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REVIEW

Corrosion of Metallic and Structural Elements Exposed to Acid Mine Drainage (AMD)

Juan Carlos Fortes[1,2] · **José Miguel Dávila**[1,2] · **Aguasanta Miguel Sarmiento**[1,2] · **Ana Teresa Luís**[3] · **María Santisteban**[1,2] · **Jesús Díaz-Curie**[4] · **Francisco Córdoba**[5] · **José Antonio Grande**[1,2]

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Abstract

Mining equipment and structural elements (e.g. bridges, mining exploration equipment), which are mainly made of steel and concrete, undergo corrosion processes that are strongly accelerated in these extremely acidic environments, with the further aid of acidophilic bacteria that act as catalysts.

Keywords Concrete · Bacterial activity · Dissolved oxygen · Acidity

Introduction

There are several types of corrosion, but this review focuses on the two types caused by acidic mine waters (AMD): chemical corrosion, caused by sulphur compounds and other acidic agents; and microbiological corrosion, in which biological organisms cause the alteration or accelerate the corrosion process (Javaherdashti 2008; Rawat 1976). When metals are submerged in water, they tend to corrode due to their thermodynamic instability (Evans 1937; Pourbaix 1987; Uhlig 1964). Most mining machinery is constructed from different alloys of steel and is very sensitive to severely acidic water. Corrosion can lead to thinning, brittle fractures, fatigue cracking, and failure. Both metallic elements and artificial materials, such as rubber seals or conveyor belts, can corrode because of the chemical composition of the AMD and their microorganisms.

Corrosion reactions can be stimulated by the activity of microorganisms, particularly when they contact the surface of the metal, creating a biofilm (Little and Wayner 1992; Videla 2001). The outcome of this process is identified as biocorrosion or corrosion influenced by microorganisms (MIC). There are several species of the acidophilic bacteria in the genus Acidithiobacillus, which thrive in low pH conditions in a variety of geo-climatic contexts (Aguilera 2013; Amils et al. 2011, 2014; Colmer et al. 1950; González-Toril et al. 2003). These bacteria are also sources of environmental pollution due to their ability to accelerate AMD generation and corrode cement and concrete structures. This causes big losses since it involves the destruction of equipment, waste of working hours, and loss of production, with the final cost estimated to be as high as $551.4 billion per year all over the world (Koch et al. 2005), and $310 billion in China alone in 2015 (Hou et al. 2017). Metallic materials form the infrastructures of industrial complexes, machinery, and installations. The machines' metallic elements that contact with AMD, suffer continuous cracking or corrosion, as can be seen in Fig. 2 (Subrahmanyam and Hoey 1975; Wu et al. 2018b). As in all other industries, corrosion is a constraining obstacle in mining, the more so because, with increased mechanization, the problem of corrosion is only getting worse (Salazar-Jiménez 2015).

✉ Juan Carlos Fortes
jcfortes@uhu.es

[1] Department of Water, Mining and Environment, Scientific and Technological Center of Huelva, University of Huelva, 21004 Huelva, Spain

[2] Sustainable Mining Engineering Research Group, Department of Mining, Mechanic, Energetic and Construction Engineering, Higher Technical School of Engineering, University of Huelva, Avda. de las Fuerzas Armadas, S/N, 21071 Huelva, Spain

[3] Department of Geosciences, GeoBioTec Research Unit, Campus de Santiago, 3810-193 Aveiro, Portugal

[4] Escuela Técnica Superior de Ingenieros de Minas, Ríos Rosas 21, Madrid, Spain

[5] Department of Environmental Biology and Public Health, Faculty of Experimental Sciences, University of Huelva, Huelva, Spain

In the Iberian Pyrite Belt (IPB), several mining operations have been reactivated due to the high price that minerals have reached in recent times (Grande et al. 2018). However, the companies have serious corrosion problems and so a multidisciplinary research team was assembled, through two funded projects. This team found that this problem has been poorly addressed and that relevant information is scattered; hence, the idea for this work.

