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Diffusivity of a noble metal solution, as applied in nuclear reactors

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DIFFUSIVITY OF A NOBLE METAL SOLUTION,
AS APPLIED IN NUCLEAR REACTORS

A Thesis

Presented to

The Faculty of the Mechanical and Aerospace Engineering Department

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Sandra Britt Diefenderfer

May 1997

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ABSTRACT

DIFFUSIVITY OF A NOBLE METAL SOLUTION, AS APPLIED IN NUCLEAR REACTORS

By Sandra B. Diefenderfer

This thesis addresses the application of noble metal chemical addition (NMCA) as an approach to stress corrosion cracking mitigation in boiling water reactor (BWR) vessel internals and components. The chemical solution consists of Pt and Rh in water at an inlet concentration of 60 ppb Pt to 20 ppb Rh. The purpose of this study is:

- to characterize the noble metal deposition process
- to explain the applicability of the data taken in each experiment, and
- to predict the noble metal chemical additive solution average diffusion coefficient

For operating conditions specified for application in a BWR hot shutdown environment, the average calculated diffusivity values as a function of Reynolds' number are as follows:

	laminar ($Re \approx 1000$)	turbulent ($Re \approx 14,000$ to 40,000)
D_{ab} , Pt (cm^2/sec)	6.78E-06	1.43E-05
D_{ab} , Rh(cm^2/sec)	1.35E-05	5.90E-05

These values are transferable to reactor geometries, given constant geometric scaling between reactor and experimental setup.

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TABLE OF CONTENTS

1. INTRODUCTION	1
1.1 Background	1
1.2 Statement of Problem.....	4
2. EXPERIMENTAL METHODS and TESTING	5
2.1 Test Objective	5
2.2 Test Description	6
2.3 Test Plan.....	8
2.3.1 Noble Metal Injection System Operation.....	8
2.3.2 Sample System Operation	8
2.3.3 Sample Collection and Return System Operation.....	8
2.4 Sampling	9
2.4.1 Liquid grab samples.....	9
2.4.2 Coupon analysis.....	10
2.4.3 Corrosion and Particle Samples.....	10
2.5 Summary of Tests Performed	12
2.6 Measurement Error.....	13
2.6.1 Water Grab Samples.....	13
2.6.2 Surface Samples.....	14
3. ANALYSIS.....	16
3.1 Convective Controlled Transport.....	18
3.1.1 Water Chemistry Data Derivation.....	18
3.1.2 Surface Data Derivation.....	23
3.1.3 Chilton-Coburn Analysis	24
3.2 Kinetically Controlled Transport	26

3.2.1 Molecular (Ionic) Diffusion and Reaction Kinetics.....	26
3.3 Mixed Control Transport	30
4. RESULTS	31
4.1 Test Data Trends	32
4.1.1 Deposition as a Function of Temperature	32
4.1.2 Deposition as a Function of Time.....	34
4.1.3 Deposition as a Function of Distance from Injection Point	36
4.1.4 Deposition as a Function of Flow.....	38
4.1.5 Deposition as a Function of Inlet Concentration	38
4.2 Diffusivity Coefficient Calculations	38
4.2.1 Molecular Diffusion.....	38
4.2.2 Diffusion - Water Chemistry Data Derivation.....	39
4.2.3 Diffusion - Surface Data Derivation.....	40
4.2.4 Chilton-Coburn Heat to Mass Transfer Analogy	41
4.2.5 Summary of Diffusivity Values at 250°F.....	41
5. DISCUSSION	43
5.1 Dimensional Analysis and Experiment Design	43
5.1.1 Scaling Considerations	46
5.1.2 Geometry of Various Reactor Regions	49
5.2 Hypothesized Mechanisms for Noble Metal Deposition	50
5.2.1 Diffusion Controlled Deposition - Convection	53
5.2.2 Kinetics Controlled Deposition	56
5.2.3 Mixed Control Deposition.....	58
6. CONCLUSIONS.....	60
7. REFERENCES	62

LIST OF TABLES

Table 2.5-1	Summary of Tests Performed	12
Table 2.6.1-1	Average Pt Concentration with Mean Standard Deviation	14
Table 2.6.1-2	Average Rh Concentration with Mean Standard Deviation	14
Table 4-1	Summary of Diffusivity Results	31
Table 4.2.2-1	Diffusivity from Solution Concentration Data	39
Table 4.2.3-1	Diffusivity from Surface Loading Data	40
Table 4.2.4-1	Diffusivity from Heat to Mass Transfer Analogy	41
Table 4.2.5-1	Calculated Diffusivity values for Pt	41
Table 4.2.5-2	Calculated Diffusivity values for Rh	42
Table 5.1.2-1	Geometric and Dynamic Similarity between Experiment and Reactor	50

LIST OF FIGURES

Figure 1	NMCA Protectable Regions in the BWR	65
Figure 2a	Coupon Platinum Loading as a Function of Temperature, at 48 hours	66
Figure 2b	Coupon Rhodium Loading as a Function of Temperature, at 48 hours	67
Figure 3	Platinum/Rhodium Deposition Rate vs Reciprocal of Absolute Temperature	68
Figure 4	Noble Metal Inlet Concentration Control over Time	69
Figure 5	Pt Outlet Concentration for Turbulent Flow: $Re > 25,000$	70
Figure 6	Pt Loading for 3/4" Tube with $Re > 20,000$ Operating Temperature approx. 250°F	71
Figure 7a	Coupon Surface Pt Loading as a Function of Time and Re No.	72
Figure 7b	Surface Load Rate as a Function of Distance from Inject Point and Re No.	73
Figure 7c	Normalized Surface Loading over Time, $Re = 30,000$, Operating Temperature $\approx 450^\circ F$	74
Figure 8	NMCA Coupon and Tube Sample Surface Analyses, Test X-12	75
Figure 9a	Effect of Water Concentration on Platinum Deposition Rate	76
Figure 9b	Effect of Water Concentration on Rhodium Deposition Rate	77
Figure 10a	Calculated Diffusivity of Pt, Various Methods. vs Flow Regime: 250°F, 60 ppb Pt/20 ppb Rh. inlet	78

LIST OF FIGURES (continued)

Figure 10b	Calculated Diffusivity of Rh, Various Methods, vs Flow Regime: 250°F, 60 ppb Pt/20 ppb Rh. inlet	79
Figure 11	NMA II 60 foot Test Loop Schematic	80
Figure 12	60 foot Loop Sample Panel: Rear View	81
Figure 13	Mass Diffusion: Diffusion or Kinetic Control	82
Figure 14	Diffusivity variation due to Boundary Layer Assumption	83
Figure 15	Average Pt and Rh Solution Concentrations, Mean Standard Deviation	84
Figure 16	NMCA Zircoloy Tube Samples, Run X-20	85
Figure 17a	NMCA Coupon Surface Analysis, Run X-4 and X-6 (Pt)	86
Figure 17b	NMCA Coupon Surface Analysis, Run X-4 and X-6 (Rh)	87
Figure 18	Normalized Loading on Zircoloy Tube Samples, Run X-20	88

NOMENCLATURE

A	area	cm ²
c	solute concentration	ppb
D _{ab}	mass diffusivity	cm ² /sec
D _H	hydraulic diameter	inches (cm)
ΔE	activation energy for diffusion	cal/mole
f	friction factor	
h	mass transfer coefficient	cm/sec
$\dot{m}$	mass flow	kg/sec
$\dot{m}''_{loading}$	surface loading rate	μg/cm ² sec
P	perimeter	cm
$\dot{r}$	surface reaction rate	μg/sec
Q	volumetric flow rate	gal/min
R	Universal Gas Constant	
T	temperature	°F, °C, K
V _A	molar volume	cm ³ g-mole ⁻¹
v	bulk fluid velocity	cm/sec
x	distance along x coordinate axis	cm
δ	boundary layer thickness	cm
φ	geometric scaling factor	
ν	kinematic viscosity	cm ² /sec
ρ	fluid density	kg/m ³
Ψ	solution association parameter	
Re	Reynolds Number	$\frac{V_{\infty} x}{\nu}$
Sc	Schmidt Number, relative rates of growth of velocity and concentration boundary layers	$\frac{\nu}{D_{ab}}$
Sh	Sherwood Number, dimensionless mass transfer	$\frac{hL}{D_{ab}}$
St	Stanton Number, mass transfer velocity relative to bulk fluid velocity	$\frac{h}{V} = \frac{Sh}{ReSc}$

1. INTRODUCTION

1.1 *Background*

Stress corrosion cracking of the boiling water reactor (BWR) vessel internals and components is a costly side effect of a corrosive operating environment, and the consequences of such unanticipated phenomenon on the internals are regular crack inspection programs, component redesign (using noble metal alloys) and replacement, and corrosion mitigation programs such as hydrogen water chemistry, noble metal coatings, and noble metal chemical addition.

Electrochemical Corrosion Potential (ECP)

The important influence of ECP on stress-corrosion cracking (SCC), irradiation assisted SCC, flow assisted corrosion of carbon steel, and other facets of BWR operation is well established. Early attention was focused on the relationship between the corrosion potential and SCC, which resulted in the discovery that SCC can be markedly suppressed if the potential is maintained below about -0.23V, thereby reducing the thermodynamic driving force for crack advance.

Under normal reactor operating conditions, the exposure of water to gamma and neutron radiation create steady state concentrations of very oxidizing O_2 and H_2O_2 radiolysis

products in stoichiometric excess of reductants (H_2). This radiolytic decomposition of water in the core is expressed by the following reaction:

This resulting high electrochemical potential established by the corrosion oxidation reduction reaction is a primary determinant of SCC susceptibility of structural materials in high temperature water.

The objective of GE Nuclear Energy's corrosion mitigation programs is to shift the red-ox balance in favor of lower corrosion potentials.

