordinary") diffusivity, depending on the region of the coolant under consideration.

We now consider some of these processes and how they affect inventory dispersion within the system.

II. THEORY OF DISPERSION OF SPECIES

It is necessary to distinguish two basic kinds of dispersion processes: gross, or macroscopic dispersion which applies to movement and accumulation of relatively large masses of one or more elemental constituents of crud in various parts of the system, and local, or microscopic dispersion which describes the detailed processes that affect corrosion product species in a particular region of the system, e.g., coolant-borne crud in a boundary layer. The present discussion is concerned with macroscopic dispersion; microscopic dispersion processes for the three major regions containing corrosion product inventory (core surfaces, coolant, and oxide films on structural surfaces) are discussed below.

Of interest here are factors that permit corrosion products to escape their surface of origin and govern the distribution of these highly mobile species throughout the system. We wish to describe the existence and magnitude of potentials for transport and the physical phenomena that influence them.

A physical process such as corrosion product transport will exist only because a potential difference, or driving force, exists and permits or demands such transport. In simple cases, such as current flow due to a voltage difference across a pure resistance, all variables are easily defined and the transport rate easily calculated. With corrosion product transport, however, if we accept an electrical analogy, the circuit is probably composed of a complex of highly nonlinear resistive and capacitive elements in parallel and series array. The equations that describe such a system are correspondingly complex; however, they are tractable and analogous to the equations of circuit theory. Indeed, this latter fact suggests strongly that analog computer studies would be of great value in this work.

The major problem in describing macroscopic corrosion products dispersion is formulation of a realistic, useful model that reflects accurately the influence of physical variables on the various potentials and thus has predictive capacity. Such a model is suggested here. The present description of the model is restricted to definition of regions of concern, statement of the transport processes in each region, and a largely qualitative discussion of the nature and interaction of these transport processes and how they affect macroscopic transport. Detailed description of processes in each region are given below.

The regions defined to be of concern to macroscopic dispersion are (1) the oxide film on the surface of the base metal that is the source of the corrosion product inventory; (2) the fluid boundary layer adjacent to the oxide film; (3) the bulk volume of the coolant; (4) the fluid boundary layer adjacent to the deposition surface; and (5) the deposit on the deposition surface. The deposition surface may be another area of corroding crud-supplying surface, in which case the deposit is characterized by its own oxide film, or it may in the limit be completely "inert" (e.g., zirconium fuel surfaces in the core, which do not contribute to the corrosion product inventory), in which case the material on the surface is more strictly a "deposit", since it is composed entirely of elemental species foreign to the base metal beneath.

The simplest model representing these regions assumes they exist in series with macroscopic transport occurring, successively through each region, from the base metal containing the oxide film to the deposition surface. For each region a "characteristic concentration," $C_1, C_2, \dots C_5$, is specified, and clearly defined interfaces with no resistance capacitance are postulated. Transport processes in each region may then be identified as listed below and shown in Figure 1.

FIGURE 1. Basic Corrosion Product Transport Processes

REGION I, OXIDE FILM

1. Oxidation (formation of ions)
2. Irreversible retention on surface.
3. Transport from oxide film to fluid boundary layer.

REGION II, FLUID BOUNDARY LAYER

4. Redeposition on surface
- 4a. Redeposition on surface after transport delay.
5. Transport delay (migration as a result of fluid motion, etc.).
6. Transport from boundary layer to bulk coolant.
- 6a. Transport from boundary layer to bulk coolant after delay. Because of the delay, the form of the species may have changed.

REGION III, BULK COOLANT

7. Loss by removal in ion exchanger.
8. Transport delay.

9. Transport from bulk coolant to fluid boundary layer near the deposition surface.

REGION IV, FLUID BOUNDARY LAYER ON DEPOSITION SURFACE

10. Transport to the deposit.
- 10a. Transport to the deposit after delay.
11. Transport delay.
12. Escape back to bulk coolant after transport delay.
13. Transport from the deposit.
14. Escape of deposit-released material to bulk coolant.
- 14a. Escape of deposit-released material to bulk coolant after delay.
16. Redeposition of deposit-released material.
- 16a. Redeposition of deposit-released material after delay.

REGION V, DEPOSIT

15. Permanent retention in the deposit

10, 10a, 13, 16, and 16a as described above.

The objectives of effort to describe corrosion product dispersion phenomena include, or should include, determination of the mechanisms and rates for each of these processes. Some detailed discussion of the mechanisms and significance of these processes is possible and will be given below. Present discussion is confined to description of net transport and dispersion in terms of the characteristic concentrations C_1 , etc.

Accepting the existence of a net transport process (and it must exist if the corrosion rate remains finite and corrosion products accumulate in the ion exchanger and on inert surfaces), the process may be described in terms of potentials, here measured by the characteristic concentrations and appropriate transfer coefficients. At steady state the net rate of transport between adjacent regions will be the same, so that

$$\begin{aligned}
 R_T &= k_{12} (C_1 - C_2) = K_{23} (C_2 - C_3) = k_{34} (C_3 - C_4) \\
 &= k_{45} (C_4 - C_5)
 \end{aligned}
 \tag{3}$$

where R_T is the net rate of transport, C is the characteristic concentration for the region designated by its subscript, and k is the transfer coefficient for transport between adjacent regions as indicated by the subscripts. The transport rate may also be expressed in terms of an overall transfer coefficient, k_o , and the overall potential difference, $(C_1 - C_5)$:

$$R_T = k_o (C_1 - C_5) \quad (4)$$

Using Equation (3), factors that affect the transport and dispersion of corrosion products may be examined. First, it may be noted that any of the individual $k_{ij} (C_i - C_j)$ terms may control the net transport rate. Such control may be exerted as a result of low potential difference or as a result of a small transfer coefficient. Additionally, reference to Equation (4) shows that the transport rate, which may ultimately be identified with the corrosion rate,* may be affected by the overall potential difference in the system. This is the origin of the previous statement that the corrosion rate of a surface may depend on the characteristics of the system in which that surface exists. If, for example, there is present in the system a "sink" for corrosion products which is large and highly effective, the low potential end of the driving force [C_5 in Equation (4)] may vanish to zero, and R_T would increase from values obtained in a system which is identical in all respects except that C_5 is larger. Alternatively, changes in other system parameters such as the surface area to liquid volume ratio, stream velocity, coolant chemistry, etc., may change k_o and/or C_1 and produce a corresponding change in R_T . All applications of test data from autoclaves and loops which assume in-service corrosion rates will be the same make the tacit assumption that phenomena in the oxide film totally

* If the oxide film weight is constant, the transport rate, corrosion release rate, and base metal corrosion rate are identical.

control the corrosion rate, so that Equations (3) or (4) do not apply at all. At least one careful experiment denies the validity of such an assumption.⁽⁷⁾

The characteristic concentration of the fluid boundary layer, C_2 , is related to the chemical solubility of the species. The influence of chemical solubility on the net transport rate and magnitudes of the individual transport processes is quite subtle, however. If it is assumed that the characteristic concentrations C_2 and C_3 are proportional to the chemical solubility,

$$C_2 = A_2 S_2; C_3 = A_3 S_3 \quad (5)$$

where A is a constant and S is the solubility, substitution in Equation (3) yields

$$R_T = k_{23} (C_2 - C_3) = k_{23} (A_2 S_2 - A_3 S_3). \quad (6)$$

Equation (6) may now be interpreted to show the basis for some of the phenomena seen in reactors. If the system is truly isothermal, or S_2 and S_3 do not differ significantly, Equation (6) becomes

$$R_T = k_{23} S (A_2 - A_3) \quad (7)$$

which shows that under isothermal conditions the driving force for transport is not chemical solubility per se but the factors that govern the parameters A_2 and A_3 . Equation (7) shows also, however, that the rate of transport will be proportional to the actual solubility. This fact has been utilized in practice by taking advantage of the variation of solubility with pH; the solubility is a minimum at about pH 10, and reactor systems are run, when possible, with a coolant pH of 10 because experiments have confirmed that corrosion is minimal under these conditions.^(5,8,9)

If the system is not isothermal, a temperature gradient will exist in the fluid and S_2 will be larger or smaller than S_3 , depending on whether heating or cooling is occurring at the surface and whether the solubility of the species follows the usual rule of increasing solubility with increasing temperature (nickel, at least, does not follow this rule;⁽¹⁰⁾ other corrosion product species may also exhibit "negative temperature coefficients of solubility"). In any event, differences in values of S_2 and S_3 may be expected under such circumstances, and the species may tend to dissolve or precipitate in passing from the boundary layer to the bulk coolant. The magnitude and direction of the net transport rate is not fixed, however, without knowledge of the phenomenological coefficients A_2 and A_3 .

Something of the nature of these phenomenological coefficients defined by Equation (5) may be illustrated by returning to consideration of transport processes in the boundary layer itself. The definition of the effective concentration in terms of A and S implies that this effective concentration will be some multiple (measured by A) of the chemical solubility. Physically, it is to be expected that what this multiple actually is will depend on how rapidly material is transported into and out of a unit volume of fluid in the boundary layer.

These concepts may be expressed quantitatively in terms of a rate balance on C_2 given in terms of transport coefficients:

$$\frac{dC_2}{dt} = \gamma_3 C_1 - (\gamma_4 + \gamma_{4a} + \gamma_6 + \gamma_{6a}) C_2 \quad (8)$$

where $\gamma_3, \gamma_4, \dots, \gamma_{6a}$ are the transport coefficients for the boundary layer transport processes identified in Figure 1. Each has units of $(\text{time})^{-1}$ and represents the fractional rate of turnover of C_2 due to the process designated by the subscript. In Equation (8), $\gamma_3 C_1$ is the corrosion release rate, R , and if steady state is assumed,

$$C_2 = \frac{R}{(\gamma_4 + \gamma_{4a} + \gamma_6 + \gamma_{6a})} = A_2 S_2 \quad (9)$$

which relates C_2 to two fundamental quantities, the corrosion release rate and the chemical solubility.* The parameter A_2 is defined by the ratio

$$A_2 = \frac{C_2}{S_2} = \frac{R/(\gamma_4 + \gamma_{4a} + \gamma_6 + \gamma_{6a})}{S_2} \quad (10)$$

and, as previously suggested, dependent on the transport rates. In the limit, $C_2 = S_2$, and $A_2 = 1.0$, but there is no physical necessity for this limit to be achieved.

Equation (9) may be used to interpret several well known phenomena:

1. For a fixed chemical solubility (and, therefore, temperature) the release rate may vary. The existence of this possibility was noted previously; Equation (9) suggests the variations are the consequence of variations in transport rates.
2. As the transport coefficients increase, the characteristic concentration C_2 will decrease for fixed chemical solubility. The effect of a change in the sum of the transport coefficients on the net transport rate is not immediately obvious, since by Equation (3) the $(C_2 - C_3)$ driving force will decrease and $(C_1 - C_2)$ will increase. More insight may be gained, however, by considering which of the transport coefficients change. If the transport coefficients representing the release processes (γ_6 and γ_{6a}) are dominant, in the limit redeposition and resistance to transport to the turbulent core of the fluid vanish. An adherent oxide film is not formed, and corrosion behavior corresponds to situations such as oxidation

* The relationships exist only by assumption and definition. It must be kept in mind that this development and others in this section are models which seek to express and explain observed phenomena. The present discussion is restricted to a very simple and phenomenological model.

of copper in acidic solution, where the mass transport rate can be correlated with the local Reynolds number. Conversely, if redeposition processes (γ_4 and γ_{4a}) dominate, an oxide film will build rapidly, corrosion rates will decrease in accordance with the rate of film growth,* and transport rate behavior will be characteristic of film-forming metals such as stainless steel and aluminum.

3. When a fixed corrosion rate prevails in a fixed transport regime, net transport rates for different species will depend on the chemical solubilities of the individual species. To illustrate this concept, it will be useful at this point to demonstrate a need for careful definition which appears not to have received sufficient attention historically.

In previous discussion the transport rate $\gamma_3 C_1$ was identified as the corrosion release rate, R . This release rate is not, however, necessarily the net transport rate, R_T . Reference to Figure 1 shows that the actual net transport rate from the surface is the sum of the rates for the transport processes numbered 6 and 6a, and a material balance on the material in the boundary layer gives

$$R = R_4 + R_{4a} + R_6 + R_{6a} \quad (11)$$

$$\text{or } R = R_4 + R_{4a} + R_T \quad (11a)$$

and hence, the corrosion release rate is numerically equal to the net transport rate only when the redeposition processes R_4 and R_{4a} are zero. Historically, the process defined here as the net transport rate, R_T , has been called the release rate. This is perfectly logical (and in most cases satisfactory) since R_T in Equation (11a) is the quantity most easily measured by net metal loss determinations.

* Simple models of film growth are discussed by Gardner.⁽¹¹⁾

However, for studies relevant to nuclear reactor systems it is imperative that the distinction indicated by Equation (11a) be made. The release rate identified here as R (or, in keeping with the above nomenclature, R_3 would be appropriate) is probably the rate process that governs the rate at which radioactivity is picked up by the film, as will be shown below.

Returning to consideration of the effect of solubility on the net transport rate, manipulation of Equations (9) and (11a) yields the relationship

$$R_T = (\sum \gamma_i) A_2 S_2 - (R_4 + R_{4a}) \quad (12)$$

wherein $\sum \gamma_i = (\gamma_4 + \gamma_{4a} + \gamma_6 + \gamma_{6a})$ and, by postulate, the values of $\sum \gamma_i$ and A_2 are fixed. Equation (12) indicates that the net transport rate will be directly proportional to the solubility, but also depend on the redeposition rates. Thus, the net transport rate can be no higher than the rate indicated by the magnitude of the term $(\sum \gamma_i) A_2 S_2$, but may be diminished from this value if the redeposition rates are significant. In the limit, all material may redeposit so that the net release rate is zero.

Equation (12) may be expressed alternatively as

$$R_T = (\gamma_{6a} + \gamma_{6a}) A_2 S_2 \quad (13)$$

which again illustrates the dependence of the net transport rate on solubility and also describes this rate in terms of the transport coefficients γ_6 and γ_{6a} , which measure the processes by which corrosion products escape the surface.