The main objective of this project was to complete a bibliographical review on the nature and outcomes of corrosion by acid mine water on metallic and reinforced concrete elements. Between February and August 2018, a bibliographic study of published work was conducted, using various documentary sources such as: ScienceDirect, Scopus, Web of Science, and Journal Citation Reports, using the descriptors: acid mine drainage, acid rock drainage, corrosion, electro erosion, oxidation pyrite, pH and corrosion, electrochemical corrosion, and microbiological corrosion. An internet search was also carried out in the search engine "Google scholar" with the same terms. The reports obtained were screened to suit the requirements of the project and those that did not meet it were discarded. The searches gave results ranging from 16 to 1685 records after combining the different keywords. The documents that were relevant to corrosion of mining machinery and structural elements with acid mine water were selected for this review.

Factors Influencing AMD Corrositivity

Interactions between AMD and mechanical and concrete elements are a critical corrosion issue. The rate of corrosion in this water is affected by several variables: dissolved oxygen concentration, pH, temperature, microbial activity, and the characteristics of the solution itself, etc. These variables are also interrelated.

Dissolved Oxygen

Metal corrosion in water is proportional to the dissolved oxygen (DO) concentration. DO is an important parameter intimately correlated with physical, chemical, and biochemical processes in water. Oxygen is required for respiration of the iron-oxidizing bacteria (Kleinmann 2006). The DO decreases as the temperature rises (Fig. 1).

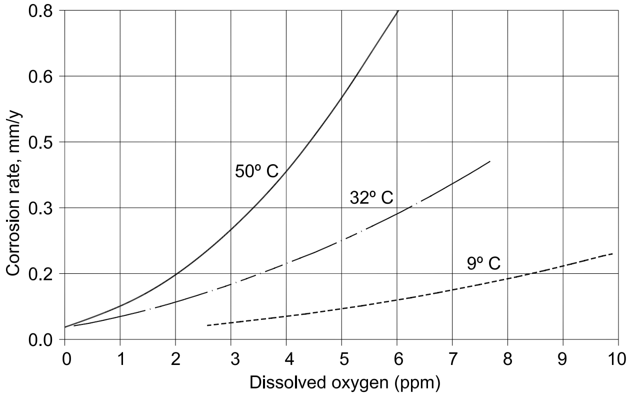

Fig. 1 Effect of oxygen concentration on the corrosion rate at different temperatures [modified from IEA (2010)]

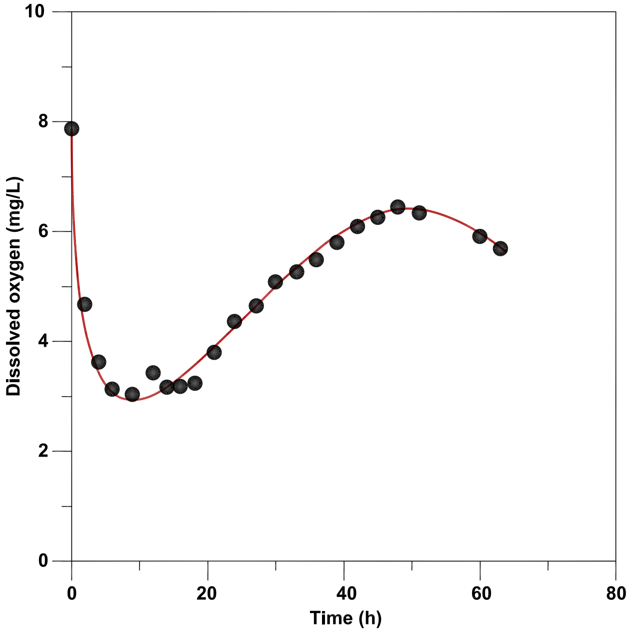

Fig. 2 Dissolved oxygen concentration as a function of time in mine ponds [modified from Lee et al. (2016)]

Lee et al. (2016), while working on the relationship between flow and water quality in mine ponds, also found variations in DO concentration (Fig. 2). After the AMD was put into the tank, the DO concentration decreased for the first 6 h due to the fast oxidation process. After that, the oxygen supplied by the water surface and the oxygen consumed by Fe^{2+} oxidation reached an equilibrium, keeping the DO at a constant level. After 20 h, the oxygen supply started to exceed consumption, allowing the DO to increase. After 45 h, the DO concentration dropped and then gradually decreased as the AMD moved towards the main outflow of the pond (Fig. 2).

