

Catalytic Acceleration of Supplied Corrosion Under Hypergenesis Conditions

BRAGIN V.I., MIKHAILOV A.G., ZHIZHAYEV A.M.

Institute of Chemistry and Chemical Technology SB RAS, 50
Akademgorodok str. Akademgorodok, 50, bild. 24, 660036, Krasnoyarsk, RUSSIA

Abstract: Ecological safety of the natural environment depends on chemical activity in conditions of hypergenesis. The catalytic role of dispersed platinum in corrosion processes of metals and sulfide minerals was described. A sharp increase in the share of platinum in the slurry fraction is experimentally substantiated. The essential fact is that platinum is redistributed in a slurry even before sulfides of nonferrous metals and iron are completely oxidized. It was found that the main cause of the initial stage of sulfide corrosion is the process of pitting. It has been experimentally established that the accelerated corrosion on the sulfide surface is determined by the catalytic action of the metal causing activation of the anodic process.

Key words: corrosion, dispersed particles, pitting, surface, sulfide, electrochemical inhomogeneity

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1. Introduction

Ecological safety of the natural environment depends on chemical activity in conditions of hypergenesis, where there is unlimited access of oxygen from the atmosphere. Ecological hazard is high in the territorial zone confined to the industrial development of natural resources. It is especially characteristic for industrial objects of mineral resources development, including sulphide mineral forms. Oxidative transformation of sulfides in conditions of hypergenesis is kinetically high in the presence of moisture. Under hypergenesis conditions, fluctuations in external conditions, mainly temperature and humidity, are highly dynamic. The most dynamic structural transformations occur under the influence of such climatic factor as freeze-thaw (FT) cycles [1,2]. This favours the growth of the surface contact of minerals. The indicators of granulometric composition, porosity, and fracturing change significantly [3]. The presence of temperature cycles leads to physical changes in the cohesion of particle aggregates in the array [4,5]. Structural changes under the influence of FT are related to crystallisation pressure [5, 6, 7]. This process leads to an increase in the porosity value of the array structure. Physical destruction of aggregates significantly increases the contact area of the available surface area of the array particles, which accelerates the material chemical [8,9] and biochemical [10,11] transformations of the array. Climatic cyclic oscillations initiate phase transformations [12]. In conditions of hypergenesis, the most intensive transition of natural minerals, including sulfides, into soluble form is noted [13, 14, 15]. The possibility of filtration mass transfer is

a determining factor of material transformation of the massif. This principle is the basis of technological solutions of in-situ leaching for metal ores [16, 17,]. The initial process of mineral destruction is important and largely determines the direction of substance transformation [17,18]. Transformation of sulfides in conditions of hypergenesis is directed to the balance of chemical activity. Deviation from chemical equilibrium entails a change in the energy potential, which predetermines the kinetics of substance transformation. In the conditions of natural hypergenesis, the balance fluctuations are very dynamic. The most dynamic structural transformations occur under the influence of the climatic factor of freezing-thawing (FT) [1]. In this case, the massif parameters in terms of granules composition (contact surface area), porosity and fracturing change significantly [2]. The presence of temperature cycles leads to physical changes in the continuity of particle aggregates in the array [3], [4]. Structural changes under the influence of FT are related to crystallization pressure [5, 6, 7, 8]. This process leads to an increase in the porosity value of the array structure. Physical destruction of aggregates significantly increases the contact area of the accessible surface of the array particles, which accelerates the material-chemical [9] and biochemical [10] transformations of the array. Climatic cyclic fluctuations initiate phase transformations [11]. In conditions of hypergenesis, the most intensive transition of natural minerals, including sulfides, into soluble form is noted [12, 13, 14]. The possibility of filtration mass transfer is a determining factor in the transformation of the massif material. This principle is the basis of

technological solutions for in-situ leaching of metals [15, 16]. The initial process of mineral destruction is important and largely determines the direction of substance transformation [17].