Hydrogen Water Chemistry

The hydrogen water chemistry (HWC) program is designed to shift the oxidation/reduction balance by providing a hydrogen rich environment. If excess hydrogen is present in a high radiation field, short-lived radiolytic species catalyze the recombination of H_2 with H_2O_2 and O_2 to reform H_2O (Reference 35):

HWC has several undesirable consequences. First, there is a high cost associated with hydrogen addition. Secondly, the reducing environment caused by the presence of excess hydrogen causes the formation of NH_4^+ and partitions ^{16}N to the steam phase,

which causes a significant increase in steam radiation level in the main steam lines and the turbine. Finally, there is increased deposition of radioactive ^{60}Co on reactor internals.

Noble Metal Alloys, Coatings, and Chemical Addition

Noble metals have long been recognized as recombination catalysts for oxygen and hydrogen dissolved in water. In particular, platinum group metals are known for their catalytic activities for numerous chemical reactions, and the catalysts containing these metals can be deposited from solution. A basic understanding of the mechanisms that drive these processes is limited (Reference 26).

However, it was recently discovered that the corrosion potential of a surface containing small amounts of noble metals dropped to very low values when hydrogen was present in stoichiometric amounts, even in the absence of complete volume recombination of O_2 and H_2 in the water. The efficiency with which the corrosion potential is increased as a function of hydrogen addition is greatly improved, such that very low potentials are obtained once a stoichiometric concentration of hydrogen (versus oxygen) is achieved. In addition, this protective coating will aid in mitigating stress corrosion cracking, as well as minimizing the increase in radiation levels in the main steam lines and turbine building due to ^{16}N carry-over and ^{60}Co deposition (Reference 1).

1.2 Statement of Problem

An approach has been developed to deposit noble metals on the stainless steel surfaces of vessel internals and components in the BWR. The method involves injecting a dilute noble metal chemical solution directly into the high temperature water that is in contact with the metal surfaces to be treated. The areas of the reactor to be protected by noble metal chemical addition are illustrated in Figure 1.

Experimental testing has demonstrated that an effective noble metal deposit can be achieved by maintaining the noble metal solution concentrations to a level of approximately 60 ppb over a period of 48 hours during the injection process. After treatment, analysis of test specimens demonstrates that the noble metal is present to a depth of 200 to 500 Å (Reference 2). The experimentation that forms the basis for this paper was originally designed as a “proof-of-concept” for the test application currently implemented at a domestic BWR. The purpose of this study is:

- to describe the test setup and explain how the various regions within the test section (entrance region, bends, coupon units) simulate various flow regions within the reactor
- to characterize the noble metal deposition process based on the data gathered through experimentation
- to explain the basis behind the range of tests made and the applicability of the data taken in each experiment and
- to predict the noble metal chemical additive solution average diffusion coefficient relative to the following application process parameters:

Temperature	250°F
Platinum Chemical	$\text{Na}_2\text{Pt}(\text{OH})_6$
Platinum Concentration	60 ppb as Pt
Rhodium Chemical	$\text{Na}_3\text{Rh}(\text{NO}_2)_6$
Rhodium Concentration	20 ppb as Rh
Electrical Conductivity (@ 25°C)	< 10 $\mu\text{S}/\text{cm}$
pH (@ 25°C)	4.7 - 9.6

Tests have shown that in order to optimize surface treatment, NMCA must be conducted between 200°F and 300°F. However, reactor operating temperatures are typically 550°F. Therefore, NMCA must be applied during a refueling outage, when the reactor is in a “hot shutdown” mode. This factor is the primary determinant for the application process operating parameters.

2. EXPERIMENTAL METHODS and TESTING

2.1 Test Objective

The test objective is to determine the extent and effectiveness of noble metal deposition on test coupons as a function of temperature, exposure time, distance from injection point, and flow rate. This effectiveness is assessed by measuring noble metal concentrations in the fluid stream and on the piping surfaces at various distances from the injection point. By varying these parameters, the results of the pipe test should be transferable to the different flow regimes in the reactor, which can be characterized into

stagnant/creeping flow regions (where the jet pumps connect to the shroud), to fully developed tube flow (through the fuel bundles), to highly agitated, non-developed regions (in the lower plenum around the control rod drive housings). “Segment scaling,” which involves a flow path similar to full size, but confined to convenient experimental boundaries, is utilized for this deposition application, by constructing a fluid path so that a portion of the fluid stream undergoes changes which are similar to a corresponding full size path. Thus, geometric scaling is the primary element of comparison. Both chemical and thermodynamic conditions are assumed to be similar between experiment and application. Therefore, kinematic similarity is assumed within the range of Reynolds numbers from near stagnant conditions ($Re \leq 1000$) to highly turbulent flow (Re up to 50,000). The test setup is heated and insulated, so that the bulk fluid temperature remains constant throughout the test.

2.2 Test Description

The noble metal solution was injected at high pressure into the NMA II 60 foot Test Loop (Figure 11). The noble metal solution is comprised of a hexahydroxyplatonic acid $[H_2Pt(OH)_6]$ and a rhodium salt $[Na_3Rh(NO_2)_6]$. The loop inlet noble metal concentration was controlled by injecting a concentrated solution of noble metal additive at known concentrations into the loop inlet water. The loop flow was controlled by a positive displacement pump and measured upstream of the injection point using a calibrated flow meter. The loop effluent was cooled in a regenerative heat exchanger, directed to a filter,

demineralizer and to the inlet water storage tank. The purpose of the heat exchanger is to cool the solution in order to allow for safe removal of product samples. The sections containing the test coupons were located at the inlet and outlet of the NMA II loop.

Sample panels were connected to the loop inlet, midpoint (30 feet from the inlet) and outlet. The sample panels provided water grab sample and corrosion product sampling capability. In addition, dissolved gas and conductivity measurements were made immediately upstream on the injection and at the end of the test loop.

The sample panel (Figure 12) is connected to the test loop with 0.125 inch outer diameter (OD) stainless steel tubing lined with 0.070 inch inner diameter (ID) teflon tubing.

Sample panel valves, fittings, and tubing are 0.125 inch OD stainless steel. The heat exchanger is 0.125 inch OD stainless steel (lined with teflon) inside a 0.375 inch OD by 0.035 inch wall copper tube. The heat exchanger length is 9 feet. At the heat exchanger outlet, the flow is split in order to provide grab sample and filter sample capability. The tubing and fittings which supply the grab sample and corrosion product sample are teflon lined. The filter holder effluent and bypass lines are 0.125 inch OD by 0.080 inch ID unlined stainless steel tubing.

2.3 Test Plan

2.3.1 Noble Metal Injection System Operation

The noble metal was injected by means of a high pressure pump, whose upstream supply reservoir consisted of a 20 liter polycarbonate carboy filled with the 60 ppb Pt/20 ppb Rh solution and blanketed with a nitrogen cover gas to prevent carbon dioxide absorption, and the resulting platinum compound precipitation. The noble metal injection system was initially tested with deionized water.

2.3.2 Sample System Operation

The sample panels provided water grab samples, corrosion product samples, and particle samples at a 100 cc/min rate and at temperatures less than 140°F.

2.3.3 Sample Collection and Return System Operation

During baseline testing and noble metal injection testing, there was continuous flow through the sample panels. In order to replenish the volume of loop water lost during the sampling period, the sample panel effluent was collected and pumped back to the loop. The effluent return was downstream of the 60 foot test loop, and upstream of the loop cleanup system. The particle analyzer was connected to the grab sample port.

2.4 Sampling

Prior to test sampling, baseline testing was conducted with the primary purpose to establish a benchmark for the various analytical techniques which were utilized in evaluating the sample data.

2.4.1 Liquid grab samples

The objective of the liquid grab samples was to evaluate the Pt and Rh concentrations in bulk fluid stream as a function of test run time, distance from injection point, temperature, and noble metal concentration.

Liquid grab samples were collected from each of the three sample panels and the 20 liter carboy reservoir. These samples were analyzed for Pt and Rh by ion chromatography and direct current plasma methods.

2.4.1.1 Ion Chromatography (IC)

IC was utilized to quantify soluble Pt in the +II and +IV oxidation states. Some of the samples were stabilized with ammonium hydroxide, which elevates the sample pH in order to preserve $\text{H}_2\text{Pt}(\text{OH})_6$ solubility. The minimum detection limit for this method is approximately 2 ppb Pt.

2.4.1.2 *Direct Current Plasma (DCP)*

DCP was used to measure Pt concentrations in the liquid grab samples. Unlike IC, DCP cannot be used to differentiate between the noble metal oxidation states. Also, the minimum detection limit for this method is approximately 20 ppb Pt.

2.4.2 Coupon analysis

The objective of the coupon samples was to evaluate the Pt and Rh concentrations deposited on the tubing and coupon surfaces as a function of test run time, distance from injection point, temperature, and noble metal injection concentration.

In each of the inlet and exit sections of the 60 foot loop, stainless steel specimens (coupons) were housed in Swagelock union assemblies. The inlet assembly contained seven coupons, and the outlet assembly contained six. The coupons were made from 0.5 inch OD by 0.065 inch wall Type 304 stainless steel tubing. Prior to installation, the coupons were oxidized for one week at 550°F in an autoclave containing air-saturated water. These conditions are representative of normal BWR operating environment conditions.

2.4.3 Corrosion and Particle Samples

Because Pt and Rh can exist in three different oxidation states, it was important to measure and quantify all the Pt species existing in the test loop.

The objective of corrosion product sampling was to determine the form of Pt and Rh in the test loop bulk solution, namely whether these elements are in ionic or particulate form. The corrosion product sample holder housed one 0.45 μ millipore filter paper, one cation exchange resin, and one anion exchange resin. These samples were digested with aqua regia to permit characterization of the form of Pt (soluble or insoluble). Additionally, these samples provided insight with respect to the ammonium hydroxide stabilizer compound, that it was performing its design intent to prevent noble metal from premature precipitation.

The objective of particle analysis is to supplement the corrosion product sample evaluation of the Pt and Rh, by determining the size and form of any insoluble Pt and Rh species. Further, these samples provided insight into the effect of miscellaneous particles (crud) on the noble metal deposition rate.