In a given fluid regime the rate constants γ_6 and γ_{6a} would be expected to be the same for all species. Hence, release rates for various species will differ in proportion to their relative solubilities. In addition, if the corrosion rate (rate of formation of ions) and the corrosion

release rate are sufficiently high to maintain C_2 at its appropriate saturation level (i.e., dC_2/dt in Equation (8) equal to zero), for equal release rates the redeposition rate must increase with decreasing solubility. This may be illustrated by indicating the various rate processes with arrows of length proportional to their magnitude; for equal release rates, the differences between high-solubility and low-solubility species would be as sketched below:

These qualitative statements may be generalized by noting that if the corrosion release rate is sufficiently high to "force" the boundary layer and maintain saturation, the distribution of the released corrosion products between redeposition and net transport will depend on the solubility and the individual transport processes measured by the transport coefficients. For situations where the transport coefficients are invariant for all species and all positions in the system, the net transport rate relative to the release rate will be governed by chemical solubility.

An example of these concepts is available through comparison of chromium and iron corrosion products

from stainless steel. It is well known^(12,13) that chromium accumulates selectively in the adherent film, increasing in amount from the 18% characteristic of the base metal to about 60% (of metals present) in the oxide film after about two years of exposure. Elemental iron in the oxide film is about 25% of the metallic constituents rather than the 67% in the base metal.

Assuming stoichiometric corrosion of the base metal, these composition changes clearly suggest a high net transport rate for iron relative to chromium. Indeed, material filtered from the coolant and deposited on Zircaloy fuel element surfaces in reactors are found usually to contain about 95% iron and hardly any chromium.

This disproportionation of species may be explained in light of the above arguments when it is noted that the apparent* solubility of iron is ten times or more larger than that of chromium.⁽¹⁰⁾ Thus, since the two species originate from the same surfaces and same boundary layer regimes, the iron will be readily transported, while the low solubility of chromium forces high rates of in situ deposition.

Summary

Factors that influence the movement and dispersion of corrosion products have been discussed in terms of a model which identifies five transport regimes and twenty-one individual transport processes in a reactor system. Driving forces for corrosion product transport have been described in terms of characteristic concentrations for each of the transport regimes. The effect of chemical solubility and the individual transport processes on these

* Jones' widely quoted data⁽¹⁰⁾ were obtained by separating "solubles" from particulates with a metallic filter element. The "true" chemical solubility of corrosion products is not really known.

characteristic concentrations and net transport of corrosion product species was demonstrated, with emphasis on the fact that the individual transport processes and their interactions play an important role in dispersion phenomena. Application of the model was illustrated by using it to explain qualitatively several phenomena characteristic of corrosion product dispersion in reactors.

III. TRANSPORT PROCESSES AND PHYSICAL CHARACTERISTICS OF COOLANT CRUD

The reactor coolant is the vehicle by which all transport of corrosion products from one surface to another takes place. The transport may involve large displacements of individual corrosion products in distance and time (e.g., transport from an out-of-flux structural surface to the core deposit, retention in the core deposit for some period of time, and re-release from the deposit to the coolant) or small displacements in which crud moves only a few inches or less from point of origin to a deposition site. In any event, all crud that finds its way into the coolant is subjected to mixing with species from all other parts of the system; individual ions and the larger agglomerates lose identity with respect to point of origin; and the manner in which the coolant disperses these materials will be statistical in the sense that the origins of species in a given element of fluid are indeterminately distributed. The net dispersion of species by the coolant will, however, be consistent with prevailing driving forces and net transport processes described above. For example, the elemental iron in a packet of fluid as it passes through the core may have originated from such diverse sources as release from the deposit on the adjacent core surface and corrosion release from out-of-flux structures; if the net driving force for iron crud is in the direction of deposition on the core, however,

enough such packets of fluid over a long enough period of time will suffer a net loss of iron to core surfaces and produce deposit buildup. Some of this deposit buildup may involve redeposition of material released from these same deposits.

The basic transport processes for crud in the coolant are easily identified: material enters by escape from surfaces that constitute the coolant boundary and leaves by deposition on these same surfaces and accumulation in the purification system. Crud which gets to the purification system is assumed to be removed irreversibly from the system as a whole; crud that engages in deposition on surfaces is not even necessarily removed irreversibly from the coolant, since possibilities for subsequent release and exchange exist. In general, purification is to be considered the only irreversible sink in the system.

These basic transport processes may be expressed in a simple, over-all material balance for each elemental species in the coolant. If N_i^C is the total mass of the i -th elemental constituent in the coolant (e.g., iron),

$$\frac{dN_i^C}{dt} = R_i - (\gamma_D + \gamma_p)N_i^C \quad (14)$$

where R_i = net rate of input of the i -th elemental species from all sources

γ_D = effective deposition rate constant for all deposition processes, units of $(\text{time})^{-1}$

γ_p = purification rate constant, calculated as (purification flow rate)/(coolant volume), in units of $(\text{time})^{-1}$.

Equation (14) is a gross simplification of details of coolant crud transport that need to be considered, as will be shown below. However, it is instructive in several respects. First,

a steady-state coolant inventory will not be achieved unless R_i , γ_D , and γ_p are constant with time. The rate constants γ_D and γ_p may both, as a first approximation, be taken to be constant; the input rate is, however, identified ultimately with the overall net transport rate which is possibly related directly to the corrosion rate. Thus, early in system history when corrosion rates are changing rapidly the coolant inventory should also change.

If steady-state is achieved, the corresponding coolant inventory will depend on both the input rate and the removal rates. The steady-state inventory is given by

$$N_i^C = \frac{R_i}{(\gamma_D + \gamma_p)} \quad (15)$$

which suggests that in different systems with equal deposition and purification rate constants, the crud level will depend on the net input rate alone. If BWR's and PWR's were identical in terms of primary system corrosion input and the transport rate constants, the BWR system should have higher crud levels because of input from the feedwater heaters. Also, carbon steel systems should have higher crud levels than identical stainless steel systems.

Equation (15) shows also that for fixed crud input and purification rates, coolant crud inventories may be controlled ultimately by the deposition processes. The deposition rate constant γ_D may be very large compared to γ_p , in which case the purification system competes very ineffectively as a sink for coolant species. It may be noted here that the competition between γ_D and γ_p (a function of factors such as coolant velocity, surface to volume ratio, and purification flow rate) is in most reactors probably such that γ_D does completely overshadow γ_p . Hence the common complaint that the purification system doesn't seem to be very effective.

As a first step in describing details of significant transport processes for coolant crud, consider the factors that influence γ_D . It is quite naive to assume--even if it is acceptable to postulate the existence of such a parameter--that γ_D would be constant everywhere in a reactor system. We must first recognize that γ_D is descriptive of events in which material is actually removed from the coolant by adherence to a surface. The sum of the rates of all such events relative to the coolant inventory then defines γ_D :

$$\gamma_D \equiv \frac{\text{total mass deposited per unit time}}{\text{mass inventory of the coolant}}$$

and it should be recognized that γ_D may differ for each of the thirty or so species previously mentioned(i.e., γ_D should be subscripted γ_{Di}).

We may consider then the factors involved in each deposition event:

1. Material in the turbulent core of the fluid must be transported to the boundary layer adjacent to the surface. Such transport would occur by convective motion and be relatively rapid.
2. Material that arrives at the boundary layer must be transported to the surface. The mechanism by which this transport occurs is, for some cases at least (deposition on core surfaces), a subject of conjecture considered in detail in later discussion. For present purposes, it may be noted that if such transport occurs by conventional mass transfer processes, the rate of transfer may approach that characteristic of molecular processes and would therefore be relatively slow. The distance through which such transport must occur (i.e., the boundary layer thickness) is a function of stream velocity and the physical properties of the species.

3. Material transported to the surface must stick. This sticking must persist in spite of factors such as the existence of a shear force exerted by the flowing stream (which will tend to tear the material from the deposit), possibly poor spatial orientation of the delivered material relative to deposition sites on the surface (this presumes a process involving particles), and possibly adverse temperature and/or electrostatic charge fields.

Obviously, many factors act to inhibit deposition. The parameter γ_D describes, however, the species which survive the adversities and arrive at a surface with a sticking probability of unity. Considering, then, the spectrum of adversities and the spectrum of species, it is clear that the γ_{D_i} are dependent not only on properties of the species but also local system properties such as temperature gradient, stream velocity, and deposit morphology. An evaluation of γ_D for a given element therefore requires proper evaluation and weighting of all constituent γ_{D_i} : those for each individual species containing that element, and, for each of these, the variation with position in the system.

Apparent values of the γ_{D_i} , which may be said to reflect "depositability," are also strongly dependent on the physical properties of the species in the coolant. At present, this dependence is more intuitively than quantitatively obvious. Some reasonable speculation on what physical properties are important for the various coolant species is, however, possible.

A property of obvious interest (obvious, perhaps, because it is rather easily measured) is chemical composition. Measurements of coolant crud composition presumably reflect something of the transport of species and the composition of material available for core deposition and activation. But

several subtle details are required for this information to be of real use:

1. Does the measured overall composition reflect the composition of each constituent particle, or is it the net result of contributions from pure-iron particles, pure-nickel particles, etc.? The difference could be of fundamental, far-reaching importance. Pure-nickel oxides, for example, might deposit selectively on core surfaces as a result of the negative temperature coefficient of solubility, whereas iron deposition might be extremely limited.
2. Is the composition constant for various cuts in the size range? Variation of composition would indicate independent size spectra for the individual elemental constituents of crud and hence coexisting, independent matrices for each elemental species. Again, depositability could vary greatly among species and throughout the size distribution for each species.
3. Is the composition constant with time? Selective input rates (e.g. wear of high-cobalt alloys) could cause the composition and again, depositabilities - to change with operating history.

In short, awareness of the existence of a spectrum of species and variable transport and deposition rates makes it clear that proper, detailed information on such simple concepts as chemical composition is essential to evaluate crud characteristics and treat crud problems effectively.

Another property of coolant crud expected to be of fundamental interest is its particle size distribution. Size distributions are known to exist,⁽¹²⁾ and the characteristics of the distributions would be expected to be intimately related to transport processes for coolant crud. The size distribution is,

therefore, as seen by reference to previous discussion on variation of deposition coefficients, expected to be a property highly dependent on the system itself, i.e., size distribution should vary in reactors of different designs. The variation can have strong bearing on crud problems in the system, since it is probable that one particular fraction of the distribution is primarily responsible for core crud deposition. Current knowledge does not, however, define what that fraction is.

Consider now in detail the size distribution of coolant species and factors that affect it. For present purposes two basic aspects are of interest: experimental measurement of the distribution and the concomitant problem of interpretation of the data, and consideration of the fundamental physicochemical factors that influence and produce the distribution as it actually exists. This latter question of the existence of the distribution will be considered first since it will suggest the problems that must be anticipated in an experimental effort.

The fact that a distribution does exist shows that the ions formed as the initial corrosion product species tend to agglomerate. But what are the constituents of the distribution? As previously noted, for each elemental constituent of crud (e.g., iron) a variety of individual species exists (e.g., $\text{Fe}(\text{OH})_2$, FeOOH , Fe_3O_4). These several species exist as a result of a "chain" of chemical reactions in which one species is formed from another, and the chain is maintained by continuous corrosion input of ions at the minimum-size end of the spectrum. All species coexist simultaneously, and each identifiable particle of each individual species is at any instant of time subject simultaneously to three possible processes: (1) change of size, as a result of agglomeration (or possibly disintegration); (2) change of species, as a result of chemical reaction; and (3) deposition. The population distribution is therefore dynamic, with continuous input (corrosion) to sustain it and numerous internal conversions and losses occurring within the distribution.

The continuous input to the distribution allows several major possibilities for changes in the existing distribution:

1. The distribution changes with time. The number of particles at the small-size end of the spectrum might increase with time because of the input of ions; alternatively, the population in the large-size end of the spectrum, which is the sink for the agglomeration process, might increase with time.
2. The size distribution within the spectrum might remain invariant in time, but the total population would increase with time (i.e., crud levels would increase with time).
3. The size distribution and the total population of the distribution are both invariant with time, with the input rate representing also a throughput rate, this throughput being accumulated in the ion-exchanger and deposits in the system.

Present data do not definitively indicate which of these situations actually is obtained in a reactor; apparently, the possibilities have not been recognized and/or investigated. However, available data suggest that crud levels in a given system remain essentially constant within sometimes wide limits. Such information suggests steady-state throughput, but does not necessarily require an invariant size distribution. Many, more thorough studies are required to determine what the real state of affairs is in a reactor coolant. What these studies should be is suggested in later discussion.

The interaction of these simultaneous input, reaction, agglomeration, and deposition processes may be organized for purposes of quantitative consideration as shown in Figure 2. The amounts of material of a given kind and given size are

Identification of Rate Processes:

FIGURE 2. Quantum-Species Matrix for Coolant Crud

represented as unit volume elements and possible inputs and outputs for each of these "quantum-species" are indicated by the arrows. The possibility of feedback due to break up of large particles is indicated (for only one species, in order to preserve some clarity in the diagram) as well as the processes of reaction, agglomeration, and deposition previously mentioned.

The matrix formed by this array of quantum-species elements represents the total possible number of species that will contribute to the total mass of a given element such as iron in a unit volume of coolant, i.e., the mass of iron in a unit volume of coolant is the sum of the masses of iron in all quantum-species. A similar matrix will exist for each of the elemental constituents of crud (e.g., Fe, Ni, Cr, Co, Mn).

The representation given in Figure 2 therefore makes an important fundamental assumption: no interaction of species, i.e., iron corrosion products will not contain nickel, etc. Such interactions could be allowed for, however, by stacking the matrices for each element and indicating interaction between matrices. A three-dimensional array of coupled matrices, each comparable to that given in Figure 2 would then be obtained.

Another fundamental assumption made by this representation is that the various species of a given element do not coexist in a given particle of a given size. In other words, the possibility that a given particle might consist, for example, of stable oxide in the center, an intermediate species in a middle layer, and ions on the surface is not permitted.

If we accept these limitations, the model given in Figure 2 provides an excellent basis for theoretical study and definition of sampling and experimental requirements. Considering first the theoretical aspects, the processes defined in Figure 2 provide explicit statements of some of the input and output processes previously given in general terms in Equation (2).

