Microbial Life in Geothermal Waters

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Abstract
Geothermal waters usually contain many salts, often in varying concentrations. Some of these salts, especially if they consist of oxidizable or reducible ones, can be subject to microbial conversion and/or (bio)precipitation. Microorganisms can oxidize, sometimes even under anoxic conditions, reduced sulfur compounds, iron(II)ions, manganese(II)ions to mention just a few important ones. On the other hand, partially or fully oxidized compounds can be reduced by microorganisms. To be mentioned are sulfur compounds, iron(III)ions, manganese(IV)ions, nitrogen oxides like nitrite and nitrate, and finally bicarbonate and carbonate ions. If organic compounds are present, these may also be oxidized or reduced. A plentiful of microorganisms exists, which are able to perform such metabolism under aerobic or anoxic conditions. All these (bio)processes allow bacteria to grow and proliferate. Consequences may be biocorrosion and biodeterioration. The growth requirements and the biodeterioration mechanisms will be discussed in this review.

Introduction
Micobial life in geothermal waters has been detected quite some time ago. The most important contribution results from the work of Brock and coworkers on the occurrence of such life forms in Yellowstone Park, USA. Although earlier evidence existed, Brock was the first to analyze and describe on a large scale microorganisms thriving in hot geothermal waters. In the course of this pioneering work all types of metabolism, from auto- via mixo- to heterotrophic were found and described. Also, the use of various energy sources, lithotrophic, phototrophic, and/or organotrophic, besides aerobic or anaerobic metabolism were detected. Consequently, Brock openend the door to a new microcosm, which thrived under these, previously unexplored conditions. In the following years many researchers have added evidence to the diversity of life in such environments (deep sea hydrothermal vents, continental deep drilling program, long term underground storage of radioactive wastes, volcanic sites in general, etc). Nowadays it is widely accepted that such geothermal environments are suitable habitats for many microorganisms and, thus, in case of technical use problems due to the interference of these microbes with the technical installations may arise.
Geothermal waters usually contain many salts, often in varying concentrations. Some of these salts, especially if they are oxidizable or reducible ones, can be subject to microbial conversion and/or (bio)precipitation. Microorganisms can oxidize, sometimes even under anoxic conditions, reduced sulfur compounds, iron(II)ions, manganese(II)ions to mention just a few important ones. On the other hand, partially or fully oxidized compounds can be reduced by microorganisms. Such compounds are the various sulfur compounds (including elemental sulfur, giving rise to sulfide), iron(III)ions, manganese(IV)ions, nitrogen oxides like nitrite and nitrate (giving rise to nitrogen gas or ammonium ions), and finally bicarbonate and carbonate ions (to be reduced to methane). If organic compounds are present, these may also be oxidized or reduced giving rise to carbon dioxide. A plentiful of microorganisms exist, which are able to perform such metabolism

under aerobic or anoxic conditions. All these (bio)processes allow bacteria to grow and proliferate.
The growth of microorganisms is generally, thus also under geothermal conditions, limited by the availability of nutrients, carbon compounds, water, and temperature. Besides these, other parameters like pH, redoxpotential, availability of trace nutrients etc plays an important role. In the following the most important chemical and physical parameters are explained, which regulate the proliferation of (microbial) life.

Microbial growth conditions

There are several factors influencing the growth of microorganisms, among these are availability of water, minerals, nutrients, oxygen or other gases, temperature, redoxpotential, and pH. All these factors influence the composition of the microbial biocoenosis in a habitat. Each factor has a broad range, which microorganisms can tolerate, mostly separated into more narrow areas for different kinds of microorganisms. Not all factors are of equal importance to geothermal habitats, but have to be taken into account, at least in cases of unprecedented problems.
Water. The most important factor for microbial growth is the availability of water. The measure for availability is the water activity, a_w. It is given as the quotient of the vapour pressure of a solution containing dissolved compounds, P, divided by the vapour pressure of distilled water at the same temperature, P_0:

