

# Electrochemical corrosion of steel balls in wet grinding<sup>①</sup>

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**Abstract:** Rest potentials for the steel ball electrode and the pyrite electrode as well as the combination potentials and the galvanic currents developed in the pyrite-steel ball couple were measured. The data demonstrate that the galvanic couples are going to form between the pyrite particles and the steel balls when they contact with each other. The initial combination potential and the initial galvanic current of the pyrite-ball couple while bubbling with oxygen are greater than those in aeration of air. The combination potential and the galvanic current decrease more quickly with time while bubbling with oxygen than they do in aeration of air. In an experiment of simulating wear differences, a galvanic current, which is smaller than that developed in the pyrite-ball couple, exists between two different ball electrodes in wear degree on the surface of them. Under different grinding time conditions, the equivalent corrosion current density calculated from marked ball wear data by applying Faraday's law correlates well with those estimated from polarization curves of pyrite and ball electrodes, and the former is always greater than the latter.

**Key words:** electrochemical corrosion; grinding medium; steel ball wear; wet grinding

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## 1 CORROSION CELL OF STEEL BALL

Steel balls used in the practice of grinding are generally made from metal or alloy materials. Their corrosion course and behavior are subject to the laws of metallic corrosion. The ball corrosion is essentially a kind of oxidation-reduction taking place on its surface. This reaction may occur in two ways: chemical corrosion and electrochemical corrosion.

In the electrochemical corrosion, the oxidation-reduction is carried out by the anodic reaction (oxidation) and cathodic reaction (reduction) occurring simultaneously and respectively, which is similar to a cell. Consequently, the electrochemical corrosion process of the ball can be described by a corrosion cell circuit<sup>[1, 2]</sup>.

When steel balls and sulfide minerals are in electrical contact with each other, on their interface a current flows from the mineral with higher corrosive potential acting as a cathode to the ball with lower corrosive potential acting as anode, so as to form a coupling corrosion cell.

In the system of sulfide ore grinding, there is a difference in the corrosive properties of the ball due to different individual rest potentials on the surface of the component minerals and the balls. The electrode potential values of common sulfide minerals and steel in neutral solution are listed in Table 1<sup>[3-9]</sup>.

It is observed that the rest potentials of different minerals are different. Even for the same mineral, there is also a marked difference in its potential values measured due to different places of origin or electrolytes. But in general, the rest potential of steel medium is the lowest and that of pyrite is the highest in the system of sulfide ore grinding. When sulfide minerals contact with steel balls, or different sulfide minerals contact with each other, the galvanic couples are going to form due to the difference of their surface rest potentials, and the coupling corrosion is going to take place certainly<sup>[10-13]</sup>.

When two or more kinds of sulfide minerals exist in the grinding pulp, the multiphase coupling corrosion is going to form, in which the ball acts as an anode and the oxidation takes place on it, and the sulfide mineral with more noble potential contacting with the ball acts as a cathode and the reduction takes place on it. In addition, between sulfide minerals forms an additional coupling corrosion according to their rest potentials, thus making the corrosion behaviors and the solution-chemistry properties of grinding system complicated.

## 2 MEASUREMENTS OF POTENTIAL AND CURRENT

For the measurements of rest potentials, py-

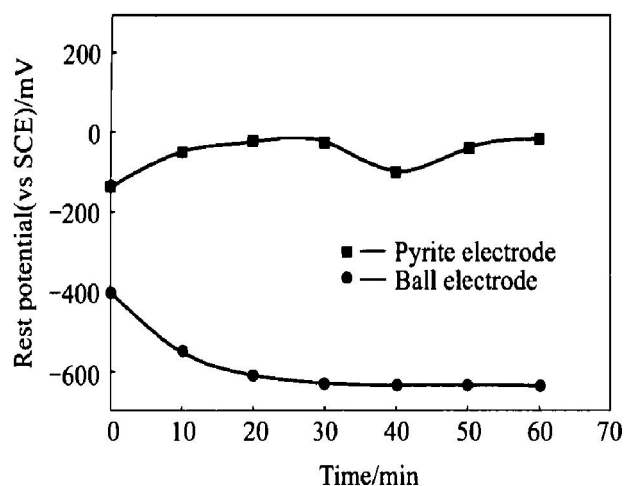
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**Table 1** Rest potentials of sulfide minerals and steel in neutral solution