2.5 Summary of Tests Performed

Table 2.5-1: Summary of Tests Performed

Test	Pt/Rh (ppb)	Temp (°F)	Flow (gpm)	Re No	Time (hrs)	Sample Types	Purpose
X-4	60/20	519	0.68	55483	120	coupon ¹	2
X-5	60/20	450	0.68	48316	96	coupon ¹	2
X-6	60/20	510	0.65	52876	40	coupon ¹	2
X-7	60/20	447	0.67	47480	48	coupon	2
X-7A	60/20	430	0.67	45611	48	coupon	2
X-8	60/20	530	0.066	5553	48	coupon	2
X-9	60/20	339	0.68	35041	96	coupon, tube	2
X-10	60/20	346	0.066	3627	48	coupon	
X-11	60/20	443	0.066	4645	48	coupon	
X-12	60/20	251	0.65	24160	40	coupon, tube	3
X-13	15/5	252	0.66	24640		tube	3
X-14	60/20	296	0.66	29878	40	coupon	3
X-15	15/5	297	0.67	30317		tube	3
X-16	60/20	188	0.66	18692	40	coupon, tube	
X-17	60/20	117	0.67	9762	40	coupon, tube	
X-18	60/20	250	0.049	1817	48	coupon	5, 7
X-19	60/20	250	1.4	5110	48	4" pipe	5, 7
X-20	59/8.8	253	1.14	31000 to 52000	48	bare zirc oxidized zirc 1/2" tube 3/4" tube	3, 4, 6
X-21	61/20	255	1.68	37840	48	3/4" tube	5
X-22	69/23	247	0.046	1001	48	3/4" tube	5

¹ the surface condition is un-polished

² deposition dependence on operating temperature

³ deposition dependence on inlet concentration

⁴ deposition dependence on tube and coupon surface conditions

⁵ deposition dependence on flow regime

⁶ deposition dependence on substrate material type

⁷ geometry effects

2.6 Measurement Error

2.6.1 Water Grab Samples

In each test, X-12, 18 through 22, there are inconsistencies in the recorded Pt and Rh concentration data. Per discussion in Section 4.1.2.1, it appears that these anomalies are attributable to either data transcription errors or to measurement errors. Figure 4 shows, by comparing the data scatter of all tests performed at 60 ppb Pt/ 20 ppb Rh, that the ability to establish an accurate reading has a discrepancy band (data scatter) of approximately ± 10 ppb for Pt, ± 5 ppb for Rh; these bands are confirmed by calculating standard deviation on each data set. However, by averaging the multiple readings at the inlet, midpoint, and outlet and calculating the corresponding mean standard deviations, the total measurement error is less than 10%. Tables 2.6.1-1 and 2.6.1-2 show these values.

Error (data repeatability) is to be differentiated from the measurement uncertainty of 0.1 ppb for the water grab samples. Since the data scatter is greater than the uncertainty for a data point, it can be concluded that there are inconsistencies in the measurements, and the amount of data scatter is significant, probably attributable to accidental errors in data collection (like transposing readings).

Table 2.6.1-1: Average Pt Concentration with Mean Standard Deviation

Test	P1, ppb Pt (inlet)		P2, ppb Pt (midpoint)		P3, ppb Pt (outlet)	
	avg	σ	avg	σ	avg	σ
X-12	61.1	0.7	45.8	1.7	N/A	N/A
X-19	57.4	0.4	57.6	0.8	55.9	2.6
X-20	55.6	1.1	49.4	0.3	46.8	1.9
X-21	56.6	0.5	48.2	1.4	N/A	N/A
X-22	59.0	3.5	45.4	3.3	43.0	3.0

Table 2.6.1-2: Average Rh Concentration with Mean Standard Deviation

Test	P1, ppb Rh (inlet)		P2, ppb Rh (midpoint)		P3, ppb Rh (outlet)	
	avg	σ	avg	σ	avg	σ
X-12	19.7	0.1	16.8	0.2	N/A	N/A
X-19	20.3	0.1	20.6	0.1	20.1	0.1
X-20	9.2	0.1	9.3	0.1	9.0	0.1
X-21	21.4	0.1	19.5	0.1	N/A	N/A
X-22	21.1	1.2	15.2	1.0	16.2	1.0

2.6.2 Surface Samples

In various tests, there are inconsistencies in the recorded Pt and Rh surface loading data.

Per discussion in Section 4.1.2.2, it appears that these anomalies are attributable to either data transcription errors or to measurement errors. In test X-18, for example,

examination of the rhodium surface data indicates that there is net rhodium generation in the system. Since there is no rhodium source material in the system, and since the plating reaction is not known to be reversible, this cannot occur. It is postulated that several data points are transposed, or that the measurements taken are outside of the measurement tolerances. Comparison with the water chemistry data for rhodium confirms this hypothesis, except for the last two data points, which also seem erroneous. Examples like this occur in several tests. The measurement uncertainty for the loading samples is $0.05 \mu\text{g}/\text{cm}^2$ for the water grab samples. It is not possible to get a sense of scatter for the surface loading data because no test was repeated. This deficiency in the test program needs to be addressed in order to determine the uncertainty in the calculations of D_{ab} based on these data points. Collecting multiple readings for each measurement would assist in detecting random sources of error, and expressing them through a calculated standard deviation from a mean.

Standard propagation of error techniques applied to the calculations, provides a means for assessing the accuracy of the calculations based on measured data, but provides no estimate on the analysis method itself.

3. ANALYSIS

Many mass transport dominated processes are expressed mathematically through equations derived from analogy to heat transfer correlations. In general, in order to make the analogy between heat and mass transfer, the following must be assumed:

- constant physical properties
- small rate of mass transfer
- no chemical reactions in the fluid
- no viscous dissipation
- no emission or absorption of radiant energy
- no pressure diffusion, thermal diffusion, or forced diffusion
- 'infinitely' dilute solution

It is necessary to assume a small mass transfer rate from the initial bulk noble metal concentration to the wall, so the velocity and concentration profiles retain the same shape as those applied to heat transfer in laminar and turbulent flow environments.

In general, an electro-chemical reaction is considered to be diffusion controlled when the rate of deposition is dependent on the rate of supply of material from the main body of the fluid by diffusion or convection. The diffusion model applied for this evaluation assumes a non-reactive, two-component solution, and considers the diffusion flux resulting from a concentration gradient of the diffusing component, as well as convective driven diffusion. Most studies of molecular diffusion have been devoted to the

estimation of diffusivities in very dilute solutions (Reference 36), whereas other correlations used for the diffusion coefficient are primarily based on data for the evaporation of liquids in a wetted wall column (Reference 23), or for electroless plating of nickel from solution (References 7, 12). The dilute solution assumption is defined by the diffusing species transported at the same velocity as the bulk fluid and neglects the interactions of the multiple diffusing species.

In general, the mathematical expression for species flux is as follows:

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i v \quad \text{equation 3 - 1}$$

where the first term represents ionic diffusion controlled by reaction kinetics, the second term represents mass diffusion in the absence of convective flow, and the third term represents the contribution due to convective flow.

The following analysis attempts to quantify each of these contributors to species flux, as derived from experimental data. The diffusive and convective mass transport terms are derived based on dimensional analysis coupled with experiment, approximate boundary layer analysis, and a mass, momentum, energy transport analogy as expressed via the Chilton-Coburn relations. The ionic diffusion term is derived based on the simplified kinetic theory of liquids, where transport is related to reaction rates and solute mobility.

3.1 Convective Controlled Transport

In the absence of forced convection, the flux of a transporting species, “j”, in the absence of migration and bulk flow is

$$N_j = D_{ab} \frac{d\rho}{dx} \quad \text{equation 3.1-1}$$

Generally, the diffusivity is a property of the transporting species solution system and can be estimated or measured (Reference 7). Mass transfer coefficients (h_D) can be estimated from mass transfer correlations for particular system geometries and flow regimes.

Similarly, boundary layer thicknesses for classical geometries and flow regimes can be applied to estimate D_{ab} from the measured value of h_D , since

$$h_D = \frac{D_{ab}}{\delta} \quad \text{equation 3.1-2}$$

The following sections summarize a variety of methods used for determining D_{ab} .

3.1.1 Water Chemistry Data Derivation

The transient diffusion equations for species ‘a’ or ‘b’ diffusing in the fluid boundary layer toward the plate surface is determined by establishing a one-dimensional control volume, assuming a flat plate model, as illustrated below:

The reaction is driven by a concentration gradient, which is determined from the following definitions for the mass terms:

$$\dot{m}_{in, Pt} = (\dot{m}_{in, H_2O}) (C_{in, Pt}) \quad \text{equation 3.1.1 - 1}$$

$$\dot{m}_{out, Pt} = (\dot{m}_{out, H_2O}) (C_{out, Pt}) = \dot{m}_{out} \left[C_{in} + \frac{\partial C}{\partial x} dx \right] \quad \text{equation 3.1.1 - 2}$$

$$M = (\rho_{H_2O} A dx) (C_{Pt}) \quad \text{equation 3.1.1 - 3}$$

Therefore, the time rate of change of mass within the control volume can be expressed as

$$\frac{dM}{dt} = \frac{\partial (C \rho_{H_2O} A dx)}{\partial x} \quad \text{equation 3.1.1 - 4}$$

Recall the general equation for conservation of mass on the control volume defined above is

$$\dot{m}_{out} - \dot{m}_{in} + \frac{dM}{dt} = 0 \quad \text{equation 3.1.1 - 5}$$

where

$$\frac{dM}{dt} = \dot{m}_{reaction} \quad \text{equation 3.1.1 - 6}$$

and

$$\dot{m}_{\text{reaction}} = \dot{r}Pdx = h_d \rho (C - C_\infty) \quad \text{equation 3.1.1 - 7}$$

Substituting 3.1.1-1, 3.1.1-2, and 3.1.1-7 into 3.1.1-6 results in the following unsteady formulation for species concentration:

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} - \frac{\dot{r}}{\rho_{\text{H}_2\text{O}} D_H} \quad \text{equation 3.1.1 - 8}$$

