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The Resistance of an Enamelled Material to Biochemical Leaching †

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Abstract: This article describes the resistance of chemically durable enamelled surfaces against the effects of chemical leachate and enzymes of bacteria *Acidithiobacillus ferrooxidans*, which are commonly used in biohydrometallurgy today during the biochemical leaching of ore. For many years now, the Vítkovice ENVI company has successfully used steel parts protected by the tested enamel in the construction of wastewater treatment plants and biogas stations. This article summarizes the results of a study that dealt with verifying the possibility of usage of widely applied enamel in the field of biochemical leaching during the treatment of raw materials. From the performed experiments, it follows that enamel can endure the effects of leaching solutions, but on poorly treated areas such as the edges and corners of parts, a quick onset of corrosion occurs.

Keywords: leaching; biochemical leaching; enamelled material; *Acidithiobacillus ferrooxidans*

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1. Introduction

In an effort to expand the product range of Vítkovice ENVI beyond storage tanks, WWTPs and biogas stations, there was a need to add tanks designed for processing lean ores and metal-bearing waste using chemical and biochemical leaching. It was therefore necessary to verify the resistance of the enamel commonly used in the company's current production to leaching media and enzymes produced by microorganisms. The initial verification experiment took place in laboratory conditions, simulating leaching in both the presence and absence of microorganisms. In today's practice, tanks made of steel or concrete scalded with a plastic liner, which protects these materials against corrosion and biocorrosion, are used to leach poor ores. Enamel could be widely used in this industry (in terms of its durability and price).

2. Theory

Testing enamel's resistance to leachates used in biohydrometallurgy is not mentioned in the literature. There is only some limited information about the leaching of enamel in order to determine which metals may be released during its use, especially during food preparation [1].

The issue of the resistance of the enamelled surface is addressed by the author Rolf Lorentz [2], who already in 1983 exposed enamelled parts of various qualities to several polar solvents (distilled water, steam, water mixed with Na_2CO_3 and water mixed with $CaCl_2$ and HCl) at different temperatures and pressures. Subsequently, he evaluated the resistance of the enamelled surface on the basis of its weight loss. Based on the performed experiments, he came to the conclusion that distilled water does not cause the corrosion of the enamel at normal temperatures; however, tap water does cause a slight corrosion on the enamelled surface. When the pH deviates, whether towards an acidic or basic area, a corrosion of the enamelled surface occurs. The author states that the pH value and the temperature of the solution are decisive for the corrosion of the enamel.

The effect of the leachates and enzymes produced on the enamelled surface itself has not yet been addressed.

3. Materials and Methods

Experimentally, samples of enamelled sheet metal were exposed to four potential leaching solutions with and without microorganisms (Table 1).

Table 1. Distribution of samples and composition of leaching solutions.

Sample 1	9K nutrient medium with *Acidithiobacillus ferrooxidans* bacteria
Sample 2	
Sample 3	Sterile nutrient medium 9K
Sample 4	Demineralized water acidified with H_2SO_4
Sample 5	$Fe_2(SO_4)_3$ solution acidified with H_2SO_4

Sheets with the trade name KOSMALT E 300 were manufactured by VSŽ Košice and are currently conventionally used for the production of enamelled parts in the Vítkovice ENVI company. The dimensions of the sheet samples used in the experiment were 120 × 120 mm. These samples were subsequently enamelled by Vítkovice ENVI. The enamelled surface produced is referred to by the manufacturer as a chemically highly resistant enamelled surface. The enamel layer in this case consists of a cover and a base layer.

The base enamel was made from a slurry prepared from a 22EC frit manufactured by Ferro. This combination has been used successfully for many years at Vítkovice ENVI. The covering enamel surface was fired from an enamel slurry, which was ground up from a PP40821 frit manufactured by Mefrit together with clay, water and pigment (RAL 6009). According to its colour, this enamel is referred to internally as "green enamel". The samples produced in this way are commonly used by this company to simulate various situations to which enamelled parts will be exposed in practice.