$$a_w = \frac{P}{P_0}$$

Bacteria and expecially fungi can resist "dryness" to a considerably larger extent than plants, animals, and especially human beings. Whereas human life already becomes restricted at a_w-values of 0.999, bacteria can resist to these conditions easily. The a_w-values for bacteria are in the range of 0.9 - 0.8, with the lowest value found for halophiles (in salines) of 0.75. Fungi are even more resistant. Their lowest value is about 0.6. An example is the extremely dangerous *Xeromyces bisporus*, which grows in the lumber construction of roofs. For the degradation of the lumber the fungus needs water. Thus, it sends its hyphae often over distances of more than 30 m into the cellar/soil for water acquisition. On its way the hyphae are able to penetrate stone, mortar, or even concrete. Consequently, if a roof is infected with this fungus, all lumber has to be exchanged plus parts of the (mineral) walls, etc. to avoid reinfection. This makes such an infection very expensive for the owner. Besides, due to the danger of infection of neighbouring buildings such cases have to be notified to the local authorities.
Minerals. (Micro)organisms need for their metabolic processes a variety of minerals. To be mentioned are N, S, P, K, Ca, Mg, and Fe, which are needed in quite large amounts, and the trace minerals like Mn, Mo, Zn, Cu, Co, Ni, V, B, Cl, Na, Si, Si, and W. The latter are used for the complementation of specific enzymes, electron transfer compounds, etc as central atoms of prosthetic groups. Besides, some microorganisms need a supply of vitamins for growth. The need for these minerals and vitamins can be very specific and varies from one microorganism to another. In case of specific deterioration causing bacteria this need may allow for very efficient countermeasures.
Temperature. Microbial growth is limited by the availability of water and the stability of the cellular compounds like membranes, enzymes, etc. Thus, it is difficult to define a lower limit, since highly concentrated salt solutions have even after being frozen at –30°C niches with liquid water. In these niches a few adapted microorganisms may survive, as research in Siberia and Arctica/Antartica has shown. Consequently, it is difficult to determine an absolute lowest value

for growth. The upper known value for life is at present at 116°C, temperatures found in the deep sea at hydrothermal vents. Around 130°C starts the spontaneous decomposition of nucleic acids and proteins, consequently life should not be expected at temperatures considerably above the current limit of 116°C. The term to describe the various temperature ranges, in which microorganisms grow, are the following:

psychro- or kryophiles	temperature range	< 0°C up to 20°C
psychrotrophs	temperature range	0°C to 30°C
mesophiles	temperature range	10°C to 40°C
moderate thermophiles	temperature range	35°C to 55°C
thermophiles	temperature range	50°C to 85°C
extreme thermophiles	temperature range	75°C to 95°C
hyperthermophiles	temperature range	> 90°C

Oxygen usage. Microorganisms may also be distinguished by their oxygen demand/usage. Strict aerobes have a fully oxygen-dependent metabolism. Facultative aerobes may use oxygen, but also are able to use other electron acceptors like inorganic Fe(III), Mn(IV)) or organic (succinate, pyruvate, etc.) compounds. The same is valid for facultative anaerobes, only that these organisms grow in contrast to the previously mentioned ones preferably under anaerobic conditions. Finally, the strict anaerobes need to be mentioned. These are organisms, for which oxygen is toxic and cannot be used for any type of metabolism.

Redoxpotential. The redoxpotential is an indication of the oxidative/reductive potential of anions and cations in solution. The value does not determine the growth of microorganisms, but allows to deduct the metabolic type to be present. Microbial life occurs in the range between (roughly) –500mV and +800mV. At pH 7 and standard conditions these values resemble the potentials of H_2 and of O_2, respectively. All metabolic processes take place in the range between these upper and lower limiting values (biological oxygen/hydrogen-reaction). The redoxpotential can be assigned to various types of metabolism. An addition of these compounds to the medium consequently will result in the modification of the dominant type of metabolism. This is simply a consequence of thermodynamics, since the larger the difference between electron donor and acceptor, the more energy is available for the growth of a microorganism. Consequently, the organisms able to use oxidants (electron acceptors) with a more positive redoxpotential grow better and, thus, outcompete those growing only with more reduced electron acceptors.

pH. The pH is an important parameter for description and limitation of microbial growth. Basically, three main categories need to be distinguished. At high proton concentrations acidophiles grow. They are subdivided into strong and moderate acidophiles with pH-ranges of < 0 to 3 and 2 to 5, respectively. The second category are the neutrophiles growing between pH 5 and 9. Finally, at low proton concentrations the alkaliphiles take over. These organisms are able to grow even at pH as high as 12, as has been found in alkaline lakes (lake Natron in Africa). Interestingly, fungi are more resistant to pH-extremes than bacteria. Organisms like *Aspergillus niger* have been shown to occur at pH 2 and at pH 10. However, at these extreme values generally specialized bacteria are the dominant microorganisms. Furthermore, in most cases fungi prefer slightly acidic conditions, whereas most bacteria thrive under neutral to slightly alkaline ones.

