Corrosion: The Most General Problem of Materials Science

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The following chapters systematically address varied aspects of the field known as corrosion.[1] In this introductory overview, an effort will be made to touch only lightly the breadth and depth of corrosion - the most general problem of materials science.

For the first step to developing an overview, a meaning to the word corrosion needs expression. To my wife, corrosion means that there is a dirty brown splotch on the side of the car which means it is worn out and time to trade in is here. They don't make them as well as before! This brings our attention to the classic meaning of corrosion as being a loss in value for some solid object which has been suffering from chemical attack at the surface. I suspect that for many this feeling of decreased value through corrosion leads to a negative feeling towards the topic. Corrosion, in general, is used to describe degradation in value of useful objects.

An alternative perspective is present in corrosion engineer anecdotes. "Nope, we don't have any corrosion problems in this plant. The pumps wear out every six weeks and we replace them." Or alternatively, "We just dump the scrap here and as soon as we can fill a railroad car we haul it to a hole a hundred miles away and bury it. Some day when the corrosion finishes the junk off, we'll build condominiums on the land." Or yet another one - "Hey, would you believe that with six months' data they want me to warrant that tank for 50 years of radioactive waste storage?" Yes, these do represent some famous last words. Enough for the anecdotal description; we are not gathered here to be entertained.

Corrosion is a serious, costly materials science problem. In the years ahead as our resources are increasingly utilized to the limits of practicality,

and conservation and recycling are watchwords, not catchwords; the corrosion engineer will be at the forefront.

May I emphasize again the title, "Corrosion: The Most General Problem of Materials Science." So many I encounter speak in a disparaging voice about corrosion problems - that it's just a black art - without supportive science. Just go in there and do your thing - don't bother me with the facts. As a matter of fact, however, there is so much science in this show that a constipation of words readily sets in before the constipation of ideas is even approached.

For the next 90 minutes or so let us explore this field - CORROSION. We shall travel in two distinct ways. One is to bring your attention to arrays of key words and concepts. The other is to formulate a pattern of solid state surface structural chemistry which may be useful as a framework for remembering complex options and for exploring new options. The latter will be within two areas: (1) exchange current descriptions of corrosion potentials and (2) the nature of corroding surfaces.

The empiricism that appears to follow the corrosion engineer arises from the multi-factor, multi-component situations which are present within all common articles of commerce, be they made from iron, aluminum, or more exotic material combinations. The variables are continually interacting in increasingly complex ways so we can become engrossed for even a lifetime with just one problem in performance such as airfoil stress corrosion cracking, boiler feed water stabilizations, or corrosion inhibiting paints, and many more. But does this mean the work lacks for glamour and excitement?

Well, the materials engineer is frequently caught with orders to select materials combinations in a practical situation giving desired property balances with adequate performance designed to first or to life costs. Alternatively, he selects model Mark II materials to cover model Mark I mistakes. More important today, material selections must avoid warranty payouts capable of corporate bankruptcy as well as extended personal liability. How indeed are R & D data predicting field reliability? What is a valid test?

The corrosion engineer is frequently the pragmatist - so what is the problem - get rid of the offending material. Another approach is "Hey, what can we add to, introduce to, or otherwise coat the system with so the problem will disappear long enough to keep the customers adequately happy? Or at least not

seriously disappointed in the value received? We can't
sell many gold-plated Cadillacs." Or the customer asks
how can I cheaply save money in the long run without
paying the factory? Ziebart it!

Well, enough commercials - who is this corrosion
engineer and what is he like? How many years has he
spent in the ivory towers? Or has he ever visited them?

Well, if I had my druthers, I would see to it that
the corrosion engineer had a bit of flavoring from
materials science as shown in Figure 1. In these days
of specialization, it would be nice to train some gen-
eralists. As an expert responsible for the future
behaviors of most of our solid materials, surely a
mastery of the full range covered by chemistry, physics
metallurgy, and just a few other incidental fields
would be consistent with assigned responsibilities. If
he feels a bit short, clearly recourse will be taken to
the consultants and the colleagues forming his support-
ive technical society.

What, you think the survey is facetious and out of
place? Let's take a look at a corrosion smörgåsbord of
terminology in Figure 2. The experiences of a corro-
sion engineer are represented by the term array. Sampl-
ing them at random, it seems to be a jumble. However,
it is an overview.

Who, then, is the corrosion engineer? For many
here, he has an exciting, responsible way of doing
complex materials science in service to our society.
This individual may never have deliberately planned the
career which developed. Rather as a civil engineer, a
mechanical engineer, a chemist, a physicist, an analyst,
one day suddenly he has a responsibility thrust on him
relating to materials reliability, to materials perfor-
mance or just to solve that problem before we are broke.

Thus, many routes lead to a corrosion engineer's
responsibility as is reflected in Figure 3. He con-
tributes to A Priori Problem Solving but economics of
first costs frequently lead to Post-Factum Problem
Solving. For, too often, corrosion is tied directly
to systems' weakest link variables. Much of the needed
knowledge is absorbed almost by an osmosis process
because there just aren't simple valid descriptions of
general use. All quickly become specific.

Ladies and gentlemen - if you were to examine the
agenda for the next few weeks, quickly a recognition
would develop that the key-words have touched on the
program exposures each will experience - can you see
the beauty of the toughest materials science problems
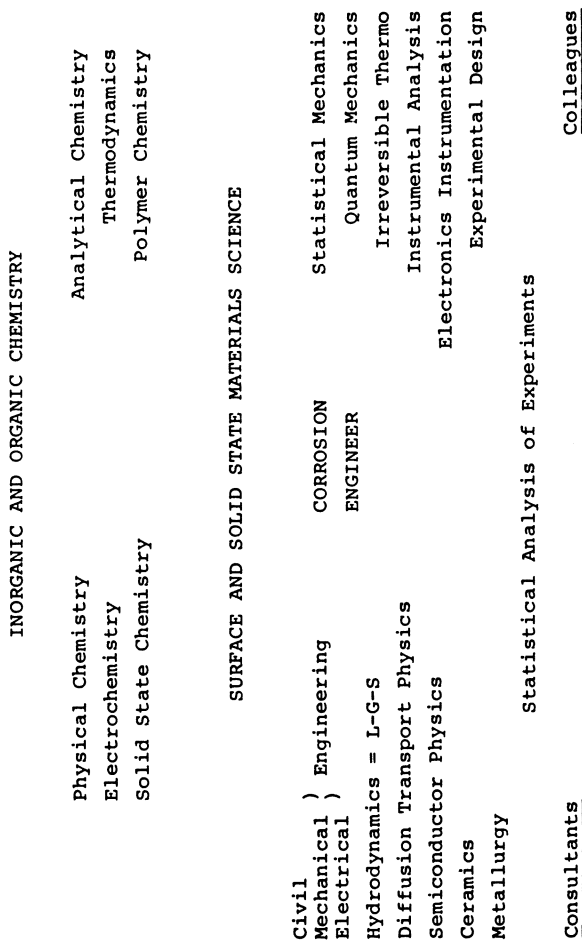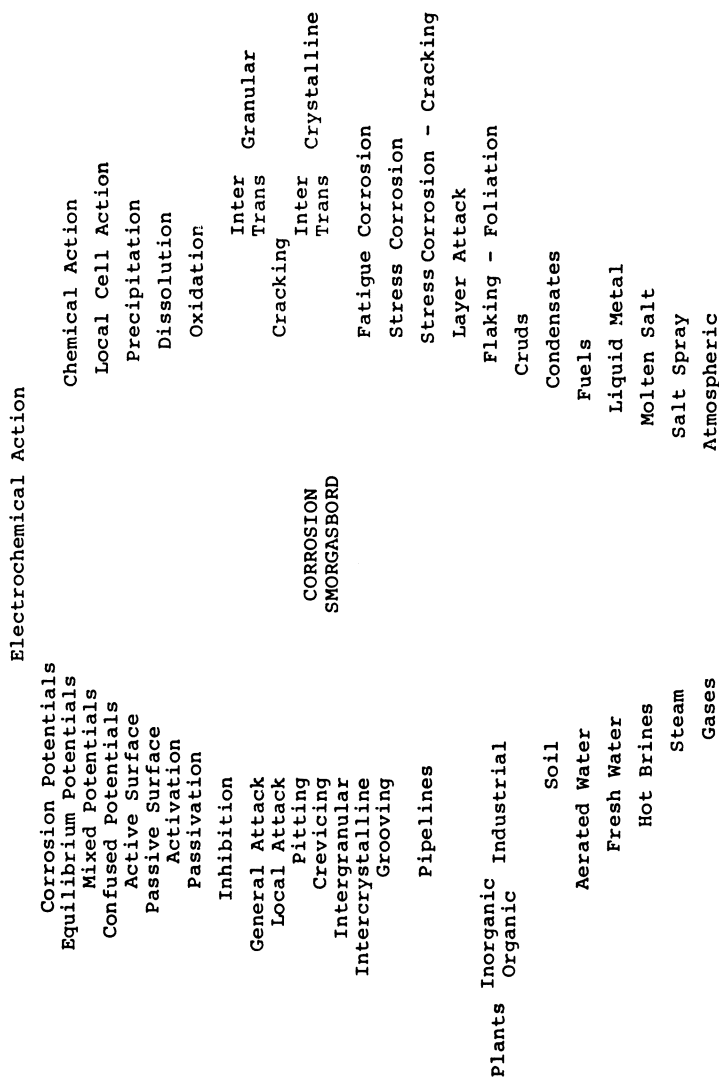emerging through the program?