The solutions used were prepared from chemicals of analytical purity. The pH of all solutions was adjusted with sulfuric acid. *Acidithiobacillus ferrooxidans* bacteria used in the experiment were obtained from the database of microorganisms of the Institute of Environmental Engineering VŠB-TU Ostrava. The distribution of the samples and the composition of the individual leaching solutions are given in Table 1.

4. Experiment

Sample 1 experiments were performed in laboratories at 20 °C. The samples of enamelled sheets were leached for 64 weeks in plastic beakers with the prepared media. The leach solution was aerated during the experiment with a small air pump to bring the experiment as close as possible to the practical conditions of aerobic leaching and also to provide sufficient oxygen for the bacteria *Acidithiobacillus ferrooxidans*.

The pH was maintained at 1.5 during the experiment. Sulfuric acid was used in the experiment to correct the pH. The temperature of the leaching media was maintained between 22 and 26 °C throughout the experiment.

During and after the leaching process, the condition of the enamelled surface was visually evaluated. All samples were weighed before the start of the experiment. Samples 1 and 2 were exposed to 9K leaching medium in the presence of said bacterial inoculum, while sample 3 was exposed to sterile 9K medium. Samples 4 and 5 were exposed to a solution of ferric sulphate acidified with sulfuric acid.

Two samples were exposed to the effects of the 9K medium, in the presence of the microorganism *Acidithiobacillus ferrooxidans*, due to the fact that in practice it is one of the most commonly used leaching media for leaching lean ores. This reduced the uncertainty of the results obtained for the possible practical use of enamelled surfaces in the construction of leaching tanks. The remaining three samples had the character of rather comparative samples without the presence of the mentioned microorganisms (Figure 1).

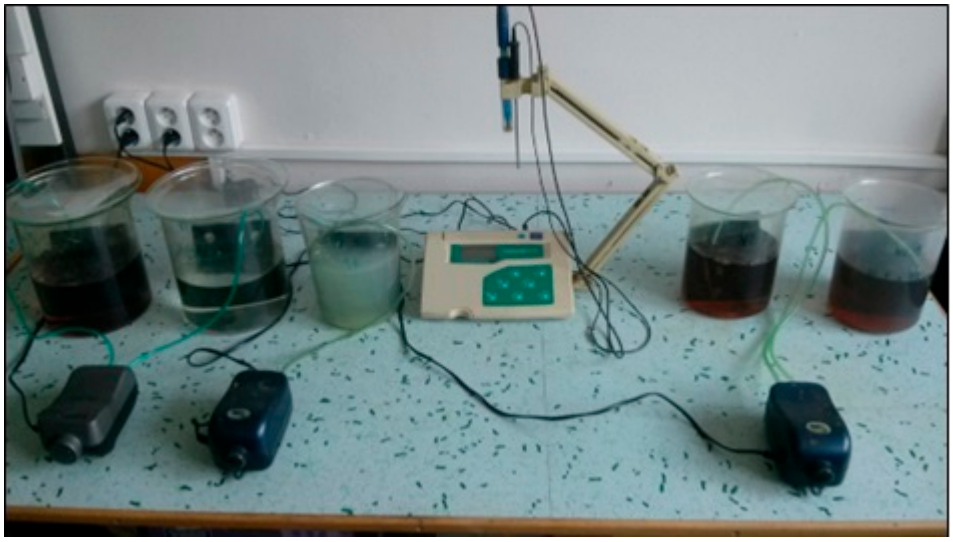

Figure 1. Resistance testing of enamelled samples in leachates.

5. Results

The surface of the enamelled parts showed no visual wear during the experiment. The enamel sufficiently protected the metal from the corrosive effects of the leaching solutions. However, this did not apply to the enamelled surface on the edges of the panels of samples 1, 2 and 5, which were exposed to solutions containing Fe^{3+} ions (Figures 2–4), where the initial visible deterioration of the enamel already occurred after 15 days of leaching. In the case of samples 3 and 4, there was an initial peeling of the enamel (also on the edges), which did not appear until after 30 days of leaching; these samples were exposed to solutions containing only Fe^{2+} ions (medium 9K) and water acidified with H_2SO_4 (Figure 5).