2. Mechanism of transformation of metals and sulphides from the surface

Weathering of sulfide-containing materials is determined by oxidation of sulfides with formation of hydrated iron oxides and free sulfuric acid [19]. Weathering of sulfides containing platinum has peculiarities expressed in the fact that the rate of release of dispersed platinum particles from the sulfide matrix is significantly higher than the rate of oxidation of the sulfide itself. As a result, there is a sharp decrease in the proportion of platinum in large classes and its concentration in the sludge.

The aggregate of the obtained data allows us to put forward, as a working hypothesis, an explanation of the accelerated, as compared to the main sulphide matrix, weathering of platinum. The mechanism consists in the catalytic action of platinum group metals on oxidation of sulfide matrix.

It is known that the presence of platinum (even traces) on the surface of steel leads to accelerated pitting corrosion of the metal [20, 21]. Increased destruction of the mineral structure is characteristic in the presence of inclusions with different electrochemical properties. Sharp acceleration of the process is also characteristic in the presence of halide ions in solution, even in insignificant amounts (primarily chlorine ions).

Pitting corrosion is characterised by intensive destruction of very limited areas of the surface [22], while the rest of the surface may be in a stable passive state. The main condition for the formation of pitting is a shift of the electrochemical potential, due to the presence of oxidants in the solution, to a positive value above some critical value, the so-called pitting potential. The pitting surface is the anode and is destroyed at a high rate due to contact with the rest of the surface, which is a non-polarisable cathode. Pitting nucleation is due to potential differences between individual surface areas. At these sites, accelerated destruction of oxide films occurs. At the moment of nucleation the corrosion rate is the highest. Nucleation sites can be non-metallic inclusions on the grain surface. The occurrence of pitting depends on the nature of anions and their concentration. The growth of pitting is associated with the operation of a corrosion galvanic cell. The efficiency of such a corrosion cell depends on the amount of

depolarisers as well as the pitting in the active state. In most cases, the corrosion process slows down over time until it stops completely.

3. Experimental studies Material and methods

To test the hypothesis, corrosion of sulfide samples: pyrite, pyrrhotite with inclusions of chalcopyrite and pentlandite was investigated. The surface of mineral samples is polished. Experiments were carried out for each sulfide in three variants: with the presence of metallic platinum on the surface; with the presence of chloride ions in a solution with a concentration of 0.01n HCl; without activating additives (as a control). In all variants, a humid atmosphere was maintained throughout the experiment.

Experimental studies with the presence of metallic platinum on the surface had the following features. Platinum was applied to the surface in the form of an aqueous solution of nanoparticles (coarseness - 20÷30 nm). The solution was preliminarily dispersed by ultrasound in distilled water.

The surface of the samples was subjected to microscopic analysis sporadically with evaluation of the process kinetics. The fracture products were evaluated by elemental and mineralogical analysis. The distribution of elemental contents by size classes was taken into account. The surface of the samples was microscopically analysed sporadically with evaluation of the process kinetics. Fracture products were evaluated by elemental and mineralogical analysis. The distribution of elemental contents by size classes was taken into account.

4. Results and discussion

The experimental data obtained are consistent with the proposed mechanism of pitting transformation of sulfides.

Namely:

- Platinum is present in sulphide minerals mainly in the form of dispersed inclusions. This creates inhomogeneities in the form of corrosion centres on the surface of minerals in places where platinum nanoparticles are present;
- Since platinum has catalytic properties and increased adsorption capacity to oxygen, hydrogen overvoltage on the surface is close to zero, in contrast to the surface of sulphides. Therefore, dispersed platinum inclusions are centres of sulphide corrosion;

- Selective, focal, destruction of the sulfide mineral structure and accelerated transition to thin slurry size classes is observed only for sulfides with inclusions of platinum group metals. It can be assumed that as a result of pitting corrosion of sulphides developing near inclusions of platinum group metals, the latter fall out of the sulphide matrix and pass into slimes. A multiple increase of platinum content in fine size classes (-0.044mm) in the first days of the experiment was noted;

- The process is accelerated in the presence of halide ions (chlorine ions).

