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BIOFOULING CONTROL PROGRAM

PRODUCTS AND APPLICATIONS

The development of biofilms, and the role they play in corrosion and deposition processes, is a relevant factor in the treatment of industrial water systems. This short introduction is designed to provide a basic understanding of biofilms, the problems they cause and the INTECNA's products range and application.

Biofilm consists of microbial cells (algal, fungal or bacterial) and the extracellular polymer they produce. Bacterial biofilms are often responsible for fouling heat transfer equipment for the formation of unpleasant odours, for corrosion attacks, for pipes and heat exchangers plugging and other phenomena. In cooling towers and spray ponds, algal biofilms are also a concern. Algal biofilms foul distribution decks and tower fill, and provide a nutrient (organic carbon) that will help support the growth of bacteria and fungi.

Algae do not require organic carbon for growth but instead use CO₂ and the energy provided by the sun to manufacture carbohydrate. Growth and dispersal of algal cells will provide nutrients that can support a larger and more diverse population of microorganisms.

Microorganisms are found in both the bulk water and on the surfaces of industrial water systems. Bacteria adhere to surfaces by proteinaceous appendages referred to as fimbriae. Once a number of fimbriae have "glued" the cell to the surface, detaching the organism is very difficult. One reason bacteria prefer to grow on surfaces is the organic molecules adsorbed there provide needed nutrients. Once attached, organisms begin to produce slime or extracellular biopolymer

The biopolymer produced can greatly exceed the mass of the microbial cell and may help to provide a more suitable environment for the survival of the organism

The extracellular biopolymer consists primarily of polysaccharide and water. An example of a bacterial-produced biopolymer is xanthan gum. This biopolymer is used as a thickening agent in a variety of food and consumer products. Gellation of some biopolymers can occur upon the addition of divalent cations, such as calcium and magnesium.

The electrostatic interaction between carboxylate functional groups and divalent cations results in a bridging effect between polymer chains. Bridging and crosslinking of the polymers stabilizes the biofilm, making it more resistant to shear

Once bacteria colonize surfaces and produce biofilms, numerous problems arise including reduced heat transfer efficiency, fouling, corrosion and scale

When biofilms develop in low flow areas, such as cooling tower fill, they may initially go unnoticed because they might not interfere with flow or evaporative efficiency. With time, the biofilm becomes more complex, developing a matrix that accumulates debris and impedes flow. Biofilms cause fouling of filtration, ion exchange and heat transfer equipment.

Fouling of heat exchangers can occur quickly either due to a process leak or influx of nutrient. A sudden increase in nutrient can send bacterial populations into an accelerated growth phase with rapid biofilm accumulation.

Algal biofilms foul cooling tower distribution decks, fill and basins. Portions of these may break loose and transport to other parts of the system, causing blockage and accelerated bacterial and fungal growth.

Biofilms can also lead to the formation of mineral scales. Calcium ions are fixed into the biofilm matrix by carboxylate functional groups present on the polysaccharides. Calcium ions held in place by biofilms on heat-transfer surfaces are readily available to react with carbonate or phosphate anions. This process provides crystal growth sites that would not normally be present on a biofilm-free surface.

Additionally, biofilms trap precipitated calcium salts and corrosion by-products from the bulk water that act as crystal growth sites. The growth of bacteria and formation of biofilms can result in another problem: corrosion. **MICROBIAL INDUCED CORROSION (MIC)** may be defined as corrosion that is influenced by the growth of microorganisms. Simply stated, corrosion occurs on a metal surface due to some inherent or environmental difference between one area on that surface and another. These differences create anodic and cathodic sites, setting up a basic corrosion cell

The anode is the area at which metal is lost, while electrons are consumed at the cathode. MIC is an electrochemical corrosion where microorganisms have some influence in the creation or acceleration of corrosion processes.

Microorganisms can influence corrosion in a number of ways. When iron or manganese oxidizing organisms colonize a surface, they begin to oxidize these elements and produce a deposit. In the case of iron-oxidizing organisms, ferrous iron is oxidized to the ferric form ($Fe^{++} \rightarrow Fe^{+++} + 1e^-$) with the electron being utilized by the bacterium for energy production.