Figure 2. Damage to the edges of samples 1 to 3 (from left to right) after 15 days of leaching.

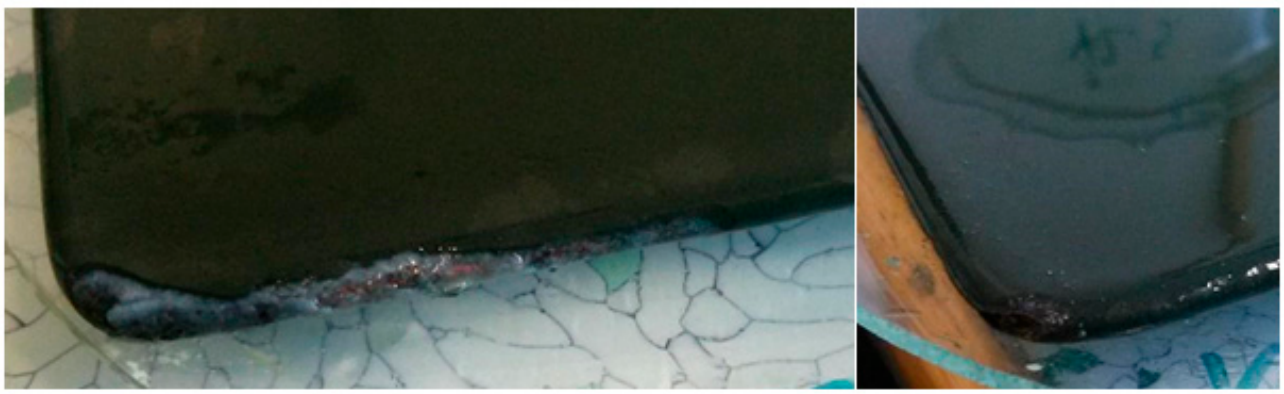

Figure 3. Detail of edge damage for samples 1 and 2 (from left to right) after 15 days of leaching.

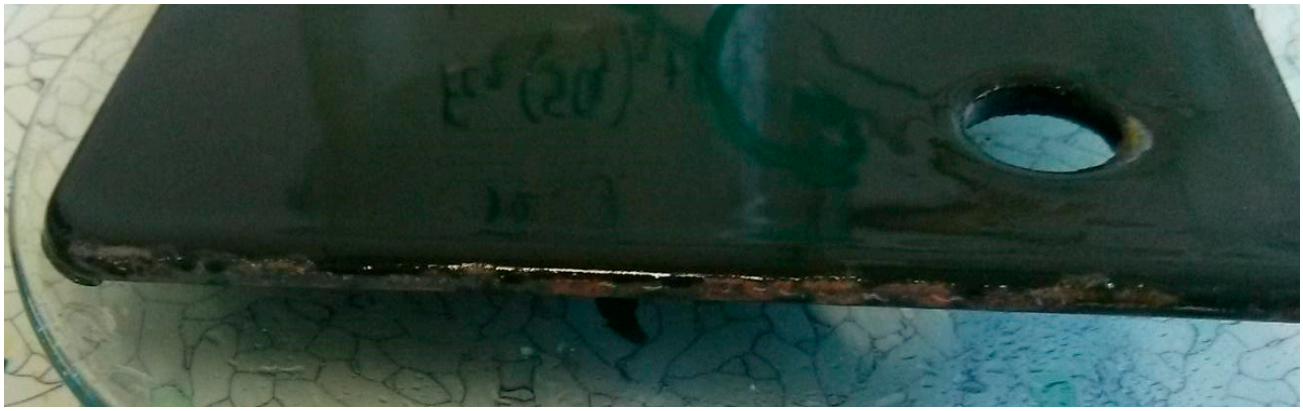

Figure 4. Detail of sample 3's damaged edges after 15 days of leaching.



Figure 5. Sample 4 and 5's damaged edges after 30 days of leaching.