Carbon- and energysource. An important differentiation of microorganisms results from their source of carbon and/or energy (electrons). As shown in Table 3, several types need to be taken into account. If the energy results from solar radiation, the organism is called phototroph, whereas any chemical reaction is resulting in chemotrophy. In case of chemotrophy, again two sources need to be differentiated. In case of an inorganic electron donor the term is lithotrophy, whereas in case of an organic one organotrophy results. Finally the carbon source may be inorganic CO_2 from the air with the resulting term autotrophy or the carbon source may be another organic compound causing heterotrophy. By combination of these terms, the metabolism of a strain may quite precisely be described.

Obviously, light may be neglected in case of underground installations. However, in case of geysers etc, it may play an important role as energy source.

Biofilm and biofouling. A biofilm is an assembly of microbial cells, living or dead, embedded in extracellular polymeric substances (EPS). In addition, organic and inorganic particles may be present, too. Biofouling is a technical expression indicating that fouling, which took place on a technical surface, is caused by living organisms. In the consequence of this process, technical characteristics of materials and/or apparatus may be changed. Osmosis membranes do not function anymore due to biofilm/biofouling meaning that a film has formed, which clogs the pores causing an increased pressure to be necessary for functioning. Heat exchangers loose their exchange capacity by biofouling, because of an insulating biofilm. Even corrosion may result from the formation of biofilm/biofouling, due to the formation of aeration/corrosion cells under biofilm covered and non-covered areas (cathode/anode). The primary process is caused by the adhesion of microorganisms to materials surfaces. As previously discussed, the EPS confer to microorganisms a means for attachment to surfaces of materials and, besides, seem to be involved in the degradation of insoluble substrates. Recent ecological research has indicated that about 90% of all microorganisms in the natural environment occur attached to surfaces. Only a small percentage seems to be free-living as planktonic organisms. The reasons for this behavior are the prevailing nutrient conditions. Under natural conditions a surplus of nutrients only extremely rarely exists. Thus, the natural nutritional state of a population is hunger. Only under artificial, man-made conditions this may be changed (pollution, biotechnology, etc.) and will result in totally different populations and behaviour of these. In case of a hunger, meaning a shortage of nutrient, it is much more advantageous for a microorganism to remain at one site (attached) and not to use energy for movement in order to actively search for nutrients. Besides, due to turbulences the available nutrients may be transported to the site of the attached organism. Consequently, the attached mode of growth is considerably more advantageous than the planktonic one. Further benefits of attached growth are the protection, a biofilm may confer against desiccation, action of biocides, and/or other toxic compounds, grazing of protozoa (amoebae), and the possibilities for exchange of genetic material for adoption of new metabolic capabilities (lateral gene transfer).

It also became obvious in the last years that the biofilm mode of growth confers to the cells an enlargement of their radius of action. E.g. it is known for a long time that exoenzymes are responsible for the cleavage of polymers like cellulose, lignin, or protein. This fact was never connected with biofilm/biofouling. Recent evidence indicates that the exoenzymes are deliberately excreted and, somehow, in a yet unkown way, the cells collect the cleavage products. Thus, their radius of action becomes considerably enlarged, as has been shown for the process of bioleaching of pyrite (which can also be called a biocorrosion of a metal sulfide). Consequently, leaching bacteria are mainly found to be attached to surfaces of metal sulfides. This principle may in general be valid for organisms growing at the expense of solid substrates. Therefore also sulfate reducing bacteria, SRB, need to be included in this scheme, since in a biofilm they are protected against oxygen and, furthermore, the Fe(II)ions are delivered directly to the cells, to react with the metabolic endproduct H_2S for detoxification by a formation of insoluble iron sulfides, FeS and FeS_2.

Summarizing it has to be pointed out that the precise knowledge of all these growth parameters is of utmost importance in case of countermeasures to be applied against biodeterioration. Although never pure cultures are responsible for such problems, a change in the parameters discussed above often results, at least temporarily, in a substantial reduction of the problem. Therefore, a careful examination is needed to allow for a successful measure. Even more, it might help to avoid the often recommended chemical weapon of biocide usage, which always is also detrimental to the environment.