Specifically (and with detailed discussion given below), Equation (2) becomes, for a given quantum-species of size r_n (i.e., the equation applies to just one of the blocks in Figure 2):

$$\begin{aligned}
 \frac{\partial}{\partial t} M_i^k(r_n) + \vec{v} \cdot \nabla M_i^k(r_n) &= D_i^k(r_n) \nabla^2 M_i^k(r_n) \\
 + \rho_n v_n \sum_{m=1,2,3,\dots,n-1}^m P_{n-m,m}(N_{n-m}^k)(N_m^k) &- \rho_n v_n \sum_{m=1,2,3,\dots,n-1}^m P_{n,m}(N_n^k)(N_m^k) \\
 - \alpha_D^k(r_n) M_i^k(r_n) + \rho_n v_n \sum_{p \neq n} \alpha_F(i,k,r_p) N(i,k,r_p) \\
 + k_i^{k-1} M_i^{k-1}(r_n) - k_i^k M_i^k(r_n) & \quad (16)
 \end{aligned}$$

in which the only thing immediately obvious is that corrosion product technology is not immune to the practice of concealing ignorance in elegant equations. Equation (16) is, however, potentially capable of providing great physical insight. The individual terms are defined and have physical meaning as follows:

$\frac{\partial}{\partial t} M_i^k(r_n)$: time rate of change of the mass (in unit volume of fluid) of the particular quantum-species being considered. In a steady-state system, this term is zero.

$M_i^k(r_n)$ = mass of the k^{th} species (e.g., FeOOH) of the i^{th} element (e.g., Fe) of size r_n .

$\vec{v} \cdot \nabla M_i^k(r_n)$: transport of the quantum-species by convection.

v = velocity components in the three spatial coordinate axes.

$\nabla = \frac{\partial}{\partial t} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$, where x , y , and z designate the coordinate axes.

$D_i^k(r_n) \nabla^2 M_i^k(r_n)$: transport of the quantum-species by diffusion. In the turbulent core of the fluid, this term will be insignificant; in the boundary layer, it may predominate.

$D_i^k(r_n)$ = diffusion coefficient for the quantum-species

$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$; x , y , and z as defined above

$$\rho_n v_n \sum_{m=1,2,3,\dots,n-1}^m P_{n-m,m} (N_{n-m}^k) (N_m^k):$$

formation of the quantum-species by agglomeration of smaller particles of the same species. The reasons for this formulation of the agglomeration process are discussed in detail below.

$P_{n-m,m}$ = probability of union of particles of sizes r_{n-m} and r_m to produce an agglomerate of size r_n .

N_{n-m}^k = number of particles of the k^{th} species and size r_{n-m} present in the unit volume of fluid

N_m^k = number of particles of the k^{th} species and size r_m present in the unit volume of fluid

ρ_n = density of particles of size r_n

v_n = volume of a particle of size r_n

$\sum P_{n,m} (N_n^k) (N_m^k)$: loss of the quantum-species by agglomeration to form larger particles of the same species.

$P_{n,m}$ = probability of union of particles of size r_n with particles of size r_m (note that m is unrestricted; particles of size r_n can join with particles of any size) to form larger agglomerates

N_n^k = number of particles of the k^{th} species and size r_n present in the unit volume of fluid

N_m^k = number of particles of the k^{th} species and size r_m present in the unit volume of fluid.

$\sum \alpha_D^k(r_n) M_i^k(r_n)$: loss of the quantum-species by deposition. Note that this term exists only for fluid elements adjacent to a deposition surface. For other fluid elements, this term is properly taken as a boundary condition.

$\alpha_D^k(r_n)$ = deposition coefficient for the k^{th} species of size r_n . As previously noted, this coefficient can vary with size, species, and location in the system.

$\rho_n v_n \sum_{p>n} \alpha_F(i, k, r_p) N(i, k, r_p)$: input of the quantum-species as a result of breakdown of larger particles. The larger particles might be agglomerates of several particles of size r_n .

$\alpha_F(i, k, r_p)$ = feedback coefficient for breakdown of particles of the k^{th} species of i^{th} element with size r_p .

$N(i, k, r_p)$ = number of particles of the k^{th} species of the i^{th} element with size r_p .

$k_i^{k-1} M_i^{k-1}(r_n)$: formation of the quantum-species by chemical reaction of the precursor in the reaction chain. Note that this formulation assumes the reaction is first-order.

k_i^{k-1} = reaction rate constant for the $k-1$ species of the i^{th} element, where $k-1$ is the reaction precursor of the k^{th} species.

$M_i^{k-1}(r_n)$ = mass of the $k-1$ species of the i^{th} element of size (r_n) .

$k_i^{kM_i^k}(r_n)$: loss of the quantum-species by chemical reaction to form the next species in the reaction chain.

k_i^k = reaction rate constant for the k^{th} species of the i^{th} element.

Similar equations may be written for each quantum-species identified in Figure 2, for each quantum-species of the other elemental constituents of crud, and for each uniquely definable region of the coolant. A very large number of such equations is therefore possible. However, some reduction in this number may be obtained through imposition of reasonable physical constraints.

Figure 2 illustrates all the possible species of a given chemical element that might exist in the coolant. However, all species need not be expected to exist and probably do not; if rational means can be used to predict which quantum-species will actually exist, the properties of the coolant crud will be predicted, the number of relationships such as Equation (16) will be greatly reduced, and, with digital computers such relationships may actually be used to predict crud dispersion.

Thermodynamics provides a basis for predicting which quantum-species will actually ~~exist~~ exist. Only a qualitative statement of what thermodynamics might be expected to predict is given here; it is hoped that these concepts will stimulate more detailed, rigorous work in the future.

The matrix in Figure 2 may be considered to represent a plane of free energy, since each quantum-species has associated with it a characteristic free energy. Surface free energy is probably most important. We may then determine, within this

Could, as defined by energetics, but not necessarily in practice. The energy levels are not sufficient to define the actual path.

framework, the surface free energy of each of the possible quantum-species. The plane of the matrix may then be converted into a contour surface of free energy, and the line of minimum free energy in this contour surface may be determined. This line should pass through the compartments (in Figure 2) for the quantum-species of minimum surface free energy and thereby define, to a first approximation, the species actually present in coolant crud.

Extending these speculative and intuitive concepts to a present conclusion, it appears -- without any quantitative study -- that the line of minimum surface free energy should lie approximately along the left-front to right-rear diagonal of the matrix in Figure 2, i.e., from smallest particles of the first member of the reaction chain to largest particles of the last member of the reaction chain. Quantum-species in the matrix that lie far from the diagonal would not be as stable and would be less likely to exist in coolant crud because their surface free energy is too high.

This prediction is obviously based on the expectation that the surface energy of large particles of elementary species (e.g., $\text{Fe}(\text{OH})_2$) and small particles of more stable species (e.g., Fe_3O_4) will prove to be intolerably high. Factors other than surface free energy may also be important, however. For example, it is possible that large particles of $\text{Fe}(\text{OH})_2$ cannot exist because they cannot hold on to the many waters of hydration; or reaction rate constants (here kinetics enters for consideration) may be sufficiently high that all $\text{Fe}(\text{OH})_2$ reacts to form other species before particles have a chance to grow. Similarly, extremely small particles of Fe_3O_4^* may be unable to survive because of a strong tendency to dissolve or agglomerate to form larger particles or to grow to form larger crystals.

* Note that the smallest possible particle of Fe_3O_4 - a single molecule - will be considerably larger than a ferrous ion or a single molecule of $\text{Fe}(\text{OH})_2$.

It is clear that these concepts are at present highly speculative; no detailed study has been made. Rigorous application of the principles of physical chemistry should indicate, however, if these concepts have any real merit.

Such approaches will serve to restrict the number of relationships such as Equation (16) that must be considered and also predict experimental requirements and results. For the equations to be of use, however, the various terms in them must be predicted from first principles or measured--with accuracy--by experiment. Possibilities for prediction and requirements for experimental determination of the various parameters in Equation (16) will now be considered.

Some of the parameters in Equation (16) are relatively simple, at least in principle, to determine. For example, diffusion coefficients may be predicted using the Stokes-Einstein equation or a relationship developed by Wilke.⁽²⁾ The reaction rate constants may be determined with appropriate kinetic experiments; some such data are already available.⁽¹⁴⁾ Similarly, volumes of particles may be established by assuming or determining their shape, and values of densities are available in the literature.

Estimates of the agglomeration rates may be made from theoretical considerations. Consider, for example, formation of particles of a given size from smaller particles. At first glance, an almost infinite array of possibilities would seem to exist. However, the number of possibilities is actually quite limited as may be demonstrated with the following arguments.

All particles will be of finite size, ranging from the smallest possible (an ion) to the size under consideration, assumed to be represented by r_n . Only those particles whose sizes add to produce size r_n need be considered. Many such

combinations are possible, but if we make the realistic assumption (with the exception discussed below) that only binary collisions are possible, the spectrum of possibilities is immediately reduced to collisions of only those binary pairs whose sizes add to r_n . The range of these possibilities may be shown (see Figure 3) to be represented by the combination of terms $(N_{n-m})(N_m)$, $m = 1, 2, 3, \dots, n-1$, and if a probability of interaction, $P_{n-m,m}$, is assigned to each possible collision, the rate of production of species of size r_n is the sum of all possible collisions:

$$\sum_{m=1}^{n-1} P_{n-m,m} (N_{n-m})(N_m) \quad m = 1, 2, 3, \dots, n-1.$$

Hence the formulation of the agglomeration term in Equation (16).

Estimates of the variation of the probability of interaction, $P_{n-m,m}$, may also be obtained from theory. Detailed discussion of this theory will not be given here; rather, it may simply be noted that the theory of the mechanics of particulate populations is quite well developed.^(15,16)

The exception to the restriction of binary collisions occurs in situations where one particle is very large compared to the other. An example would be collision of ferrous ions with a large particle of Fe_3O_4 . Under such circumstances, the large particle might intercept many mean free paths for the small particles and if the small particles are sufficiently numerous, collision of many small particles with the large one could occur simultaneously. The writer has not investigated the circumstances for which such collisions are possible or probable; it seems, however, that the subject should be amenable to theoretical treatment and indeed may already have been treated in the literature of precipitation from solution.

In General: Rate of Formation of Size $n = \sum_{m=1, 2, 3, \dots, n-1}^m P_{n-m, m} (N_{n-m}) (N_m)$

$P_{n-m, m}$ = Probability of Collision Between Sizes $(n-m)$ and m

N_{n-m} = No. of Particles of Size $(n-m)$

N_m = No. of Particles of Size m

FIGURE 3. Possible Processes for Formation of Agglomerates by Binary Collisions

The term in Equation (16) representing loss of the quantum-species by agglomeration may be treated by noting that since collision may occur with any other particle of the k^{th} species,* the factor $\sum N_m^k$ represents the entire population of the k^{th} species. This term may then be evaluated through knowledge of the size distribution for that species and the probability of interaction as a function of size.

Problems involved in determining the deposition coefficient have been discussed previously. Reviewing briefly, the numerical value of this coefficient will depend on

* Note that the possibly unrealistic assumption of no collision with species of a different kind has been made. Certainly, such a collision would produce a new species of mixed origin and remove the particle from the population of the k^{th} species.

factors such as transport in the turbulent regime, transport in the boundary layer, and the sticking probability. By far, the most difficult of these to evaluate is the sticking probability. It is also, however, the most critical to evaluate. Experience with reactors indicates that deposition dominates corrosion product dispersion and corrosion product activity distribution. It certainly is a key factor in formation of core crud deposits, which are the source of all corrosion product problems. In present context, deposition processes may govern the nature of the size distribution.

A particularly acute area where important knowledge is lacking is the variation of deposition with particle size. Classical aerosol theory⁽¹⁵⁻¹⁸⁾ predicts a strong dependence of deposition on particle size; it is not at all obvious, however, that concepts which describe deposition from a low density phase will apply in an aqueous phase, particularly when the presence of ionizing radiation may overshadow normal hydrodynamic phenomena and be selective with regard to particle sizes affected.

A need for detailed analytical and experimental study of deposition phenomena is therefore clearly evident. The primary focus of the effort should be what has here been called the "sticking probability"; effects of the transport regime are predictable within reasonable limits. Concomitant effort on the effect of ionizing radiation should also be pursued, however. The radiation field may change the driving force for transport from hydrodynamic control to electrostatic control or some other mechanism.

The term in Equation (16) that represents feedback input from destruction of large particles is probably the most elusive and difficult of all to evaluate. If the large particles are of high integrity (e.g., reasonably well-formed crystals) such processes should not exist except perhaps for shedding of

ions by dissolution. On the other hand, particles deemed "large" by conventional deterministic methods have often proven on closer examination to be merely loose agglomerates of smaller particles. Perhaps such "large" particles do not exist at all in the strong shear field of the coolant. If they do, however, the feedback term in Equation (16) could be a strong contributor to the material balance for the quantum-species. The first need in this area is therefore to establish experimentally whether or not large particles that are relatively loose agglomerates of smaller actually exist in reactor coolant under operations conditions.

This latter point stresses one of the experimental needs pinpointed by this theoretical treatment: the need to obtain accurate data on conditions as they actually exist in the coolant. In addition, many other factors demand what amounts to in-situ measurement. All may be summarized by noting that answers to two basic questions (with the data soundly supported and interpreted by theory) will provide the necessary information. These questions are:

1. For each elemental constituent of crud, what size and number distribution exists in the coolant under operating conditions, and what quantum-species are present in each size range?
2. Is there extensive interaction of chemical species, e.g., does nickel mix freely with iron, etc.?

Theoretical considerations can predict, at least to a first approximation, what results might be obtained. If the idea that the diagonal of the quantum-species matrix defines the existence region should prove valid, for example, iron crud should consist of $\text{Fe}(\text{OH})_2$ in the small size range, FeOOH in the intermediate sizes and Fe_3O_4 at the large size end of the spectrum. The number distribution should be studied to confirm the presence of these species as well as to establish the number distribution itself.

The question of mixing of elemental species may be studied theoretically by considering, for example, the extent to which nickel atoms are compatible with the Fe_3O_4 spinel structure. Data on solid solutions of mixed oxides may also be available or obtained. Experimental verification of conditions in reactor crud will be essential, however, since the opportunities for complete and intimate mixing provided in theoretical or laboratory studies might not exist in reactor coolants.