In contrast to the enamel on the surface of the part, the enamel on the edges of the samples is always less resistant and may show small pores (it is not inspected by the poroscope, compared to the surface of the sample) and cracks caused by sample handling. Despite the fact that during the production process, the edges of the parts to be enamelled are rounded, the enamel on the edges of the parts and on the circumference of the holes necessary for the assembly of the tanks is always less durable.

A rapid process of metal oxidation followed from the damaged places on the edges of the parts. It is clear that as the corroded area became larger, the rate of metal oxidation increased. It is also worth noting that during the progressive corrosion of the metal, it was possible to observe on the individual samples the formation of small overhangs (Figure 6) formed by the enamelled surface, which remained intact. The resulting overhangs were very fragile and easily crumbled.

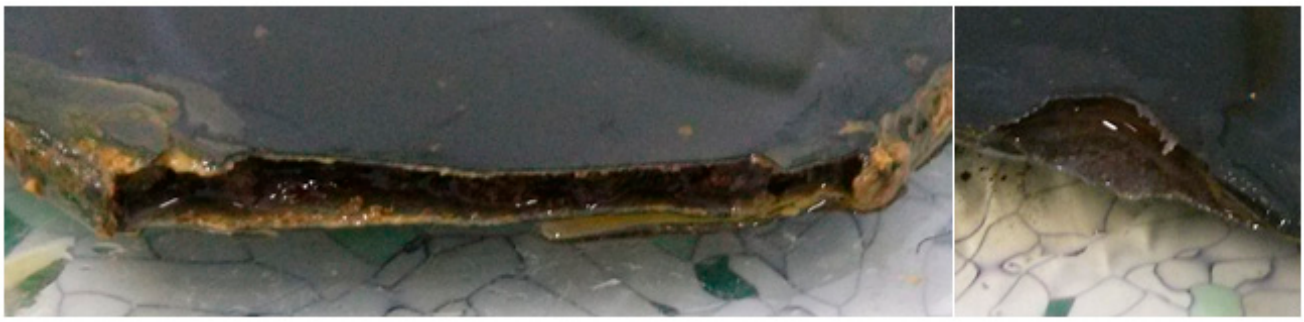

Figure 6. Portals formed by the enamel during the degradation of the base plate.

During the next 60 weeks of leaching, a considerable corrosion of the enamelled parts occurred (Figures 7 and 8), but the initial points of corrosion were always the edges of the enamelled parts, from where the corrosion spread below the amorphous enamel phase. The enamelled surface withstood all leachates used in the experiment. The metal protected by the layer of enamel was free of signs of corrosion in all samples (after cutting) even after 15 months of exposure to leachates (Figure 9).

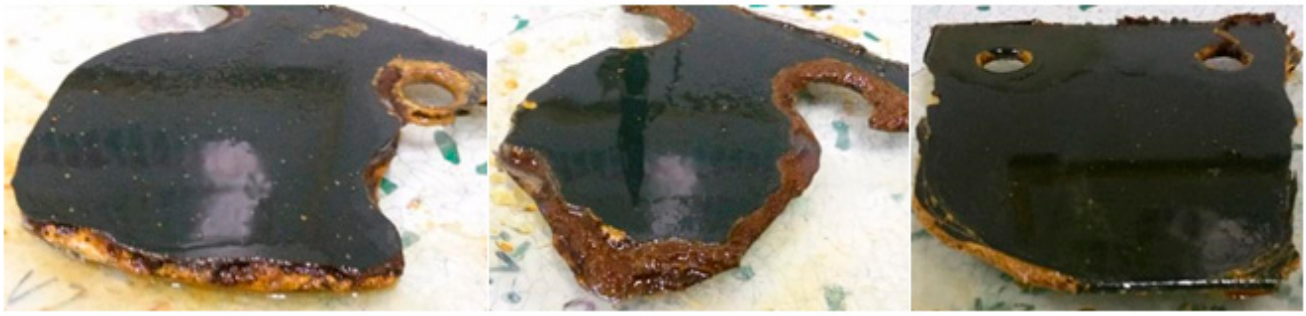

Figure 7. Portals formed by the enamel during the degradation of the base plate.