Mechanisms of microbial deterioration

Despite the many varying factors involved, the mechanisms of biodeterioration can be described by a few main categories. An overview of the mechanisms is given in Table 1.

Physical presence of microbial cells. Sometimes, the physical presence of microbial cells is sufficient to cause damage of equipment. The electronics industry, for example, is sensitive in this respect. Because of the tiny dimensions of electronic conductors, a 4-MB chip has a critical lateral defect size of 0.15 µm, with a size for the smallest structures of 0.5 µm. Sedimented microbial cells with dimensions of about 0.3-2 µm diameter and fungal cells of about 5 µm and above will result in a connection of neighbouring electronic conductors. As a consequence, this type of industry has to use clean air technology to keep this type of failure at a minimum.

Inorganic acids (including CO_2). Two important strong inorganic acids are produced by microorganisms as an end-product of their metabolism-nitric and sulfuric acid. Only highly specialized, lithoautotrophically growing bacteria are able to produce these acids. If these bacteria are growing on a material (substratum) that may react chemically with the acids (e.g. concrete or iron), deterioration may result (corrosion). Sulfuric acid is generated mainly by bacteria belonging to the genera Thiobacillus and Acidithiobacillus. Nitric acid is usually formed by nitrifying bacteria of the genera Nitrosomonas (or Nitrosovibrio) and Nitrobacter. Acidithiobacilli and thiobacilli are acidophilic or at least acid-tolerant bacteria and are able to fix CO_2. The species Acidithiobacillus thiooxidans and At. ferrooxidans survive values below pH 1. Because of this ability, they are of importance in acid attack on materials. The requirements for nutrients are modest. The sources of energy are reduced inorganic sulfur compounds. A few species, for example Thiomonas intermedia or T. novellus, need an additional supply of vitamins such as biotin. Organic compounds often inhibit the growth of these bacteria.

The nitrifying bacteria are not as acid-resistant as thiobacilli. They also have modest growth requirements. Most of them build up their cell material by CO_2-fixation. The sources of energy are ammonium compounds, urea, nitrite, and possibly NO. Besides trace elements, a few may use organic compounds. Both groups are lithoautotrophic microorganisms and have been shown to cause considerable damage to mineral materials, e.g. concrete, natural stone, glass, etc.

All living organisms excrete carbon dioxide as an end-product of their metabolism. Although it is a weak acid, carbon dioxide may cause also serious deterioration of susceptible materials. In the case of cementitious-bound concrete, the system CaO/ $Ca(OH)_2$/CaSiO2 will react with CO_2 to form $CaCO_3$, a reaction known as 'carbonatization'. This results in a serious reduction of the (alkaline) pH in the surface water on concrete: it falls from about 12.5 (fresh concrete) to 8.5. Because this pH is no longer prohibitive for microorganisms, they may start to grow and, for example by acid production, reduce the pH even further, leading to an acid attack on concrete. However, even if no further acid attack ensues, at a pH of 8.5, the iron/steel reinforcements of concrete become susceptible to corrosion because the passivation by the strongly alkaline pH no longer exists. This type of corrosion is usually a slow process. However, taking into account that sewage pipelines shall have a service life of about 50 to 80 years, this biogenic attack may, nevertheless, cause considerable problems. In any case, the effect of carbonatization, the attack of a weak acid on concrete/lime, may be characterized as a permissive effect allowing microorganisms to grow in a previously hostile environment and excrete deleterious end-products. Besides concrete (cementitious-bound), materials such as limestone, marble, etc. may be endangered.

Table 1.. Main Biological Stress Factors Affecting Materials

Mineral Acids	Sulfurous Acid (H_2SO_3) Sulfuric acid (H_2SO_4) Nitrous acid (HNO_2) Nitric acid (HNO_3) Carbonic acid (CO_2/H_2CO_3)
Organic acids	Oxalic acid ($H_2C_2O_4$) Gluconic acid ($H_8C_6O_7$) Citric acid ($H_8C_6O_7$) Formic acid (H_2CO_2) ...and many more
Organic solvents	Ethanol, acetone. propanol, butanol
Hydrogen sulfide	H_2S (to sulfuric acid or to metal sulfide precipitate)
Nitrous oxides	NO, NO_2
Salts	Hygroscopic (= increased water content = increase of crystal volume by inclusion of watermolecules = swelling attack in pores)
Biofilm	Clogging of pores Decrease of porosity Increase of humidity (enhanced physical attack as freezing-thawing)
Exopolymers	Nucleation sites (= precipitatations, scaling)
Enzymes	Degradation of organic constituents
Complexing/emulsifying compounds	Organic acids Phospholipids Lipoproteins Lipopolysaccharides