INORGANIC AND ORGANIC CHEMISTRY

Analytical Chemistry
Thermodynamics
Polymer Chemistry

Physical Chemistry
Electrochemistry
Solid State Chemistry

SURFACE AND SOLID STATE MATERIALS SCIENCE

Statistical Mechanics
Quantum Mechanics
Irreversible Thermo
Instrumental Analysis
Electronics Instrumentation
Experimental Design

CORROSION
ENGINEER

Colleagues

Civil
Mechanical) Engineering
Electrical)

Hydrodynamics = L-G-S
Diffusion Transport Physics
Semiconductor Physics
Ceramics
Metallurgy

Statistical Analysis of Experiments

Consultants

Figure 1. Corrosion engineer

Electrochemical Action

Corrosion Potentials
Equilibrium Potentials
Mixed Potentials
Confused Potentials
Active Surface
Passive Surface
Activation
Passivation

Inhibition

General Attack
Local Attack
Pitting
Crevicing
Intergranular
Intercrystalline
Grooving

Pipelines

Plants Inorganic Industrial
        Organic

Soil

Aerated Water
Fresh Water
Hot Brines

Steam

Gases

Chemical Action
Local Cell Action
Precipitation
Dissolution
Oxidation

Inter Granular
Trans
Cracking
Inter Crystalline
Trans

Fatigue Corrosion
Stress Corrosion
Stress Corrosion – Cracking
Layer Attack
Flaking – Foliation
Cruds
Condensates
Fuels
Liquid Metal
Molten Salt
Salt Spray
Atmospheric

CORROSION
SMORGASBORD

Figure 2.   Corrosion term smorgasbord

THE CORROSION ENGINEER'S RESPONSIBILITY

Aesthetics   Environments   Economics   Performance

Practical Engineering
Property Balance

THE PROBLEM

A Priori Materials Selection

A Useful   Limited Useful Product Life
Product Life

Recycle   Disposal   Degradation

Post-Factum Solutions

Corrosion and Weakest Link Variables
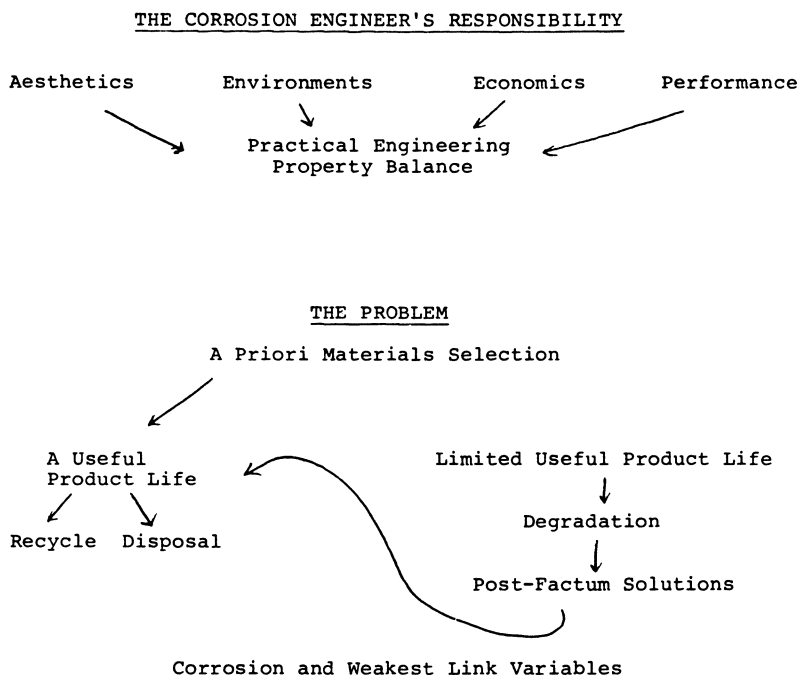
Figure 3.   Corrosion engineer's responsibility

Let us look at another pair of smörgåsbord figures on corrosion. The first, Figure 4, focusses largely on surface phenomena from a physical chemist – electrochemist or surface chemist context. Do the words have a familiar meaning? Should I define a few or perhaps we should look at another, Figure 5, which outlines another set of, probably less familiar to most, key words. These are related to the description of solid state structures which are encountered on the solid side of the electrical double layer. It is the disturbing phenomena proceeding within the solid surface side that gives rise to the diverse experiences of the corrosion engineer.

For an overview we clearly could spend much time on each word, learning what meaning was experienced by each of us. Each would be surprised what a range could be revealed by the dialogue. This is why so much of the management end of the talent spectrum is inclined to say, please practice your art without fully recognizing or experiencing the complex beauty present. For it is only art to the beholder – let us continue sketching the canvas.

Did you ever stop to contrast the conceptualization of chemists' common models, or for that matter, most descriptions of solid material behaviors? In Figure 6 we are examining the phenomenological situation over which we spend so much time puzzling. The mental images usually do not assign detailed structure to the solid phase. We can clearly see it before us – it is so obvious.

The model we are usually speaking about is shown in the lower left corner – a structureless solid behaving in an environment of liquid, or gas, more rarely an imperfect, impure vacuum. The latter environment has the spatial extent.

More truly as in the lower right corner the solid is defined by x-y-z coordinates which define what is actually happening where as a function of time in an experiment.

Still more precisely, the solid in the experiment is being space averaged to produce the data in the figures above.

The solid is best described generally for the corrosion engineer's purposes as a
  "polyphase inhomogeneous solid containing
   heterogeneity homogeneously dispersed."
The description is rather precise according to Webster's Unabridged Dictionary. This reference can be cited if the statement requires substantiation.