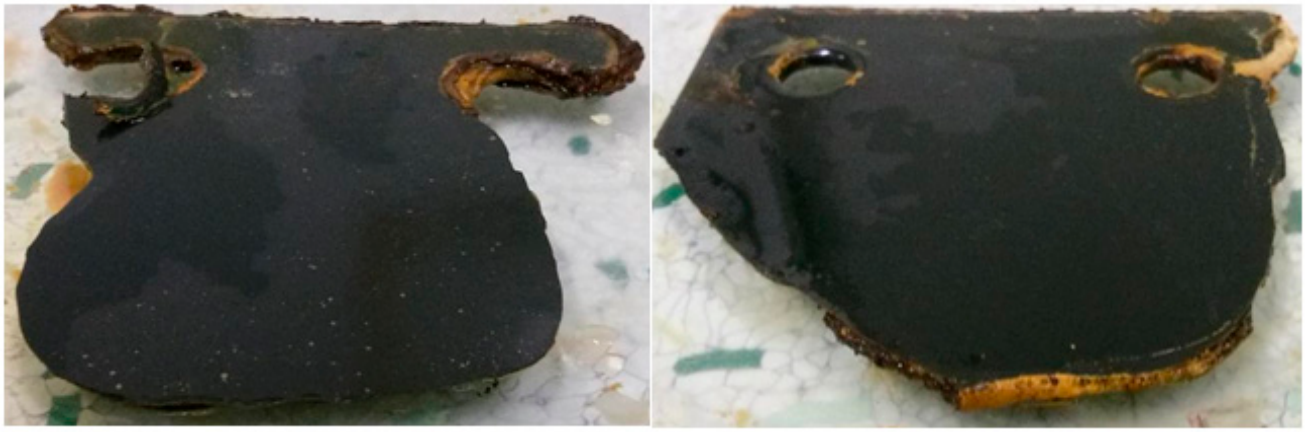

Figure 8. Extensive corrosion of samples 4 and 5 after almost 15 months of leaching.



Figure 9. View of the cut sample.

The obtained results show that the proportion of Fe^{3+} ions in the solution (whether formed purely chemically or biochemically) has the greatest influence on the destruction

of metal in the areas where the enamel was damaged. The influence of direct enzymatic processes of *Acidthiobacillus ferrooxidans* on metallic material, in this experiment, cannot be unambiguously demonstrated and evaluated.

During the construction of tanks, the Vítkovice ENVI company uses only sheets without enamelled edges, because these do not come into contact with the solutions present in the tank. All joints are covered with sealant, and the degree of resistance of the sealant to the liquids used in the experiment has not yet been determined. It is obvious that in the case of minor damage to the tank, the corrosion proceeds briskly through the enamelled part. This fact must be taken into account when considering the possibility of using enamelled parts for the construction of tanks for the leaching of metal-bearing raw materials, where high abrasion can be expected, especially under kinetic leaching conditions.

6. Conclusions and Recommendations

Experiments have shown that sheets with an enamelled surface of chemically resistant enamel, manufactured by Vítkovice ENVI, resist the effects of the 9K nutrient medium, both with and without the presence of the microorganism *Acidithiobacillus ferrooxidans*, provided that the edges of these parts (although enamelled) do not come into contact with this solution. Enamelled edges and especially corners are subject to the effects of leaching due to the natural occurrence of pores and defects on the edges. However, in practice, the edges of the sheets do not come into contact with the solutions inside the tanks, because they are separated from the solutions by high-quality sealants.

The part would also be destroyed in the event of damage to the enamelled surface, such as abrasion. The extent of this risk needs to be further investigated, and it is questionable how long it would take for such damage to the enamel to occur during the leaching process, especially in kinetic leaching.

Before planning the production of these tanks, it would also be necessary to determine whether the sealants used will be resistant to the leachates used.

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Conflicts of Interest: The authors declare no conflict of interest.

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