Organic acids. Generally, most microorganisms excrete organic acids, while metabolizing organic and inorganic compounds. Organic acids may react with working materials by two mechanisms: by the action of protons and by chelation of metal ions. The acidic effect of organic acids is comparable to that of mineral acids. However, a distinction needs to be made between strong and weak organic acids. Acetic, gluconic, glucuronic, oxalic, oxalacetic, succinic, malic, glyoxylic acid are worth mentioning in this context. Besides `simple' organic acids, molecules, such as amino acids or polysaccharides with ionic groups, may be excreted. The second important effect, chelation, will be discussed below. The excretion of organic compounds is usually the result of an unbalanced growth. Because of metabolic bottlenecks and/or a surplus of substrate and/or a limiting supply of nitrogen or phosphorous compounds, organic compounds are excreted into the medium during metabolism. In some cases, the organic compounds are end-products of metabolism, e.g. in the case of acetic acid, which is excreted by some sulfate reducers or by acetic acid-generating bacteria.

Organic solvents. Many microorganisms are capable of metabolizing organic compounds via fermentation. As a result, other organic compounds are formed, which, in many instances are organic solvents. Organic acids like acetic, formic, or butyric acid as well as alcohols (ethanol, propanol, butanol, etc.) and ketones are noteworthy. These solvents may react with materials of natural and/or synthetic origin, causing swelling, total or partial dissolution and, finally, deterioration.

Salt stress. Anions, the final product of microbial metabolism, react with cationic components of ceramic materials to salts. These salts are often highly water soluble and, thus, are hydrated. Their presence results in an increased water content of porous mineral. If dryness causes desiccation, a formation of salt crystals results. Often, the crystals require an increased volume, which causes a 'blasting' deterioration of porous materials.

Furthermore, the increased water content renders ceramic materials susceptible to a physical attack like the freeze-thaw attack. This attack is an example of a complex interaction of an microbiological effect with a physical attack, in which the impact of microorganisms cannot be distinguished from the impact of physical forces (and, hence, not separately be quantified).

Noxious compounds-hydrogen sulfide and nitrogen oxides. Hydrogen sulfide is produced predominantly by anaerobically growing microbes. SRBs reduce oxidized sulfur compounds, such as sulfate, sulfite, thiosulfate, thionic acids, and sulfur, to H_2S. The reaction is used as a sink for electrons originating from organic substrates. It enables SRB to grow oxidatively under anaerobic conditions. For some reactions, e.g. if sulfate is used as an electron acceptor, the available energy is only slightly lower than for aerobic oxidative metabolism with O_2. Sulfate as the most important sulfur compound is ubiquitously present in water. Thus, H_2S may be produced, whenever anaerobic conditions occur. However, recent work has shown that SRB may be oxygen-tolerant or even may be able to use some oxygen (under reduced partial pressure) for an oxidative metabolism. As a consequence, the general opinion on oxygen toxicity for SRB needs to be reevaluated. In addition, H_2S is a result of the degradation of sulfur-containing amino acids. Under aerobic conditions, the amino acid cystein (and the dimer cystin) is degraded to H_2S, NH_3, and CO_2. In biotopes containing such amino acids like sewage, the aerobic degradation is a source of hydrogen sulfide. Hydrogen sulfide may cause several problems. From the chemical point of view, it is a weak acid and reacts with cations to sulfidic compounds. With heavy metal ions, insoluble metal sulfides form and precipitate. In the case of metals, this may result in severe corrosion. In the case of mineral materials, H_2S is important as a nutrient source for aerobic thiobacilli producing sulfuric acid (either directly or after autooxidation of H_2S to sulfur with O_2).

A variety of nitrogen oxides occurs in the atmosphere, in soil, and in water. The most important are nitrous oxide (N_2O), the nitric oxides NO and NO_2, nitrite NO_2^-, and nitrate NO_3^-. The importance of nitrate, the anion of nitric acid, has been explained above. Nitrite, the anion of nitrous acid, is a reactive compound, and may be oxidized to nitric acid by bacteria (genus Nitrobacter) or may be reduced to NO either by microorganisms (aerobically and/or anaerobically, denitrification) or by a chemical reaction with a compound such as sulfur dioxide (chemodenitrification).