Goodness, with this complexity where do we go from

(Liquid Phase)
Model Components

Thermodynamic
Oxidation-Reduction
Free Energy
Heat Content
Entropy
Electrode Potentials
Polarization Potentials
Activation Polarization
Concentration Polarization

CORROSION

I^2R Loss
Open-Circuit Potentials
Short-Circuit Potentials
Cell Potentials
Over Potentials
Anodic-Cathodic Potentials
Mixed Potentials

Kinetic
Atomic Polarization Fields
Ionic Fields
Electric Dipole Fields
The Helmholtz Planes
Diffuse Double Layer
Compact Double Layer
Potential Transients
Constant Current
Constant Potential
Faradaic Processes
Non-Faradaic
Ideal Polarizable

Electrochemical
Potential
Exchange Currents

Figure 4. Corrosion smorgasbord (continued)

Mass Transport Imperfections   Charge Transport

Vacancies - Interstitials   Imperfections

Associated Defects   Insulator-Semiconductor
                                    -Metal

Zeolite to Perfect Crystal -

Solid Phase   Charge Transfer
                                    Catalysis
Inhomogeneous-Heterogeneous-   Surface Defects
    Heterogeneity
Metastable Solutions   Surface States

Solid Solutions   CORROSION   Electrons and Holes

Electronegativity   Surface Potentials

Ionic-Covalent   Work Functions

Dopant States   Fermi Levels

Impurity States   Dislocations

Trapping States   Impurity Bands

Valence Bands   Conduction Bands

Band Structure

Space Charge Potential   Flat Band Potential

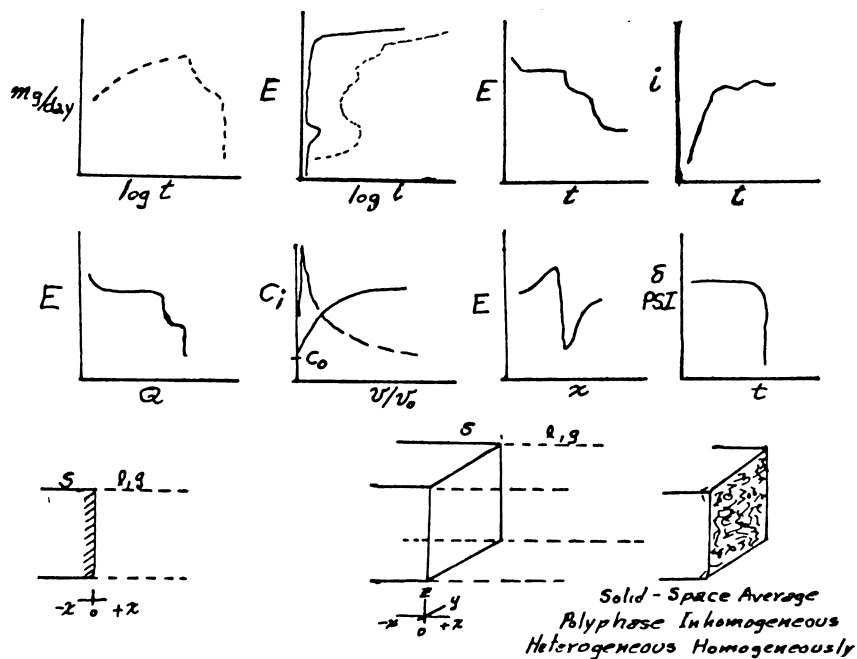*Figure 5.   Corrosion smorgasbord (continued)*

Figure 6. Phenomenological view of a one-dimensional solid contrasts with the three-dimensional reality of most solid systems.

here? Well, let's just acknowledge that this has
always been the stage on which most of us are acting
out our professional lives.

Thus, in Figure 7, <u>Solids</u> are described as being
ideally perfect versus ideally imperfect with most
being in the latter category. A sharp consequence was
taught to me many years ago by Leroy Dunham of the
Edison Primary Battery. When I smartly described a
statistical quantum-mechanics model of charge transfer
catalysis of oxygen reduction on an electrode surface,
he smiled as if he was enjoying himself. He had been
forced to leave school at the eighth grade level.

Later in the day as he and I strolled through the
production plant making his electrodes, he quietly
said, "Don, I enjoyed your comments so very much.
Back in the '30's when I was doing the development work
many confusing results came from experiments. In the
evenings I have enjoyed reading the Encyclopedia
Britannica. One day it dawned on me that the distri-
bution of people in the United States versus other
areas resembled the charge transfer behavior. To
change things the people must move around, get into
and out of cars, trains, planes.

What a memorable moment - the theory did not have
to be absolutely right to be useful in guiding exper-
iments.

Why have I taken such a circumspect path to reach
this point? Well, I wish to present a conceptualiza-
tion of the problems which has been useful to me. It
has helped to bridge the chasm separating different
experimental situations.

The following Figure 8 indicates that the lectures
could be placed in a variety of categories. First, the
familiar metal-electrolyte system with gas evolution
potentially present. Second, the systems involving
metals separated from the liquid by a covering film
structure, and third the metal separated from a gas by
an intermediate phase layer. There is some ambiguity
evident in this description; however, in the next few
minutes perhaps some new perspectives for thought
organization can emerge.

In a more general sense surface corrosion pro-
cesses can be described in terms of the phases present
as shown in Figure 9. Here the solid is not identified
simply as a metal but a more general term S is being
used with L representing liquid phase and G gas phase.
The systems locally present can be represented by the
notations S-L, S-L-G, S-G or, if a covering chemically
altered layer exists on the surface, then S_1-S_2 is
present with S_1 the starting material.

12   CORROSION CHEMISTRY
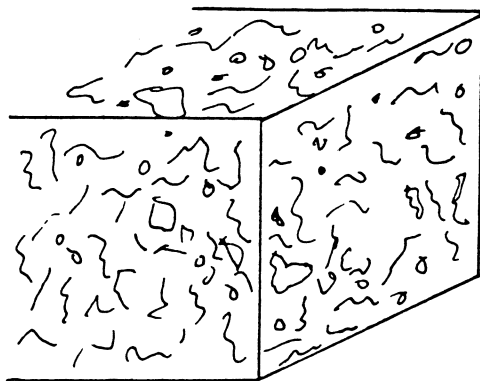
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               Solids

Ideally Perfect          Reality → Ideally Imperfect


              THEORY:

    if it leads to experiments
        does not need to be

              RIGHT

      to be very valuable.
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Figure 7.   Modeling

Metal-Electrolyte-Gas

Corrosion Electro-
  chemistry
Iron Dissolution
  Mechanisms
Corrosion Inhibition
  and Inhibitors
Stress Corrosion
  Cracking

Metal-Solid-Liquid

Solid Electrolyte-Ionic
  Electronic Transport
Iron Passivation
Valve Metals Dielectric
  Layers
Industrial Problem:
  Cooling Waters and
  Treatments

LECTURE SERIES

CORROSION

Metal-Solid-Gas

High-Temperature
  Corrosion
Low-Temperature
  Atmospheric
  Corrosion
Corrosion Phenomena
  Novel Energy
  Conversion Processes
Iron Passivation

Figure 8.   Corrosion lecture classifications

The perspective of simple phases and phase equilibria is adequate for many corrosion problems. This is particularly true for the cases where thermodynamic free energy data really describe what phases are present.
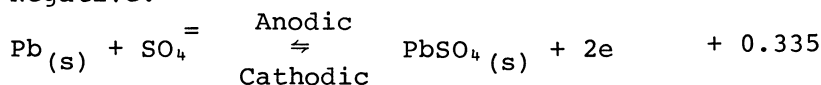
Let us examine this for a few minutes from the viewpoint of everyday experience. We will utilize the key device which was responsible for our arrival at the lecture - the black box called
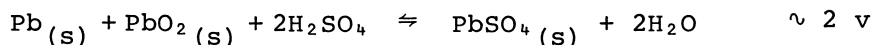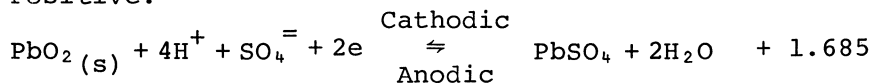
THE LEAD-ACID STORAGE BATTERY.