Mineral	Electrolyte	Rest potential (vs SHE) / mV		
		N <sub>2</sub> bubbling	Air exposed	O <sub>2</sub> bubbling
Pyrite	Distilled water	405	445	485
	0.001 mol/L Na <sub>2</sub> SO <sub>4</sub>	389	391	393
White pyrite	Distilled water	277	303	323
Cobalt pyrite	Distilled water	200	275	303
Copper pyrite	Distilled water	190	355	371
	0.05 mol/L Na <sub>2</sub> SO <sub>4</sub>	115	–	265
Pyrrhonist	Distilled water	55	160	173
	Distilled water	125	262	295
	Distilled water	155	290	335
	0.001 mol/L Na <sub>2</sub> SO <sub>4</sub>	262	277	308
	0.05 mol/L Na <sub>2</sub> SO <sub>4</sub>	58	–	190
Galena	Distilled water	142	172	218
Steel medium	Distilled water	– 355	– 255	135
	Distilled water	– 515	– 335	175
	0.05 mol/L NaCl	–	– 395	–

rite and ball (middle carbon steel, HRC59) electrodes were respectively placed in a solution exposed to open air together with a saturated calomel electrode (SCE), and 0.025 mol/L Na<sub>2</sub>SO<sub>4</sub> solution was used as the supporting electrolyte. 1 g iron scraps with size of less than 0.83 mm were put into the solution after 30 min. The potential-time curves of pyrite and ball electrodes are shown in Fig. 1. It is observed that there is a significant distinction in the variation of rest potentials of pyrite and ball electrodes with time. In the absence of iron scraps, the rest potential of the pyrite electrode increases with time, that of the ball electrode decreases, and the rest potential values of both tend to become steady after about 30 min. After adding iron scraps into the solution, the rest potential of the ball electrode still keep steady, and that of pyrite electrode decreases but increases gradually after another 10 min.

**Fig. 1** Rest potential-time curves of pyrite and ball electrodes in solution exposed to air

The combination potentials and the galvanic currents of the short-circuited pyrite-ball electrode pair were also measured. Typical examples of the potential-time and current-time curves in solution exposed to the air or bubbled with O<sub>2</sub> are presented in Fig. 2 and Fig. 3. The initial combination potential and the initial galvanic current bubbling with oxygen are greater than those bubbling with air. The combination potential and the galvanic current decrease more quickly with time in aeration of oxygen than they do in aeration of air. Because the magnitude of the current represents the rate of reaction taking place on the electrode surface, at the beginning the corrosion rate of the steel ball electrode under the condition of bubbling with oxygen is greater than that under the condition of an air-exposed. With oxidizing (passivation) of the ball electrode surface, its corrosion rate is hindered. The corrosion rate decreases rapidly with time under oxygenated condition and it does gradually with time in an air-exposure. When reaching a steady state, the corrosion rate under oxygenated condition is greater than that under an air-exposure.

But in wet grinding practice, an oxidic film (more noble) forming on the steel ball surface and hindering the corrosion rate can be timely abraded away by mechanical action and the new area (more active) exposes out, without the change of the galvanic current of the pair with time. For this reason, the corrosion rate of steel balls under the condition of bubbling oxygen is always greater than that under the condition of an air-exposure<sup>[13]</sup>.

For the presence of wear difference, not only an oxidized area but also an abrasive active area exist as well on the surface of the same ball. The rest potential of the oxidized area is relatively higher and that of

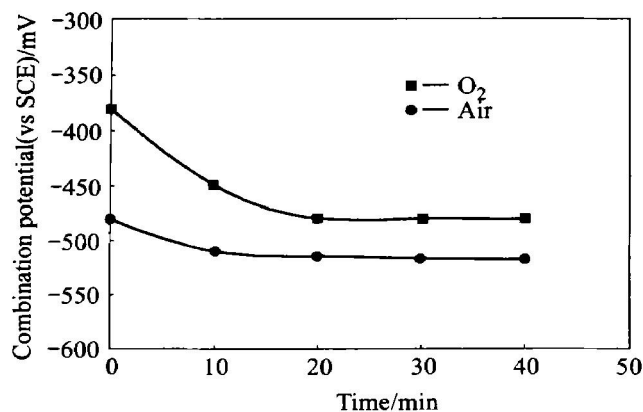


Fig. 2 Combination potential of pyrite-steel ball electrode pair as function of time under different aeration conditions

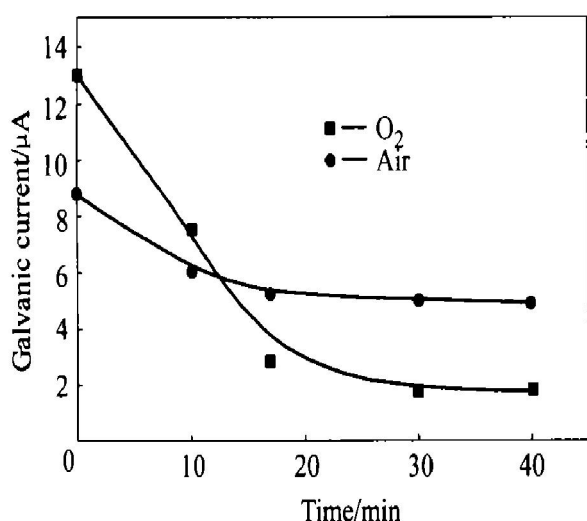


Fig. 3 Galvanic current of pyrite-steel ball electrode pair as function of time under different aeration conditions

the active area is lower. The presence of potential difference results in wear - different cells forming on the same surface. In order to simulate this wear difference, we used a surface-oxidized ball electrode and a surface-polished ball electrode to form an electrode pair. The variation of the combination potential and galvanic current of the simulated cell through time is presented in Fig. 4.

