

An investigation of the corrosive wear of steel balls in grinding of sulphide ores

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Abstract

Ball mills are common grinding equipment in mineral processing industries. Ball wear results from three mechanisms namely impact, abrasion and corrosion. Of these, the corrosion mechanism is the least investigated, due to its chemical-electrochemical nature. Therefore, the aims of this research were to investigate the grinding chemistry influence (slurry pH, solid percentage, water chemistry and gas purging) on corrosive wear of steel balls and to determine the contribution of corrosion mechanism to total wear of steel balls. The results indicated that the mass losses of steel balls could be reduced considerably by controlling the pulp chemistry inside the mill. In addition, the results showed that 73.51% of the corrosion products are generated from the oxidation of steel balls. It was also estimated that the corrosion mechanism accounts for 26.68% of the total wear of steel balls.

Keywords: *corrosion mechanism, grinding, steel balls, sulphide ore, wear.*

1. Introduction

Grinding in ball mills is an important technological process applied to reduce the size of particles, which may have different nature, and a wide diversity of physical, mechanical and chemical characteristics. However, ball mills have been widely applied in different fields such as the mining, chemical and pharmaceutical industries. One of the most popular ball mills is the tumbling ball mill, which consists of a rotating cylindrical drum with grinding media such as balls [1-3].

The use of balls in the grinding of ores is a major item in the costs of milling operations. It has been known that the total wear of grinding media in ball mills included mechanisms of abrasion, corrosion and impact, but it is difficult to isolate the contribution of each wear mechanism towards total media wear [4]. It is estimated that over half of the grinding media wear, results from corrosion or dissolution from the active nascent metal surfaces continuously exposed

during grinding [5]. Corrosive wear is defined as metal loss due to chemical and electrochemical reaction [6-9]. Corrosion of the ball is essentially a kind of oxidant-reduction reaction that takes place on its surface. Therefore, the corrosive wear of balls can be seen more in the grinding of sulphide ore. This is because most of the sulphide minerals are nobler than the media used during grinding, and as such, results in a galvanic couple between the ball and the sulphide mineral. Thus, this increases the dissolution of ferrous ions from medium, which are usually precipitated in surfaces of the sulphide minerals [5, 7] and consequently result to increase in metal losses.

In addition, there are many different factors that could have effect on the mass losses of grinding media, such as metallurgical properties of the grinding media, grinding media size, grinding media distribution, shape, charge weight, hardness of ore, work index (where the work index is defined as the specific energy (kWh/t) required to reduce a particulate material from infinite grain size to 100 microns), ore density, ore mineralogy (that is, percentage of sulphides, oxides, magnetite), particle size, speed and discharge type of the mill, throughout of grinding circuit, circulating load, grinding time and grinding chemistry (pH, percent solid, viscosity, Eh, gas purging (air, O₂ and N₂), temperature, rheological properties and water chemistry (that is, anions; Cl⁻, SO₄⁻²; cations; Ca⁺², Mg⁺², Fe⁺², Fe⁺³)) [4, 7, 9-20].

Numerous studies have been conducted [5, 7, 9-22] on the influence of these factors in the wear of grinding media during the grinding of sulphide minerals (or ores), but little attention has been given to assess the influence of grinding chemistry on the mass losses of steel balls and to determine the amount of corrosion products derived from the oxidation of steel balls inside ball mills. Nevertheless, the contribution of corrosion mechanism to the

total wear of the media used for the ball grinding of sulphide ores is yet to be reported. Thus, this study aimed to evaluate the effect of grinding chemistry (pH, solid content, water chemistry) on corrosive wear of steel balls and to determine the contribution of corrosion to total wear of steel balls, as well as to estimate the obtained corrosion products from the oxidation of steel balls in the grinding of sulphide ore.

This study was carried out on Sarcheshmeh sulphide copper ore. Sarcheshmeh copper deposit is the major producer of copper in Iran and one of the 10 biggest copper mines of the world. It is located in Kerman Province, at a distance of 60 km from Rafsanjan city.

2. Experimental

2.1. Materials

The samples obtained from the ball mills input of Sarcheshmeh copper mine were crushed in a jaw crusher (Fritsch 01.703). The size fraction of -2000 +250 microns was collected for the experiments. The samples were then homogenized and sealed in polyethylene bags. Thereafter, samples were chemically analyzed and their chemical compositions are presented in Table 1.

Two types of steel ball, including low alloy and high carbon chromium steel were employed as grinding media, and thus their chemical compositions are listed in Table 2.

Two types of water (distilled water and tap water) were used to investigate the influence of water chemistry on balls wear during grinding, and thus the chemical analysis of tap water is presented in Table 3.