The results of the formation of corrosion zones on the surface of sulfide samples depend on the conditions of the experiment. The key condition for intensive corrosion is the presence of aqueous phase

and the presence of electrical contact of nanoparticles with the sample. Corrosion in wet conditions in the control sample also appears, but insignificantly and with a 10-day lag. It is observed that the corrosion centres are randomly distributed on the surface and there is no correlation with the distribution on the surface of the nanoparticles. At the same time, samples with mechanically removed weakly bonded nanoparticles, show corrosion development in the vicinity of the nanoparticles (Figure 1). The presented image shows rounded formations of sulfide oxidation products (dark grains) around the platinum particles (light grains). Oxidation products are represented by basic iron sulphates with a small admixture of nickel and copper.

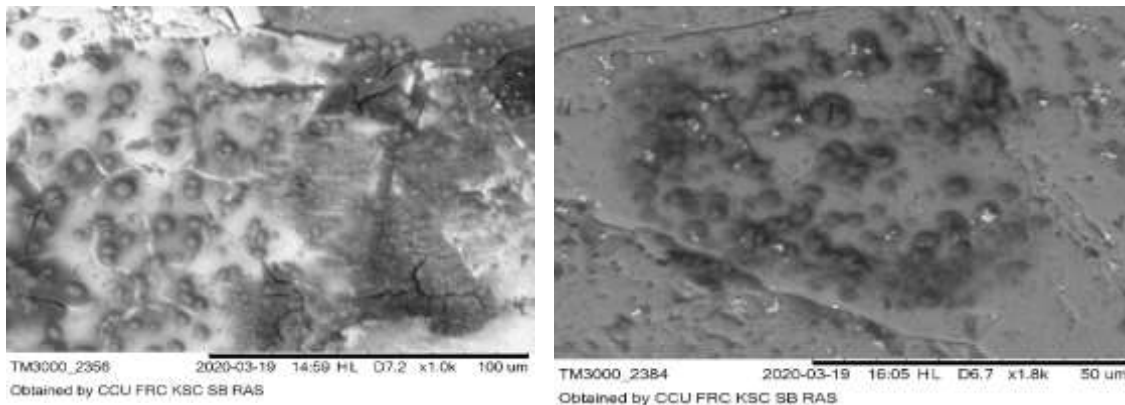


Figure 1 - Sulfide surface with platinum nanoparticles applied after 1 week of the experiment

The influence of the wet environment plays a crucial role in the oxidation of the sulfide (Figure 2). The initial aqueous film at the droplet site favoured the formation of a dense film of basic sulphate, thickening near the platinum nanoparticles.

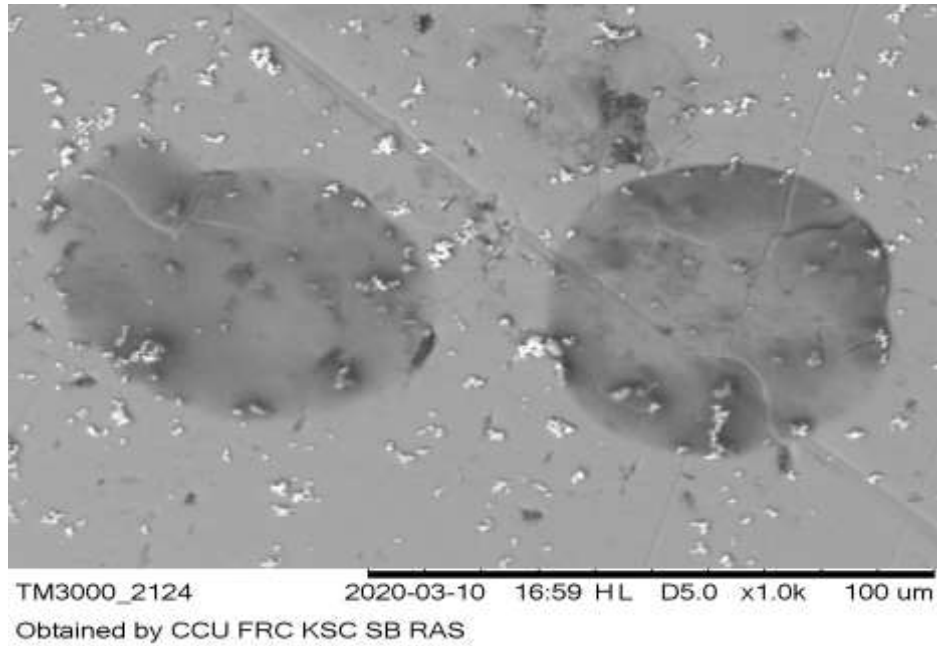


Figure 2 - Influence of aqueous medium on the character of sulphide surface corrosion

