International Biodeterioration **25** (1989) 323–326

Comment

BIOFILMS AND CORROSION: A PROCESS ANALYSIS VIEWPOINT

Fouling and corrosion are frequently mediated by microorganisms attached to the metal surface and/or embedded in a gelatinous organic matrix termed a biofilm. Biofilms substantially change the local chemistry of the adjacent metal and thereby enhance corrosion processes. The change in local chemistry is influenced by the micro-environmental conditions at the metal surface including: the number and types of microorganisms present, the dissolved oxygen concentration, the flow velocity, the buffering capacity of the bulk water, and many other factors. Since microbial corrosion is generally localized, the spatial distribution or patchiness of the microbial activity also affects the corrosion processes.

Microbial films of varied composition and thickness develop on surfaces in contact with aqueous environments. Metabolic reactions mediated by certain microorganisms residing in biofilms can promote or impede the biodeterioration of materials including metals, concrete and plastics.

Most confirmed cases of microbial corrosion are characterized as localized corrosion. Discrete mounds or columns related to tuberculation can develop on metal surfaces as a result of microbial activities. The morphology and location of deposits are sometimes indicative of the microbial species that caused the deposit. For example, distinctive hemispherical or conical tubercles on the surface of steel and subsurface

International Biodeterioration (**25**) (1989) —

pitting are characteristic of iron-oxidizing bacteria. Sulfate-reducing bacteria (SRB) produce open pitting or gouging on stainless steel. When SRB are active along the edges of gasketed joints, shallow crevice corrosion is often found under adjacent gasket areas. SRB attack on cast iron typically produces graphitization, whereby the corroded areas are filled with a soft skeleton of graphite. On nickel and cupro–nickel alloys, SRB are reported to produce conical pits containing concentric rings These types of observation have been used to document microbial corrosion problems. Despite the recognition and the documentation, the identification of specific mechanisms for microbial corrosion has remained elusive because of the complexity of microbiological processes and the lack of analytical techniques to quantify localized corrosion

The goal of our work is to integrate the physical, chemical, electrochemical, biochemical, and microbiological processes contributing to microbial corrosion with the processes of biofilm accumulation.

In most, if not all, reported research on biofilms, certain observed or measured quantities are reported: net biofilm accumulation and/or substrate (or oxygen) removal. A difficulty with these observed quantities is that they reflect the contribution of several processes of more fundamental significance. For example, net biofilm accumulation results from the combination of the following processes: a) transport of cells to the substratum, b) adsorption of cells by the substratum, c) growth and other metabolic processes within the biofilm, and d) detachment of portions of the biofilm. If all of the processes occur in series, the slowest step of the sequence exerts the greatest influence and limits the overall process rate. This step is called the 'rate-determining step' or 'rate-limiting step'. If the overall process consists of a number of parallel processes (or processes in series and parallel), the slowest process becomes the 'rate-controlling step'. Identifying the rate-controlling and/or rate-limiting step is critical to successful scale up procedures, and its determination contributes significantly to the insight gained from experimental results. Process analysis permits the determination of the rate-limiting or rate-controlling step in the overall process at different environmental, operating or physiological conditions.

Biofilm accumulation is the net result of the following physical, chemical, and biological processes:

1. Organic molecules are transported from the bulk fluid to the substratum where some of them adsorb, resulting in a '*conditioned*' substratum.
2. A fraction of the planktonic microbial cells are *transported* from the bulk water to the conditioned substratum.

3. A fraction of the cells that strike the substratum adsorb to the substratum for some finite time, and then desorb. This process will be termed *reversible adsorption*.
4. *Desorption* may result from fluid shear forces but other physical, chemical or biological factors may also influence the process.
5. A fraction of the reversibly adsorbed cells remain immobilized beyond a 'critical' residence time and become *irreversibly adsorbed*.
6. The irreversibly adsorbed cells grow at the expense of substrate and nutrients in the bulk water increasing biofilm cell numbers. The cells may also form significant amounts of products, some of which may be excreted. One class of products is the extracellular polymeric substances (EPS) which hold the biofilm together. Thus, biofilm accumulation increases through *microbial metabolism* at the expense of substrate energy in the bulk water.
7. Cells and other particulate matter attach to the biofilm increasing biofilm accumulation. *Attachment* is the immobilization of cells and other particulate matter in the biofilm while adsorption refers to the same processes occurring on the substratum.
8. Portions of the biofilm detach and are reentrained in the bulk water. *Detachment* refers to the loss of material from the biofilm while desorption is loss of cells and other material from the substratum. Detachment may be termed erosion or sloughing depending on the nature of the biofilm loss. Cell multiplication can also lead to the release of daughter cells into the bulk water.

The progression of biofilm accumulation frequently takes the form of a sigmoidal curve which can arbitrarily be classified in three phases: initial events, exponential or log accumulation, and plateau or steady state. The individual processes can be grouped into transport, interfacial transfer, and transformation processes.

Interfacial transfer processes describe the transfer of energy or material between the environment and the system in question (interphase transport), while *transport* describes the transport of energy or material from the system boundary through the system (intraphase transport). Of the fundamental processes listed above, all can be classified as interfacial transfer or transport processes except for metabolism by the immobilized cells and the production of cells and products which are transformation processes.

Transformation processes are those processes resulting in molecular transformations of matter, i.e. chemical or biochemical reactions. Transformation processes are described by rate equations or, more specifically, constitutive or kinetic expressions of the following form:

$$r = r(C_1, \ldots C_n)$$

where r is the reaction or transformation rate and $C_1 \ldots C_n$ are concentrations of the various reacting components. The microbial transformation processes can be classified further: a) microbial growth and reproduction; b) product formation, e.g. EPS; c) maintenance and d) decay.

The above processes are considered fundamental because accepted mathematical descriptions for each process exist. In addition, further detailed structuring of these processes is difficult if experimental validation of the mathematical expressions is desired.

To accomplish an analysis of microbial corrosion processes, the biofilm processes must be interpreted with the electrochemical and physical processes occurring at the metal surface. Corrosion products accumulate at the metal–bulk liquid interface and have a marked effect on the corrosion rate. Oxide films form on metal surfaces exposed to aerobic environments and provide protection against further corrosion. The extent to which these products can adhere firmly, resist removal by turbulent flows, or be restored if damaged determines the ability of an alloy to remain passive and resist corrosion. The manner in which microbial colonization influences the stability of the passive film cannot be predicted and remains the major challenge in microbially induced corrosion.

The approach to developing a unified theory of microbially induced corrosion must be interdisciplinary and include a thorough process analysis combined with well-defined electrochemistry, biochemistry, and microbiology. Specific matters which must be addressed include: 1) the influence of chemical gradients and colonization 'patchiness' on corrosion, 2) the production and accumulation of low molecular weight extracellular products in biofilms and their influence on corrosion, and 3) the role of microbially produced extracellular polymeric substances on biofilm accumulation and corrosion. Finally, the impact of corrosion on biofilm formation should not be ignored since abiotic corrosion processes undoubtedly influence biofilm accumulation.

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