Table 1. Chemical composition of the Sarcheshmeh ore sample (Wt %)

Chemical compositions (Weight, %)					
Cu	Fe	Mo	S	SiO ₂	Al ₂ O ₃
0.74	4.34	0.032	3.05	55.07	14.35

Table 2. Chemical composition of steel ball

Ball type	Chemical compositions (Weight, %)							
	C	Si	S	P	Mn	Cr	Mo	Cu
High carbon chrome steel (HS)	2.28	0.698	0.049	0	1	13.25	0.177	0.044
Low alloy steel (LS)	0.249	0.173	0.024	0.018	0.586	0.019	0.002	0.012

Table 3. Chemical composition of the tap water sample

Chemical analyze (ppm)					
Cl ⁻	Ca ⁺²	SO ₄ ⁻²	Fe ⁺²	Fe ⁺³	Mg ⁺²
37.8	24.3	40	Tr	0.02	3

2.2. Grinding

In order to investigate the effect of grinding chemistry on the mass loss of steel balls (wear), a specialized laboratory ball mill was designed in R&D of Sarcheshmeh copper mine. This mill was constructed using a stainless steel pipe with 21 cm in diameter and length of 30 cm with a wall thickness of 0.7 cm. An electrochemical apparatus associated

with gas purging was also linked to the mill. This grinding system can be used to control the chemical conditions and to study the electrochemistry inside the mill. The schematic plan of the mill is illustrated in Figure 1.

Generally, the setup experiments involved a specialized ball mill and electrochemical tools which include potentiostat/ galvanostat coupled with a personal computer for data acquisition and potential control accompanied by a three-electrode system, the gas purging system and meters for monitoring chemical conditions (Eh, pH and DO).

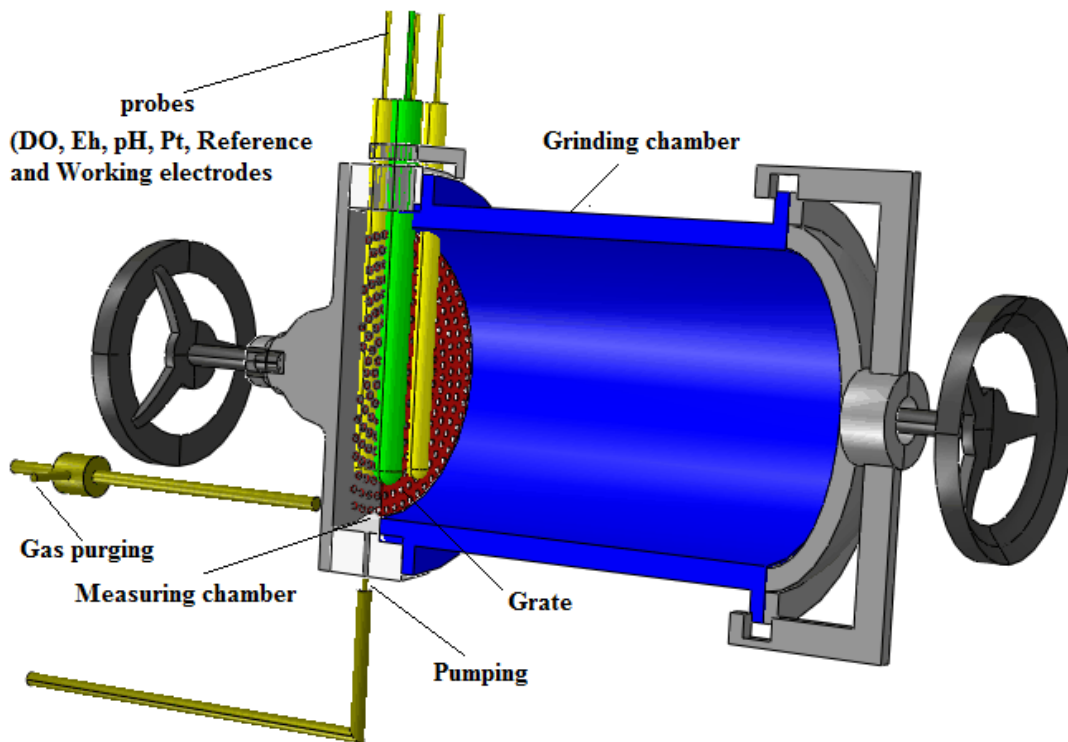


Fig. 1. Schematic representation of specially designed ball mill

2.3. Fabrication of grinding media

A grinding media electrode was fabricated to study and determine the corrosion rate of steel balls. In order to fabricate the grinding media (steel ball) electrode, samples of medium were cut into a size of 7×7 mm, to fill a Teflon tube. Then, a copper wire was connected to the back of the medium with electrically conductive silver epoxy. After that, the sample was mounted in a Teflon tube with the working surface exposed, and the central part of the tube was sealed with non-conductive epoxy resin. The surface of the electrodes were

gently polished with 500 grit silicon carbide paper prior to each test and cleaned with acetone and double distilled water. After each experiment, electrodes of the used medium were repolished and then reused.