This system permits brief descriptions of some key concepts encountered in corrosion phenomena: electrode potentials, exchange currents, mixed potentials, corrosion potentials, passive films, as well as leading to thermodynamic descriptions of systems.[2]

The redox systems of the battery are simply presented as:

Negative:

$$Pb_{(s)} + SO_4^= \quad \overset{Anodic}{\underset{Cathodic}{\leftrightharpoons}} \quad PbSO_{4(s)} + 2e \quad\quad + 0.335$$

Positive:

$$PbO_{2(s)} + 4H^+ + SO_4^= + 2e \quad \overset{Cathodic}{\underset{Anodic}{\leftrightharpoons}} \quad PbSO_4 + 2H_2O \quad + 1.685$$

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4 \quad \leftrightharpoons \quad PbSO_{4(s)} + 2H_2O \quad\quad \sim 2 \text{ v}$$

At the negative lead is oxidized to lead sulfate during discharge while at the positive lead dioxide is reduced to lead sulfate. The functioning of the battery for many cycles depends upon maintaining the reactions isolated to their respective electrodes, to having the electrons flowing through an external circuit, and only ionic currents flowing in the internal electrolyte circuit.

If the potential-current (E-i) characteristics of the individual reactions were measured, the reactions could be readily modeled as electrochemical reactions with the battery at open circuit as indicated by the processes in Figure 10. If dynamic electrode potential-current relationships were determined, the electrode is expected to show the classic Tafel slope behaviors as the exchange current of the anodic-cathodic equilibrium is shifted into either direction. From the Tafel curves a value for the E_O and i_O of the electrode could be defined.

LOCAL REGION SOLID SURFACE TRANSFORMATIONS

Solid-Liquid   Solid-Liquid-Gas   Solid Gas
   S-L   S-L-G   SG

Solid 1-Solid 2-L   Solid 1-Solid 2-L-G   Solid 1-Solid 2-G

$S_1- S_2- L$ $S_1- S_2- L - G$ $S_1- S_2- G$

Figure 9.   Corrosion system

$$PbSO_4{}_{(s)} + 2\ H_2O \rightarrow$$
$$PbO_2{}_{(s)} + 2H^+ + H_2SO_4 + 2e$$

$$PbO_2{}_{(s)} + 2H^+ + H_2SO_4 + 2e \rightarrow$$
$$PbSO_4{}_{(s)} + 2\ H_2O$$

$$PbSO_4{}_{(s)} + 2e \rightarrow Pb_{(s)} + SO_4^=$$

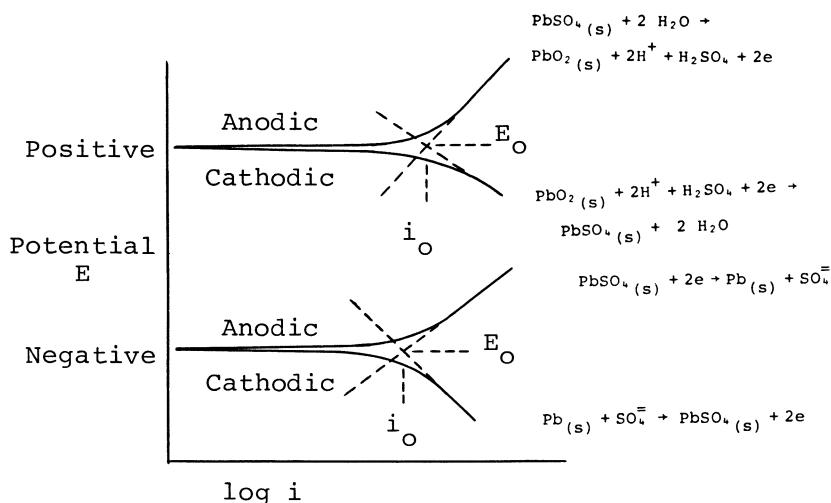$$Pb_{(s)} + SO_4^= \rightarrow PbSO_4{}_{(s)} + 2e$$

Figure 10.   Model battery anodic–cathodic reactions

If the two electrodes are short-circuited together, the cathodic process of the positive combines with the anodic process of the negative as shown in Figure 11. The battery now has a singular potential – the short circuited potential. This clearly is a mixed potential or could be viewed as a corrosion potential of the system.

Looking at Figure 12, a sketch of a single cell shows that the positive is a paste of PbO_2 in a lead grid. This electrode in the electrolyte clearly must have a mixed potential since metallic lead in the presence of lead dioxide and sulfuric acid is thermodynamically unstable. At the negative the lead grid contains pasted lead! This is also unstable with respect to charging the battery. Both electrodes represent a corrosion control problem!

Really, this is a little too simple, because if the electrodes are fully charged, the voltage may be increased so oxygen and hydrogen are evolved at the positive and negative, respectively. This is indicated by the potential-log current lines in Figure 13. These reactions convert the battery into a potential explosive by the H_2-O_2 recombination to form water if a match is used to aid in seeing how much water needs to be added. If the O_2 reduction could be made to proceed on the negative surface as a local corrosion current, and if the H_2 could be made to undergo oxidation on the positive surface, a hermetically sealed cell could be made. These electrochemical reactions, however, represent forms of local cell reactions familiar to corroding systems.

As any of these reactions proceed at the electrode surface, the surface chemistry is continuously changing. The composition of the local electrolyte in contact with the solids is changing. Thus, the simple chemistry implied by the reaction

$$Pb + PbO_2 + 2\ H_2SO_4 \rightarrow PbSO_4 + 2\ H_4O$$

really does not exist. There are numerous changes of a complex form proceeding on the metal surfaces, on the metallic heavily-doped oxide PbO_2, on the $PbSO_4$ crystallites, on the Pb particulates in the negative grid, as well as in systems of grain boundaries which are present.

Suddenly, as we peer beyond the casual solution chemistry equation, rather complex solid state chemistry is interacting with solution and gas phases processes.
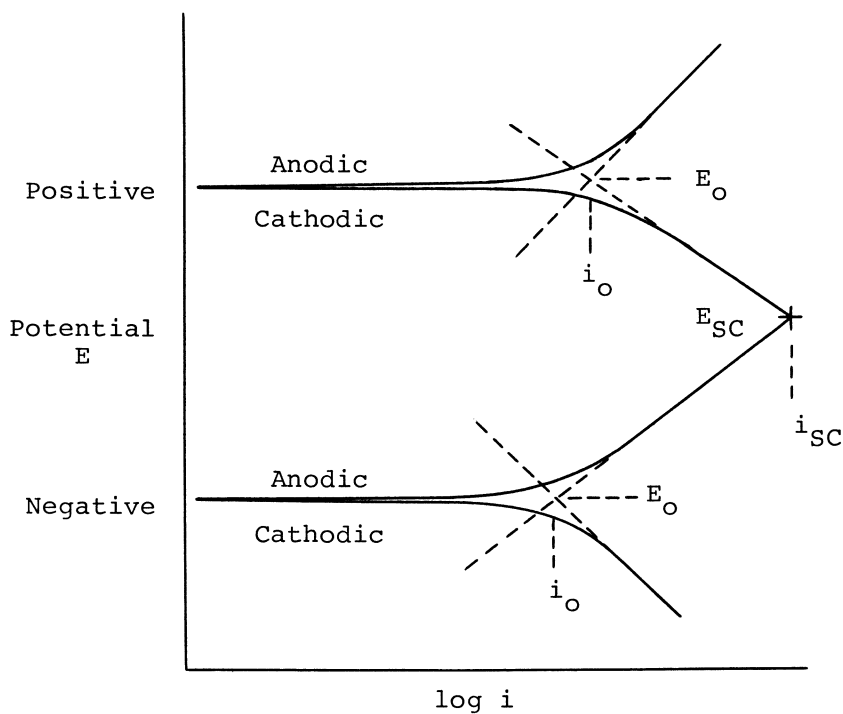
Figure 11.   Short circuit of battery terminals creates characteristic short circuit potential (E_{SC}) and short circuit current (i_{SC}).
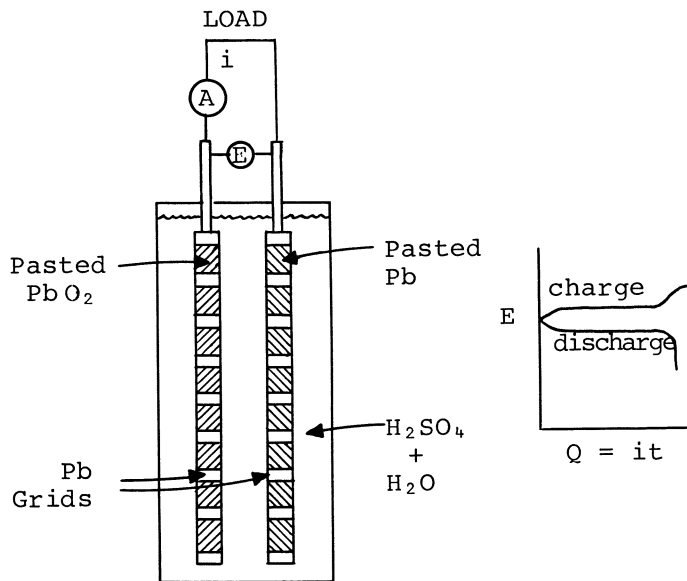
LOAD