NO may be reduced further to N_2O by microorganisms (anaerobically, denitrification). NO also may be oxidized to NO_2, e.g. by the action of ultraviolet light. Whereas NO is only slightly soluble in water (about 8 mg /L, comparable to oxygen), NO_2 is highly soluble in water. The dissolution yields nitrite and nitrate. Hence, NO_2 may be called the anhydrite of nitrous and nitric acid. Nitrous oxide, N_2O, is an intermediate product of denitrification. It will be anaerobically reduced to dinitrogen N_2. Microorganisms active in denitrification use the chemically bound oxygen for an oxidative metabolism. In the case of nitrate, this process is nearly as efficient as the use of free oxygen, O_2. From the main nitrogen oxides (many more are occurring in the environment because of the complex chemistry of nitrogen and its compounds, which may react forming dimers, etc.), only nitrous oxide seems to be of little importance for the biodeterioration of mineral materials. Nitrite is a well-known substrate for nitrifying bacteria yielding nitrate. Thus, the anion of a weak acid is transformed to the anion of a strong acid, which may react accordingly. NO_2 gives rise to nitrite and nitrate and, thus, may cause a deleterious effect. NO, as preliminary evidence suggests, may be oxidized by, for example, nitrifying bacteria via nitrous acid to nitric acid and, in this way, exert deleterious effects. Summarizing, the action of,nitrogen oxides on mineral materials may be described as an enhancement of an acid attack and/or as the generation of acidic reactants from gaseous atmospheric pollutants. Furthermore, NO_2 is a strong oxidizing agent. Recently, it has been shown that biogenic NO, resulting from the biological process of nitrification, considerably enhanced the chemical conversion of sulfite to sulfate, causing an increased sulfuric acid attack (besides an increase in the salt concentration) on natural stone. The process required the presence of a nitrifying biofilm. Further deleterious effects of NO and NO_2 may be detected in the future.

Biofouling and biofilm. Microorganisms growing on and/or in mineral materials often excrete exopolymers. Exopolymers contain ionic groups, which cause them to function like ion-exchangers. Together with metabolic end-products like acids (and the derived salts), an increased water content of porous materials results. The consequences have been described above. Biofilm and its exopolymers aggravate this problem by clogging the pores of materials reducing evaporation of water. Another important effect of clogging is a reduced penetration of protecting agents either because the pore space is occupied or because the reaction time of organic resins is already exceeded a few millimeters below the surface. This effect is dangerous because it may result in the formation of crusts, which tend to flake off in the course of freeze-thaw attacks. The layer with resin-filled pore space reacts towards temperature changes physically different from the untreated stone below (different dilatation coefficients). Thus, at the boundary, cracks and fissures occur. If the attack and its resulting deterioration are severe enough, whole surfaces of buildings may be lost.

Another type of failure results from the growth of microorganisms on surfaces, e.g. of heat exchangers. Since biofilm is preventing the direct contact between the circulating liquid and the (metallic) surface of the equipment, a reduced efficiency of the heat transfer (either in or out, depending on the use) results. Furthermore, the reduction of the void of a pipeline may cause an increased velocity of the circulating liquid or a reduced throughput. In some cases, an increased pressure may result. In the case of biofilm/ biofouling on ship hulls, a reduced cruise velocity or an increased fuel consumption is the consequence.

Another effect may be the induction of anaerobic conditions below biofilm/biofouling. In the case of susceptiple materials such as iron, the growth and activity of SRB may be furthered, causing hydrogen sulfide production accompanied by biocorrosion (see above). This may be regarded as an indirect effect.