Recalling the definition of the total derivative and applying the chain rule transforms 3.1.1-8 to a simple form that can be solved using separation of variables:

$$\begin{aligned} \frac{dC}{dt} &= v \frac{\partial C}{\partial x} + \frac{\partial C}{\partial t} \\ \frac{dC}{dt} + \frac{\dot{r}}{\rho_{\text{H}_2\text{O}} D_H} &= 0 \quad \text{or} \quad \frac{dC}{dt} + \frac{4h_d \rho (C - C_\infty)}{D_H} = 0 \end{aligned} \quad \text{equation 3.1.1 - 9}$$

which can be solved using a standard separation of variables technique to give the following expression for the concentration profile:

$$\frac{C}{C_o} = \exp \left[\frac{-4h_d x}{v D_H} \right] \quad \text{equation 3.1.1 - 10}$$

Note that the values for C and C_o correspond to the water sample data. Further, by rewriting 3.1.1 - 10 in terms of the non - dimensional parameter , $\frac{h_d}{v}$, which is known as the Stanton number (St). This is a non - dimensional mass transfer coefficient, expressed as:

$$St = \frac{Sh}{ReSc} = \left(-\frac{D_H}{4x} \right) \ln \left(\frac{C}{C_o} \right) = \frac{h_d}{v} \quad \text{equation 3.1.1 - 11}$$

Equation 3.1.1 - 11 provides a relationship in terms of measured data for the mass transfer coefficient. Additionally, an analogy to heat transfer and the assumption of fully developed flow in a circular pipe leads to an expression for Sh in the laminar flow regime (Reference 23):

$$Sh = \frac{h_d D_H}{D_{ab}} = 3.66 \quad \text{equation 3.1.1 - 12}$$

For turbulent flow regions, Sh takes the form

$$Sh = a Re^b Sc^c \quad \text{equation 3.1.1 - 13}$$

The coefficients are empirically derived (Reference 23), such that 3.1.1 - 13 becomes

$$Sh = 0.023 Re^{0.83} Sc^{0.44}$$

combining 3.1.1 - 13 with 3.1.1 - 11 provides a representation of D_{ab} in terms of measureable quantities:

$$Sc = \left[-10.87 \frac{D_H}{x} Re^{-0.17} \ln \left(\frac{C}{C_o} \right) \right]^{0.56} = \frac{v}{D_{ab}} \quad \text{equation 3.1.1.-14}$$

The resulting first order differential equation for solute concentration is solved for the concentration profile. Thus, the inlet and outlet concentrations are expressed as a function of the mass transfer coefficient, geometry, and velocity of the flow. This provides a means for determining the mass transfer coefficient based on the measured concentrations. Further, mass diffusivity can be predicted by transforming this equation, using dimensionless parameters (Re , Sc). Solving for Sc , and estimating viscosity to be that of the bulk fluid (water) at the test operating temperature, provides a means for predicting diffusivity.

In order to relate the rate of mass transfer with a fluid's rate of momentum transfer, the Schmidt number, which is a dimensionless ratio of the momentum and mass diffusivities, is applied. For a gas, its value is 1. For liquids, Sc is much higher: approximately 297 for self-diffusion in water at 25°C, and ranging into the thousands for more viscous liquids and even for water with slowly diffusing solutes.

Since theory is incomplete regarding turbulence and little experimental information exists on concentration fluctuations in a turbulent flow field, it is common to make an analogy between turbulent transfer of mass and turbulent transfer of momentum and energy in order to relate mass transfer rates to known friction factor or heat transfer data. This analogy is only valid for dilute solutions (low mass transfer rates), which is the scenario of the noble metal coating process.

3.1.2 Surface Data Derivation

Whereas the previous formulation provides a means for determining the mass transfer coefficient, h_d , in terms of the concentration profile (equation 3.1.1-11), this approach incorporates the surface loading measurements with the equations developed in the previous section.

Recall that the surface loading data was taken periodically during each test, and has units of $\frac{\text{mass}}{\text{length}^2 \text{time}}$. A steady state mass balance on the following one-dimensional control volume provides a relationship between the mass transfer coefficient and the measurable quantities, surface loading and concentration.

As in the previous section analysis, the reaction is driven by a concentration gradient, which is determined from the following definitions for the mass terms:

$$\dot{m}_{in, Pt} = (\rho A v)(C_{in, Pt}) \quad \text{equation 3.1.2 - 1}$$

$$\dot{m}_{\text{out, Pt}} = (\rho A v) (C_{\text{out, Pt}}) \quad \text{equation 3.1.2 - 2}$$

$$\frac{dM}{dt} = \dot{m}_{\text{loading}}'' = h_d A \rho (C_{\text{in}} - C_{\text{out}}) \quad \text{equation 3.1.2 - 3}$$

Rearranging 3.1.2 - 3 provides an expression for the mass transfer coefficient in terms of measured values,

$$h_d = \frac{\dot{m}_{\text{loading}}''}{A \rho (C_{\text{in}} - C_{\text{out}})} \quad \text{equation 3.1.2 - 4}$$

Applying the equations developed for the laminar and turbulent flow regimes developed in Section 3.1.1 provide a means for determining D_{ab} .

3.1.3 Chilton-Coburn Analysis

The general definition of the j-factor for mass transfer is provided as a function of Sh, Re, Sc:

$$j_D = \frac{Sh}{Re Sc^{1/3}} = \frac{f}{2} = \frac{h_D}{v} Sc^{2/3} \quad \text{equation 3.1.3 - 1}$$

As in the previous section, empirically based equations provide a relationship between h_D and D_{ab} through Sc for laminar and turbulent flow regimes.

$$\text{laminar:} \quad \frac{0.664}{\text{Re}^{0.5}} = j_D \quad \text{equation 3.1.3 - 2}$$

$$\text{turbulent:} \quad \frac{0.037}{\text{Re}^{0.2}} = j_D \quad \text{equation 3.1.3.-3}$$

Equation 3.1.2 - 4 is used to generate h_D .

Consider a fluid in turbulent flow through a tube with mass transfer taking place between the fluid and the tube wall. The mass transfer coefficient in the fluid may be assumed to be some function of the following variables:

$$h_D = \text{fnc}(d_{\text{tube}}, v, \rho, \mu, D_{ab})$$

and by dimensional analysis

$$\frac{h_D d_{\text{tube}}}{D_{ab}} = \text{fnc}\left(\frac{d_{\text{tube}} v \rho}{\mu}, \frac{\mu}{\rho D_{ab}}\right) \quad \text{or} \quad \text{Sh} = \text{fnc}(\text{Re}, \text{Sc})$$

Further, $j_D = f/2$. The ranges of validity in the case of mass transfer are (Reference 22):

$$2000 < \text{Re} < 300000,$$

$$0.6 < \text{Sc} < 2500.$$

3.2 Kinetically Controlled Transport

3.2.1 Molecular (Ionic) Diffusion and Reaction Kinetics

3.2.1.1 Non-Electrolytic Solutions (Particulates):

Diffusion in liquids occurs at a very much slower rate than in gases. Since the kinetic theory of liquids is generally not as well developed as that of gases, a typical first order approximation is that the general form of the equations applicable to diffusion in gases is applicable to the diffusion of a solute in a solvent (Reference 22).

Generally, the diffusion parameters for the momentum and energy equations (viscosity, thermal conductivity) are functions of temperature and pressure. Mass diffusivity, also a function of temperature and pressure, is additionally a function of composition. The following semi-empirical relation has been developed for non-electrolytic dilute solutions (Reference 22):

$$D_{ab} = 7.4 \cdot 10^{-8} \frac{(\Psi_B M_B)^{0.5} T}{\mu \tilde{V}_A^{0.6}} \quad \text{equation 3.2.1-1}$$

The formulation indicates that diffusivity is a function of the size of the particles (molecular volume, V_A), and that the solution's "association" parameter (ψ_B) for the solvent. ψ_B is empirically derived. This is the Wilke equation, which combines both the simple Eyring kinetic model for an ideal liquid with the hydrodynamic theory for

diffusion. The Eyring “hole” theory and hydrodynamic theory, have been postulated as possible explanations for diffusion of non-electrolytic solutes in low concentration solutions. The hole theory treats an ideal liquid as a quasi-crystalline lattice model interspersed with holes. The transport phenomenon is then described by a unimolecular rate process involving the jumping of solute molecules into the holes within the lattice model. These jumps are empirically related to Eyring’s theory of reaction rate. The fundamental equation for the specific rate constant is given as:

$$k' = Ze^{-\frac{\Delta G}{RT}} \quad \text{equation 3.2.1-2}$$

where ΔG is the Gibbs free energy, and Z is a function of Boltzmann’s constant, temperature, enthalpy, and a transmission coefficient, that is, the probability that a process actually takes place once the system is in an activated state (Reference 31). It is customary to refer to ΔG as the activation energy for diffusion (Reference 32), so another way of looking at equation 3.2.1.-2 is as follows:

$$D_{ab} = Ze^{-\frac{E_D}{RT}} \quad \text{equation 3.2.1-3}$$

The hydrodynamic theory states that the liquid diffusion coefficient is related to the solute molecule’s mobility; that is, to the net velocity of the molecule while under the influence of a unit driving force (Reference 27). In order to apply this theory to the concept of diffusion, it is necessary to assume that there is some one type of mechanism

which is responsible for the flow of molecules, and in which there is one slow step which can be identified with the activated state.

Agreement between theory and experiment is poor, but the following fundamental relationship is indicated:

$$\frac{D_{ab}\mu_B}{R} = f(\text{molal function of mixture}) \quad \text{equation 3.2.1-4}$$

The hydrodynamic theory applies Stokes' law to describe drag on large, spherical solute molecules (A) moving through a continuum of small solvent molecules (B). The equation obtained is:

$$\frac{D_{ab}\mu_B}{T} = \frac{k_b}{6\pi r_a} \quad \text{equation 3.2.1-5}$$

where k_b is Boltzmann's constant and r_a is the radius of a molecule of A. The expression is not valid for smaller solute molecules. Combining 3.2.1-4 and 3.2.1-5 results in equation 3.2.1-1. The equations suggest that the quantity $D_{ab}\mu_B/T$ is constant for a given liquid system. This relationship is found to be only approximately true but will be used here to estimate the diffusivity at the system operating temperature.