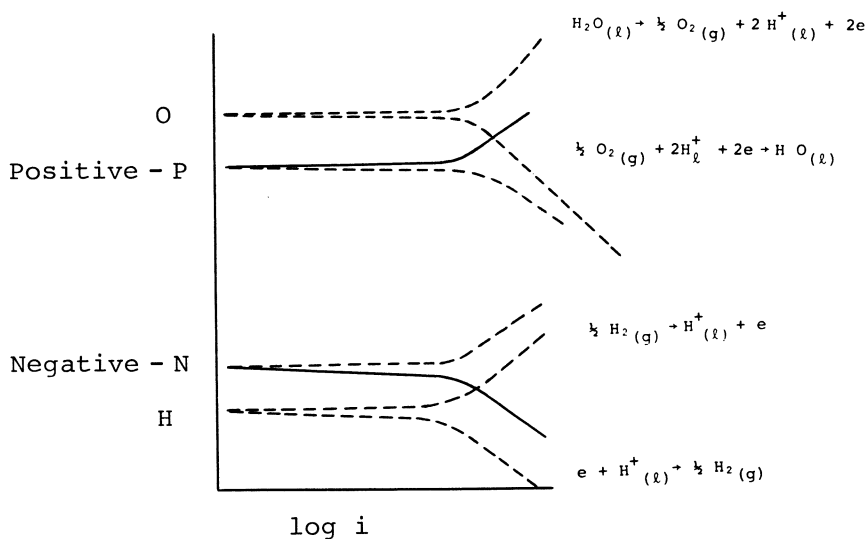*Figure 12.   Simple cell in a lead–acid battery*

Figure 13.   Hydrogen and oxygen evolution reactions at the battery electrode

Clearly the system has electrochemical-chemical exchange currents at the positives and negatives which define the potentials observed. The metal grid must show combinations of $PbSO_4$ film, PbO_2 film, as well as hydride film phenomena. Isn't corrosion chemistry exciting in that black box under the hood?

The battery electrode mixed potential brings attention to the corrosion engineer's problem of controlling either the cathodic or anodic process to minimize the corrosion current. The problems of surface passivation, the question of identifying the distinctive spatial locations of the reaction processes are frequently present in practical situations - what is cathodic to an anodic region or vice versa, what are useful ways to modify the surface processes?

Thus, when attention is given to detail, what appeared as a simple problem initially has with a little thought become complex.

For a few moments let's drop the key words and turn to creating a skeleton for the corrosion engineer's interphase transport processes. We need all the tools possible to bring the materials science resources to our aid. How can we express questions so aid can come from other experts?

Part II

This phase of the discussion is concerned with concepts of solid state chemistry rather than a detailed analysis of a particular case. The objective is to bring attention to a variety of surface chemistry perspectives. This variety can be helpful because the number of ways we can scavenge information from related materials science areas becomes expanded. Further, a variety of seemingly unconnected phenomena can be brought into related ballgames. The multidisciplinary character of real material science is its real richness.

Earlier attention was brought to the corrosion processes of liquid-solid systems. Let's start with a metal contacting an electrolyte as do all electro-chemistry texts.

The simplest model of the electrical double layer between a metal and an electrolyte is the simple capacitor visualized by Helmholtz[1] as shown in Figure 14. The diffuse ion distribution in the liquid phase was recognized by Gouy and Chapman[4,5] to form a space charge region adjacent to the electrode surface.

Stern[6] in 1924 combined the structures to form a compact double layer at the electrode surface with a
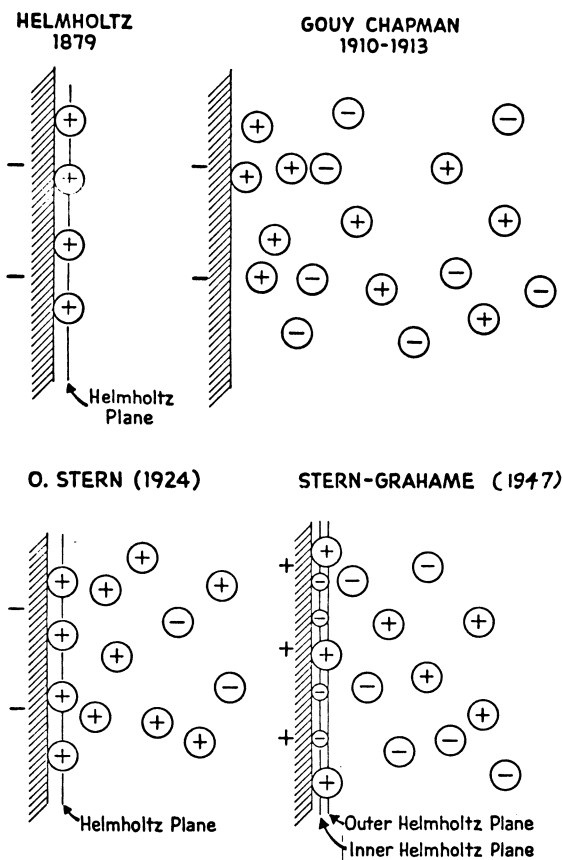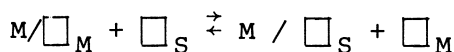
Figure 14.   Models for the electrical double layer at a metal surface

diffuse space charge. In 1947 David Grahame[2] added to
this the specific adsorption of ions forming an inner
and outer Helmholtz plane with hydrated cations not
approaching as closely as the anions at the ideal
metal substrate surface. In this ideal polarizable
electrode model perspective, no charge transfer occurs
between metal and liquid phase - i.e., no Faradaic
processes are present. It is important to visualize
this surface region as formed of atoms, molecules, and
ions having significant thermal vibrational, rotational
and translational energy. The sketched structures are
for only a moment in time but are averaging over space
adjacent to the electrode surface when measurements
are being made.

A subsequent description by Bockris and associ-
ates[8] drew attention to further complexities as shown
in Figure 15. The metal surface now is covered by
combinations of oriented structured water dipoles,
specifically adsorbed anions, followed by secondary
water dipoles along with the hydrated cation structures.
This model serves to bring attention to the dynamic
situation in which changes in potential involve
sequential as well as simultaneous responses of molec-
ular and atomic systems at and near an electrode sur-
face. Changes in potential distribution involve inter-
actions extending from atom polarizability, through
dipole orientation, to ion movements. The electrical
field effects are complex in this ideal polarized
electrode model.

The models clearly have not assigned any atomic
structure to the metal side. With a metallic substrate
Rice, in 1928,[9] showed the electric field penetration
was indeed slight. Consequently, this model was ade-
quate for the ideal polarizable electrode without
Faradaic charge transfer.