Exopolymers and nucleation sites - scaling. Recently, exopolymers have become of interest to geobiologists. The extracellular polymeric substances, exopolymers or EPS, consist chemically of the basic compounds sugars (with and without substituents), uronic acids, proteins, nucleic acids, and lipids. Besides, some metal ions like Ca^{2+} and/or Mg^{2+} have been shown to be an integral part of the EPS. In specialized environments like acidic leaching habitats iron(III)ions occur in the EPS. These complexed metal ions seem to be nucleation sites for (bio)precipitate formation. E.g. in leach environments with high concentrations of iron(III)ions besides other metal ions, cells become totally encrusted in by iron precipitates, which seem to start at the outside of the cell in the surrounding EPS-layer. The leaching bacteria Acidithiobacillus ferrooxidans and Leptospirillum ferrooxidans have been shown to contain in their EPS iron(III)ions in concentrations of up to 50g/L. Since such high concentrations are even under acidic conditions not stable and tend to precipitate (which is by these bacteria prevented by complexation with uronic acids), fluctuations in the redox potential can easily cause the formation of iron hydroxides and further the formation of coprecipitates. Thus, these iron ions can be seen as nucleation sites for precipitate formation. Microscopic observation has shown, consequently, that such precipitates are intergrown with microbial cells. EPS are thus sites, due to complexed metals, where precipitations are initiated. In this way in geothermal environments with their often high salt concentrations a microbial colonization of materials surfaces may cause extensive precipitations to occur: the scaling problem. Other effects like alkalinization, which might also be due to microbial activity, can also be relevant for this scaling problem.

Exoenzymes. Microorganisms living on insoluble compounds often excrete exoenzymes to degrade these into small fragments. The fragments then may be taken up and metabolized. An example is the biodeterioration of wood (cellulose) being degraded to cellubiose and, finally, glucose, which is used as the substrate. In the case of purely mineral materials, compounds that may serve as a nutrient source are non-existent. Thus, for these materials, exoenzymes are not important for a microbiologically, influenced attack. If, however, organic substances, such as resins, waxes, carbohydrates, or other compounds, are added to inorganic materials to achieve improved virtues, this might render them susceptible to attack by exoenzymes.

Chelating agents, emulsifying compounds. Besides the acidic action of organic acids, most of these compounds are able to complex metal ions and, thus, to dissolve these. Usually, these complexes are rather stable. Hence, `insoluble' compounds are dissolved because the cations are removed in spite of an extremely low solubility product. This may cause corrosion effects of mineral materials. Besides organic acids, exopolymers of microorganisms containing anionic groups such as amino acids, peptides, or sugar acids, may act as complexing agents. Furthermore, emulsifying compounds, such as phospholipids (excreted by microorganisms), are known to be involved in the biological degradation of insoluble compounds such as pyrite, sulfur, etc. Because of an increased hydrophilicity, the formerly hydrophobic substances become biodegradable. For example, the solubility of elemental sulfur is increased because of the excretion of an emulsifying agent, with a concentration of 5 to 20 000 µg/L, by a sulfur degrading bacterium. A similar mechanism is reported for hydrocarbons.

Conclusions

Summarizing these effects, it becomes obvious that only a few main mechanisms are involved in microbiologically influenced corrosion of mineral materials. However, these mechanisms are the result of a vast diversity of microorganisms with certain growth requirements and a different response to environmental stress factors. The microorganisms actually involved certainly differ from case to case, and a thorough investigation involving environmental parameters as well as data on the substratum are needed for an analysis of the underlying mechanisms. Only with an understanding of the complex processes occurring in microbiologically influenced corrosion countermeasures may be developed successfully. These often need simulation equipment (biotests) to develop reliable procedures/chemicals, etc. However, only rarely do appropriate biotests exist because of the complexity of the factors involved. Progress in this field requires considerable research efforts in the future.

Although this overview describes the major growth conditions and biodeterioration mechanisms, not all of them may be applicable to geothermal waters in general. However, it becomes obvious that microorganisms can interfere in many ways with man-made geothermal installations. Consequently, in case of problems like corrosion and scaling combined with clogging of water pipelines the participation of miccroorganisms should be taken into account, especially for repair or exchange. For such a purpose sampling and analyses by experienced personnel with a solid background on MIC (microbially influenced corrosion) of materials is required. Furthermore, due to the often prevailing anaerobic conditions the use of sophisticated sampling techniques combined with appropriate storage and transport of such samples is necessary. The processing of the samples also requires specialized equipment in order to be able to detect and quantify the relevant microbes and to come up with a proposal for countermeasures and/or the use of appropriate installation materials.

If such an approach would be used, it may be expected that the involvement of microbes in the currently as pure chemistry explained problems will become obvious. Furthermore, due to the unique conditions of geotheermal underground reservoirs, which have not been touched by humans so far, a plentiful of unknown microorganisms waits for their detection. In the course of the characterization of these unknown microbes may be discovered that may help to reduce their impact on affected geothermal installations.

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