Acidity

The extremely low pH values of some AMD (Sarmiento et al. 2018) makes them highly corrosive. The corrosion rate is different depending on the material type, but generally, a decrease in pH increases the corrosion rate (Prawoto et al. 2008). Figure 3 shows the behaviour of carbon steel in an aqueous solution with changing pH and the effect caused by

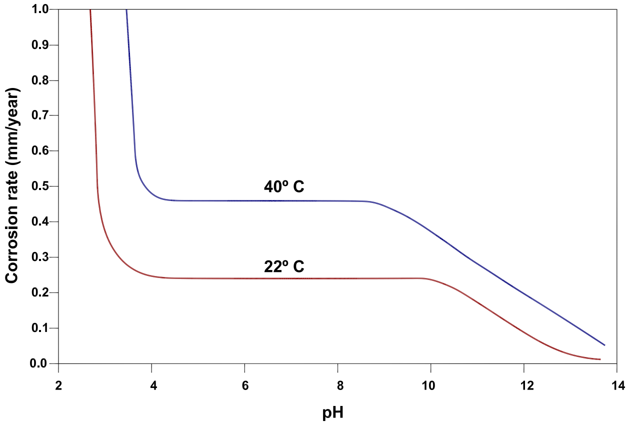

Fig. 3 Corrosion of steel in water containing 5 ppm of dissolved oxygen at two different temperatures, as a function of the water pH [modified from Roberge (2008)]

the decrease or increase of pH in the aqueous medium for steels. It can be seen that corrosion in acid water is much faster than in a neutral or alkaline media. The anodic reaction is given by:

$$Fe \rightarrow Fe^{2+} + 2^{e-}. \tag{1}$$

At low pH values, sticky corrosion products are not so obvious, although a very hard deposit form is sometimes observed. At even lower pH values, red coloured water from suspended corrosion products is more common (Fig. 4). Cast iron behaves similarly to steel at high pH values, but at low pH values, it is subject to graphitization (Fig. 5) (Roberge 2008).

Nevertheless, the corrosion rate varies due to changes in the cathodic reaction. At pH < 4, iron oxides are soluble and corrosion increases significantly. It can also be appreciated that the corrosion rate is affected by temperature, except in the pH interval from 4 to 10.

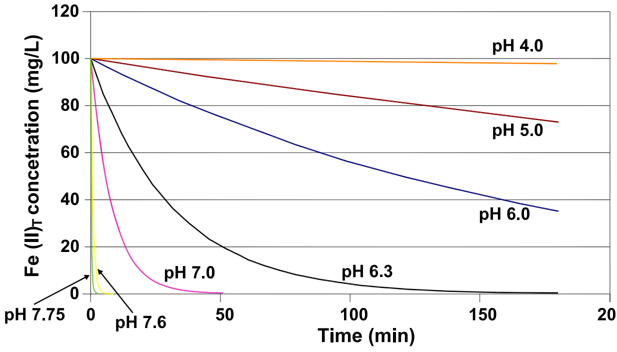

Fig. 4 Oxidation rate of soluble Fe (II) in a batch test as a function of pH [modified from Morgan and Lahav (2007)]