A further complication is introduced in Figure 16
where the presence of surface adatoms is indicated as
well as metal lattice vacancies in the substrate
surface. Within the system attention now can be drawn
to Faradaic processes involving the substrate structure.
The transfer of an atom to the surface can be expressed
by the equation

$$M/\square_M + \square_S \underset{\leftarrow}{\overset{\rightarrow}{=}} M / \square_S + \square_M$$

where $M/\square_S$, the surface adatom, is further potentially
involved in the exchange process

$$M/\square_S + n\ H_2O \rightarrow M^+ (H_2O)_n + e + \square_S$$
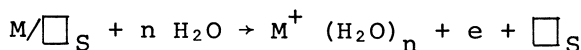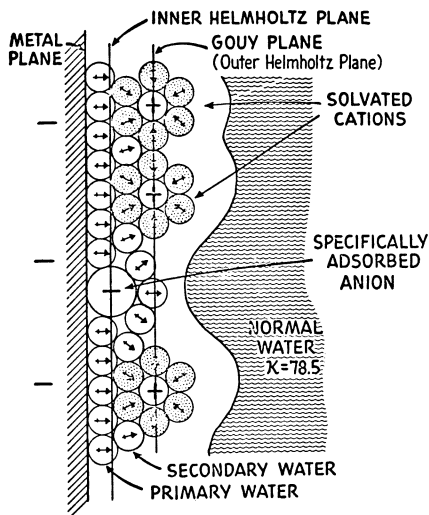
Proceedings of the Royal
Society of London

*Figure 15. Structures of the electrical
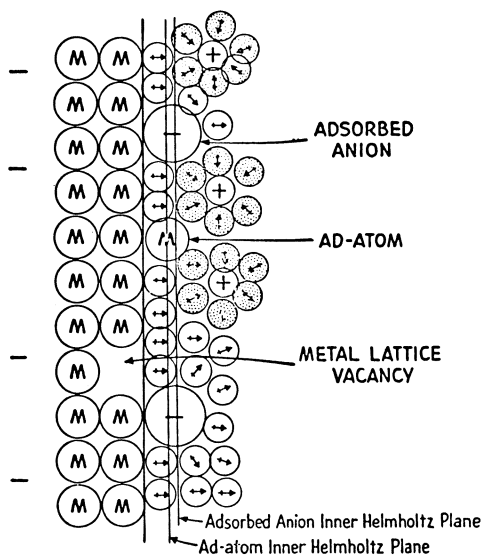double layer, ideal polarizable electrode
(8)*

Figure 16.   Electrical double layer with structure introduced on the metal side

This suggests that attention needs to be given to interphase exchange currents which involve not only electron transfer from the metal surface, but may involve atom exchanges from the bulk to the surface region. The plane metal surface associated with studying the model ideal polarized electrode behavior now becomes part of an interphase system separating metal from an electrolyte or a gas phase system.

The evolution of semiconductor electronics depended upon developing a detailed materials science, first for germanium and then for silicon. This confronted the electrochemist with a further refinement of the electrical double layer systems model. At the surface of a silicon semiconductor crystal the electronic process now is no longer simply an electron transfer from a metal but involves two distinct reactants, electrons or holes. Thus, the following two reactions are not equivalent at the surface of a semiconductor, S:[10]

$$S + OH^- \rightarrow SOH + e$$
$$S + OH^- + p \rightarrow SOH$$
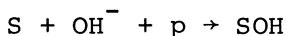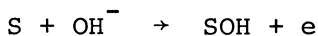
A further complication arises when attention is focussed on the electron density distribution within the semiconductor solid. This, in contrast to the metal case, now is able to vary from a low to a high concentration level as electrons in a conduction band or as holes in a valence band. The electric field on the solid side of the electrical double layer now has spatial extent - a diffuse double layer character exists within the solid. The conventional electric field effects previously associated with ion motion and ion distributions in the electrolyte have a counterpart within the solid phase.

A further complication is brought to the forefront by silicon-electrolyte electrochemical studies. This is the phenomena of surface states at the solid-electrolyte interface. These become critically involved in charge transfer reactions involving complex reactants at the surface. Thus simple electric field distributions are not present except in particular model cases.

On the other hand, rather than having a semiconductor replacing the metal, the actual situation may involve growth of semiconductor layers on a metal surface, or a dielectric film, or more generally a compound MX separating the base metal from the corrosion media. A new phase separates the corroding base from the reactants.

The examination of the material MX as a model two-dimensional lattice solid phase, AB, in Figure 17 is revealing. The material can have a variety of lattice imperfection structures[11] including

interstitial A and B atoms $A/\triangle$, $B/\triangle$
improper site A and B atoms $A/\boxminus$, $B/\boxplus$
lattice vacancies for A and B sites $\boxplus$, $\boxminus$
associated A and B vacancies $\boxed{+|-}$

as readily described by a simplified symbolism. In real systems attention must be given to defining at least conceptually the nature of the phases present. Frequently, under ordinary conditions the solid does not fit any simple stoichiometry or electrical neutrality compound model but is a structure unique to the actual system under study. Thus, useful results may come from unorthodox approaches to real systems.

If attention is given to the combination of a metal M becoming covered with MX the model as shown in Figure 18, several observations can be made as to interphase systems and the growth of the film layer. At the exterior surface a particular combination of interphase exchange currents for solid phase growth can be formulated depending on the detailed character of the solid phase, the surface states, the allowed electronic processes. Similarly, a set of interphase exchange currents can be formulated at the boundary of the metal and the MX layer again subject to constraints defined by the mass transport processes permissible in the covering layer and in the metal.

The situation is illustrated in greater detail in the following model situations where attention is given to the interphase boundary exchange currents injecting the lattice imperfections which are responsible for atom transport through the compound MX.[12]

Thus in Figure 19 lattice vacancy with a trapped hole is injected at the compound electrolyte interface, the imperfection at the metal-compound interface reacts to release a vacancy into the metal. Alternatively, in Figure 20 the exchange process injects a lattice vacancy on the cation lattice which appears at the metal compound interphase to release an electron and transfer a metal ion into the surface region.

Transport models such as these have been created to bring attention to the possibility of the boundary exchange currents injecting imperfection into a crystalline phase during an anodic process. In fact, they may determine the solid phase structures formed. Furthermore, the metal with a solid phase covering film
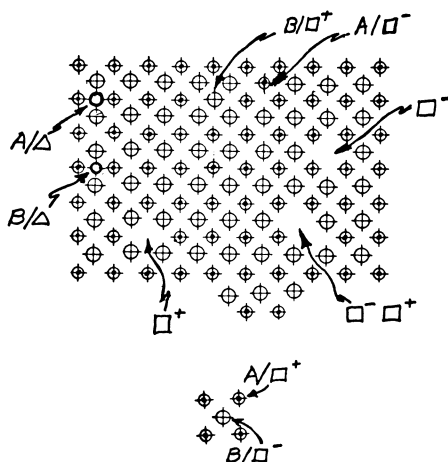
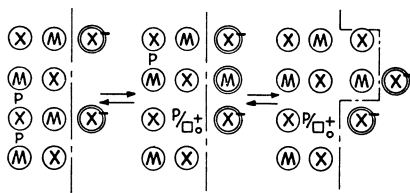Journal of the Electrochemical Society

Figure 17.   A model two-dimensional AB compound lattice illustrating simple imperfection structures expected as a systems variable (12)
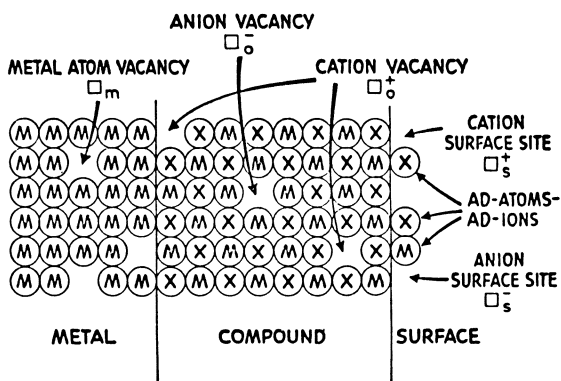
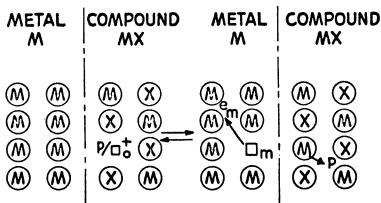Journal of the Electrochemical Society