New, highly-sophisticated experimental techniques will undoubtedly be required as part of an experimental program to determine properly the significant properties of coolant crud. The experimental program itself is clearly needed; but it must be properly supported by concomitant theoretical effort. The areas of study required, as indicated by the above discussion, may be summarized as follows:

1. Thermodynamics and kinetics of crud species.
2. Mechanics of particulate distributions in aqueous systems.
3. Existence of individual corrosion product species.
4. Size distribution of coolant crud; species in each size range.
5. Number distribution of coolant crud species.
6. Mechanisms of crud deposition.
 - a. Transport characteristics of individual crud species.
 - b. Sticking probability for individual crud species.
7. Mixing of elemental constituents in individual crud particles.

IV. CORE CRUD DEPOSITS

The core crud deposits are the source of the corrosion product problems in nuclear reactors. The ultimate objective of study of corrosion product phenomena is to eliminate or minimize formation of these deposits through improved design practice and/or control of coolant chemistry conditions. Knowledge of

the fundamental mechanisms of core deposition and the species involved is essential to achieve this goal in a manner which will permit optimum application of control practices in the wide variety of present and future water cooled reactors.

Coolant crud is the source of core deposits; hence, the detailed attention given to coolant crud in previous discussion, and, because of the expected variability of deposition, the need for detailed information on coolant species. After identification of the depositing species, however, it is necessary to consider what happens to the species that become part of the deposit; net deposit buildup and activation of crud depends on the detailed transport mechanisms.

The fact that corrosion product activity appears in large amounts in regions external to the core shows that crud that deposits on the core is not retained irreversibly. Some release of material occurs, and the processes that govern this release, in concert with the processes that govern deposition, control the net rate of deposit buildup and release of radioactive species. We now consider these transport processes for core crud deposits in some detail. Available transport processes are considered first; possible mechanisms associated with these processes are discussed later.

Deposition Processes

The basic transport processes available are those associated with the deposition surface shown in Figure 1. Four individual deposition processes are identified:

Process 10: immediate deposition on entry to the boundary layer after delivery from the turbulent core of the coolant.

Process 10a: delayed deposition, with some transport time in the boundary layer, of material delivered from the bulk coolant.

Process 16: immediate redeposition of material released from the deposit.

Process 16a: delayed redeposition of material released from the deposit.

This distinction of deposition processes is probably of great importance to radioactivity dispersion processes, as discussed later. It may or may not be of significance with regard to net mass transport. The key to possible significance for net mass transport is the transport time in the boundary layer and what happens to the individual crud species during this time. The transport delay that distinguishes Process 10a (delayed deposition of new material) from Process 10 (immediate deposition of new material) could be necessary for the depositing species to become susceptible to deposition as a result, for example, of change of colloidal charge. If such a delay is necessary, the spatial distribution of the deposit could be greatly affected; the amount of material which actually deposits might also be greatly affected.

Similarly, transport delay for redeposition can also affect the spatial distribution of the deposit. These species might also in general be expected to have physical properties quite different from those of new material, since they have been aged by exposure to radiation and retention in the core deposits.

The deposition rate on reactor core surfaces will therefore be the sum of these processes. At present there is no way to distinguish them or determine which, if any, is dominant. Nor, apparently, has any direct attempt been made to distinguish them despite their potentially great influence on spatial distribution and total amount of deposition. An experimental and theoretical program which will predict and measure the rates of these individual processes is required for future work. Careful, preliminary thought to establish the methodology of such a research program is required, however. To date, the writer has not attempted such effort.

Release Processes

Only one release process is identified in Figure 1 (Process 13); all release, no matter what the mechanism or mechanisms, will look the same and constitute the apparent release rate. Properties of released material may vary considerably, however, and the release rate itself may be variable. For example, a thermal or chemical shock may cause short-term, large-scale release which would be interpreted as a crud burst. Such macroscopic release would not, however, be the same as microscopic release which might characterize more normal transport processes. Further, the microscopic release rate may be statistical if particulate release predominates. Particles with a size distribution might be released at random intervals so that the instantaneous release rate fluctuates around a mean value.

Variation in physical properties of released material may also exist if particulate release predominates. A spectrum of residence times in the deposit would exist, and the age and amount of induced radioactivity in individual particles will vary correspondingly. Note also that several loops exist in the transport processes shown in Figure 1. Material may deposit, be released, redeposit, be re-released, etc. These possibilities broaden considerably the possible range of properties of material that is ultimately released to the bulk coolant.

Net Release and Deposition Rates

When attempts are made to determine release and deposition rates, numerous problems develop. In experiments, the quantity measured is the amount of deposit present at some time; variation of the amount of deposit with time then gives the deposit buildup rate. Such experiments never, however, measure the

deposition and release rates. The deposit buildup rate is the net difference between deposition and release,

$$\frac{dD}{dt} = \text{deposition rate} - \text{release rate} \quad (17)$$

where D is the amount of deposit present, and there is no way to tell from such measurements if the net buildup rate is a small difference between two very large rates, if deposition rates are much higher than release rates, or if any of the other possible combinations produced the observed result.

Experiments designed to provide information necessary to control core crud buildup must measure absolute deposition and release rates. The rates also must be established for the entire range of operating variables to be encountered in reactor systems. But to determine the absolute rates, it is necessary to determine the mechanisms of deposition and release.

Mechanisms of Deposition and Release

Current ignorance of the detailed mechanisms of deposition and release is phenomenal. Several possible mechanisms for the two processes may be easily defined, as described below; current data do not, however, permit definition of which mechanisms actually exist or control the transport processes. This situation exists for three basic reasons: (1) the data are insufficient in number; (2) the data are insufficiently definitive (inaccurate, and/or restricted to measurement of buildup rates, as discussed above); and (3) deposition and release are (conveniently) formulated as first-order processes, and without knowledge of the mechanisms of the processes, the rate constants for each process cannot be predicted reliably.

Some of the possible mechanisms of deposition and release are as follows:

Possible Mechanisms of Deposition

1. Convective transport control. Delivery of material to the surface would be controlled by convective processes in the fluid, and the transport process would be expressed in terms of conventional mass transfer formulations.
2. Electrophoretic control. The driving force for deposition could be a difference in electrostatic charge between the particle and surface.
3. Solubility control. As previously discussed, the temperature gradients over a heat transfer surface may produce solubility gradients that are the driving force for deposition.
4. Phase equilibrium control. This is a general term reflecting the possibility that the surface might act as an ion exchanger or a collection of adsorption sites, so that distribution of species between the solid phase and the liquid phase would be described in terms of a phase equilibrium constant.
5. Diffusion control. Molecular transport processes in the boundary layer, and the magnitude of concentration gradients may govern the deposition rate.*

Possible Mechanisms of Release

1. Dissolution. The temperature field may promote a solubility gradient which, for the deposited species, favors solubilization of the solid.
2. Recoil. Energy effects associated with nuclear reactions may cause material to be ejected to the coolant.
3. Diffusion. Concentration gradients for species in the deposit may favor diffusion-controlled transport to the coolant.

* Mechanisms 1 and 5 are distinguished here as indicated because of the possibility that the deposition event occurs on a particle which protrudes beyond the laminar sublayer.

4. Erosion. This process involves release as a result of shear forces exerted on the deposit by the coolant, or other mechanical means. Erosion may be macroscopic (large masses of material involved in each erosion event) or microscopic, in which individual particles or small aggregates of particles are involved in each erosion event.

No attempt will be made here to consider in detail the relative probability of control by these various processes; the status of current understanding decries the sensibility of such a discussion. A presentation of a formulation that might be used to describe buildup rates and deposition and release rates will, however, be given, again with the objective of demonstrating the capacity of such formulations to define variables of concern and predict experimental needs.

A Model for Deposition, Release, and Deposit Buildup Processes

The most general formulation might treat the deposit as an unusually dense concentration of material whose location in space happens to be relatively fixed in comparison with the translation of position that can occur in a flowing turbulent stream. We therefore permit, in principle at least, convective and diffusional processes for particles in the deposit and simply restrict exchange with neighboring regions (the coolant) to one plane, the deposit-boundary layer interface. This approach is highly unusual in comparison to methods used in the past. It suggests itself, however, as a result of the knowledge that the deposits are highly porous (80 to 90 percent voids) and is mentioned here largely as a suggestion for future use. In the treatment given below, the conservation equation for this general case is rapidly reduced to more conventional expressions.

The conservation equation for the deposit is quite similar to that given for coolant crud (Equation 16) when the general situation described above is considered:

$$\frac{\partial D_i}{\partial t} + \vec{v} \cdot \nabla D_i = \mathcal{D}_i \nabla^2 D_i + \text{deposition} - \text{release} \quad (18)$$

where D_i is the mass of the i^{th} elemental species in the deposit and the other symbols have the same meaning as for previous definitions [Equations (2) and (16)]. As a preliminary step in reducing Equation (18) to a specific model, the convection term may be expanded to indicate its component terms:

$$\begin{aligned} \frac{\partial D_i}{\partial t} + v_x \frac{\partial D_i}{\partial x} + v_y \frac{\partial D_i}{\partial y} + v_z \frac{\partial D_i}{\partial z} \\ = \mathcal{D}_i \nabla^2 D_i + \text{deposition} - \text{release} \end{aligned} \quad (18a)$$

where the subscripts x , y , and z denote coordinate directions. Let us now define

x = coordinate parallel to the surface in the direction of flow

y = coordinate normal to the surface

z = coordinate parallel to the surface and perpendicular to the direction of flow

and make some simplifying assumptions:

1. The deposit is uniform across the width of the surface:

$$\frac{\partial D_i}{\partial z} = 0.$$

2. Diffusion within the deposit is negligible: $\mathcal{D}_i \nabla^2 D_i = 0$

3. The deposit density is uniform: $\frac{\partial D_i}{\partial y} = 0$

Equation (18a) then reduces to

$$\frac{\partial D_i}{\partial t} + v_x \frac{\partial D_i}{\partial x} = \text{deposition} - \text{release} \quad (19)$$

and the interesting thing about Equation (19) is that it permits transport, by convection, of material within the deposit

and in the direction of flow. This transport might be formulated in terms of the transport delay processes mentioned above and might account for the often observed phenomenon of heavier deposits near the outlet end of the reactor core. This term does not exist, except possibly as an artifact, in the usual formulation of the conservation equation which assumes no internal transport processes in the deposit but perhaps permits variation of the deposition and release rates with position in the direction of flow. The time derivative then becomes a total derivative, and we arrive at the standard formulation

$$\frac{d D_i(x)}{dt} = \left(\text{deposition rate} \right)_{\text{at } x} - \left(\text{release rate} \right)_{\text{at } x} \quad (20)$$

which historically is the starting point for predicting deposit buildup rates. Here $D_i(x)$ is the amount of the i^{th} elemental species in the deposit at position x .

The obvious problem in Equation (20) is to formulate the deposition and release rates. At present, any of the mechanisms listed above might be used for this purpose. For illustration, we will select convective transport control of deposition and erosion release as the basis for formulation here.

Formulation of the Deposition Rate

Convective mass transport processes are usually formulated in terms of a transfer coefficient and a concentration driving force. A more explicit formulation is required for crud deposition, however, because, as discussed previously, the various species available for deposition are present in different concentrations and probably have different capacities to deposit, as measured by the sticking probability. A rigorous expression of these factors which also allows for depletion of coolant concentrations as a result of deposition, might be

$$R_{D_i}(x) = \sum_{r=1}^r \sum_{k=1}^k \alpha_{D_i}^k(r_n) M_i^k(r_n, x) \quad (21)$$

where $R_{D_i}(x)$ is the deposition rate of the i^{th} species at position x , and the factors under the summation signs are as identified for Equation (16). Equation (21) simply expresses the local deposition rate as the sum of all the deposition elements in the matrix of quantum-species shown in Figure 2.

Knowledge of the individual α_D 's and quantum-species concentrations is necessary for utilization of Equation (21). These terms are not at present known, however, and we retreat to an expression involving a conventional mass transfer coefficient and bulk concentration:

$$R_D(x) = [k_m(x)][\delta(x)]C_\infty \quad (22)$$

where $R_D(x)$ = total deposition rate at position x

$k_m(x)$ = local mass transfer coefficient

C_∞ = crud concentration in the coolant, assumed invariant with position

$\delta(x)$ = a "deposability coefficient," which is dimensionless

The "deposability coefficient," $\delta(x)$, may be expressed as the fraction of all coolant-borne species that is depositable, i.e.,

$$\delta(x) = C_D(x)/C_\infty \quad (23)$$

where $C_D(x)$ is the concentration of depositable species. The deposition rate can then be expressed as

$$R_D(x) = k_m(x) C_D(x) \quad (24)$$

Note that in Equations (22) and (24) the concentration of species in the deposit has been taken as zero for purposes of formulating the mass transfer driving force. In other words, deposited species are assumed not to affect the rate of deposition from the stream.

Equation (22) is more desirable to work with than Equation (24), since it expresses the concentration driving force in terms of a

fixed, presumably measurable quantity (the crud level) and, for a fixed geometry, local mass transfer coefficients may be obtained from standard correlations. The problem is therefore to formulate $\delta(x)$.

One method of formulation of $\delta(x)$ might be to assume that depositability is a linear function of time of exposure to neutron flux. The time of exposure will be simply the distance traveled in the flux region divided by the coolant velocity,* time of exposure (τ):

$$\tau = \left(\frac{x - x_0}{v} \right) \quad (25)$$

where x = position from inlet to neutron flux region

x_0 = position at inlet of flux region,

conveniently taken as zero

v = coolant velocity in the flux region

and the variation of depositability with position is then given by

$$\frac{d}{dx} [\delta(x)] = k_D \left(\frac{x}{v} \right) = k_D \tau \quad (26)$$

where k_D = a deposition coefficient, which is independent of position and has units of $(\text{length})^{-1} (\text{time})^{-1}$, and x_0 has been set equal to zero.

Integrating Equation (26),

$$\delta(x) = \frac{k_D x^2}{2v} + C \quad (27)$$

where C is a constant of integration which may for present purposes be set equal to zero. Substituting Equation (27) into Equation (22), we then have as the variation of the deposition rate with position

$$R_D(x) = [k_m(x)] \left[\frac{k_D x^2}{2v} \right] C_\infty \quad (28)$$

* This assumes the species always moves with the bulk linear velocity of the fluid.

and the actual variation of deposition with position may be determined from Equation (28) by inserting the position dependence of the mass transfer coefficient. Note that, if the mass transfer coefficient is independent of position and velocity, the deposition rate is predicted to increase with the square of downstream distance and to be inversely proportional to stream velocity. The actual variation of the mass transfer coefficient in a given system should be determined from design correlations for that system, since lack of isothermal operation could make the standard correlations⁽²⁾ inapplicable.