2.4. EDTA extraction technique

The EDTA (ethylene diamine-tetra acetic acid disodium) extraction process was used to determine the amount of oxidized iron species from minerals and/or grinding media, which was carried out on the designed mill discharge as follows [15, 23-24].

A 3% by weight solution of ethylene diamine-tetra acetic acid disodium salt was prepared and the solution's pH was adjusted to 7.5 with sodium hydroxide. In this study, 250 ml of EDTA solution was placed into a beaker and stirred using a magnetic stirrer. Further, a 25 ml sample of the pulp was collected from mill discharge. The samples were weighted to determine the mass of the pulp. The pulp was injected into the EDTA solution and then stirred for 5 min. At the end of the 5 min extraction, the sample was filtered through a 0.22 micron Millipore filter paper using a vacuum filter. The filtrate was analyzed using atomic absorption spectroscopy (AAS). However, the solids from the bulk sample, from which 25 ml of pulp was collected, were assayed. Finally, the percent of EDTA extractable iron was determined by dividing the mass of iron in the solution by the total mass of iron in the solids.

3. Results And Discussion

3.1. Effect of grinding chemistry on steel ball wear

In order to investigate the effect of grinding chemistry on the mass losses of ball, 365 samples were ground under different experimental conditions in a specialized mill using an 8 kg ball (mixing of 0.5, 0.75 and 1 inch ball in diameter), grinding time of 15 min and rotation speed of 75 rpm, such that 70% of the particles were less than 75 μm in diameter. In

determining the ball mass losses through total wear, 15 steel balls were handpicked and marked and were weighted before and after each grinding experiment. In order to investigate the influence of gas purging on corrosion rate, different gases (nitrogen, air or oxygen) were continuously injected at the rate of $6 \frac{l}{\text{min}}$ into the mill to change the oxidation conditions. The results associated with experimental conditions are presented in Table 4.

As shown in Table 4, ball loss is significantly affected by pulp pH and solid content. It can be seen that higher pH and percentage of solid, result in a smaller loss of steel ball mass. This may be attributed to the fact that high pH leads to the formation of iron salt precipitates and consequently a passive film.

In addition, injection of different gases into the mill significantly alters the oxidation-reduction environment during grinding, by providing or removing oxygen from the mill. As considered, the gas change from nitrogen to air to oxygen increase corrosion products during grinding, and consequently increases steel ball loss. When tap water was used in grinding, it was observed that the mass losses of the ball was 1.8 times higher than when distilled water was used. This is probably because of the high presence of chloride and sulfate in tap water.

Table 4. The conducted tests conditions and the calculated mass losses at grinding time of 15 min

Factors			The mass loss of balls (mg)	
pH	Solid content	Aeration type	Water type	
7-7.5	35	Without aeration	Tap	1.6
8-8.5	35	Without aeration	Tap	1.5
9-9.5	35	Without aeration	Tap	1.4
10-10.5	35	Without aeration	Tap	1.3
7-7.5	30	Without aeration	Tap	2.4
7-7.5	40	Without aeration	Tap	1.9
7-7.5	45	Without aeration	Tap	1.4
7-7.5	55	Without aeration	Tap	1.2
7-7.5	35	O ₂	Tap	2.4
7-7.5	35	Air	Tap	2.1
7-7.5	35	N ₂	Tap	0.8
7-7.5	35	Without aeration	Distilled	0.9

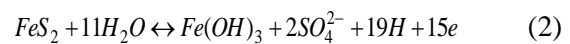
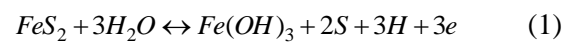
3.2. Determining the contribution of corrosion mechanism and amount of oxidation balls during grinding

An EDTA extraction technique was employed as measurement of system corrosion, as well as to determine the amount of oxidized iron species from steel balls in order to qualify the extent of oxidation of the balls, as well as how much of the corrosion products are derived from the oxidation of steel balls inside mills.

In order to determine the extent of ball oxidation, a series of grinding experiments were conducted with pure pyrite mineral, in which its chemical analysis was determined as 99% FeS₂ and 0.7% Al₂O₃. The extent of steel balls oxidation was estimated as follows.