The lack of widespread quantitative success with the theoretical approaches has led to the development of several semi-empirical relationships based on the above equations. Note that these relations for diffusivity apply to very dilute binary solutions of non-

electrolytes. There seems to be a large range of temperatures for which this formulation is applicable; however, the uncertainty associated with this introduces a source of error; Reference 31 states that this reaction is generally acceptable between 10°C and 30°C, whereas References 22, 23, 27, and others tend to maintain a more general caveat that there is a large uncertainty in the formula, depending on the types of solutes. Other methods, also derived from the Eyring hole theory, attempt to gain accuracy on the estimates of D_{ab} by eliminating the dependence on the association parameter, ψ_B , (Reference 34) but also rely on properly understanding the diffusion mechanisms. Additionally, empirical data is required to establish the constants that fit the relationship between $D_{ab}(\mu, T)$ and the solution's molal volumes. In binary systems, only one diffusivity need be defined. The situation is more complex in multi-component systems because of the interactions between the flows of the various species, and these complications increase with increasing departure of the system from ideal.

3.2.1.2 *Electrolytic Solutions (Anion/Cation):*

The diffusivity of strong electrolytes at infinite dilution may be calculated based on the Nernst equation, on the assumption of complete cation/anion dissociation (Reference 36):

$$D_{ab} = 8.931 \cdot 10^{-10} T \left(\frac{l_+^0 l_-^0}{l_+^0 + l_-^0} \right) \left(\frac{z_+ + z_-}{z_+ z_-} \right) \quad \left(\frac{cm^2}{sec} \right) \quad \text{equation 3.2.1.2 - 1}$$

where:

l_+^0, l_-^0	refers to the cationic and anionic conductances at infinite dilution,
$l_+^0 + l_-^0$	refer to the electrolyte conductance at infinite dilution
z_+, z_-	refer to the absolute value of cationic and anionic valence
T	absolute temperature, °K

Molecules of an electrolyte in solution dissociate into cations and anions which, because of their smaller size, diffuse more rapidly than the undissociated molecules. Despite differences between the sizes of the positive and negatively charged ions, this formulation assumes that both types diffuse at the same rate, so that the electric neutrality of a given solution is preserved.

This assumption would introduce a source of error into the approach for evaluating D_{ab} ; experimental data suggests that the Pt and Rd species types do not diffuse at the same rate (see Section 4.2). However, this approach is not viable for processing the data gathered; instead, applying the assumption of dilute solutions reduces this formulation to the Wilke-Chang equation addressed in the previous section (Reference 36).

3.3 Mixed Control Transport

Each partial reaction of the plating process is either under electrochemical control or under mass transfer control. The mechanics of mixed control of the plating reaction

remains undetermined based on the results of the experiments. Section 5.2.3 addresses a common approach for addressing this aspect of the problem.

4. RESULTS

Tests X-4 through X-22 were conducted to provide insights into the noble metal deposition process. However, in the interest of reducing data in order to focus on results that are most directly applicable to the reactor operating conditions during the proposed NMCA process (reactor coolant temperature of 250°F, and 60 ppb Pt/20 ppb Rh), most of the results discussed in the following sections are drawn from tests X-12 and X-18 through 22.

For the operating conditions specified for application in a BWR hot shutdown environment, the average calculated diffusivity values as a function of Reynolds number are as follows:

Table 4-1: Summary of Diffusivity Results

	laminar (Re $\approx$ 1000)	turbulent (Re $\approx$ 14,000 to 40,000)
$D_{ab, Pt}$ (cm ² /sec)	6.78E-06	1.43E-05
$D_{ab, Rh}$ (cm ² /sec)	1.35E-05	5.90E-05

4.1 Test Data Trends

4.1.1 Deposition as a Function of Temperature

The graphs of Pt and Rh deposition as a function of temperature and distance from the inlet (Figures 2a and 2b) demonstrates several phenomena:

- increasing reaction kinetics with temperature up to 350°F
- decreasing deposition as a function of ion decomposition at temperatures above 350°
- boundary layer effects on mass transfer

The temperature dependence of reaction kinetics can be explained with a simple reaction rate equation, which has been successful in predicting transport coefficients in liquids.

The fundamental equation for the specific rate constant is the Eyring equation:

$$k' = Ze^{-\frac{\Delta G}{RT}} \quad (\text{equation 4.1.1-1})$$

where ΔG is the Gibb's free energy, and Z is a function of Boltzman's constant, temperature, enthalpy, and a transmission coefficient. that is, the probability that a process actually takes place once the system is in an activated state (Reference 31).

This fundamental rate process being described by the Eyring equation is the movement of a molecule to a vacant site nearby. In order to squeeze through the "bottleneck" formed by its nearest neighbors, the wandering molecule must pass through a region of high

potential energy. It is assumed that the reaction rate, as defined in equation 4.1.1-1, is analogous to the deposition rate for a purely kinetically driven reaction. Note that the half-width of the temperature peak is approximately 150°F, after which point the reaction appears to decompose. This can be explained by noble metal ion solution decomposition occurring as temperature increases.

A log plot of noble metal deposition as a function of the inverse of temperature (Figure 3) confirms that this reaction rate model is applicable to the plating process being investigated (Reference 32). This Arrhenius type plot, derived from the Eyring equation, is approximately linear, providing a means for determining the activation energy for diffusion. Figure 3 demonstrates that the activation energy required to drive Rh plating ($\Delta E = 2.33\text{E}4$ cal/mol) is greater than that for Pt ($\Delta E = 1.26\text{E}4$ cal/mol). This might indicate that plating reaction is kinetically controlled for Rh. Section 5.2.3 provides further discussion for differentiating the diffusion and migration modes that drive this electroless plating process.

If it is assumed that the distance between molecules (related to the molecule mobility) is dependent on temperature, then diffusivity takes the form:

$$D_{ab} = C_1 \exp\left(\frac{-\Delta E}{RT}\right) \quad (\text{cm}^2/\text{sec}) \quad \text{equation 4.1.1-2}$$

and

$$\dot{m}''_{\text{loading}} = C_2 \exp\left(\frac{-\Delta E}{RT}\right) \quad (\mu\text{kg}/\text{cm}^2\text{sec}) \quad \text{equation 4.1.1-3}$$

Therefore, D_{ab} and the rate of deposition are related as follows:

$$D_{ab} = \dot{m}''_{\text{loading}} \left(\frac{C_1}{C_2} \right) \quad \text{equation 4.1.1-4}$$

4.1.2 Deposition as a Function of Time

4.1.2.1 *Water Grab Samples*

As expected by conservation of mass, the water sample concentration data generally reflects the surface loading data. As deposition to the tube walls increases, the noble metal solution bulk concentration decreases. The following discussion addresses some of the anomalies of the test data.

Examination of the grab sample data for individual tests indicates several questionable data points have been collected, with outlet concentrations higher than the inlet concentration. Since the probability of the noble metal coating stripping from the pipe wall is highly remote, then it is possible that the inlet and outlet values are transposed. Comparison with the surface analysis data confirms this hypothesis. The surface sample loading trends show an increase in deposition over time, though at a slightly lesser rate. Thus, the water concentration trend should decrease with time, which the results do

generally indicate, excepting the inconsistent data points. This discrepancy is consistent for both the platinum and rhodium water concentration data. However, by grouping test results based on operating temperature and Re, average trends are more readily visible, providing insight regarding data accuracy (see Figures 4 and 5).

4.1.2.2 *Surface Samples*

Deposition to the pipe walls increases over time, though the rate of increase appears to be a function of flow regime. The linearity of surface loading with time is illustrated in Figure 7c. The obvious implication is that the amount of surface coating is a function of exposure to plating substance. However, inspecting raw data for particular tests, as plotted as a function of exposure time, shows what appear to be deviations in the overall nearly linear increase in Pt loading. Such deviations are most likely due to fluctuations in the system's inlet concentration or to the error band in the measurements, both for the surface loading data as well as for the water concentration data. This is discussed in Section 2.6. Figures 6 and 7b illustrate that surface loading is greatest at the entrance to the test loop, for each of the tests. Examination of tests performed at other temperatures confirms this trend.

4.1.3 Deposition as a Function of Distance from Injection Point

Assuming direct correlation between deposition and reaction rate, it can be concluded that the reaction rate is very great at the entrance of the test loop. The increased reactivity can potentially be due to the following effects:

- higher solution concentration
- pipe entrance effects -- transition region eddying

More importantly, when considering the effect of concentration on deposition rate, it becomes clear that in the entrance of the pipe, where noble metal concentration is the greatest, surface deposition will have the greatest driving force (as a function of available concentration).

4.1.3.1 *Water Grab Samples*

Pt and Rh concentration data was accumulated for each of the performed tests. Figures 5 and 6 illustrate the typical trend, that Pt and Rh concentrations decrease between the inlet and outlet, as is expected.

4.1.3.2 *Surface Samples*

The surface sample data taken at the inlet and outlet of the test setup for each test performed indicates a decrease in deposition along the length of pipe. Figure 6 illustrates this for a set of tests performed at the same operating conditions.

The surface samples taken at system inlet and outlet also show a significant difference in loading, which indicates that higher solution concentrations drive higher deposition values (which occurs at the inlet). Thus, it is anticipated that the deposition rate decreases as a function of distance along the pipe, assuming no changes induced in the velocity and concentration profiles. Examination of the deposition data taken as a function of distance from the injection point for each test shows that this occurs; although the data points corresponding to 16 feet from the injection point (midpoint of test loop, characterized by a u-bend) shows an increase in deposition. U-bends are a known source of flow disruption, a fact typically characterized by large k-factor values, where the k-factor is an indicator of relative flow resistance. In general, u-bends cause a condition known as “secondary flow,” which is a rotating motion, at right angles to the pipe axis, which is superimposed upon the main motion in the direction of the axis. This condition causes eddy regions, which increase “stirring” motion, driving ionic species to the pipe walls. Several tests reveal this same trend. Figure 6 shows this trend for tests conducted at nearly the same operating conditions.