Fig. 4 demonstrates that between two different ball electrodes in wear degree exists a galvanic current, which is smaller than that between pyrite and ball electrodes. The combination potential and the galvanic current decrease with time and become steady after 20 min. In the wear-different cell, the abrasive area acts as an anode and the oxidized area a cathode.

### 3 MEASUREMENTS OF ELECTROCHEMICAL CORROSION

As it is well known, for the corrosion of steel

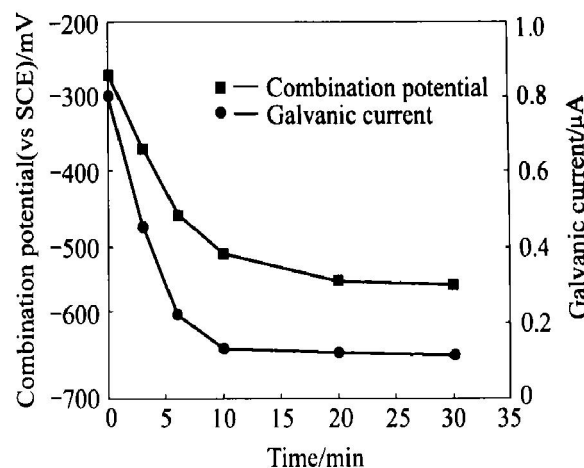


Fig. 4 Variation of combination potential and galvanic current through time for simulated wear difference cell

balls in aqueous media, oxygen plays a major role. While the pulp is in neutral solution, the cathode reaction of a coupling corrosive cell takes place mainly by oxygen reduction<sup>[2]</sup>. To control the mill atmosphere, nitrogen was introduced by a tube inserted through a hole at the center of the mill in which iron ore with 3.1% mass fraction of pyrite was ground, so as to exhaust oxygen away from the mill and inhibit the cathode reaction of electrochemical corrosion. Therefore, the ball wear flushed with nitrogen can be considered as pure abrasive wear. So it can be assumed that the difference in the ball mass losses between under the air and under nitrogen represents the corrosion wear of the ball in wet grinding<sup>[13]</sup>. The correlation of the wear by mass of the marked ball with a diameter of 30 mm with the grinding time under different aeration conditions is listed in Table 2. Clearly, the ball wears increase in all cases, when the mill atmosphere is changed from nitrogen to the air.

Table 2 Marked ball wear by mass and grinding time under different aeration conditions

Grinding time/min	Marked ball wear/mg		
	$m_{N_2}$	$m_{air}$	$\Delta m = m_{air} - m_{N_2}$
20	7.9	9.1	1.2
40	15.6	18.1	2.5
60	23.2	27.0	3.8

According to Faraday's law:

$$\Delta m = AIt/ZF \quad (1)$$

the corrosion current density of the ball,  $J$  can be obtained as

$$J = \frac{\Delta m Z F}{S A t} \quad (2)$$

where  $A$  is atomic mass;  $Z$  is electron number in an anodic reaction;  $F$  is Faraday constant;  $\Delta m$  is corrosion wear by mass of the ball, mg;  $S$  is ball surface

area,  $\text{cm}^2$ ;  $t$  is grinding time, s. Thus,

$$J = \frac{96\,500 \times 2 \times \Delta m}{28.26 \times 55.847 \times t} = 122.29 \Delta m / t \quad (3)$$

By solving Eqn. (3), the current density values are obtained in Table 3.