Figure 18.   Model situation where metal, M, is separated from corroding medium by covering-layer compound (MX) containing imperfection structures (12)

COMPOUND MX—ELECTROLYTE INTERFACE

Journal of the
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Figure 19. Model boundary interphase exchange currents involving the injection of a lattice vacancy with trapped hole at compound–electrolyte interface and vacancy release into the metal with a hole and metal ion in the compound (12)
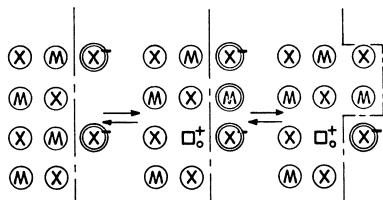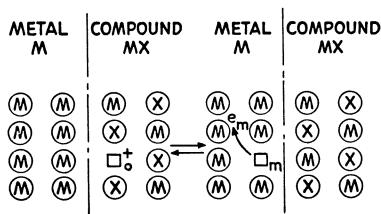
COMPOUND MX—ELECTROLYTE INTERFACE

Journal of the
Electrochemical Society

Figure 20. Model boundary interphase exchange currents involving lattice vacancy injection at the compound–electrolyte interface and vacancy exchange into the metal releasing an electron and transferring a metal ion into the compound layer (12)

can be in reversible equilibrium with an electrolyte
without having exposed metal necessarily in contact
with an electrolyte. In such a model, an increase in
the driving currents may increase the mass transport
rates (alter solid phase structures) within limits so
the rapid phase transformations (M to MX) can occur
without necessarily involving ion-solution and precip-
itation reactions in the ordinary sense.

   This discussion has brought attention to the pot-
ential presence of two classes of interphase transport
conditions in solid state systems. Let us examine
these for a moment from the perspective of forming
solid phases under model conditions.

   For the single interphase exchange process of
solid phase P_2 interactions with P_1 shown in Figure 21,
a series of model conditions are illustrated. For each
a set of interphase atom exchange reactions can be
formulated which have both thermodynamic and kinetic
interpretations. The first is the local deposition of
metallic titanium by the thermal decomposition of $TiCl_4$
gas on a hot wire. This vapor plating technique can be
performed to grow a varied crystallite structure of a
relatively pure titanium on the hot filament. More
generally, vapor plating techniques of many complex
forms are used to grow epitaxial silicon layers of
controlled impurity content onto silicon substrates.
The careful control of conditions results in an amaz-
ingly homogeneous film growth of high semiconductor
quality. The imperfection structure in a composition
and structural sense depends on technique details.

   The second example is electrolytic plating of
copper films. Contrary to some expectations growth
close to equilibrium potential conditions does not
result in the highest quality deposit. In general, the
composition and structure of the deposit depends on the
detailed combination of transport processes towards and
away from the electrode surface. Adding the local
hydrodynamic variables provides the system with an
extremely broad structural chemical range.

   The third example involves growth of a crystalline
salt phase from the saturated solution. The thermo-
dynamic description again is inadequate for describing
the detailed states of the solid. The relatively
anhydrous chloride ion readily deposits into the
surface lattice but the sodium ion must be dehydrated
to form NaCl. This means that water must be diffused
away from the surface during solidification. The white
cast of salt, termed veiling, involves solution incor-
poration during growth with a subsequent diffusion of
the solvent out of the crystal.

IP

| Substrate | P_2 | | P_1 | |

| $P_2 = S_2$ | | P_1 | |
| Filament | Ti | Ti Cl$_4$ gas | Vapor Plating |

| Fe | Cu | Cu^{++} Plating Solution | Electrolytic Plating |

| Seed Crystal | Na Cl | Saturated NaCl | Solution Precipitation |

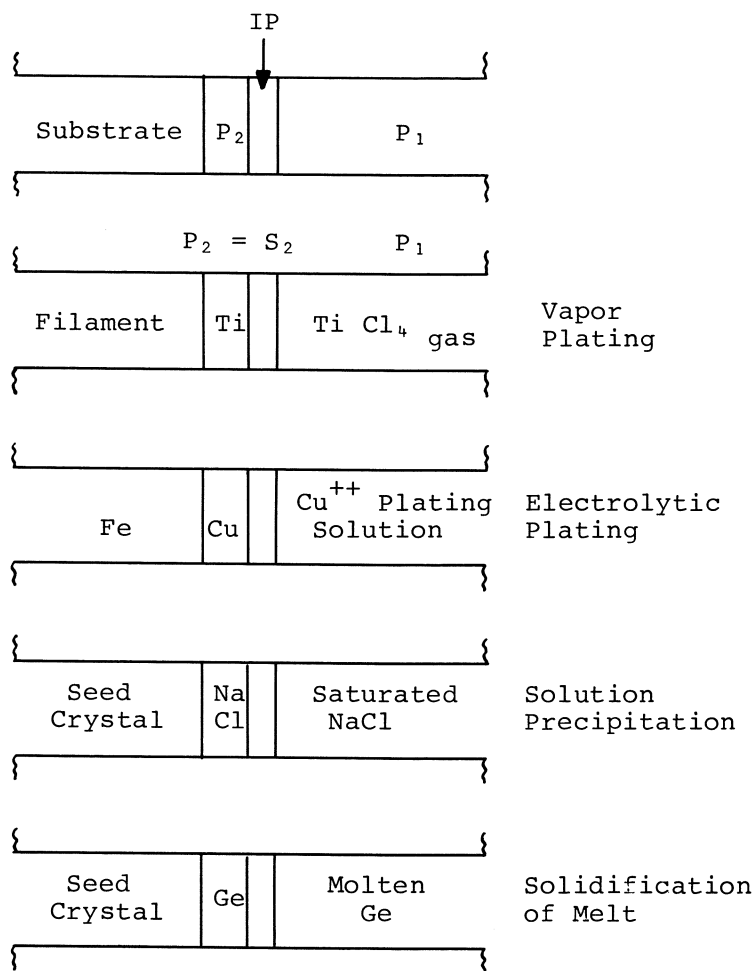| Seed Crystal | Ge | Molten Ge | Solidification of Melt |

Figure 21. Single interphase exchange current model for solid-phase formation (P_2) through interphase reactions with second phase (P_1)

The fourth example is the controlled solidifica-
tion of germanium (or silicon) to produce semiconductor
grade materials. The solid phase structure and compo-
sition depend strongly upon the interphase exchange
processes which can enhance incorporation into the
solid or into the liquid depending upon ??? This
example implicitly includes the production of most of
the metallic structural materials.

The metal alloy systems generally have both con-
trolled and uncontrolled impurities being deposited and
redistributed within the solid as a result of complex
liquid hydrodynamic interphase region processes as well
as secondary solid state diffusion and transformation
processes. This materials science is familiar to all
corrosion engineers who become involved with commercial
systems.

The second interphase transport model incorporates
the dynamic interaction of three phases with two inter-
phase exchange currents at the separated boundaries as
indicated in Figure 22 where a solid phase P_2 is formed
by interactions involving the separated phases P_3 and
P_1.