The oxidation of iron or manganese by microorganisms is not a requirement for the development of a localized corrosion cell. Corrosion can also occur when localized cells are formed, simply due to the presence of biofilm. Ammonia produced by the reduction of nitrates or nitrites may lead to severe localized corrosion on copper-based metallurgy. The production of organic acids, such as acetic, butyric or citric acid, may help solubilize protective metal oxide films. Inorganic acid, such as sulfuric acid produced by *Thiobacillus* sp., can also have detrimental effects.

Anaerobic, sulfate-reducing bacteria, such as *Desulfovibrio* sp., seek out and colonize areas deficient in oxygen, such as those found in porous corrosion tubercles, within biofilms and under debris. These bacteria are responsible for rapid and severe metal loss. This type of corrosion is easily recognizable from the characteristic sulfide by-product present within the corrosion cell.

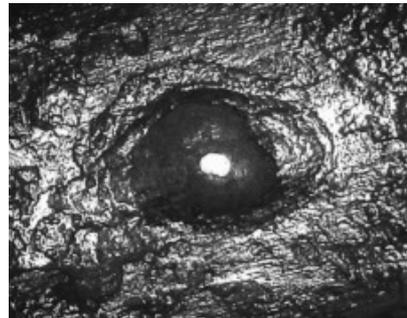
MIC (Microbial induced Corrosion) is extremely aggressive, and in its worst form, will lead to piping failures within a short period of time. Once established, MIC is extremely difficult to eliminate, and may elevate into a chronic maintenance and operating problem. The failure to totally remove MIC from deep pits and the furthest branches and dead legs of a piping system generally results in re-infection by the same microorganisms within a short period of time

When a metal surface is exposed to water, the microorganisms typically resident in the water quickly attach themselves to the surface to form a biofilm - which is a living biological mass composed of bacteria, algae and other microorganisms. Those microorganisms grow, break free, and distribute throughout the piping system. Chemical biocides are generally applied to prevent the growth of such microorganisms, although they are not always effective. Even under well controlled conditions, MIC can develop within a short period of time due to a variety of factors. Once MIC has gained a solid presence in the system, the reliance on biocides alone as a corrective measure becomes worthless

Many forms of MIC types exist to present different levels of threat. Some microorganisms are capable of producing metal dissolving metabolic by-products such as sulfuric acid, and are often identified within a classification termed sulfur reducing bacteria, or SRB.

MIC attack often results in accelerated corrosion rates exceeding 20 MPY and more - causing penetration of some metal surfaces in as little as one or two years.

The below close-up photographs will illustrate the deep penetration typical of an MIC infection. In many examples, the surrounding area suffers only moderate deterioration, or little metal loss at all.



SRB are anaerobes that are sustained by organic nutrients. Generally they require a complete absence of oxygen and a highly reduced environment to function efficiently. Nonetheless, they circulate (probably in a resting state) in aerated waters, including those treated with chlorine and other oxidizers, until they find a "ideal" environment supporting their metabolism and multiplication.

SRB are usually lumped into two nutrient categories, those that can use lactate and those that cannot. The latter generally use acetate and are difficult to grow in the laboratory on any medium. Lactate, acetate, and other short chain fatty acids usable by SRB do not occur naturally in the environment. Therefore, these organisms depend on other organisms to produce such compounds.

SRB reduce sulfate to sulfide, which usually shows up as hydrogen sulfide or, if iron is available, as black ferrous sulfide. In the absence of sulfate, some strains can function as fermenters and use organic compounds such as pyruvate to produce acetate, hydrogen, and carbon dioxide. Many SRB strains also contain hydrogenase enzymes, which allow them to consume hydrogen. Most common strains of SRB grow best at temperatures from 25° to 35°C. A few thermophilic strains capable of functioning efficiently at more than 60°C have been reported.

SRB have been implicated in the corrosion of cast iron and steel, ferritic stainless steels, 300 series stainless steels (also very highly alloyed stainless steels), copper nickel alloys, and high nickel molybdenum alloys. They are almost always present at corrosion sites because they are in soils, surface water streams and waterside deposits in general. Their mere presence, however, does not mean they are causing corrosion. The key symptom that usually indicates their involvement in the corrosion process of ferrous alloys is localized corrosion filled with black sulfide corrosion products.