4.1.4 Deposition as a Function of Flow

Deposition to the pipe surfaces increases significantly with the Reynolds number, as illustrated in Figures 7a and 7b.

Each test exhibits the flow to loading relationship because of the physical test design, which incorporates 1/2 inch and 3/4 inch regions; flow accelerates through the narrower coupons, where the corresponding deposition increases, as illustrated in Figure 8.

4.1.5 Deposition as a Function of Inlet Concentration

As platinum and rhodium inlet concentrations are increased, the deposition on the pipe surfaces increases, as shown in Figures 9a and 9b.

4.2 Diffusivity Coefficient Calculations

The calculated diffusivity as a function of Re is graphically displayed in Figures 10a and 10b. Diffusivity increases with Re.

4.2.1 Molecular Diffusion

The diffusivity values for platinum and rhodium, based on dilute solution theory (see Section 5.) for binary solutions, are independent of flow regime and dependent on temperature. For a fluid temperature and pressure of 250°F and 1250 psig, the diffusivities for Pt and Rh, based on dilute solution theory, have been determined to be:

$$D_{Pt} = 1.89^{-05} \text{ cm}^2/\text{sec}$$

$$D_{Rh} = 3.59^{-05} \text{ cm}^2/\text{sec}$$

These values are the correct order of magnitude for solutions with water as the solvent (Reference 36). However, these results imply that rhodium will exhibit a greater tendency for deposition. This is difficult to confirm based on the experiment results. Normalizing the loading data with respect to maximum values for Pt and Rh respectively, provides a means for comparing the two on the same scale. Test X-20 (Figure 18) most clearly illustrates that Pt loading is greater than Rh. This implies that there is less resistance to Pt mass transfer, and consequently the diffusivity for Pt should be greater than for Rh.

4.2.2 Diffusion - Water Chemistry Data Derivation

The average diffusivity coefficients for Pt and Rd, based on an inlet concentration ratio of approximately 60 ppb Pt to 20 ppb Rd, an operating temperature of 250°F, the same test geometry, and a concentration mass balance, are summarized below:

Table 4.2.2-1: Diffusivity from Solution Concentration Data

	$D_{Pt} \text{ (cm}^2/\text{sec)}$	$D_{Rh} \text{ (cm}^2/\text{sec)}$
laminar ($Re \approx 1000$)	4.2E-06	5.8E-06
turbulent ($Re \approx 14,000 - 40,000$)	1.0E-05	3.1E-06

This method predicts that platinum has a higher deposition rate than rhodium in the turbulent flow region.

Since these convective transport derived values are “slower” for Rh than the kinetic model’s, it can be concluded that this plating process (for Rh) is diffusion dominant.

Based on these calculated values, the opposite applies to Pt. However, to differentiate the amount of kinetic versus diffusion control, additional investigations must be conducted (see Section 7).

4.2.3 Diffusion - Surface Data Derivation

The diffusivity coefficients for Pt and Rh, based on an inlet concentration ratio of approximately 60 ppb Pt to 20 ppb Rh and a surface loading mass balance, are summarized below:

Table 4.2.3-1: Diffusivity from Surface Loading Data

	D_{Pt} (cm ² /sec)	D_{Rh} (cm ² /sec)
laminar (Re $\approx$ 1000)	1.8E-06	9.4E-06
turbulent (Re $\approx$ 14,000 - 40,000)	1.0E-05	1.9E-04

4.2.4 Chilton-Coburn Heat to Mass Transfer Analogy

In general, the results of this analysis approach indicates that platinum has a higher diffusivity than rhodium. This is in direct contradiction with the molecular model, but is in agreement with the other calculations.

Table 4.2.4-1: Diffusivity from Heat to Mass Transfer Analogy

	D_{Pt} (cm ² /sec)	D_{Rh} (cm ² /sec)
laminar ($Re \approx 1000$)	2.3E-06	3.0E-06
turbulent ($Re \approx 14,000 - 40,000$)	1.8E-05	6.8E-06

4.2.5 Summary of Diffusivity Values at 250°F

Table 4.2.5-1: Calculated Diffusivity values for Pt

Test	Re	Pt/Rh (ppb/ppb)	$D_{(molecular)}$ (cm ² /sec)	$D_{(surface)}$ (cm ² /sec)	$D_{(H_2O)}$ (cm ² /sec)	$D_{(Chilton-Coburn)}$ (cm ² /sec)
X-22	1001	69/23	1.9E-05	1.8E-06	4.2E-06	2.3E-06
X-19	5110	64/21	1.9E-05	9.6E-05	4.7E-05	9.9E-05
X-12	14330	61/20	1.9E-05	2.6E-06	1.4E-05	2.4E-05
X-21	37840	61/20	1.9E-05	1.8E-05	6.0E-06	1.2E-05
X-20	52810	59/8.8	1.9E-05	1.2E-05	7.0E-05	9.3E-05
X-18	1818	43/14	1.9E-05	4.6E-06	1.4E-05	1.9E-05

Table 4.2.5-2: Calculated Diffusivity values for Rh

Test	Re	Pt/Rh (ppb/ppb)	$D_{\text{(molecular)}}$ (cm ² /sec)	$D_{\text{(surf)}}$ (cm ² /sec)	$D_{\text{(H2O)}}$ (cm ² /sec)	$D_{\text{(Chilton-Coburn)}}$ (cm ² /sec)
X-22	1001	69/23	3.6E-05	9.4E-06	5.8E-06	3.0E-06
X-19	5110	64/21	3.6E-05	5.9E-04	1.6E-05	1.6E-05
X-12	14330	61/20	3.6E-05	1.9E-05	4.2E-06	8.8E-06
X-21	37840	61/20	3.6E-05	3.6E-04	2.0E-06	4.8E-06
X-20	52810	59/8.8	3.6E-05	9.4E-05	2.8E-06	5.6E-06
X-18	1818	43/14	3.6E-05	3.4E-06	7.8E-06	1.2E-05

5. DISCUSSION

5.1 *Dimensional Analysis and Experiment Design*

Dimensional analysis of a fluid system requires that the experiment be designed so that the results give a representative indication of noble metal deposition in the reactor flow fields. The phenomena that are expected to dominate deposition are:

- fluid velocity field
- ion diffusion to metal surfaces
- chemical reaction at metal surfaces

The fluid velocity field determines the rate at which plating material is brought into proximity with mechanical surfaces. Regions of flow parallel to straight metal surfaces would have a continuous supply of plating substance in the free stream. Concave corners will result in stagnant fluid regions, for which the only supply of plating substance would be from the moving external fluid stream. Convex corners could result in wakes, consisting of rotating fluid islands with little flow interchange with external fluid. Wherever stagnant or rotating fluid regions might occur, the substance plating rate would be slower than on a surface with forced convection. Ion diffusion is coupled with the velocity flow field. In the absence of flow, diffusive flux is proportional to the concentration gradient of the plating substance through the concentration boundary layer.

Once the ions arrive at the metal surface, it is assumed that a chemical reaction occurs which retains the plating substance.

The experiment must attempt to isolate and preserve these effects such that dynamic, kinetic, and geometric similarity arguments remain valid. The most representative small-sized experiment would involve a geometrically similar model of reactor internals with fluid and chemical properties adjusted to give a miniature replica of the full size system. Experimental measurements, when scaled up to full size by applicable scale model laws, would demonstrate how well all surfaces would plate. There are a multitude of nondimensional groups to preserve in a geometrically scaled test. Early in the development of this test program, a simple scale modeling analysis showed that it is necessary to preserve the Reynolds number (Re) and the Schmidt number (Sc).

A manageable scaling method is referred to as “segment scaling,” which involves a flow path similar to full size, but confined to convenient experimental boundaries. The deposition application considered here involves a flow path which is constructed so that a portion of the fluid stream undergoes changes which are similar to a corresponding full size path.

The phenomena of interest in this study is the noble metal plating rate, and the transferability of experimental results to reactor flow conditions. In the reactor, mechanical surfaces parallel to the flow stream occupy most of the flow path. However,

other geometric boundaries of concern are horizontal surfaces which face upward or downward, where the flow fields are complex, with swirling and/or stagnation regions occurring. While occasionally the reactor coolant flow may be entirely in laminar flow, more frequently the motion is turbulent (or in transition to turbulence). However, the no-slip boundary condition, which dictates zero fluid velocity at the fluid/solid interface, simplifies the fluid field through which mass transfer occurs; there will be a region of laminar flow (laminar sublayer of the turbulent boundary layer) adjacent to the surface (Reference 21), where it can be assumed that molecular diffusion and reaction kinetics predominate. Although a geometrically scaled section and linearly scaled flow rate could be used in the experiment to determine diffusive plateout in turbulent flow regimes, the laminar sublayer would not retain geometric similarity. However, since the laminar sublayer is a function of fluid velocity, the friction factor, and the hydraulic diameter, all quantities which can be scaled between the experiment and reactor conditions, a representative deposition rate can be determined.

The substance density in the stream will have a representative depletion in a section of length $x = L$ if the non-dimensional parameter

$$\pi_d = \frac{D_{ab}}{v} \sqrt{\frac{f}{8}} \frac{L}{D_H} \quad \text{equation 5.1 - 1}$$

is preserved between the experiment and the full size system (Reference 39). This π value is derived from continuity and the assumption of concentration gradient driving diffusion occurring through the laminar sublayer.

5.1.1 Scaling Considerations

5.1.1.1 Geometry Scaling Factor

If all linear dimensions are scaled by the same scale factor, ϕ , L/D_H will be preserved.