The classic oxidation of aluminum to form a pass-
ive surface is the first illustration. While the
second model is the anodic oxidation of aluminum, the
interphase transport phenomena here can be distributed
within more complex contexts as a result of the
boundary layer composition changes in the electrolyte.
This model is a particularly fascinating one because
several decades ago it was clear that the large
negatively charged oxygen anion could not migrate in
such oxidation processes - the metal ion +3 aluminum
was small and of course had to transport all the
current through the film. Famous last words that
created a crisis when good transport number experiments
were performed which showed both atoms move in the
film-forming process.[13]

The silver tarnishing reaction involving hydrogen
sulfide is a classic of solid state materials science
literature, and the zinc oxidation is yet another
example of a more complex protective layer corrosion
problem for which wide ranges of data exist relating
to purity, to kinetic conditions, etc.

This interphase exchange current modeling of the
solid phase formation process serves to emphasize the
varied perspectives from which useful information can
be drawn to aid in describing and understanding corro-
sion processes in varied systems. Rarely are the real
systems simple and many pieces of data are examined
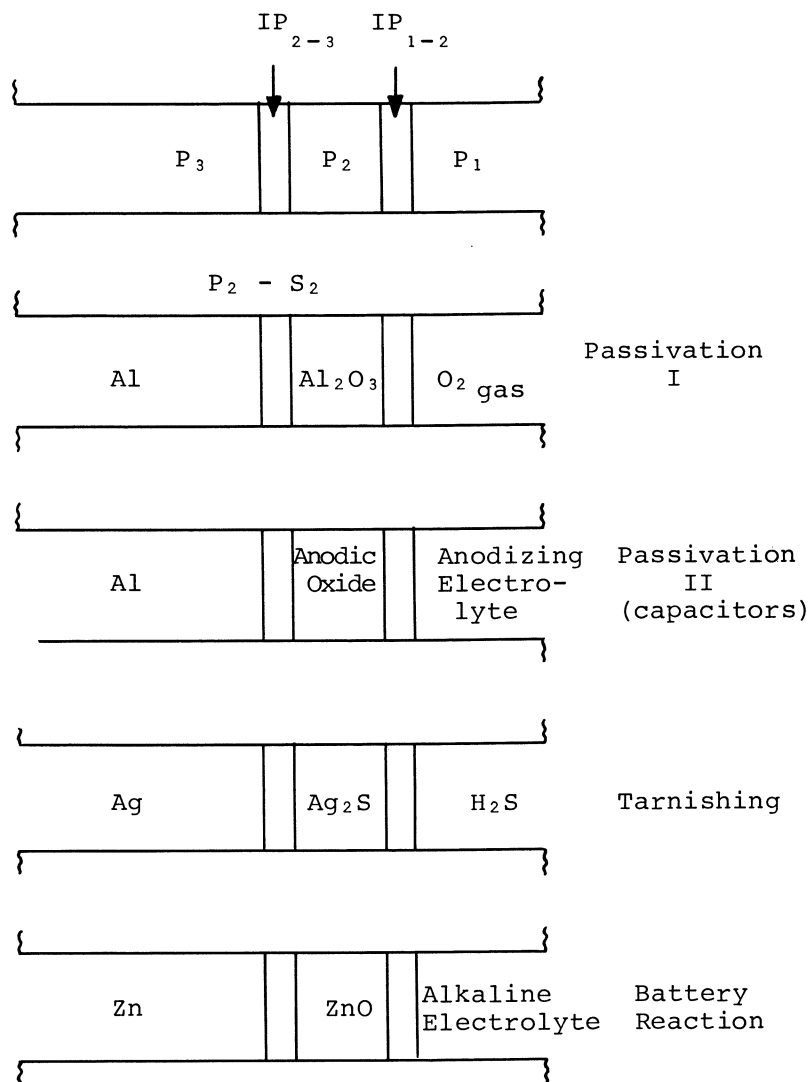before the models do incorporate the full ranges of

Figure 22.   Double interphase exchange current model for solid-phase formation
(P_2) through interphase reactions (IP) at P_2–P_3 and P_2–P_1 boundaries

variables present.

The corrosion engineer's experiences exist in a
complex synergistic relationship to the varied inter-
phase exchange current relationships present within
systems of practical concern. It is indeed rare that
his problems are expressed within any model materials
science contexts. He must necessarily work with the
economically feasible materials for the practical
applications. As the production engineers work with
steadily increasing labor costs in assembly, the
materials engineer - corrosion engineer - wear engineer
become increasingly on the spot to extract the required
values from cheaper materials. It is no joke that
the contract went to the lowest bidder.

What does this mean to all of us assembled here?

First, a recognition needs to exist that in all
practical situations materials science is a tough
ball game - it cannot remain a phenomenological art
if we are expected to warranty the performance.

Second, a recognition needs to exist that, though
the problems are complex, many new tools and skills
are increasingly available to clarify directly the
character of the problems present. The articles which
follow bring attention to this.

Third, a recognition needs to exist that organ-
ized knowledge on solid state chemistry is becoming
increasingly available to us. This is illustrated by
N. B. Hannay's multi-volume Treatise on Solid State
Chemistry.[14] As noted by Hannay in his foreword,

> "... Yet even though the role of chemistry
> in the solid state sciences has been a vital
> one and the solid state sciences have, in
> turn, made enormous contributions to chemi-
> cal thought, solid state chemistry has not
> been recognized by the general body of
> chemists as a major subfield of chemistry ...
> Solid state chemistry has many facets, and
> one of the purposes of this treatise is to
> help define the field."

If chemists are to be the atomic-molecular domain
custodians of solid state materials science, a serious
concern will need to exist for acquiring useful back-
grounds in this area. A significant related publica-
tion is the recent appearance of F. A. Kröger's second
edition of the Chemistry of Imperfect Crystals[15] in
three volumes. The defect chemistry concepts from this
area need to be incorporated more generally into the
new surface science which relates to the environmental

stability of materials.

Fourth and last, but not least, a growing recognition needs to exist that the application of the new complex instrumental techniques can clarify the surface chemistry speculations previously necessary. So frequently our conceptualizations of the real problem are wrong. I personally accept the hypothesis that the first six models when tested in detail will prove wrong. However, as the real model emerges in its complex beauty, the number of paths to optimizations have multiplied and science is no longer dead ended.

The complex instrumentations include LEED, low energy electron diffraction, which is revealing a complex model for surface structure when apparent multilayer adsorption of oxygen proceeds on clean metal surfaces.

It also includes ESCA, electron spectroscopy for chemical analysis, or x-ray photoelectron spectroscopy that can prove that the postulated covering film, by golly, is not covering, and what's the surface composition? Ever try to deal with nine surface components at once? Well, you can seriously explore that distribution for electroless nickel films being deposited on a catalyzed substrate.

It also includes Auger electron spectroscopy microprobe identification of the surface crud in the pit, or definition of the surface composition gradient previously omitted from the speculation on atom transport processes.

The scanning electron microscope provides us neophytes with a realistic look at surface structure as encountered in the system. When teamed with Auger or ESCA a confrontation can be created with self, trying to rationalize the old comfortable models that did not have to acknowledge that surface chemical structure really existed on the "polyphase inhomogeneous solid containing heterogeneity homogeneously dispersed."

Corrosion is here to stay. The wedding to materials science is implicitly reviewed in the first five figures. It is a clearly important complex materials science drawing on all the other disciplines. As the surface science of interphase mass and charge transport phenomena on solids continues to evolve then more clearly, defined new routes for product optimizations will be evident.

Would you agree that corrosion is the most general problem of materials science?

May all have fun exploring the new vistas of our physical world through the following chapters. For

indeed we are all stewards of the utilization of mater-
ials on this scene in service to all. May the mastery
of corrosion extend the resources available to all
those who will celebrate the tricentennial, for few of
us will have this privilege.

Acknowledgements

I would like to specifically acknowledge the chal-
lenge provided by Dr. Rudolph Hausler when he indicated
that preparing the overview would be an easy task. It
wasn't, but it did provide an opportunity to survey
corrosion literature and to recognize more fully the
title of this article: Corrosion (is) the Most General
Problem of Materials Science.

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