BIOFILM FORMATION CONTROL

Too often microbiological control efforts focus only on planktonic (free-floating) organisms. While useful data may be gathered from monitoring daily bacterial counts, monthly or weekly counts may have little meaningful use. Planktonic counts do not necessarily correlate to the amount of biofilm present.

In addition, planktonic organisms are not generally responsible for deposit and corrosion problems. There are a few exceptions, such as a closed-loop system, where planktonic organisms may degrade corrosion inhibitors or reduce pH.

Systems with low planktonic counts may have a significant biofilm problem and vice versa. Therefore, efforts should focus on biofilm control.

Biofilms can be controlled through the use of microbicides and biodispersants.

Biocides can be classified broadly into two groups: oxidizing biocides and nonoxidizing biocides. In general, oxidizing biocides are used only in freshwater systems because their activity is rapidly consumed by organic matter in produced waters. The nonoxidizing biocides cover a wide spectrum of chemical compounds that can be used in many different types of environments.

Oxidizing Biocides

Chlorinating compounds include bleach (sodium hypochlorite solution [NaOCl]) and calcium hypochlorite (dry chlorine [Ca(OCl)₂]). The use of these materials avoids the dangers and inconvenience of handling chlorine gas, but the materials are bulkier and more expensive. The addition of large amounts of calcium might also create scaling problems in some systems. Monographs are available to calculate the amounts of chlorinating compounds required to produce the hypochlorite ion in concentrations equivalent to those produced by chlorine.

Chlorinating compounds offer the following advantages:

- They circumvent the danger of handling chlorine; and
- They are as effective as chlorine.

Among the compounds' disadvantages are the following:

- They can cause scaling problems;
- They are expensive; and larger quantities are needed than when using chlorine.

Chlorine dioxide (ClO₂) is an effective oxidizing agent that can be used to remove organic material, biomass, and iron sulfide deposits from a system.² This makes its use in downhole cleaning of injection and disposal wells very attractive. Chlorine dioxide is effective in a wider pH range than hypochlorite and is less affected by organic material and ammonia.

Because of its sensitivity to pressure and temperature, chlorine dioxide cannot be transported and must be generated on site. Three precursors are generally used to produce chlorine dioxide: sodium hypochlorite (NaOCl), hydrochloric acid (HCl), and sodium chlorite. A two-stage reaction process is required. The first stage involves reacting 15% HCl and 10% NaOCl to produce 6% aqueous chlorine:

Chlorine dioxide offers the following advantages:

- It is pH insensitive;
- It is a good oxidizing agent for biomass;
- It tolerates high levels of organics;
- It dissolves iron sulfides.

Some disadvantages of chlorine dioxide include:

- Special equipment is required for generation;
- It is a toxic compound; and it is expensive.

Bromine (Br₂) is analogous to chlorine. Generally it is used in the form of a solid compound (1-bromo-3-chloro-5,5-dimethylhydantoin), which releases bromine hydroxide and chlorine hydroxide into the water.

The advantages of bromine are:

It is more effective than chlorine at higher pH; and

It has broad-spectrum activity.

The disadvantages of bromine are:

It is similar to chlorine compounds; and It is expensive.

Nonoxidizing Biocides

Aldehydes

Formaldehyde (HCHO) is used generally as an aqueous solution (37%). It has restricted applications because high doses are required for it to be effective.

An advantage of formaldehyde is that it is economical

Formaldehyde's disadvantages are:

It is a suspected carcinogen;

High dosages are required; and

It reacts with ammonia, hydrogen sulfide, and oxygen scavengers.

Glutaraldehyde (pentanedial, OCH[CH₂]₃CHO) is used widely in the petroleum industry.⁴ It is sometimes used in a blend with other biocides or surfactants to increase its effectiveness.

Glutaraldehyde offers the following advantages:

It has broad-spectrum activity;

It is relatively insensitive to sulfide;

It is nonionic (compatible with other chemicals); and

It tolerates salts and hardness.

A disadvantage of using glutaraldehyde is that it is deactivated by ammonia, primary amines, and oxygen scavengers.