The above development illustrates one approach for predicting deposition rates. Others are possible. The only restriction on such formulations will come from experimental data, which must confirm the predicted variation of deposition with position and stream velocity. This confirmation must, however, exist not only for the predicted deposition rate but also for the predicted release rate, which is inherently coupled to deposition.

Factors Important to Deposit Release

Some possible mechanisms of deposit release were listed above; this development considers only the mechanism called erosion release. For this mechanism we postulate that some purely mechanical applied force causes bonds to be broken so that pieces of the deposit are freed to migrate as they will. Where and how the particles migrate will probably depend on their size and original location.

Erosion release is considered to be a strong candidate as the actual mechanism of release from reactor core deposits. For this reason, it is worth listing briefly some of the factors that must be considered in formulating a detailed model of the process:

1. The erosion rate may depend inherently on the deposition rate, the amount of deposit present, or both. The model

developed below predicts that erosion is inherently coupled to the deposition rate.

2. The applied force that causes erosion may originate from several sources:
 - a. shear stress exerted by the fluid, which will depend on the local viscosity and velocity field;
 - b. thermal-stress induced deposit cracking;
 - c. internal mechanical stresses, developed as a result of
 - (1) radiation damage
 - (2) vacancy migration, etc.
 - (3) change of particle configuration as a result of deposition of more material.

Note that no matter what the exact nature of the applied force is, flow of the coolant is responsible for transport of eroded material to other parts of the deposit or system.

3. If fluid shear stress is the basic force causing erosion, we must ultimately know:
 - a. Does the stream velocity vanish to zero at the base of the deposit?
 - b. How thick is the deposit compared to the boundary layer thickness?
 - c. What is the structure of the force field the deposit is subject to? Can the shear stress at the wall be used as a measure of the force?
 - d. How does the fluid force field interact with the deposit? Is a drag coefficient type of formulation proper?
4. Other questions that must be considered include:
 - a. What happens in the interstices of the porous deposit? How does this influence the net migration of broken-off material from the surface? How much broken-off material is trapped again immediately? How much redeposits further downstream?

- b. Is there a most-probable or minimum particle dimension for which the erosion forces are effective? How would this be calculated?
- c. On the macroscale (for the entire deposit) an average, effective release rate may exist, but this release rate is probably the sum of individual erosion events that are statistically determined and position dependent. How should this be handled quantitatively?

As a final note before presenting a model for erosion release, it is important to recognize that the problem of determining the mechanism(s) and rates of release from deposits is a fundamental aspect of corrosion product technology fraught with some of the most difficult technical problems of the entire field. We wish ultimately to minimize core deposition or, failing there, to maximize core deposit release. To know which is possible requires fundamental understanding of both. Theory provides a fundamental formulation of the deposition process [i.e., Equation (21)], but no similarly "obvious" single formulation for release is at present possible. All possibilities for release listed above must be considered equally probable, and appropriate equations for each must be developed. However, to determine reliably which of the mechanisms is actually right by using the conventional technique of measuring the amount of deposit present at different times [c.f. Equation (17) and related discussion] requires one of two alternatives: (1) to know the deposition rate in terms of Equation (21), or (2) to measure release in the absence of deposition. But release occurs because the deposit exists, and the deposit exists because deposition exists. Hence, the alternative of measuring release in the absence of deposition is highly suspect and not really available. To evaluate release we are therefore forced to the need to know deposition in terms of Equation (21) or the desperate hope that a reliable,

more empirical expression for deposition [e.g., Equation (28)] can be found and, concomitantly, that the various models for release will be sufficiently different that they are experimentally distinguishable. To establish release phenomena by this latter approach will require experiments that are conceived and executed with extraordinary skill and insight.

A Formulation of the Release Rate

At present we must assume that release phenomena will have to be established from experimental testing of the postulated models. The development given herein postulates a fluid-shear induced release mechanism and shows how experiments might test the validity of the mechanism.

The basic release mechanism postulated is that the shearing force exerted by the flowing fluid causes particles to be broken off at points where weak bonds are present. The weak bonds are postulated to develop as a result of accretion of small particles to form a large particle on one side of the critical bond in question. Eventually, the particle gets large enough so that the total force exerted on it by the fluid is sufficient to break its connection with the deposit at the weakest bond. The process is diagrammed in Figure 4.

To establish the release rate within this framework, several assumptions are necessary:

1. No redeposition of eroded particles, either immediately or further downstream within the same deposit.
2. Erosion force is proportional to the local fluid-exerted forces and constant throughout the thickness of the deposit.
3. Average deposit characteristics are constant. In particular, time-average spectrum of bond strengths at a given point is constant.
4. The deposition rate is constant in time at a given downstream position.
5. Bond breakage occurs when the total force applied to a bond reaches the bond strength.

FIGURE 4. *Postulated Mechanism of Deposit Release*

These assumptions postulate that every bond fracture contributes material to the release rate, and that the fracture rate is a function of downstream position only. The force per unit area exerted by the coolant will be a constant at any downstream position, so the increase in force on a bond occurs as a result of increasing particle area only. The erosion event, corresponding to bond fracture, will then occur somewhere in time after the bond is first formed, with the time of fracture occurrence depending on the rate at which the total force on the bond increases. The rate of increase of total force will depend on the local fluid viscosity and deposition rate. Schematically,

These concepts may be expressed quantitatively as follows. The rate of change of total force applied to the bond, F_B , may be given by

$$\frac{dF_B(x)}{dt} = \frac{d}{dt} \left\{ A_p(x) \cdot F''(x) \right\} = F''(x) \left\{ \frac{dA_p}{dt} \right\} \quad (29)$$

where $F_B(x)$ = force applied to the bond at position x

$A_p(x)$ = projected area of the particle joined to the deposit by the bond

$F''(x)$ = effective applied force per unit area exerted by the flowing fluid on the particle in question.

where the expression on the right reflects the assumption that the fluid shear force is constant at any position. We now assume that the particle grows (i.e., $dA_p(x)/dt$ exists and therefore $dF_B(x)/dt$ exists) because of deposition of fresh material:

$$\frac{dA_p(x)}{dt} = \phi a_p \frac{dN_p(x)}{dt} \quad (30)$$

where a_p = projected area of the individual depositing particles

ϕ = an "effectiveness factor" for the projected area

$N_p(x)$ = number of particles in the deposit.

But
$$\frac{dN_p}{dt} = \frac{R_D(x)}{\rho v_p} \quad (31)$$

where ρ = density of the particle

v_p = volume of the individual particle

$R_D(x)$ = local deposition rate at position x , expressed as mass/unit time

$$\text{therefore } \frac{dA_p(x)}{dt} = \frac{\phi a_p}{\rho v_p} R_D(x) \quad (32)$$

$$\text{and } \frac{dF_B(x)}{dt} = \frac{F''(x) \phi a_p}{\rho v_p} R_D(x). \quad (33)$$

If all parameters on the right-hand side of Equation (33) are independent of time, the force on the bond is therefore predicted to increase linearly with time,

$$F_B(x) = \frac{F''(x) \phi a_p}{\rho v_p} R_D(x) t \quad (34)$$

and since we postulate that bond fracture and the erosion event occur when the applied force achieves the bond strength, Equation (34) really defines the residence time, t_R :

$$t_R = \frac{F_B(x) \rho v_p}{F''(x) \phi a_p R_D(x)}. \quad (34a)$$

Equation (34a) offers some interesting predictions:

1. Residence time is not constant, but should vary with position in the reactor core.
2. As would be expected, residence time increases as bond strength increases.
3. Also as would be expected, residence time decreases with increasing applied shear stress.
4. Residence time decreases as the deposition rate increases. This results from more rapid deposition causing more rapid achievement of critical bond strengths.

These results therefore suggest an experimental program to test this model of the release mechanism. The following experiments and measurements should be made:

1. Apparent residence times should be determined (from induced radioactivity) as a function of position in the flux region.

If the postulate that deposition increases with downstream position is correct, the apparent residence time should decrease with increasing downstream position.

2. A series of isothermal experiments at different temperatures should be run. This will vary the applied shear force, $F''(x)$ and should produce corresponding changes in absolute values of residence time without changing the position profile.
3. Nonisothermal experiments with known temperature fields should be run. This should change the residence time profiles in a predictable manner.
4. A series of experiments with varying crud levels should be run. Residence times should decrease with increasing crud level.
5. The above experiments should be run with constant neutron flux levels along the length of the experimental section. To test redeposition, which was assumed out of the model, experiments should be run with neutron flux gradients present. Comparison of results with the no-gradient data should provide a measure of redeposition.

Thus, this model indicates directly the experiments that are needed to test it.

It remains to formulate an expression for the release rate. To be consistent with the postulated model, the expression should have the form

$$\text{Release rate} \propto (\text{existing fluid force}) \left(\frac{\text{mass achieving break-off}}{\text{size/unit time}} \right) \quad (35)$$

The present model gives the product of the terms on the right-hand side of Equation (35) as Equation (33); thus we may write

$$R_e(x) = \xi \frac{F''(x) \phi_a R_D(x)}{\rho v_p} \quad (36)$$

where $R_e(x)$ = the release rate due to erosion
 ξ = an appropriate constant which establishes
the absolute release rate.

Equation (36) expresses the release rate in terms of several unknown parameters and is based on numerous assumptions. These are obvious shortcomings. The major virtue of Equation (36) is not, however, intended to be its capacity to predict release rates. Rather, its importance lies in the fact that it predicts release that is inherently coupled to deposition and a direct dependence on fluid shear force. Other models based on other mechanisms should predict dependence of release on other parameters. The predictions should be capable of experimental test just as the postulates of this model are subject to meaningful experiment as described above.

Combination of Deposition and Release Expressions

Equations (28) and (36) may now be combined for substitution in Equation (20). The expression obtained is

$$\frac{dD(x)}{dt} = [k_m(x)] \left[\frac{k_D x^2}{2v} \right] C_\infty - \xi \frac{F''(x) \phi a_p}{\rho v_p} R_D(x) \quad (37)$$

or

$$\frac{dD(x)}{dt} = \left\{ 1 - \frac{\xi F''(x) \phi a_p}{\rho v_p} \right\} [k_m(x)] \left[\frac{k_D x^2}{2v} \right] C_\infty \quad (38)$$

which may be compared to a frequently used formulation,

$$\frac{dD(x)}{dt} = (1 - k_e) R_D(x) \quad (39)$$

where k_e is the "erosion coefficient." Equation (38) therefore indicates that the erosion coefficient may be defined by

$$k_e = \frac{\xi F''(x) \phi a_p}{\rho v_p} \quad (40)$$

and consequently predicts that this coefficient is dependent on the shear force exerted by the fluid and the physical properties of the depositing particles. In general, Equation (38) may be examined to determine the expected dependence of deposit buildup rate on various parameters such as crud level, coolant velocity, position, etc. Experiments may then be run to test specifically and individually these predictions. One important prediction to be tested is that, if all parameters are time-independent as postulated, the deposit should increase in amount linearly with time. This prediction should be the first to be tested in careful experiments, since the consequences are of great significance to reactor operations. If the prediction is verified, study of the individual parameters in Equation (38) should be pursued. If a nonlinear dependence of deposit buildup on time is found, the results themselves will have to dictate what revisions to the model and the experimental program are made.

V. CORROSION PRODUCT FILMS ON STRUCTURAL SURFACES

Corrosion products on the surface of materials that provide crud inventory by corrosion are uniquely complex because all the transport processes in Figure 1 except those restricted to the bulk coolant occur on the same surface; i.e., the oxide film and the deposit become synonymous. This greatly enhanced multiplicity of transport processes is of enormous practical importance: the origin of material on the base metal surface

cannot be determined without knowledge of the rates of the individual transport rates. Similarly, simple measurements of the amount of material present cannot be used to determine the individual transport rates. The complexity of the situation may be illustrated by writing the general rate balance for the mass of a given elemental species in the film:

$$\begin{aligned} \frac{dD_i}{dt} &= \sum (\text{all input rates}) - \sum (\text{all output rates}) \\ &= (R_1 + R_4 + R_{4a} + R_{10} + R_{10a} + R_{16} + R_{16a}) \\ &\quad - (R_3 + R_{13}) \end{aligned} \quad (41)$$

where R_1 , R_3 , R_4 , etc. designate the transport processes identified in Figure 1. The chances of determining the individual transport processes in Equation (41) are clearly quite limited unless some special means of tagging, measuring, or predicting some of the individual rates is used. That these processes and rates are important is indicated by the rather startling conclusion reached in a study of corrosion product films on the stainless steel cladding of Yankee fuel elements: all film material came from sources external to the fuel rod cladding.^{(19)*}

Corrosion Film Transport Processes and Mechanisms

The range of possible transport processes for corrosion film on crud-source surfaces includes all surface-to-coolant exchange processes previously identified. Similarly, the potential mechanisms for occurrence are basically the same as

* The conclusion was drawn without, of course, access to detailed information such as that indicated herein to be necessary.

previously noted: convective transport, electrophoresis, solubility, phase equilibrium, or diffusion may control deposition; dissolution, diffusion, or erosion may control release. The rates at which the various processes occur may, however, differ considerably from those characteristic of deposits on inert surfaces, as a result of the mass flux of fresh corrosion products at the surface.

Input of two species--fresh corrosion products and coolant-borne species--to the boundary layer over a crud-source surface may alter transport rates and promote more rapid deposition or escape to the coolant than will exist for deposits on an inert surface. The "characteristic concentration" (see discussion under Part II, Theory of Dispersion of Species) in the boundary layer adjacent to a crud-source surface may differ from that adjacent to an inert deposition surface because the dual input of species forces higher concentrations over the crud-source surface. The transport rates for the crud-source surface would then be higher--for equal fluid regime effects--simply because characteristic concentration in the boundary layer is higher.

An additional factor that could lead to different transport rates for crud-source and inert surfaces is that most of the crud-source surfaces in a reactor system are not exposed to a high-intensity radiation field.* The effect of radiation on deposition is not clear, as previously noted, but presumably it does alter transport processes markedly.