The scaled dimensions are represented as:

$$L_{\text{experiment}} = \phi L_{\text{reactor}}$$

$$D_{H, \text{experiment}} = \phi D_{H, \text{reactor}}$$

and

$$\left(\frac{L}{D_H} \right)_{\text{experiment}} = \left(\frac{L}{D_H} \right)_{\text{reactor}} \quad \text{equation 5.1.1.1-1}$$

5.1.1.2 Flow Rate Scaling Factor

Since Reynolds number should be preserved in order to assure the same friction factors, and since kinematic viscosity is the same between reactor and experiment, then the velocity scaling becomes

$$v_{\text{experiment}} = \frac{v_{\text{reactor}}}{\phi}$$

The volumetric flow rate scaling is determined as a function of flow area and velocity:

$$Q_{\text{experiment}} = (Av)_{\text{experiment}} = \phi^2 A_{\text{reactor}} \frac{v_{\text{reactor}}}{\phi} = \phi (Av)_{\text{reactor}} = \phi Q_{\text{reactor}}$$

Thus, the volumetric flow rate must be scaled by the geometric scaling factor.

5.1.1.3 Time Scaling Factor

To determine how the chemical additive residence time scales between experiment and the reactor, consider a particle traveling at a velocity, V , through a flow path of length, L , such that the reference time for the distance traveled is:

$$t_{\text{reactor}} = \frac{L_{\text{reactor}}}{V_{\text{reactor}}} \quad \text{equation 5.1.1.3 - 1}$$

The experiment residence time is related to the reactor residence time by the geometric scaling factor as follows:

$$t_{\text{experiment}} = \frac{\phi L_{\text{reactor}}}{\left(\frac{v}{\phi}\right)} = \phi^2 t_{\text{reactor}} \quad \text{equation 5.1.1.3 - 2}$$

Thus, chemical residence time scales as a second order function of the dynamic scaling factor, ϕ .

5.1.1.4 Mass Scaling Factor

The amount of substance plated onto mechanical surfaces depends on the diffusive mass flux and the time of exposure to the flowing stream. Therefore, the mass deposited on the metal surfaces scales as:

$$\left(\frac{M}{A}\right)_{\text{reactor}} = \dot{m}''_{\text{reactor}} t_{\text{reactor}} \quad \text{equation 5.1.1.4 - 1}$$

where

$$\dot{m}''_{\text{reactor}} = D_{ab} \frac{(\rho_{\infty} - \rho_o)}{\delta'} = D_{ab} \frac{\rho_{\infty} v_{\infty}}{5\nu} \sqrt{\frac{f}{8}} \quad \text{equation 5.1.1.4 - 2}$$

With all physical parameters the same between experiment and the reactor, then $\dot{m}''$ scales as the velocity, or

$$\dot{m}''_{\text{experiment}} = \frac{\dot{m}''_{\text{reactor}}}{\phi} \quad \text{equation 5.1.1.4 - 3}$$

It is expected that diffusion of the substance from the main stream to mechanical surfaces parallel to the flow will occur through the laminar sublayer of a turbulent boundary layer. Outside the laminar sublayer, the fluid is assumed to be sufficiently mixed so that the

substance concentration is uniform at any cross-section. This is based on the assumption of fully developed flow.

5.1.2 Geometry of Various Reactor Regions

The scaling relations are applied to the various flow zones within the reactor to assure complete plating within all reactor flow regions. This has been performed in support of demonstration testing at a domestic BWR.

For commercial grade pipe, the Re that defines the onset of transition region flow is generally accepted to be approximately 2300; fully developed turbulent flow begins around 4000. Since most of the tests were performed at $Re > 10,000$, the assumption of fully-developed flow is valid. To check whether the test results apply to typical reactor geometries, apply the following condition for determining entrance lengths (Reference 37) for commercial grade pipe:

$$\frac{L}{D_H} \approx 0.06 Re \quad \text{for laminar flow}$$

$$\frac{L}{D_H} \approx 4.4 Re^{1/6} \quad \text{for turbulent flow}$$

An examination of some of the critical reactor flow region L/D_H values, demonstrates that the turbulent flow relations applied in the analysis are valid for the reactor flow fields of interest:

Table 5.1.2-1: Geometric and Dynamic Similarity between Experiment and Reactor

Reactor Region	Re	L/d, actual	L/d, calc	Flow Regime
<u>Reactor</u>				
shroud	2.53E+03	56.52	152	transition
Fuel	1.90E+04	320	23	fully developed
Fuel bypass	1.12E+04	57	21	fully developed
<u>Test</u>	1000	960	60	fully developed
	50000	960	27	fully developed

This table compares the geometric L/D_H with the L/D_H required to ensure fully developed flow for a given Re. The actual dimensions are sufficient for 'transition' region effects to be neglected.

5.2 Hypothesized Mechanisms for Noble Metal Deposition

The driving mechanisms of the noble metal coating process are only slightly understood.

The intent of this evaluation is to develop an empirical basis for the noble metal deposition mechanism. In general, the plateout rate can be considered to be driven by

concentration gradients, convective transport, and chemical reaction kinetics on the reactor's internal metal surfaces. This is expressed mathematically as (Reference 30):

$$N_i = -z_i u_i F c_i \nabla \phi - D_i \nabla c_i + c_i v$$

The first term accounts for movement of species due to an electric field/species charge (electro-chemical reaction), the second term accounts for the concentration gradient, and the final term for the bulk flow of the fluid. When the reaction rate is relatively rapid compared to the rate of diffusion, the process is said to be diffusion controlled. In contrast, the process is said to be kinetically controlled when the rate of mass transfer is limited by the reaction step. Figure 13 illustrates this in simple terms.

Though it can be hypothesized that the presence of each noble metal species in the mixture may effect the other's reaction kinetics, any such coupled effects are considered to be negligible. This assumption allows Pt and Rh to be independently evaluated.

Another intent of this study is to characterize the plating reaction as diffusion or kinetic dominant. For noble metal coating processes, two fundamental techniques exist: autocatalytic and displacement; both are categorized as electroless plating techniques. Autocatalytic deposition of a metallic coating occurs by controlled chemical reduction that is catalyzed by the metal or alloy being deposited. The electric power needed to drive the reaction is not provided by electrodes, but instead is supplied by chemical reduction of metallic ions in an aqueous solution containing a reducer. Once the reaction

is initiated, the metal deposited serves as the catalyst, thus ensuring a continuous buildup of material on the surface of the metal (Reference 26). Plating is initiated upon the catalyzed surface, and the plating reaction is sustained by the catalytic nature of the plated metal surface itself. This definition of electroless plating eliminates solutions that spontaneously plate on all surfaces through a process known as “homogeneous chemical reduction.” The particulate test conducted proved that this scenario is not occurring. In this test, iron oxide particulates were introduced in the bulk water flow as suspended matter, as would be expected in the reactor coolant. Particulate sampling data demonstrated that negligible plateout occurred on these particles. Therefore, it can be concluded that particulate surfaces did not introduce sufficient catalytic surface for plating to occur (Reference 12).

Displacement reactions are differentiated from autocatalytic reactions by the fact that the reaction ceases as soon as the substrate material is completely covered, thus allowing no further displacement of the metal salts and substrate. Displacement coatings are formed when noble metal ions in solution are displaced from their ionic state by the less noble metal ions onto the substrate. The reaction is limited by the access and renewal of the solution to the substrate surface, which implies that forced convection of the fluid past the plating surface will facilitate the reaction. The experimental methods employed do not readily facilitate assessing the type of electroless plating reaction that is occurring. It is recommended that coating thicknesses be measured as a function of exposure time in

order to determine whether the reaction is continuous and ongoing or a function of time. Preliminary tests results seem to indicate that a displacement reaction may be occurring, since (a) the plating layer is approximately on the order of an atomic thickness and (b) there is a steep drop off in the plating rate (Reference 3).

The following sections explain some of the principal approaches and assumptions behind mass transfer in the following modes:

- diffusion control
- kinetic control
- mixed potential control

5.2.1 Diffusion Controlled Deposition - Convection

Simple filter tests have demonstrated that the noble metal solution remains in ionic form, rather than becoming a dilute particulate solution. As a simplifying model of the coating process, it is assumed that diffusion of the Pt and Rh ions is slow, while the electron exchange at the metal surface is fast. Therefore, diffusion effects dominate.

5.2.1.1 *Empirically Based Models and Simplifying Assumptions*

A commonly applied model for mass diffusion is borrowed from classical solutions to convective heat transfer equations and recognizes that molecular diffusion most readily occurs in laminar flow fields, whereas convective mass transport dominates in turbulent flows. In this approach, the entire concentration difference is attributed to molecular

diffusion within an effective film thickness. The concentration gradient in the film is assumed to be characteristic of steady state. This assumption is a valid approximation, even though the test setup does not have obviously discernible stagnant fluid regions. The flow boundary condition at the surface to be plated can be idealized as a zero velocity, “no-slip” condition, which provides for a region of predominantly laminar flow adjacent to the surface through which molecular diffusion predominates (Reference 29). This is an important simplifying approach, since it eliminates the complexity of turbulence, where there will be a physical movement of packets of material across streamlines, transported by the eddies present in the turbulent flow.

Both the water chemistry and Chilton-Coburn analytical approaches explained in Sections 3.1.1 and 3.1.3 take advantage of semi-empirical convective heat transfer correlations developed for both laminar and turbulent flow regimes. D_{ab} is calculated for the laminar sublayer boundary layer model, as well as for a completely turbulent flow model. A comparison of the range of D_{ab} values due to convective transport is shown in Figure 14. Of key importance in the formulation of nearly all these analogies is the structure of the velocity distribution and the corresponding distribution of eddy diffusivities between a solid boundary and the bulk or core of the turbulent stream. Reference 36 provides, for a variety of variations on the structure of the turbulent boundary layer, complex relationships between the velocity profile and concentration distribution. A ‘next step’ would be to compare these improved formulations to a

solution with known D_{ab} characteristics, and back out the diffusivity based on surface loading data for the flow model of interest.

5.2.1.2 *Improving the Boundary Layer Model*

The ensuing discussion of the relationship between surface roughness and boundary layer development is relevant because it leads to the recommendation that classifying the surface roughness will determine the turbulent boundary layer model to be applied, and how to apply the eddy diffusivity term through a turbulent sublayer region within the boundary layer. In other words, the ability to more accurately specify the flow field will directly affect the determination of mass diffusivity. The tests do demonstrate that surface roughness affects plating. In fact, test X-20 (Figure 16) shows that oxidized surfaces promote increased surface plateout over non-oxidized surfaces. Additional comparison of polished and unpolished coupon samples taken in tests X-4 and X-6 (Figure 17) indicate that rougher surfaces (unpolished) promote increased loading.