Acrolein(H₂C=CHCHO; 2-propenal) is a highly reactive material that is an effective biocide and sulfide scavenger. It is a gas at ambient temperature and extremely irritating to eyes and mucous membranes, so it must be handled carefully. It is injected by pumping or displacement using oxygen-free nitrogen.

Acrolein has the following advantages:

It is a broad-spectrum biocide; and

It penetrates deposits and dissolves sulfide constituents. Acrolein's disadvantages are:

It is difficult to handle;

It is reactive with polymers, scavengers, etc.; and it is highly toxic.

Quaternary amine compounds ([R₁R₂R₃R₄ N]⁺ X⁻) have been used for many years in the oil industry.

The products are generally used in low-total dissolved solids waters. Generally these compounds function best at alkaline pH levels. Quaternary amine compounds have such advantages as:

They have broad-spectrum activity;

They have good surfactancy;

They have persistence; and

They have low reactivity with other chemicals.

The compounds' disadvantages include:

They are inactivated in brines;

They are foaming; and

They are slow acting.

Amine and diamine biocides also are used. The most commonly used amine/diamine (R-NH₂, R-NH-R-NH₂) is the cocodiamine. These materials usually are neutralized with an acid, such as acetic acid, to form a watersoluble salt.

The advantages of amines and diamines are:

They have broad-spectrum activity;

They have some inhibition properties;

They are effective in sulfide-bearing waters; and

They are surface active.

Their disadvantages include:

They react with other chemicals, particularly anionics; and

They are less effective in waters with high levels of suspended solids.

Halogenated Compounds

Bronopol ($C_3H_6BrNO_4$, 2-bromo-2-nitropropane-1,3-diol) is a dry product sold as a powder or compressed into a solid stick. It has been used in drilling and completion fluids as well as produced fluids.

Its advantages are:

Its broad spectrum activity;
Its low human toxicity; and
Its ability to degrade.

Bronopol's disadvantages are:

It is a dry chemical; and
It breaks down in high pH.

Another compound, **DBNPA** (2,2-dibromo-3-nitrilo propionamide $CHBr_2CNCONH_2$), also has been used. DBNPA's advantages are:

It has broad-spectrum activity; and
It is fast acting and effective.
Its disadvantages are that it is:

Expensive; and
Affected by sulfides.

Sulfur Compounds

Isothiazolone (C_4H_4NOCIS) has been used for several years to kill sessile bacteria. It is inactivated by sulphide, so it may not be effective in killing sulfate-reducing bacteria (SRB) in mature big films.

Its advantages are:

It has broad-spectrum activity;
It is compatible with brines;
It has good anti-sessile bacteria activity;
Low dosages are required; and
It is degradable.

Isothiazolone's disadvantages are:

It cannot be used in sour systems; and
It is expensive.

Carbamates (alkyl thiocarbamates) may be a better choice than isothiazolone in some circumstances.

The advantages of using carbamates are:

They are effective against SRB and spore formers;
They are effective in alkaline pH; and
They are useful for polymer solutions.

Carbamates have certain disadvantages:

High concentrations are required; and
They react with metal ions and other compounds.

Quaternary phosphonium salts $[(CH_2OH)_4P-X]$ (X = anion, for example, Cl^- , SO_4^{2-} , PO_4^{2-}) are new to the oilfield biocide market. They have been reported to travel through the formation with injection water and have been analyzed in injection water returns at the producing facility.

Their advantages include:

They have a broad spectrum of killing activity and good stability;
They have low toxicity; and
They are stable and unaffected by sulfides.

Because the use of quaternary phosphonium salts is recent, its disadvantages are unknown.

BIOFOULING CONTROL GUIDELINES

Microbicides, both oxidizing and non-oxidizing, can be effective in overall biofilm control when applied properly. The oxidizing microbicides, such as chlorine, bromine, chlorine dioxide and ozone, can be extremely effective in destroying both the extracellular polysaccharide and the bacterial cells.

When using oxidizing microbicides, a sufficient residual residence time must be maintained to effectively oxidize the biofilm.