It should be noted that in addition to corrosion near the contact with platinum, oxidation of sulphides occurs along other inhomogeneity's, in particular near inclusions of sulphides of different composition, rock-forming minerals (Figure 3, Figure 4, Figure 5).

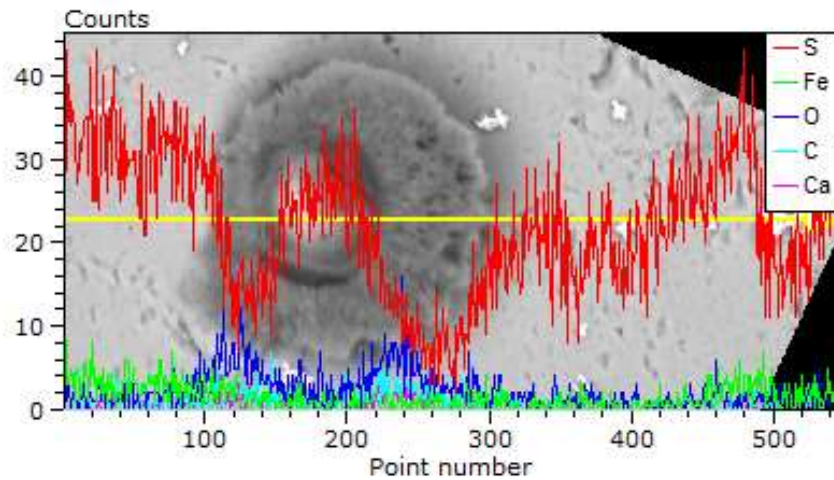


Figure 3 - Oxidation centre formed by an inclusion in pyrite

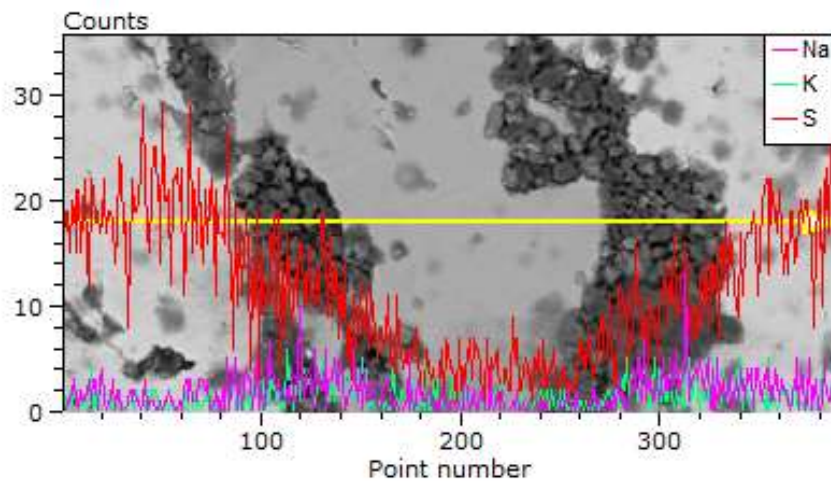
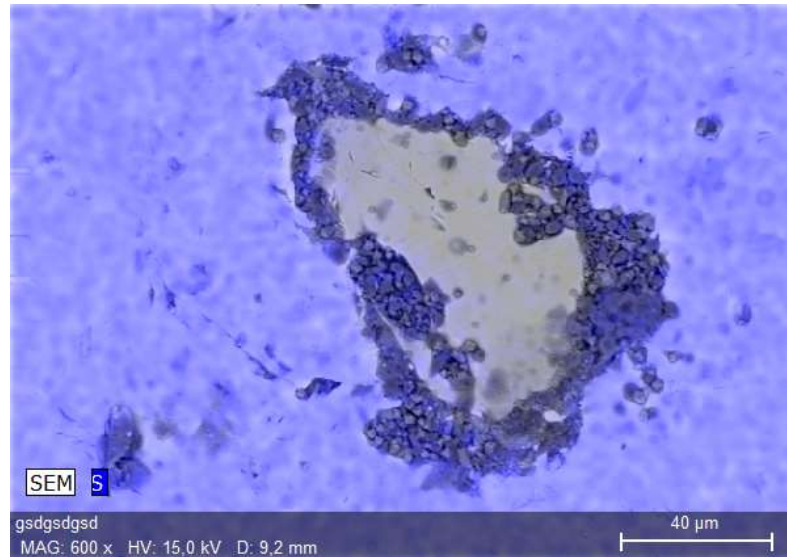