Differences in fluid regimes could also lead to different transport rates for crud-source and inert surfaces. Some of the differences are obvious, e.g., differences in stream velocity will produce different boundary layer thicknesses, different

* This presumes the usual arrangement of inert (e.g., Zircaloy) fuel cladding and ferrous- or nickel-based alloys as the basic material of construction. Systems with stainless-steel clad fuel elements will have crud-source surfaces both in flux and out of flux.

erosion rates, etc. (these differences apply, of course, to all materials, similar or dissimilar, exposed to different velocities). It is also possible, however, that differences in species present in the fluid boundary layers (e.g., a predominance of young species in boundary layers adjacent to out-of-flux, crud-source surfaces; a predominance of aged species near in-flux, inert surfaces) could lead to markedly different transport rates--even for similar fluid regimes--as a result of different deposition coefficients for the various quantum-species.

The significant conclusion to be drawn from the above brief, qualitative discussion is that although the same transport processes may exist for crud-source and inert surfaces, the rates of the individual processes may differ markedly. It is therefore improper to assume that rates determined for transport with an inert surface will apply to a crud-source surface. Separate experiments are required to determine transport rates for the crud-source surface. However, it will be difficult, if not impossible, to distinguish the rates and mechanisms.

Significance of Transport Processes at Crud-Source Surfaces

Is it necessary to study all transport processes for crud-source surfaces and determine each in detail? Probably not. Only two factors relevant to phenomena at crud-source surfaces are of real practical concern: (1) the magnitude of the mobile-crud source (pertinent factors: base metal corrosion rate and the net transport rate), and (2) the capacity of the corrosion film to pick up and retain corrosion product activity. Indeed, we must hope and anticipate that these are the only factors of concern; discussion given below under activity dispersion processes suggest that the problems associated with attempting to sort out the various transport processes are hopelessly complex.

Theory and common sense predict that corrosion rates should be minimized to minimize crud problems if the method of

minimization does not adversely affect crud transport characteristics.* If we accept the premise that minimized corrosion rates are desirable, it remains to consider requirements and methods for study of the capacity of corrosion films to pick up and retain activity. Since it is activity pickup that is of concern, this discussion will be deferred to a later section, even though the process basically involves retention of mass.

Closing Remarks on Corrosion Product Films

The brevity of this discussion reflects the writer's present opinions that: (1) detailed study of transport mechanisms for corrosion product films on structural surfaces in reactor systems is not an urgent requirement for current research programs; and (2) the problem may prove to be intractable. Experiments could be designed in which some of the transport processes would be selectively tagged (e.g., by making the base metal radioactive in one case and the coolant crud radioactive in another), and limited conclusions might be drawn from simplified models. Such experiments would, however, of necessity uncouple the surface under study from the dynamics and dispersion processes characteristic of reactor systems. This uncoupling would be a severe limitation to the utility of results, since (a) local transport rates that prevailed during the experiments might be quite different from those that prevail in reactors; (b) results would have to be interpreted in terms of simplified models, and these models might describe the experiments but not the reactors; and (c) the experiments might not reflect properly the area of real concern: pickup and retention of activity.

The present need is therefore to determine, on a relatively empirical basis, the rate at which a reactor surface will accumulate corrosion product activity. The activity accumulation

* The possibility that minimized corrosion rates may actually aggravate some crud problems is discussed in detail below.

rate will depend on the availability of activity and the physical processes occurring at the surface. A method of attack in this area is suggested below.

VI. DYNAMICS OF CORROSION PRODUCT ACTIVITY DISPERSION PROCESSES

In principle, corrosion product activity dispersion provides a tag for the mass dispersion processes described previously. Indeed, corrosion product activities would be of interest only as a tag--or of no interest at all--if it were not characteristic of reactor systems that these activities accumulate in corrosion films on structural surfaces and, thereby, produce radiation dose rates that can inhibit accessibility to the system for maintenance.

Radiation dose rates from corrosion products have, unfortunately, been a problem in some reactors; decontaminations and/or high radiation exposure to personnel have been required. Such problems might be tolerable if dose rates did not get so high that frequent decontamination or large numbers of maintenance personnel were required. But all available evidence suggests that dose rates experienced to date may be far below those that might ultimately be achieved in present reactor systems and those now in construction or design.*

Hence, there is some urgency to be able to eliminate corrosion product radiation dose rates or--as a considerably inferior alternative--reliably predict expected dose rate build-ups in any water-cooled reactor system. The latter will at least indicate decontamination requirements and permit appropriate scheduling of system downtime for this purpose.

* The major contributor to corrosion product dose rates is ^{60}Co , with a half life of 5.3 years. Observed rates of dose rate increase and this long half life combine to predict that radiation dose rates in systems now operating might become 30 to 100 times higher than they are now within the system's lifetime.

The possibility that dose rate buildup cannot be held to insignificant levels must be recognized, at least in the framework of current technology. The need for reliable prediction of dose rate buildup is therefore obvious, and the purpose of this section is to describe the quantitative methods and knowledge necessary to accomplish this goal. Before embarking on this discussion of quantitative methods, however, some brief comments on factors relevant to activity buildup and past methods of attack of the problem will be offered.

Activity Buildup Phenomena--General Discussion

Two basic possibilities exist as modes of control of activity buildup rates: control of the number of target nuclides available for activation, and control of the dispersion of activity in the system.

1. Target Nuclide Control

The obvious way to minimize the number of target nuclides is to minimize corrosion product inventory input. Of specific concern here is the input of elemental cobalt, since ^{60}Co (produced for all practical purposes only by the reaction $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$) is the major contributor to corrosion produce dose rates.

The amount of elemental cobalt found in reactor corrosion product inventories consistently exceeds that expected on the basis of structural materials composition by approximately a factor of ten. The source of this large amount of excess cobalt is apparently corrosion and wear of high-cobalt alloys used in valve facings and other wear surfaces.

Development of noncobalt alloys that will be satisfactory for wear applications therefore suggests itself as a means of greatly reducing corrosion product dose rates. It might even be most economical to use alloys which might require more frequent replacement; this could be determined by comparing decontamination economics and replacement economics after a reliable means of predicting activity buildup is available.

There are three basic possibilities for minimizing or eliminating dose rates due to radioactive corrosion products on out-of-flux surfaces: (a) eliminate deposition on core surfaces; (b) eliminate release from core surfaces; and (c) eliminate activity pickup by out-of-flux surfaces.

Another, more subtle method of control is to increase core deposit release rates. This would serve the dual purpose of decreasing in-flux residence times and the amount of deposit present. The net effect of this procedure would, of course, be that of decreasing deposit buildup rates.

One factor pertinent to both activity and total inventory control that will bear further study is the effect of various pH agents and pH levels. Lithium hydroxide, for example, is widely touted for its capacity to reduce corrosion rates and produce dense adherent films. These dense films might, however, produce more problems in the long run than they cure: core

[illegible]

deposit buildup might be more persistent (i.e., no equilibrium achieved); the deposits might have a very high thermal resistance; and activity pickup on out-of-flux surfaces might be more irreversible. Experience to date is really insufficient to confirm or deny these adverse characteristics.

Operation with chemical shim adds another new dimension in the case of PWR's. In these systems, corrosion product inventories will be higher because of higher corrosion rates. Experience with such systems is not yet sufficient to indicate the magnitude and type (core fouling? radioactivity?) of corrosion product problems with this mode of chemistry control. Ideally, a soundly conceived research program will provide answers to these questions without need to wait for any problems to become obvious.

Past and Present Methods for Predicting Activity Buildup

Awareness of the possibility that corrosion product dose rates might eventually achieve intolerable levels has led to development of numerous past and present methods for predicting activity buildup. These methods have ranged from the very simple to the very detailed and sophisticated; no attempt will be made to list or review them here.

Most present methods that achieve some success (at least in matching observed activities) are quite detailed and take advantage of modern high speed digital computers. These methods use equations which represent models of the transport processes that are in some cases as detailed as the representations presented here. For example, one method, not available in the open literature, permits different deposition coefficients for each uniquely describable region of the system. Models which are similar in concept but differ in the number of regions specified for a system or in the degree of sophistication used to predict the transport coefficients are also available in the open literature.⁽¹⁹⁻²¹⁾

These present models have two major weaknesses: (1) the transport coefficients, which are defined as in this report, are, at worst, derived from available data and, at best, predicted from models which are unsubstantiated by adequate experiments; and (2) none of the models accounts for the range of species and properties of coolant crud. One of the best recognizes only two coolant species: solubles and particulates.

The upshot of these weaknesses is that none of the predictive methods has proven to be capable of reliable prediction of activity buildup in the wide variety of water-cooled systems now operating or planned for the future. It is true that few, if any, of the methods have been severely tested by attempting to apply them to a spectrum of widely different systems. It is doubtful, however, that such attempts would be successful; present understanding of the factors that influence the significant quantities--deposition, release, and the properties of coolant crud--is simply too inadequate.

It is the writer's opinion that no really adequate method for predicting activity buildup rates exists today.

Activity Production in Core Deposits

Spatial variations of neutron flux, neutron absorption cross section, amount of deposit, and deposit release rate must be taken into account in order to calculate core deposit activation with accuracy. As a further refinement the possibility that release is not uniform through the depth of deposit should be recognized; the need for this refinement can be established in the experiments on release mechanisms (e.g., by comparing the specific activity (dpm/mg parent) of released material with that remaining in the deposit).

The equation for the inventory of a specific radionuclide in the core deposits therefore should be given in a form such

$$\frac{dN_j}{dt} = \int_{x,r} \sigma(x,r) \phi(x,r,t) N_T(x,r,t) - \int_{x,r} R_j^R(x,y,r,t) - \lambda_j N_j \quad (42)^*$$

which presumes radial symmetry in the reactor. In Equation (42) the terms are defined as follows:

N_j = total number of radionuclides of the j^{th} kind in the whole core deposit

x = spatial direction measured along the direction of coolant flow in the core

y = spatial direction measured through the depth of the deposit (perpendicular to x)

r = radial direction in the core

$\sigma(x,r)$ = neutron absorption cross section for the target isotope. The cross section may vary with position because of temperature variations in the core.

$\phi(x,r,t)$ = effective neutron flux for activation. Dependence on time is indicated to account for variations in power level.

$N_T(x,r,t)$ = number of target atoms (for production of j^{th} radionuclides) present in all core deposits

$R_j^R(x,y,r,t)$ = release rate for k^{th} nuclides. It may vary with time, depth of deposit, and core position

λ_j = radioactive decay constant for the j^{th} nuclide

t = time

Equation (42) can actually be used to calculate radionuclide inventories in core deposits; the core can be subdivided into appropriate regions and the activation rate calculated numerically for each region. Equation (42), or one

* Note that Equation (42) does not recognize deposition of activity-bearing material as a significant contributor of radionuclide inventory. This is consistent with previous discussion which postulated negligible redeposition.

like it, should be used for all corrosion product activity calculations. Simplified forms which assume uniform deposits, an average neutron flux, and an average release rate (usually derived from data and a simple model) are inadequate.

The number of target atoms will be established from a relationship such as Equation (38), which will give the amount of deposit of a given element as a function of position and time, i.e., $D_i(x,r,t)$.^{*} The number of target atoms for production of the k^{th} nuclide is then calculated by use of the isotopic abundance and Avogadro's number:

$$N_T(x,r,t) = \frac{A_{T_i} D_i(x,r,t) N_a}{A_i} \quad (43)$$

where $D_i(x,r,t)$ = mass of deposit of the i^{th} element

A_{T_i} = fractional isotopic abundance of the target atoms for production of the k^{th} nuclide

N_a = Avogadro's number

A_i = atomic mass of the i^{th} element.

Release of Activity from Core Deposits

The release term in Equation (42) is most difficult to evaluate. A reliable expression for release is essential, however, because this term constitutes the input rate of activity to the coolant and also probably far exceeds radioactive decay as a mechanism of loss of activity from core deposits.

The mechanism of activity release might nominally be expected to be the same as the mechanism of mass release, discussed in Part IV, Core Crud Deposits. Activity release would then be the result of one or more of the release mechanisms previously listed, i.e., dissolution, recoil, diffusion, or erosion.

^{*} *In deriving Equation (38), deposit buildup was assumed to be independent of radial position. Such dependence is easily added, and might enter from radial variation of fluid shear force, depositability, etc.*

Assumption of similar release mechanisms for activity and mass in the core deposits is a good starting point. However, the possibility of additional, selective activity release mechanisms must be considered. For example, a concentration gradient for mass diffusion release of an elemental species might not exist; however, strong concentration gradients for the radionuclide might be present, and isotopic diffusion could then be a major release mechanism. Similarly, recoil release is restricted to radionuclides at the moment of formation, and in practice even further restricted to only those nuclides formed from fast neutron reactions (i.e., ^{58}Co and ^{54}Mn). The recoil ranges for the various nuclear reactions are entirely predictable, and a good estimate of recoil release as a function of deposit thickness and structure may therefore be made.

Another detail in a comparison of activity and mass release that could be of great significance is the possibility that most of the release occurs from a "skin" on the deposit rather than with equal probability for the entire depth of the deposit. Such selective release (from what has been called the "exchange layer") would be of little significance to mass accumulation rates. It would be highly significant in terms of activity release, however. Most of the exchange of mass between the deposit and the coolant might occur as a result of high transport rates for this exchange layer. The specific activities of this exchange layer would then be quite different from those of the adherent layer beneath. In other words, the apparent residence times of the two layers would differ.

Thus, activity release adds a new dimension to the needs for experimental study of release mechanisms. Not only must the basic mechanism of release (e.g., erosion) be established, but any release mechanisms that are selective in terms of activity must be quantitatively identified.

The experiments described in Part IV are therefore required to test erosion as a mass release mechanism, but additional measurements are required to determine if this release is equally effective throughout the deposit depth. These measurements should include:

1. Determination of the specific activity of the released material and comparison with the material in the deposit. Careful study and experiment will be required to determine if this practice provides a valid measurement. The released material will mix with undeposited, nonradioactive species in the coolant and changes in specific activity of the deposited material during the course of the experiment must be properly accounted for.
2. A better assessment of nonuniform release may come from detailed examination of the structure of the deposits. Such examinations should be made for a variety of purposes (e.g., to permit reliable calculation of the thermal resistance of the deposit), but activity release provides one of the greatest demands for such examinations.