Unfortunately, concern for the corrosive nature of the oxidizing microbicides leads to insufficient residual/microbe contact necessary for effective control. Low residual oxidant levels may significantly reduce planktonic counts but may not be sufficient to control biofilm. The level of oxidant and duration required will vary.

In some systems it may be more effective to maintain a higher residual for a shorter duration than it is to continuously maintain a very low residual.

In some cases, continuous low-level feed may not achieve a residual sufficient to oxidize the biofilm.

It is well known that chlorine is ineffective for controlling microorganisms at elevated pH. Hypochlorous acid (HOCl) is significantly more microbicidal than the hypochlorite ion (OCl⁻).

However, the hypochlorite is very effective at oxidizing the extracellular polysaccharide and the proteinaceous attachment structures. Therefore, the use of chlorine in alkaline cooling waters can still be an effective biofilm control strategy. This is especially true when combined with a compatible non-oxidizing microbicide, such as Quaternary or Phosphonium salts.

Non-oxidizing microbicides are also effective in controlling biofilm. Control is greatly dependent on the frequency of addition, concentration and the resistance of the incumbent population to the product being fed. A typical application may include the addition of product two to five times per week. As with oxidizing microbicides, frequency and dosage will depend on the system conditions.

It is generally most effective to alternate non-oxidizing microbicides to ensure broad spectrum control. Most non-oxidizing microbicides will have little effect in destroying extracellular biopolymer, although some microbicides may be able to penetrate and kill organisms found within the biofilm.

The combined use of non-oxidizing and oxidizing microbicides is an effective means of biofilm control. When using non-oxidizing microbicides in conjunction with an oxidizing agent, no oxidant residual should be present at the time of addition. Sufficient time should be allowed for the non-oxidizing microbicide to work before resuming oxidant feed unless an oxidant-compatible microbicide is being used .

Biofilm control programs can be made more effective through the use of biodispersants. Products that penetrate and loosen the biopolymer matrix will help to slough biofilm and expose the microorganisms to the effects of the microbicide. These are especially effective when dealing with systems that have a high nutrient load and a tendency to foul.

In the following scheme are reported the suggested conditions, the average dosages and the products more diffused to biofouling INTECNA's program

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MICROORGANISM	REQUIRED DOSAGE (ppm) average	SUGGESTED PRODUCT HYCOR RANGE NON OXIDIZING BIOCIDES	SUGGESTED TREATMENT
BACTERIA			
ASPERGILLUS FOETIDUS	30	AK - PHG - IG	Coupling with Oxidizing Biocide
ASPERGILLUS NIGER	40	AK - PHG - IG	Coupling with Oxidizing Biocide
ASPERGILLUS ORIZAE	25	AK - PHG - IG	Coupling with Oxidizing Biocide
CANDIDA ALBICANS	25	AK - PHG - IG	Coupling with Oxidizing Biocide
CLADOSPORIUM RESINAE	25	AK - PHG - IG	Coupling with Oxidizing Biocide
LENTINUS LEPIDEUS	30	AK - PHG - IG	Coupling with Oxidizing Biocide
PENICILLUM FUNICOLOSUM	30	AK - PHG - IG	Coupling with Oxidizing Biocide
PENICILLUM VARIABILE	20	AK - PHG - IG	Coupling with Oxidizing Biocide
AUREOBASIDIUM PULLULANS	20	AK - PHG - IG	Coupling with Oxidizing Biocide
SACCHAROMYCES CEREVISIAE	10	AK - PHG - IG	Coupling with Oxidizing Biocide
ACHROMOBACTER PARVULUS	10	AK - PHG - IG	Coupling with Oxidizing Biocide
ALCALIGENES FOECALIS	10	AK - PHG - IG	Coupling with Oxidizing Biocide
AZOTOBACTER VINELANDII	10	AK - PHG - IG	Coupling with Oxidizing Biocide
ENTEROBACTER AEROGENES	25	AK - PHG - IG	Coupling with Oxidizing Biocide
FLAVOBACTERIUM SUAVEOLENS	30	AK - PHG - IG	Coupling with Oxidizing Biocide
NITROBACTER AGILIS	10	AK - PHG - IG	Coupling with Oxidizing Biocide
PROTEUS VULGARIS	30	AK - PHG - IG	Coupling with Oxidizing Biocide
PSEUDOMONAS AERUGINOSA	30	AK - PHG - IG	Coupling with Oxidizing Biocide
PSEUDOMONAS CEPACIA	10	AK - PHG - IG	Coupling with Oxidizing Biocide
PSEUDOMONAS FLUORESCENS	10	AK - PHG - IG	Coupling with Oxidizing Biocide
PSEUDOMONAS OLEOVERANS	30	AK - PHG - IG	Coupling with Oxidizing Biocide