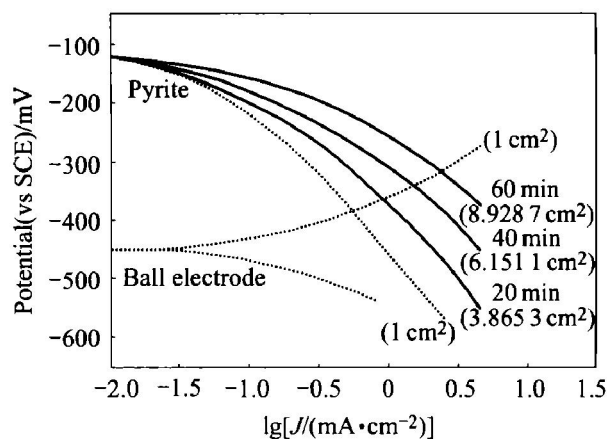
**Table 3** Comparison of corrosion current densities obtained by two methods ( $\text{mA}/\text{cm}^2$ )

Grinding time/min	Marked ball wear test	Polarization curve
20	1.152 0	0.936 7
40	2.399 9	2.016 5
60	3.647 9	3.095 8

The marked ball surface area is converted from its mass. The surface areas of the feed and the products are determined on the basis of size analysis data and specific surface tested, respectively. Since the pyrite surface area and the ball surface area are different at different grinding times, in order to simplify the calculation, the arithmetic average of the initial and the final values is approximately used as the ball surface area, and similarly the pyrite surface area is assumed to be the arithmetic average of the initial and the final values of the ground products multiplied by the respective percentage of pyrite in the ore mixture<sup>[8]</sup>, supposing pyrite component possesses the same size distribution as the ore mixture. The correlation of surface areas of pyrite particles and steel balls with grinding time is shown in Table 4.

It can be found from the data listed in Table 4 that the pyrite surface area increases with the grinding time, without the obvious variation of the ball surface area. Consequently, the ratio of pyrite surface area to ball surface area increases with the grinding time. In fact, the increase of pyrite surface area increases the cathode surface area, enlarges the current density of an anode and accelerates the anodic reaction rate or the corrosion wear rate of the ball.

Fig. 5 illustrates the procedure for the corrosion current density determination. Measured po-



**Fig. 5** Estimation of corrosion current densities for pyrite-steel ball system

(Solid lines—Cathodic polarization curves;  
Dashed lines—Measured polarization curves)

larization curves of pyrite and ball electrodes are presented in dashed lines, while the polarization curves of pyrite expressed in terms of the unit surface area of balls are presented as solid lines. According to the corrosion theory<sup>[1,2]</sup>, the points at which the solid lines meet the cathodic polarization curve of the steel ball electrode determine the corrosion current densities of the ball<sup>[8,13]</sup>. The results illustrated by the polarization curves are compared in Table 3 with the corresponding corrosion current densities estimated from the marked ball wear data by applying Faraday's law.

The data listed in Table 3 indicate that at different grinding times, the equivalent corrosion current densities calculated from the marked ball wear data by applying Faraday's law correlate well with those estimated from polarization curves of pyrite and ball electrodes, and the former is always greater than the latter. This is because the current densities from the polarization curves only represent those between pyrite and steel balls. But there are some other sulfide minerals besides pyrite in grinding samples, and multiplicity couples in fact exist in the grinding system so as to accelerate the electrochemical corrosion wear of steel balls.

**Table 4** Pyrite and ball surface areas at different grinding times

Grinding time/min	Ball surface area/ $\text{cm}^2$			Pyrite surface area/ $\text{cm}^2$			Relative surface ratio
	Initial	Final	Average	Initial	Final	Average	
20	1 376.05	1 375.87	1 375.96	1 655.80	8 981.16	5 318.48	3.865 3
40	1 375.87	1 375.49	1 375.68	1 655.80	15 267.97	8 461.89	6.151 1
60	1 375.49	1 374.95	1 375.22	1 655.80	22 901.96	12 278.88	8.928 7

## 4 CONCLUSIONS

1) Electrochemical determining data demonstrate that the rest potential of the pyrite electrode increases with time and that of the ball electrode decreases in the absence of iron scraps. The rest potential of the ball electrode still keeps steady, and that of the pyrite electrode tends to decrease after adding iron scraps into the solution. The galvanic couples will exist between the pyrite particles and the steel balls when they contact with each other, because the rest potential of the steel ball electrode as an anode is lower and that of the pyrite electrode acts as a cathode is higher.

2) The initial combination potential and the initial galvanic current of a pyrite-steel ball couple in aeration of oxygen are greater than those in aeration of air. The combination potential and the galvanic current decrease more quickly in aeration of oxygen than they do in aeration of air.

3) In an experiment of simulating wear differences, between two different ball electrodes in the wear degree exists a galvanic current, which is smaller than that between the pyrite electrode and the ball electrode. In the wear difference cell, the abrasive area acts as an anode and the oxidized area acts as a cathode.

4) The equivalent corrosion currents calculated from the ball wear data by applying Faraday's law correlate well with those estimated from the polarization curves and the former is always greater than the latter. This is because the current densities from the polarization curves only represent those between pyrite and the ball. But there are some other sulfide minerals besides pyrite in grinding samples, and multiplicity couples in fact exist in the grinding system so as to accelerate the electrochemical corrosion wear of

steel balls.

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