Because of factors such as nonuniform erosion release, selective release processes such as recoil, the spectrum of properties of the various quantum-species for a given element, and the several elemental constituents of crud, it would be wise to accept from the beginning the possibility that release rates will be different for each radionuclide of concern (^{60}Co , ^{58}Co , ^{59}Fe , ^{54}Mn , ^{56}Mn , ^{51}Cr). Individual determinations of the release rates for each nuclide are therefore required. In a world of good fortune, such measurements can be made simultaneously and the release mechanism will be found to be the same for all nuclides. If early experiments show, however, that these ideal circumstances do not exist, attention should be focussed on the nuclide(s) of concern, e.g., ^{60}Co . If the

release mechanisms should prove to be the same, it will still be possible to restrict measurements to only one nuclide, with the advantage that results will be applicable to all. Again, ^{60}Co should be used for this purpose since its long half life permits simplification of the equations.

Activity in the Coolant

Activity release from the core deposits is the major source of radioactivity in the coolant, although release from corrosion films on structural surfaces not in the core region may make some contribution. The activity in the coolant is in turn the source of radioactivity found in corrosion films on out of flux surfaces. Parenthetically, it may be noted that the driving force for activity dispersion is therefore in the direction core-to-structures; the driving force for mass dispersion is in the opposite direction, structures-to-core (cf. discussion under Part II, Theory of Dispersion of Species).

These oppositely-directed driving forces meet and mix in the coolant. The practical problem is then to describe adequately, in terms of all appropriate variables, corrosion product radioactivity in the coolant. The description must be sufficient to use coolant activities as a source term in equations that reliably predict activity accumulation in corrosion films on structural surfaces.

As was the case with core deposit release phenomena, the need to consider radionuclides adds new dimensions to the description of coolant crud. The coolant crud may be thought of ideally as consisting of three fractions: (1) radioactive species released from core deposits; (2) radioactive species released from noncore surfaces; and (3) nonradioactive species generated from fresh corrosion products. The latter fraction would be described in terms of a matrix of quantum-species, as described in Part III, Transport Processes and Physical Characteristics of Coolant Crud.

But the two kinds of radioactive species will also exist in a matrix of quantum-species. In addition, the "existence domain" for each of these matrices might differ from each other and that of the nonradioactive quantum-species. Thus, the coolant crud may be thought of as consisting of three different spectra of species, each with its own characteristic size, number, and depositability variation for the constituent quantum-species. In effect, three matrices such as that shown in Figure 2 exist side by side, and if this viewpoint is followed to its logical conclusion the task that must be accomplished to describe coolant crud is to establish the existence and properties of all quantum-species in all three matrices.

Such an approach is obviously not going to produce much practical success. It is also probably quite wrong since the description given does not recognize mixing between matrices (e.g., agglomeration involving one particle from one matrix and another from one of the other matrices). The whole concept is mentioned here primarily to indicate the dimensions of the problems involved in attempting to describe the radioactive properties of coolant crud. However, the concept might ultimately have practical use and should be kept in mind. For example, if it can be established that release from noncore surfaces is negligible, and the existence domain for species released from core deposits can be established (this domain might be quite limited, e.g., particles of a narrow size range), interactions between the two matrices can be recognized quantitatively and the overall properties of coolant crud established.

The theoretical and experimental work required to calculate activity dispersion is indicated, at least in part, by the relationship for activity in the coolant. This relationship has the general form

$$\frac{dN_j^C}{dt} = R(N_j^R) - R(N_j^D) - (\lambda + \lambda_p)N_j^C \quad (44)$$

where N_j^C = total number of atoms of the j^{th} radionuclide in the coolant
 $R(N_j^R)$ = rate of introduction of j^{th} nuclides to the coolant from all release processes
 $R(N_j^D)$ = rate of removal of j^{th} nuclides from the coolant by all deposition processes
 λ_p = purification rate constant, units of (time) $^{-1}$

Equation (44) is useful only if the release and deposition terms can be formulated properly. Release will include core deposit release and release from noncore deposits; the $R(N_j^R)$ term may therefore be represented more explicitly but still quite generally by the relation

$$R(N_j^R) = \int_{x,r} R_j^R(x,y,r,t) + \sum_{n_s}^{n_s} N_j^R(n_s,t) \quad (45)$$

where $\int_{x,r} R_j^R(x,y,r,t)$ = core deposit release rate [Equation (42)]
 $N_j^R(n_s,t)$ = rate of release of j^{th} nuclides from n^{th} noncore deposit
 n_s = number of uniquely describable noncore deposits in the system

The problems associated with determining $N_j^R(n_s,t)$ are described in some detail below.

Similarly, deposition may be represented as a summation of deposition rates for all uniquely describable deposits:

$$R(N_j^D) = \sum_{n_s+n_c}^{n_s+n_c} N_j^D(n,t) \quad (46)$$

where $N_j^D(n,t)$ = rate of deposition of j^{th} nuclides in the n^{th} deposit

n_c = number of core deposits

$n = n_s + n_c$ = total number of deposits in the system.

In keeping with previous discussion and methodology, the deposition rate may be further detailed to reflect the contribution of the individual quantum-species and their deposition coefficients [cf. Equation (21)]:

$$R(N_j^D) = \sum_{n=1}^{n_s+n_c} N_j^D(n,t) = \sum_{n=1}^{n_s+n_c} \left\{ \sum_{r=1}^r \sum_{i=1}^k \alpha_{D_i}^k(r_n, n) N_j^k(r_n, n, t) \right\} \quad (47)$$

where

r = designator of quantum-species size

$\alpha_{D_i}^k(r_n, n)$ = deposition coefficient for the quantum-species in the n^{th} region

$N_j^k(r_n, n, t)$ = number of j^{th} nuclides available for deposition in the n^{th} region

and a similar formulation might be given for release by defining a release coefficient, α_R .

Equation (44), with Equations (45) and (47) substituted into it, then expresses the coolant activity for a given nuclide within the present framework. This model incorporates, however, two major and important assumptions: (1) complete mixing of the coolant, and (2) each quantum-species is considered to be homogeneous, i.e., radioactivity is uniformly distributed among all particles in a quantum-species, and all particles have the same deposition coefficient. The validity of the latter assumption is subject to experimental testing, and will depend on the degree of interaction between nonradioactive and radioactive particles. Indeed, this assumption and this discussion in general point out that study of the way radioactive species distribute in the coolant crud population is a fundamental need of a research program to advance the art.

The assumption of complete coolant mixing can be obviated by considering the coolant to be composed of n boundary layer regions (one for each of the n deposition regions) plus the turbulent core. There will then be an Equation (44) for each of these coolant regions. Some modifications of Equation (44) would be necessary to allow for convective transport between adjacent boundary layers and to remove the purification term as appropriate. This approach would lead to greatly increased complexity because of the large number of equations and boundary conditions involved. Again, however, modern computers make it feasible.

We may note for emphasis at this point that this discussion of coolant activities reaffirms the needs for fundamental knowledge previously established, viz., mechanisms of deposition and release and detailed knowledge of all properties of coolant crud. An additional fundamental requirement has been added: the need to establish the distribution of radioactivity among the various coolant species.

Activity Accumulation in Corrosion Films

Opportunities to conceal ignorance in undetermined coefficients cease at the payoff point: accurate prediction of activity accumulation in corrosion films on noncore structures. To make accurate predictions, the transport processes associated with the film must be adequately describable and the amount of activity available to the surface, from the coolant, must be known. As seen above, the availability of coolant activity depends on core release and what happens to the activity after it gets into the coolant. In turn, core release depends on core deposition, and core deposition depends on the mass dispersion characteristics of the system. Thus, every facet of corrosion product transport and dispersion phenomena is important to activity accumulation.

Even if all important phenomena in this chain of dependence are adequately understood, the problems in predicting activity buildup appear to be quite formidable because of the number and complexity of the transport processes associated with the material on the surface. The nature of these problems was indicated briefly in Part V, Corrosion Product Films on Structural Surfaces. A more quantitative discussion is given herein.

Reviewing briefly, the accumulation of mass in the material on the surface was described by Equation (41),

$$\frac{dD_i^n}{dt} = (R_1 + R_4 + R_{4a} + R_{10} + R_{10a} + R_{16} + R_{16a}) - (R_3 + R_{13}) \quad (41)$$

where the superscript n has been added, to give D_i^n , because we now recognize that mass buildup rates are unique to the region; there are therefore n equations of the form of Equation (41), and the individual transport rates may be different in each. Equation (41) has frequently been simplified in the past in terms of more conventional parameters, viz.,

$$\frac{dD_i^n}{dt} = R_{C_i}^n + R_{D_i}^n + R_{R_i}^n \quad (48)$$

or

$$\frac{dD_i^n}{dt} = R_{C_i}^n - R_{T_i}^n \quad (49)$$

where D_i^n = mass of the i^{th} elemental constituent in the film
in the n^{th} region

$R_{C_i}^n$ = corrosion rate

$R_{D_i}^n$ = net deposition rate

$R_{R_i}^n$ = release rate (as defined in Part II)

$R_{T_i}^n$ = net transport rate (as defined in Part II)

The acceptability of simplified relationships such as Equation (48) or (49) for predicting activity buildup is a matter of considerable concern. Each of the simplified terms is a combination of several of the individual transport processes, and how well these equations will describe activity accumulation depends on how the activity is distributed among the individual transport processes. The following arguments illustrate the problems involved. To simplify notation somewhat, it is to be understood that the equations apply to one corrosion product radionuclide (e.g., ^{60}Co) and one element (e.g., Co); therefore no nuclide-designating or element-designating subscripts will be indicated.

We first recognize that two basic measurements are possible: the mass of an element, and the specific activity, as dpm/mg of element. The activity balance for the deposit may then be written

$$\frac{dA_D^n}{dt} = A'_1 R_1 + A'_4 R_4 + A'_{10} R_{10} + A'_{16} R_{16} - (A'_3 R_3 + A'_{13} R_{13}) - \lambda A_D \quad (50)$$

where the transport delay processes identified in Figure 1 have been ignored. In Equation (50),

A_D^n = activity in the film in the n^{th} region, dpm

A' = specific activity of species involved in the designated process, dpm/mg species

R = transport rate for the designated process, mg species per unit time

λ = radioactive decay constant.

But we must recognize that the total amount of activity in the film changes because of changing amount of film and changing specific activity. Hence

$$A_D^n = A_D' D^n \quad (51)$$

and therefore

$$\frac{dA_D^n}{dt} = \frac{d}{dt} (A_D' D^n) = D^n \frac{dA_D'}{dt} + A_D' \frac{dD^n}{dt} \quad (52)$$

where A_D' is the specific activity of the film and D^n is the mass of the film. The expression on the right of Equation (52) must be substituted into Equation (53), with the expectation that both time derivatives are finite.

The problem now is to determine the individual specific activities in Equation (50). Because of the way the transport processes are defined, these specific activities will be related to the specific activity of the film itself and/or the specific activity of coolant species. The relationship will depend, however, on how these species interact. Two extremes of interaction are possible: no mixing in the coolant with complete mixing in the film, and complete mixing in the coolant and the deposit. These extremes lead to quite different formulations of activity buildup in the deposit.

1. No Mixing in Coolant, Complete Mixing in the Film

For this situation, the specific activities of the individual transport processes may be equated to deposit and coolant activities as follows:

$$A_1' = 0 \text{ (if the surface is not exposed to neutron flux)}$$

$$A_4' = A_D'$$

$$A_{16}' = A_D'$$

$$A'_3 = A'_D$$

$$A'_{13} = A'_D$$

$$A'_{10} = A'_C$$

where A'_C is the specific activity of the coolant species. Equation (50) then becomes

$$D^n \frac{dA'_D}{dt} + A'_D \frac{dD^n}{dt} = A'_D (R_4 + R_{16} - R_3 - R_{13}) + A'_C R_{10} - \lambda A'_D D^n \quad (53)$$

or, in terms of the net transport rate,

$$D^n \frac{dA'_D}{dt} + A'_D \frac{dD^n}{dt} = R_{10} (A'_C - A'_D) - A'_D R_T - \lambda A'_D D^n \quad (54)$$

where A'_C is to be determined from relationships such as Equations (44), (45), and (47) which describe coolant activity.

2. Complete Mixing in Coolant and Film

In this case, it is necessary to define an effective specific activity for the coolant boundary layer, A'_B . This specific activity will depend on the specific activities of species involved in transport processes for the boundary layer:

$$\begin{aligned} \frac{dA_B^n}{dt} = & A'_3 R_3 + A'_{13} R_{13} - R_6 A'_B - R_4 A'_B - R_{10} A'_B - R_{16} A'_B - R_{14} A'_B \\ & + R_9 A'_C - R_{12} A'_B - \lambda A_B^n \end{aligned} \quad (55)$$

where A_B is the total activity in the boundary layer and A'_B is the specific activity of boundary layer species. Again we must write

$$A_B^n = A'_B M_B^n \quad (56)$$

and

$$\frac{dA_B^n}{dt} = M_B \frac{dA'_B}{dt} + A'_B \frac{dM_B^n}{dt} \quad (57)$$

where M_B^n is the mass of species in the boundary layer. It is reasonable to assume that the derivative dM_B^n/dt is zero (i.e., the boundary layer concentration is constant); Equation (55) then becomes

$$M_B^n \frac{dA_B'}{dt} = A_3' R_3 + A_{13}' R_{13} - R_6 A_B' - R_4 A_B' - R_{10} A_B' - R_{16} A_B' - R_{14} A_B' + R_9 A_C' - R_{12} A_B' - \lambda A_B' M_B \quad (58)$$

Equation (58) only defines the boundary layer specific activity; specific activities for the transport processes must now be defined in terms of the boundary layer activity:

$$A_1' = 0 \text{ (out of flux)}$$

$$A_4' = A_B'$$

$$A_{10}' = A_B'$$

$$A_{16}' = A_D'$$

$$A_3' = A_D'$$

$$A_{13}' = A_D'$$

and the equation for activity in the film becomes

$$D^n \frac{dA_D'}{dt} + A_D' \frac{dD^n}{dt} = (R_4 + R_{10}) A_B' - (R_3 + R_{13} - R_{16}) A_D' - \lambda A_D' D \quad (59)$$

or

$$D^n \frac{dA_D'}{dt} + A_D' \frac{dD^n}{dt} = R_D A_B' - R_R A_D' + R_{16} (A_D' - A_B') - \lambda A_D' D \quad (60)$$

in which A_B must be determined by solution of Equation (58), which again requires utilization of Equations (44), (45), and (47).