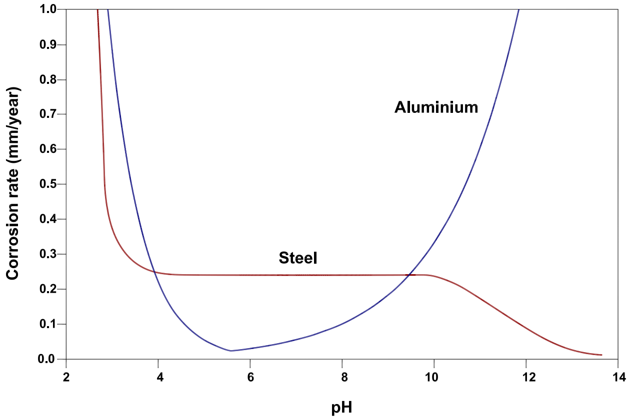

Fig. 5 Corrosion rates of steel and aluminium as a function of pH at the same temperature (22 °C) [modified from Roberge (2008)]

The corrosion of carbon steels in groundwater depends on the ion and pH content (Baranwal et al. 2017; Fang et al. 2003).

Temperature

Temperature accelerates the corrosion rate of metals because the higher the temperature, the higher the corrosion rate (Prawoto et al. 2009). The motors of the machines used in a mining environment are heated to temperatures much higher than 40 °C, and this heat is transmitted to nearby elements, increasing equipment corrosion.

Sulphate Concentrations

The degradation suffered by concrete in the presence of sulphate ions is well known and occurs abundantly in AMD-affected waters (Ekolu et al. 2016). The sulphate anion reacts with CaOH, which is released during concrete hydration, forming gypsum, and with the hydrated tricalcium aluminate, forms stringite (calcium aluminate sulphate). Both of the reactions result in an expansion, a loss of strength, and the cracking of concrete (Neville 2004). The current regulations on structural concrete differentiate three environments, depending on the aggressiveness and with respect to the concentration of sulphates, pH, and the presence of other salts in the environment, either in soil or in water. Table 1 lists some of these parameters related to environments contaminated by metal sulphides, obtained from the Structural Concrete Instructions (ACI 318-14 2014).

It can be said that the type of exposure is "strong attack" for an aqueous medium, since in media contaminated by AMD, the pH can be < 4, and the concentrations of sulphate and Mg can even be in concentrations of g/L. AMD can also contain a high concentration of metallic elements, some of which, according to their standard reduction potential, are

Table 1 Classification of chemical aggressiveness

Type of aggressive medium	Parameters	Exposure type		
		Qa	Qb	Qc
		Weak attack	Medium attack	Strong attack
Water	PH value according to UNE 83.952	6.5–5.5	5.5–4.5	< 4.5
	ION Mg (mg/L) according to UNE 83.955	300–100	1000–3000	> 3000
	ION SULPHATE (mg/L) according to UNE 83.956	200–600	600–3000	> 3000
Soil	Degree of acidity Baumann-Gully (mL/kg) according to UNE 83.962	> 200		
	Sulphate ion (mg/kg dry soil) according to UNE 83.963	2000–3000	3000–12,000	> 12,000

capable of oxidizing solid or native iron. Previous studies (Sarmiento et al. 2019) show how mechanical elements in contact with AMD present high concentrations of elements that are not found in the initial composition of the steel.

Microorganisms

The main types of bacteria associated with metals in terrestrial and aquatic environments are sulphate-reducing bacteria, sulphur-oxidizing bacteria, iron-oxidizing/reducing bacteria, manganese-oxidizing bacteria, and organic and slime acid-secreting bacteria (Beech and Coutinho 2003). These can coexist in naturally formed biofilms, forming important consortia on metal surfaces (Kjellerup and Ohlsen 2003). Some of these bacteria can increase corrosion by increasing the acidity and hence, the corrosivity, of mining waters (Baker and Banfield 2003; Dong et al. 2018; Hedrich et al. 2011; Johnson and Hallberg 2003; Jones et al. 2015; Joshi 2014; Klein et al. 2013; Kleinmann et al. 1981; Korehi et al. 2014; Schippers et al. 2010; Singer and Stumm 1969). Some of these bacteria and others can also directly cause metal corrosion; this form of biocorrosion is discussed in more detail below.