SALMONELLA TYPHOSA	30	AK - PHG - IG	Coupling with Oxidizing Biocide
BACILLUS SUBTILIS	20	SB	
SARCINA LUTEA	30	SB	
STAPHYLOCOCCUS AUREUS	20	SB	
STAPHYLOCOCCUS EPIDERMIDIS	20	SB	
STREPTOMICIS ALBUS	10	SB	
IRON BACTERIA – SRB			
THIOBACILLUS NOVELLUS	50	SB	
LEPTOTHRIX DISCOPHORA	50	SB	
HYPOMICROBIUM INDICUM	50	SB	
SPHAEROTILUS NATANS	50	SB	
ALGAE			
CHLORELLA OLEOFACENS	10	AK	Coupling with Oxidizing Biocide
CHLORELLA PYRENOIDOSA	10	AK	Coupling with Oxidizing Biocide
SELENASTRUS CAPRICORNUTUS	10	AK	Coupling with Oxidizing Biocide
ULOTHRIX FIMBRIATA	10	AK	Coupling with Oxidizing Biocide
ULOTHRIX ACUMINATA	10	AK	Coupling with Oxidizing Biocide

PRODUCTS PROFILE

HYCOR SB

HYCOR SB is a totally water soluble biocide.

The product is effective in controlling biological fouling and microorganism populations in a variety of water system and particularly indicated for the water to be used in cooling circuits, paper production, pipeline hydrotesting procedures, sugar production, milk derivatives production etc.

The active principle of HYCOR SB reduce the microorganism levels which lead to biofilm formation and allow the growth of anaerobic Sulphate Reducing Bacteria. The product requires a dosage of 50 - 200 ppm depending on the conditions of the system to be treated. HYCOR SB is normally injected directly in the system without dilution.

HYCOR AK

HYCOR AK is a totally water soluble biocide.

The product shows a strong bactericidal and fungicidal efficiency, so it is effective in controlling biological fouling in a variety of water system and particularly indicated for the water treatment in paper production .

The active substances of HYCOR AK (Dimethyl - Alkyl Ammonium Chloride - Alkyl Phosphonium derivatives) reduce the microorganism levels which lead to biofilm formation and allow the growth of anaerobic Sulphate Reducing Bacteria. The product requires a dosage of 50 - 200 ppm depending on the conditions of the system to be treated. HYCOR AK is normally injected directly in the system without dilution.

HYCOR IG

HYCOR IG is a totally water soluble biocide. The product is effective in controlling biological fouling and microorganism populations in a variety of water system and particularly indicated for the water to be used in cooling circuits, paper production, pipeline hydrotesting procedures, sugar production etc.

The active principles of HYCOR IG (Glutaraldehyde/Isothiazolones) reduce the microorganism levels which lead to biofilm formation and allow the growth of anaerobic Sulphate Reducing Bacteria. The product requires a dosage of 50 - 200 ppm depending on the conditions of the system to be treated. HYCOR IG is normally injected directly in the system without dilution.

HYCOR PHG

HYCOR PHG is a totally water soluble biocide. The product is effective in controlling biological fouling and microorganism populations in a variety of water system and particularly indicated for the water to be used in cooling circuits, paper production, pipeline hydrotesting procedures, sugar production etc.

The active principles of HYCOR PHG (Glutaraldehyde/Phosphonium Salts) reduce the microorganism levels which lead to biofilm formation and allow the growth of anaerobic Sulphate Reducing Bacteria. The product requires a dosage of 50 - 200 ppm depending on the conditions of the system to be treated. HYCOR PHG is normally injected directly in the system without dilution.