Thus we arrive at a rather dismaying situation. Prediction of activity buildup rates requires solution of Equation (54) and its antecedent equations or the coupled Equations (58) and (60) and the same antecedent equations for coolant activities, core deposit release, core deposit deposition, and mass dispersion. Equations (58) and (60) probably

are more nearly correct because of the mixing and loss of identity of species that occurs in the coolant. Either method, however, requires identification of at least some of the individual transport processes associated with the film. At present, it does not appear possible to measure and identify these processes experimentally.

We are therefore forced to a need to find a way to reduce the "complete" equations to useful working models. Considerable thought and study should be put into this effort, because the "best" way to accomplish this simplification is not at present obvious. Parametric computer studies using Equations (58) and (60) and available data might prove useful; so also might carefully conceived experiments designed to explore the relative importance of the various transport processes.

As a concomitant to this effort, it should be kept in mind that predictions of activity buildup rates should not really be necessary if reduction or elimination of core crud deposits is achieved (and/or elimination of elemental cobalt is achieved). Effort on activity buildup predictions is mandatory at present, however. It would be dangerous to assume that core deposition will be controlled in the near future (or that the methods evolved can be applied to existing systems), and the effort on activity buildup may provide considerable input and insight for other aspects of effort.

In closing this section, it may be noted that Equations (58) and (60) demonstrate why simplified models used in the past have had such limited success in predicting activity buildup. Details of knowledge required far exceed those now available.

VII. SUMMARY OF QUANTITATIVE RELATIONSHIPS

For convenience, the quantitative relationships developed here and deemed necessary for description of corrosion product

and corrosion product activity dispersion are summarized in Table I. It should be kept in mind that even this formidable array is only representative; for variables such as quantum-species in the coolant and activity buildup on noncore surfaces, there are as many equations as there are individual variables or regions that are convenient or necessary to define. The entire system of relationships probably forms an array of several hundred equations. This large number of equations does not, however, preclude their use; similar sets of equations are commonly used in the physics design of reactor cores. In short, there is no operational limitation to the use of these relationships.

It will be noted that all relationships in Table I are highly interrelated. The mass dispersion and activity dispersion equations are internally coupled, and there is complete cross-coupling between the two systems. This, of course, is to be expected, and it illustrates the fact that our capacity to use these relationships is no better than the weakest link of knowledge in the entire system.

The equations all express the dependent variables in terms of physical parameters or phenomenological coefficients that are in principle theoretically predictable or experimentally determinable. Thus, the theory predicts, in reasonable explicit fashion, exactly what parameters and phenomena are of concern. As shown throughout the body of this discussion, detailed application of theory also defines the experiments to be performed, the variables to be considered, and limitations for experimental work and current theory.

The equations in Table I represent only one collection of models for transport processes important to corrosion products. Other models are possible, and may indeed be found to be necessary as knowledge increases. The models given here represent,

in the writer's opinion, the best representation of current theory and, therefore, provide the best basis for theoretical and experimental work in the near future.

TABLE I. Summary of Equations for Corrosion Product Transport

MASS DISPERSION	ACTIVITY DISPERSION
Formation of Species:	Activation of Core Deposits:
$A \xrightarrow{k_1} B \xrightarrow{k_2} C \xrightarrow{k_3} \dots N$	$\frac{dN_j}{dt} = \int_{x,r} \sigma(x,r) \phi(x,r,t) \frac{A_{T_i} D_i(x,r,t) N_a}{A_i}$
Driving Force Transport:	$\int_{x,r} R_j^R(x,y,r,t) - \lambda_j N_j$
$R_T = k_{ij} (A_i S_i - A_j S_j)$	Activity in the Coolant:
Coolant Quantum-Species:	$\frac{dN_j^C}{dt} = \int_{x,r} R_j^R(x,y,r,t) + \sum_{n_s} N_j^R(n_s,t)$
$\frac{\partial}{\partial t} M_i^k(r_n) + \nabla \cdot \nabla M_i^k(r_n) = D_i^k(r_n) \nabla^2 M_i^k(r_n)$	$\sum_{n_s+n_c} \left\{ \sum_{r,k} \alpha_{D_i}^k(r_n,n) N_j^C(r_n,n,t) \right\}$
$+ \rho_n \nabla_n \sum_{n-m,m}^m (N_{n-m}^k) (N_m^k) - \rho_n \nabla_n \sum_{n,m}^m (N_n^k) (N_m^k)$	$- (\lambda + \lambda_p) N_j^C$
$- \sum \alpha_D^k(r_n) M_i^k(r_n) + \rho_n \nabla_n \sum_F(i,k,r_p) N(i,k,r_p)$	Activity Accumulation on Structural Surfaces:
$+ k_i^{k-1} M_i^{k-1}(r_n) - k_i^k M_i^k(r_n)$	$M_B^n \frac{dA_B}{dt} = R_9 \lambda N_j^C + (R_3 + R_{13}) A_D - (R_6 + R_4$
Core Deposit Buildup:	$+ R_{10} + R_{16} + R_{14} + R_{12} + \lambda M_B) A_B$
$\frac{\partial D_i}{\partial t} + v_x \frac{\partial D_i}{\partial x} = \sum_{r=1}^r \sum_{k=1}^k \alpha_{D_i}^k(r_n) M_i^k(r_n, x)$	$D_i^n \frac{dA_D}{dt} + A_D \frac{dD_i^n}{dt} = (R_4 + R_{10}) A_B$
$- \frac{\xi F''(x) \phi a}{\rho v_p} \sum_{r=1}^r \sum_{k=1}^k \alpha_{D_i}^k(r_n) M_i^k(r_n, x)$	$- (R_3 + R_{13} - R_{16}) A_D - \lambda D_i A_D$
Corrosion Products on Structural Surfaces:	
$\frac{dD_i^n}{dt} = (R_1 + R_4 + R_{4a} + R_{10} + R_{10a} + R_{16} + R_{16a})$	
$- (R_3 + R_{13})$	

VIII. SUMMARY OF REQUIREMENTS FOR FUTURE WORK

This discussion has pinpointed clearly defined subjects for theoretical and experimental work to advance the art.

These areas of study may be summarized as follows:

A. Theoretical and Experimental Studies of the Properties of Coolant Crud

1. Thermodynamic and kinetic limitations on existence of species.
2. Mechanics of particle distributions in aqueous systems.
3. Determination of depositability as a function of particle size, species, and deposition environment.
4. Determination of size and number distributions for coolant crud. Species present in each size range.
5. Determination of extent and mechanism of mixing of elemental constituents in a given crud particle.
6. Distribution of radioactivity among species.

B. Theoretical and Experimental Studies of the Mechanism(s) of Crud Deposition

1. Identification of depositing species.
2. Identification of deposition mechanism.
convective transport
electrophoresis
solubility-induced precipitation
phase equilibrium
diffusion
3. Effect of ionizing radiation.
4. Definition and determination of the sticking probability.
5. Deposit buildup as a function of time and position.

C. Theoretical and Experimental Studies of the Mechanism(s) of Release from Deposits

1. Experimental study of the model for erosion release.
residence time gradients

isothermal experiments at different temperatures
nonisothermal experiments
varying crud levels
experiments with neutron flux gradients
specific activities of released material and deposits
structure of deposits

2. Theoretical (and experimental, as required) study of other release mechanisms.
recoil
diffusion
dissolution

D. Activity Accumulation in Corrosion Product Films

1. Theoretical parametric studies to determine influence and significance of various transport processes.
2. Definition of a program for meaningful experiments.

ACKNOWLEDGEMENTS

The experience which led to preparation of this report has been gained in large measure by feeding on the ideas and knowledge of others.

Major influence and impetus were provided by Dr. Stephen Yerazunis of Rensselaer Polytechnic Institute; his originality and insistence on thoroughness have contributed beyond measure to current understanding of corrosion product transport.

Sherman L. Williams, of Knolls Atomic Power Laboratory, has also been a valuable mentor and leader. His depth of knowledge of the field and demands for effective performance have prompted much of the thinking behind this effort.

Dr. Robert L. Dillon of Battelle-Northwest Laboratories contributed many hours of useful discussion which greatly aided sifting and focussing of ideas. His facilities also provided the opportunity and stimulating environment necessary for preparation of this paper.

cr back

REFERENCES

1. Hermann Schlichting. Boundary Layer Theory, McGraw-Hill Book Co., Inc., New York, 1960.
2. R. B. Bird, W. E. Stewart, and E. N. Lightfoot. Transport Phenomena, John Wiley and Sons, New York, 1960.
3. Irving Kaplan. Nuclear Physics, Addison Wesley Publishing Co., Inc., Reading, Massachusetts, 1955.
4. A. S. Kesten and L. S. Lasher. Decomposition of Solid Ferrous Hydroxide in High Temperature Water, WAPD-CDA(AD)-526. Westinghouse Electric Corp., Pittsburgh, Pennsylvania, February 1959.
5. G. E. Galonian, J. W. Bartlett, and S. L. Williams. Conditions to Minimize High Temperature Water Corrosion Products from Inconel, January, 1964. Presented at 20th Annual NACE Conference, Chicago, Illinois, March 1964.
6. J. W. Bartlett, C. M. Mills, and T. J. Kabele. Dispersion of Corrosion Products from a Film-Forming Metal Exposed to an Aqueous Stream. Presented at 23rd Annual NACE Conference, Los Angeles, California, March 1967.
7. R. L. Dillon. "Observations on the Mechanisms and Kinetics of Aqueous Aluminum Corrosion," Corrosion, vol. 15, p 336t, 1959.
8. R. L. Dillon. Dissolution of Aluminum Oxide as a Regulating Factor in Aqueous Aluminum Corrosion, HW-61089. General Electric Company, Richland, Washington, August 31, 1959.
9. J.-Ph. Berge et al. Studies of Steel Corrosion in High Temperature Water and Steam, EURAEC-1625, dated April 29, 1966. Distributed by Clearinghouse for Federal Scientific and Technical Information, Springfield, Virginia.
10. M. E. Jones. The Solubilities of Ni-Cr-Fe- Alloy 600 Corrosion Products, KAPL-3017. Knolls Atomic Power Laboratory, Schenectady, N. Y., 1964.
11. G. S. Gardner. Corrosion, vol. 19, p 81t, 1963.
12. W. D. Fletcher. Interactions Between Stainless Steel Corrosion Products and Boric Acid Solutions, WCAP-3730. Westinghouse Electric Corp., Pittsburgh, Pennsylvania, March 1964.

13. G. R. Taylor and Paul Cohen. "Corrosion Product Behavior in Stainless Steel Clad Water Reactor Systems," Nuclear Applications, vol. 1, p 446, 1965.
14. O. Kubaschewski and B. E. Hopkins. Oxidation of Metals and Alloys, Academic Press, New York, 1953.
15. N. A. Fuchs. The Mechanics of Aerosols, The Macmillan Company, New York, 1964.
16. V. G. Levich. Physicochemical Hydrodynamics, Chapter 5. Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962.
17. J. E. Quon and L. F. Mockros. "The Equilibrium Size Distribution of an Aerosol Continually Reinforced with Particles," Int. J. Air Water Poll., vol. 9, p 279. 1965.
18. L. F. Mockros, J. E. Quon, and A. T. Hjelmfelt, Jr. "Coagulation of a Continuously Reinforced Aerosol," J. of Colloid and Interface Science, vol. 23, p 90. 1967.
19. L. F. Picone and G. R. Taylor. "Chemical Evaluation of Yankee Core I Fuel Cladding Corrosion Products," WCAP-6072. Westinghouse Electric Corp., Pittsburgh, Pennsylvania, August 1966.
20. G. N. Walton and E. Hesford. "Activated Corrosion Products in High Pressure Water," Corrosion of Reactor Materials, Proceedings Conference, Salzburg, June 4-8, 1962, vol. 2. International Atomic Energy Agency, Vienna, 1962.
21. G. N. Walton. "Activity Transport in Pressurized Water Reactors from Measurements in Loops," Amer. Nucl. Sci. Trans., vol. 7 No. 1, p 180. 1964.

DISTRIBUTIONNo. of
Copies

2	<u>AEC Chicago Patent Group</u> C. H. Lee R. K. Sharp (Richland)
265	<u>AEC Division of Technical Information Extension</u>
2	<u>AEC Library, Washington</u> Division of Reactor Dev. and Tech. L. J. Colby D. E. Erb
2	<u>AEC RDT Site Representative - PNL</u> P. G. Holsted
2	<u>AEC Richland Operations Office</u> C. L. Robinson Technical Library
1	<u>Atomic Energy of Canada Ltd.</u> <u>Chalk River Project</u> H. K. Rae
1	<u>Atomic Energy of Canada Ltd.</u> <u>Whiteshell</u> S. R. Hatcher
3	<u>Battelle Memorial Institute</u>
5	<u>Douglas United Nuclear, Inc.</u> T. W. Ambrose W. Kratzer M. Lewis J. Riches Files
1	<u>General Electric Company APED</u> <u>San Jose</u> W. L. Pearl
2	<u>General Electric Company</u> <u>Pleasanton</u> F. J. Brutschy W. Reas

No. of
Copies

- 1 Knolls Atomic Power Laboratory
 Niskayuna, New York
 Sherman Williams
- 2 Oak Ridge National Laboratory
 Oak Ridge, Tennessee
 Dr. J. C. Greiss
 G. H. Jenks
- 2 Westinghouse Electric Corporation
 Pittsburgh, Pennsylvania
 Paul Cohen
 W. D. Fletcher
- 1 Culcheth Laboratory, UK AEA
 Attn: Dr. C. Tyzack
 Wigshaw Lane, Culcheth
 Warrington, Lancashire
 England
- 1 UK Atomic Energy Research Establishment
 Attn: G. N. Walton
 Metallurgy Division
 Harwell, Didcot,
 Berks, England
- 1 UK Atomic Energy Research Establishment
 Attn: J. N. Wanklyn
 Metallurgy Division
 Harwell, Didcot,
 Berks, England
- 1 University of Rochester
 Attn: Professor John W. Bartlett
 Dept. of Chemical Engineering
 Rochester, New York 14627
- 1 Rensselaer Polytechnic Institute
 Attn: Professor Stephen Yerazunis
 Department of Chemical Engineering
 Troy, New York 12180

No. of
Copies

27

Battelle-Northwest

F. W. Albaugh
J. A. Ayres
D. R. de Halas
J. R. Divine
R. L. Dillon (10)
V. F. FitzPatrick
B. Griggs
H. Harty
L. D. Perrigo
R. Purcell
R. B. Richman
Technical Files (5)
Technical Publications (2)