Corrosion of Mechanical Elements

Chemical reactions that vary from material to material are favoured by the presence of liquid water on the surface, or in the interior of pores of the solid material. Metal corrosion (Jones 1996; Leygraf and Graedel 2000) is the destructive result of a chemical reaction between a metal and its environment, and hence also includes oxidation, which is the first form of metal decay (Fig. 6). Metallic corrosion involves the transfer of electronic charges in aqueous solutions. Due to this, in the presence of water, metals tend to combine with other chemical compounds and return to the natural minerals from which they are extracted (Camuffo 2014).

In 1953, a study was commissioned by the U.S. government to evaluate the corrosion of different materials in the drive pumps of the mines in the Anthracite region of Pennsylvania, due to the high costs to mining companies. (Ash et al. 1955). Early literature on the corrosivity of mine water dealt mainly with pumping water and the effect on fresh steel pipes carrying water (Higginson and White 1983; Rawat 1976; Singh 1988). These studies found that, due to the presence of aggressive ions such as chlorides and sulphates, the Langlier saturation index (LSI) (Rivas-Romero et al. 2016), which predicts the deposition of protective scaling on steel surfaces, is not applicable to mine waters.

Fig. 6 Corroded mining pumping equipment

Studies on mechanical elements subjected to the chemical stress of AMD have shown that metal resistance to fatigue is significantly reduced in acidic conditions (pH values of 2.4–6) (Sanabria et al. 2015). Fatigue resistance limits are determined using the ladder method recommended by ISO 1143 (2010) and ISO 12107 (2012), with a 50% confidence level and a 10% failure probability. Finally, the fracture surfaces were analysed and the higher the acidity, the greater the damage.

Stress corrosion cracking (SCC) of cable bolts in underground mines is a universal issue with limited cost effective solutions. Recent research has shown an increase in the frequency of bolt failure caused by SCC (Chen et al. 2018; Craig et al. 2016; Galvin 2016; Wu et al. 2018a).

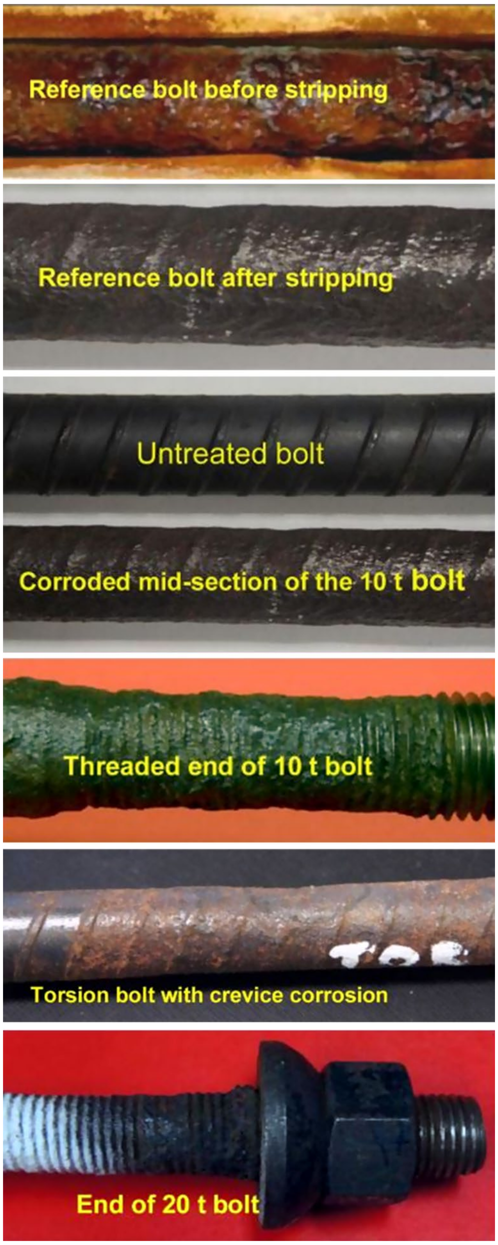

Fig. 7 Photos of parts of various corroded bolt sections compared with uncorroded section [modified from Aziz et al. (2014)]

While testing mine cable bolts in acidic water (Aziz et al. 2014; Wu et al. 2018a), significcant reductions in failure resistance in post-corroded bolts was discovered (Fig. 7), ranging from 21 to 39%. These studies were undertaken in an environmentally controlled laboratory under different bolt loading conditions and demonstrated the influence of pH, temperature, DO content, surface condition, and hydrogen sulphide concentrations on the corrosion rate (Spearing et al. 2010). Similar corrosion studies were done in Finland (Satola and Aromaa 2005) and Australia (Hassel et al. 2005), with identical results.