These results are consistent with well documented results of heat transfer in laminar and turbulent flow; heat transfer increases with turbulence. In general, surface roughness promotes turbulence. Therefore, the ability to characterize the surface oxidation in terms of quantifiable roughness factors (in terms of the height of surface protrusions) will further assist in appropriately categorizing the turbulent boundary layer model (to have an eddy sublayer or a turbulent sublayer, as influenced by the height of the surface

protrusions due to oxidation levels). It is clear that in the reactor flow environment, where crud buildup as well as oxidation exists on the reactor internals' surfaces, that the expectation of a laminar sub-layer is a simplification of reality. The presence of noble metal on the substrate surface after deposition was confirmed by various analytical techniques such as Auger electron spectroscopy, X-ray photoelectron spectroscopy, and surface analysis by laser ionization (Reference 3). These methods demonstrate that the surface coating process was successful, and even assessed the film thickness. However, the uniformity of the coating, and the effect of surface unevenness on the plating thicknesses remains unknown.

5.2.2 Kinetics Controlled Deposition

The analytical approach to kinetically controlled deposition is presented in Section 3.2.1.1, but is only investigated from the perspective of the generalized rate equation. In this postulated scenario, the electron exchange at the metal surface is slow relative to the diffusion from the bulk fluid stream to the wall. In general, the kinetics can be expressed in terms of a reaction rate, k , which is generally a function of concentration, temperature of the fluid stream, and the ionic activation energy, as described by the Eyring approximation, which applies for dilute solutions only. Dilute solutions are defined in terms of ppb of solute for the purposes of this evaluation, and this approximation provides a means for simplifying the problem, such that each species (Pt, Rh) can be

treated independently. It is assumed that each species diffuses independently according to its own concentration gradient and diffusion coefficient (Reference 30).

However, it is recognized that for an electroless plating process the solute species do not diffuse independently. It has been proposed that whereas D_{ab} for a binary solution is a function alone of concentration gradient and convective transport, for electrochemical systems or systems containing charged species, it is the gradient of activity rather than concentration that is the driving force. In other words, species migration is a function of another driving force, the electrostatic potential. The Eyring rate formulation is an attempt to quantify this driving force by the estimate of energy required to drive diffusion.

A tool that enables quantifying the kinetic driver to mass transport is the Arrhenius reaction rate, which quantifies the temperature effects between molecular diffusion, as expressed in equation 3.2.1-2. Based on experimental data (Figure 3), the activation energies for deposition of Platinum and Rhodium are 1.26E4 cal/mole and 2.33E4 cal/mole, respectively. More energy is required to activate Rh in a kinetic sense. Note that the graphs of plating rates for Pt and Rh generally confirm this; Rh normalized plating rates, as compared to Pt, are less. The plating rates required normalizing in order to eliminate the initial inlet concentration difference from the comparison (Figure 18).

5.2.3 Mixed Control Deposition

The question remaining is how to determine the amount the deposition process is controlled by an electro-chemical potential (activation control) driving ion migration to the surface or by diffusion of the reactants to the surface. This scenario combines the diffusion and kinetics effects. In other words, neither is dominant, but instead share in driving mass transfer; one of the partial reactions is diffusion controlled, the other is activation controlled. Electroless plating of metals typically involves a reaction proceeding at a rate limited by diffusion.

One method for confirming the empirically derived values for platinum and rhodium diffusivity in water at 250 °F, is to measure current density due to diffusion of these metal ions to the plating surface. This can be performed using standard rotating disk electrode experiments, where the velocity fields are fully defined. The current due to the diffusion of metal ions to a rotating disk is given by:

$$i_M = B_M (C_{M\infty} - C_{Ma}) \sqrt{\omega} \quad \text{equation 5.2.3 - 1}$$

where $C_{m,\infty}$ is the bulk concentration of the metal ions, C_{ma} the surface concentration, and B_m is a diffusion parameter given by

$$B_M = 0.62 n_m F D_M^{2/3} \nu^{-1/6} A \quad \text{equation 5.2.3 - 2}$$

where,

- D_m , diffusion coefficient of the metal ions
- ν , kinematic viscosity
- n_M , number of electrons involved in the metal deposition reaction
- F , Faraday
- A , area of the disk

When the other reaction is under electro-chemical control, the current voltage curve is described as

$$E = E_R^0 - b_R \ln n_R F k_R - b_R \ln C_R^\infty + b_R \ln i_R \quad \text{equation 5.2.3 - 3}$$

where

- k_R rate constant
- n_R number of electrons involved in the reaction
- b_R Tafel slope. $b_R = \frac{RT}{(1 - \alpha_R)n_R F}$

Combining these equations gives an expression for the mixed potential in terms of ω and $C_{M\infty}$:

$$E_{MP} = E_R^0 - b_R \ln n_R F k_R - b_R \ln C_R^\infty + \frac{b_R}{2} \ln B_M'^2 \omega + b_R \ln C_M^\infty \quad \text{equation 5.2.3 - 4}$$

Embedded in this formulation is some knowledge of the diffusion boundary layer thickness and its correlation to the plating rate (Reference 7) via some volumetric flux

through the boundary layer, which is why a thorough understanding of the flow field development is so crucial; the concentration profile is a function of the velocity profile. Further, the bulk solution potential drop is determined by the solution conductivity and is generated by ion migration (Reference 5). Much of this data has been accumulated in other related investigations, in terms of studying the effects of noble metal alloying on the corrosion potential of stainless steels (Reference 1). Since limited conductivity data is available from the experiments, a similar approach is possible, by relating classical solutions for tube flow (through the entrance region, fully developed tube flow, through the u-bends) to the concentration profile. It is recommended that the electro-chemical approach using RDE methods be pursued in order to specify diffusion in a known flow field.

6. CONCLUSIONS

Note that the original design intent to the sets of tests conducted at the GE Pipe Test Lab that form this basis for this work was as a “proof-of-concept” in a geometrically scaled laboratory setup, such that noble metal plating would occur in flow fields considered to be similar to those seen in the reactor hot shutdown environment. It was desired then to make a first approximation of diffusivity from these tests. The uncertainty of the analysis method itself is undetermined. Therefore, it is recommended that either (a) the accuracy of the analysis assumptions and methods be benchmarked against a solution with a well

characterized D_{ab} correlation or (b) use established electro-chemical methods (i.e., rotating disk electrode (RDE) experiments) for deriving diffusivity correlations as a function of temperature, concentration, and flow.

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8. FIGURES

Figure 1: NMCA Protectable Regions in the BWR

Figure 2a: Coupon Platinum Loading as a Function of Temperature, at 48 Hours

Figure 2b: Coupon Rhodium Loading as a Function of Temperature, at 48 Hours

Figure 3: Platinum/Rhodium Deposition Rate vs Reciprocal of Absolute Temperature

Figure 4: Noble Metal Inlet Concentration Control over Time

Figure 5: Pt Outlet Concentration for Turbulent Flow: $Re > 25,000$
inlet: 60 ppb Pt/20 ppb Rh

**Figure 6: Pt Loading for 3/4" Tube with Re > 20,000
Operating Temperature approx 250 deg F**

Figure 7a: Coupon Surface Pt Loading as a Function of Time and Re No.

Test X-12, 251 F, 60 ppb Pt/20 ppb Rh

Test X-18, 250 F, 60 ppb Pt/20 ppb Rh

**Figure 7b: Surface Load Rate as a Function of Distance
from Inject Point and Re No.**

Figure 7c: Normalized Surface Loading over Time, Re = 30,000
Operating Temp approx 450 F

Figure 8: NMCA Coupon and Tube Sample Surface Analyses
Run X-12, 250°F, 2.1 ft/s, 16 ft, 6/1/20

Figure 9a: Effect of Water Concentration on Platinum Deposition Rate
Test X-12, X-13, Test X-14, Test X-15

Figure 9b: Effect of Water Concentration on Rhodium Deposition Rate
Test X-12, X-13, Test X-14, Test X-15

Figure 10a: Calculated Diffusivity of Pt, Various Methods, vs Re
 250 F, 60 ppb Pt/20 ppb Rh, inlet
 Test X-12, 21, 22: 3/4" Tube Samples

Figure 10b: Calculated Diffusivity of Rh, Various Methods, vs Re
250 F, 60 ppb Pt/20 ppb Rh, inlet
Test X-12, 21, 22: 3/4" Tube Samples

Figure 11: NMA II 60 foot Test Loop Schematic

Figure 12: 60 foot Loop Sample Panel: Rear View

a) Diffusion Controlled Reaction

$$\frac{\partial c}{\partial x} \propto \frac{c^{\text{bulk}} - c^{\text{surface}}}{\delta}$$

b) Kinetics Controlled Reaction

$$k = Ae^{\frac{-\Delta E}{RT}}$$

Figure 13: Mass Diffusion: Diffusion or Kinetic Control

**Figure 14: Diffusivity Variation due to Boundary Layer Assumption
Mass Transfer through Laminar or Turbulent Sublayer**

Figure 15: Average Pt and Rh Solution Concentrations, Mean Standard Deviation
Tests X-12, 19, 20, 21, and 22 (250 F)

Figure 16: NMCA Zircoloy Tube Samples
Run X-20, 253°F, 2.5Zr-2.26OZr-4.5&1.6SS fps, 5.4 ft, 59/8.8

Figure 17a: NMCA Coupon Surface Analysis
Run X-4& X-6, 550°F, 2 ft/s, 60 ft

Figure 17b: NMCA Coupon Surface Analysis
Run X-4& X-6, 550°F, 2 ft/s, 60 ft

Figure 18: Normalized Zircoloy Tube Samples
Run X-20, 253oF, 2.5Zr-2.26OZr-4.5&1.6SS fps, 5.4 ft, 59/8.8
Oxidized Zirconium Tube