Figure 4 - Corrosion of pyrrhotite along the rock inclusion boundary

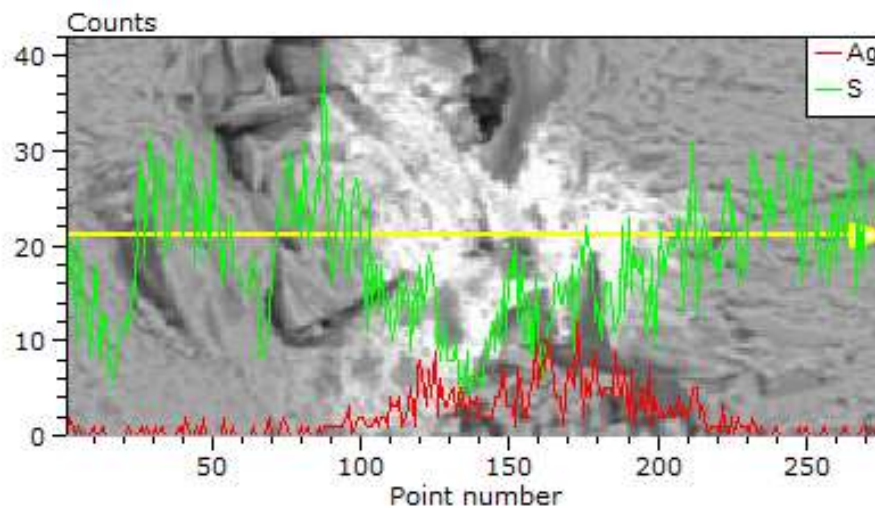


Figure 5 - Corrosion of pyrrhotite surface near natural silver inclusion

The main factor in the mechanism is oxygen depolarisation of the cathode. Inclusions that catalyse the depolarisation reaction increase the cathode current and thus accelerate the process. The sulphide corrosion centre develops until the oxidation products (sulphates) block access to the surface.

5. Conclusions

As a result of studies, the acceleration of weathering of sulfides near inclusions in the contact zone with dispersed platinum particles has been experimentally demonstrated. A pitting mechanism of weathering acceleration has been proposed.

The factors determining the accelerated weathering from the surface of sulfides are the quality of electrical contact between the metal particle and the surface and the presence of moisture. Under favourable conditions, corrosion of the sulphide develops with the formation of wells filled with oxidation products, represented mainly by basic sulphates located in the immediate vicinity of the corrosion zone. Accelerated destruction of the sulfide surface under these conditions is determined by the catalytic action of platinum, leading to depolarisation of the anode and an increase in the cathodic current.

A similar process of focal corrosion from the surface was observed on a pyrrhotite sample without the addition of platinum nanoparticles. The corrosion degradation involves platinum in the mineral.

With further development of the corrosion process on the surface of the sulphide, the formation of continuous iron-oxide films including dispersed platinum particles occurs. This oxidation process explains the zones of platinoid enrichment in slurry fractions detected during the study of waste tailings from the Norilsk industrial district.

Thus, the conducted studies explain the process of weathering of sulphides with platinum group metals and platinum concentration in slurry weathering products.

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Conflict of Interest

The authors have no conflicts of interest to declare that are relevant to the content of this article.

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