Fig. 8 Concrete support and metal mine beam affected by acidic water

Corrosion of Reinforced Concrete

Reinforced concrete is the most used construction material in the world (Xi et al. 2018). Both the high compressive strength provided by the concrete and the excellent mechanical properties that characterizes steel makes it an ideal composite for all types of structures. Yet, one of the principal weaknesses of this material is that exposure to aggressive environments such as acidic water can cause the reinforcing steel to corrode, which shortens the service life (Saraswathy and Song 2007). This is due to the diffusion of chloride and sulphate ions to the iron (Xi et al. 2019). These ions penetrate the concrete and also react with the components of the cementitious matrix (Al-Sodani et al. 2018), inducing diverse expansive chemical reactions. The evidence of attack is a gradual loss of cement paste strength, caused by a decline in the cohesion among the hydration products (Fig. 8). Furthermore, the expansion of these products can induce concrete cracking, which raises the permeability of the material and favours the entrance of other agents that can further accelerate the decay (Bertolini et al. 2004; Mehta 2006).

$$Ca(OH)_2 + SO_4^{2-} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^-. \tag{2}$$

Biocorrosion

The initial work in this field on the role of bacteria in metal corrosion processes was done by Von Wolzogen-Kuhr (1923), who in 1923 highlighted the electrochemical mechanism of the attack of iron by sulphur-reducing microorganisms. Principally, the excretion of metabolic intermediates and/or end products, as well as exoenzymes is what causes the microbial corrosion involved. Bacteria, cyanobacteria, algae, lichens and fungi, together with protozoa, are classified as microorganisms (Harbulakova et al. 2009) and part of the biocorrosion phenomenon.

Microorganisms growing on surfaces perform diverse metabolic reactions, the by-products of which may promote the deterioration of the underlying substratum. The result of corrosive microbial products on underlying metal surfaces is aggravated when their concentrations are allowed to increase to a high level, as may occur when the microorganisms grow on a biofilm surface (Luís et al. 2018). The biofilm contains exopolymers, which restrain the diffusion of solutes and gases between the surface and the bulk aqueous phase. The biofilm also allows the evolution of highly structured microbial communities on the surface. The diverse species are able to collectively perform metabolic activities that are potentially more than could be achieved by a single species on his own.

Metal oxidation is a mechanism which depends on pH and Eh (redox potential). In other studies, (Grengg et al. 2018; Singh et al. 1988) an approach which intertwines microbial spatial distribution with chemical, mineralogical, and structural micro-aspects, was presented. They demonstrated the presence of microbes within corrosion layers, which is unequivocally correlated with pH levels. *Acidithiobacillus ferrooxidans* is one of the most highly corrosive organisms.

Experiments have shown the influence of biogenic sulphuric acid production on short term corrosion rates (Gutierrez-Padilla 2010). Figure 9 shows the profile of pH measurements as an additional indication of biological activity over two cycles. The pH of the solution dropped from 6.87 to 3.42 over 40 days, followed by a period of slowly declining pH for the next 45 days. This pH drop was consistent with the production of sulphuric acid by the bacteria. In the second cycle, the pH dropped even faster, from 6.22 to 3.12 in 12 days. Compared to the biokinetic studies, the pH drop in both cycles relates to the activity of *A. ferrooxidans* species, as the pH is favourable for these species, except *A. thiooxidans*.

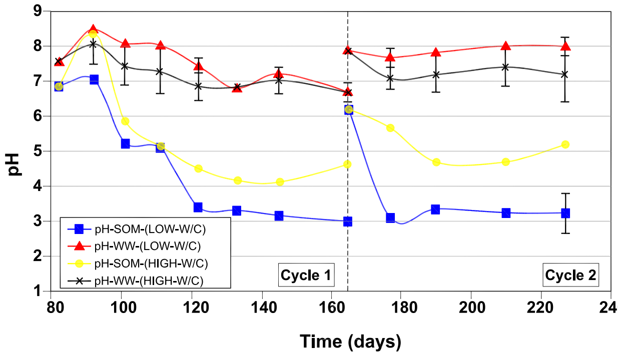

Fig. 9 Profiles of pH measurements of the solution during two cycles [modified from Gutierrez-Padilla (2010)]

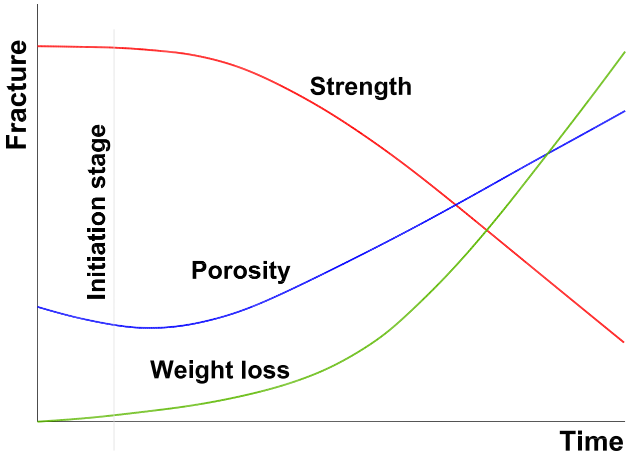

Fig. 10 Material changes trend from biodeterioration [modified from Márquez (2013)]

Microorganisms are the biological factor that mostly deteriorate concrete and metals. The most important biodeteriogens are bacteria, especially the sulphur-oxidizing bacteria, such as *A. thiooxidans* and the sulphate-reducing bacteria (e.g. *Desulfovibrio* spp.).

In addition, the growth of microorganisms can make concrete and materials more vulnerable to chemical attack (e.g. due to chlorides), negatively affecting the material integrity (Márquez et al. 2013; Fig. 10).

A great variety of organisms can cause concrete deterioration (Wei et al. 2014). The action of microorganisms on concrete structures can be classified by their effects on concrete surfaces, concrete matrices, and on cracking and crack growth (Amann et al. 1990; Aviam et al. 2004). According to Sanchez-Silva and Rosowsky (2008), the effects of microorganisms are principally the erosion of the exposed surface, which reduces the protective cover depth, and increases porosity. Another effect is the transport of the degrading materials into the concrete, which accelerates cracking, spalling, and other damage, diminishing its lifespan.

Conclusions

Corrosion is a universal problem in industry in general and in the mining industry, due to the extreme conditions to which installations are subjected and the effect of these conditions various material's mechanical integrity. Acidic mine water is a global problem and can aggressively attack materials, such as steel and concrete, subjecting them to chemical stress, which can cause safety problems, significant economic costs, and environmental pollution.

Corrosion depends on many factors, including pH, DO, the ions present in the water, biological activity, and temperature. The presence of certain bacteria, such as *Acidothiobacillus ferrooxidans,* contribute to increase the acidity of mine water, with an acid formation rate greater than in the absence of bacteria, thus increasing the corrosion rate.

Microbiological corrosion is the result of biogenic substances produced by the metabolic activity of proliferating microorganisms. It must be considered that microorganisms cause both the initiation, as well as the intensification of the corrosion processes of metals and concrete. However, the true role of bacterial activity in metals and concrete, especially in their natural environment, remains poorly understood (Shipping et al. 2013).

To sum up, corrosion is a widely studied problem, but it remains a difficult and expensive problem. This work reveals the need to deepen the study of corrosion for the mechanical and structural elements in contact with AMD, to analyse the chemical and electrochemical processes that are produced and the factors that notably increase the degradation process of these materials.

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