It is hypothesized that pyrite is oxidized by the reactions presented in Equation 1 or 2 [25-28]. On the other hand, the two equations show that the amount of dissolved sulphur is twice that of EDTA extractable iron formed from pyrite oxidation. Therefore, the oxidation amount of steel balls ($Q_{Ox, Ball}(t)$) is the amount of EDTA extractable iron ($Q_{EDTA, Fe}(t)$) minus half the dissolved sulphur ($\frac{Q_{DS}(t)}{2}$) given in Equation 3 [16]. The value of EDTA extractable iron from mineral and grinding media, the oxidation value of steel ball (different of EDTA extractable Fe and

half the dissolved sulphur) and the percentage of corrosion products of steel balls associated with experimental conditions are presented in Table 5. In Table 5, the percentage of corrosion products obtained from oxidation of steel ball were attained from dividing the amount of ball oxidation (the produced Fe percentage from steel ball in inside mill) to the EDTA extractable Fe percentage (the produced Fe from steel ball and pyrite). If it is averaged from the last column of Table 5, it can be seen that 73.51% of the corrosion products were averagely generated from the oxidation of steel balls in ball mills:



$$Q_{Ox, Ball}(t) = Q_{EDTA, Fe}(t) - \frac{Q_{DS}(t)}{2} \quad (3)$$

In order to determine the contribution of corrosion mechanism to total wear of steel balls, ten grinding experiments were conducted. In eight experiments, low alloy steel balls were used but in the other two experiments, high alloy steel balls were used as grinding media. The steps involved in qualifying the contribution of corrosion mechanisms are as follows:

Table 5. The obtained corrosion products (%) and EDTA extractable Fe (%) from the oxidation of steel balls

pH	Factors				EDTA extractable Fe (%)	Difference EDTA Fe and the half dissolved sulphur (%)	The amount of Corrosion (%)
	Solid %	Aeration type	water Type	ball Type			
7-7.5	35	Without aeration	Tap	LS	0.185	0.139	75.14
10-10.5	35	Without aeration	Tap	LS	0.095	0.069	72.63
7-7.5	55	Without aeration	Tap	LS	0.089	0.066	74.16
7-7.5	35	Without aeration	Distilled	LS	0.091	0.064	70.33
7-7.5	35	Oxygen	Tap	LS	0.501	0.419	83.63
7-7.5	35	Air	Tap	LS	0.362	0.289	79.83
7-7.5	35	Nitrogen	Tap	LS	0.064	0.045	70.31
7-7.5	35	Without aeration	Tap	HS	0.084	0.06	71.43
7-7.5	35	Without aeration	Tap	HS	0.058	0.043	74.14
7-7.5	35	Without aeration	Tap	HS	0.049	0.037	75.51
7-7.5	35	Without aeration	Distilled	HS	0.057	0.039	68.42
7-7.5	35	Oxygen	Tap	HS	0.196	0.146	74.49
10-10.5	55	Air	Tap	HS	0.121	0.089	73.55
7-7.5	35	Nitrogen	Tap	HS	0.032	0.021	65.63

Step 1. The ball mass losses through total wear (m_{wear}) were determined by weighting the marked steel balls before and after each grinding test.

Step 2. The corrosion rate of balls was determined using electrochemical equipments (potentiostat/galvanostat and three electrode system) linked to the ball mill in which the three-electrode system was comprised of an Ag/AgCl (3.0 M KCl) electrode as a reference electrode, Pt wire as the counter electrode and grinding media electrode as working electrode. Measurements were carried out using a computerized potentiostat/ galvanostat (SAMA500 Electrochemical Analysis System, SAMA research center, Iran) by Tafel extrapolation method and technique of linear sweep voltammetry. Thereafter, the corrosion rate was calculated using the following formula [29]:

$$CR = \frac{0.1288 \times EW \times j_{corr}}{\rho} \quad (4)$$

where CR is the corrosion rate, j_{corr} is the corrosion current density ($\mu A/cm^2$), EW is the equivalent weight of metal (g) and ρ is the density of metal (g/cm^3).

The potentiostatic parameters j_{corr} and E_{corr} were obtained from the confluence of slopes of linear polarization curves (Slopes of cathodic and anodic branches). For example, the polarization curves of the experiment are presented in Figure 2.

Step 3. After determining the corrosion rate, the losses in ball mass through corrosive wear (m_{corr}) were determined using the following equation [30]:

$$CR = \frac{534 \times W}{\rho \times A \times t} \quad (5)$$

where CR is the wear rate (CR can also be impact, abrasive or corrosive wear rate) in mils penetration per year (mpy), W is weight loss in milligrams, ρ is the density in grams per cubic centimeter, A is area in square inches, and T is time in hours [30].

Step 4: The contribution of corrosion mechanisms was obtained by dividing the mass losses of corrosion with the mass losses of total wear ($\frac{m_{corr}}{m_{wear}}$). The experimental conditions accompanied by the results are presented in Table 6.

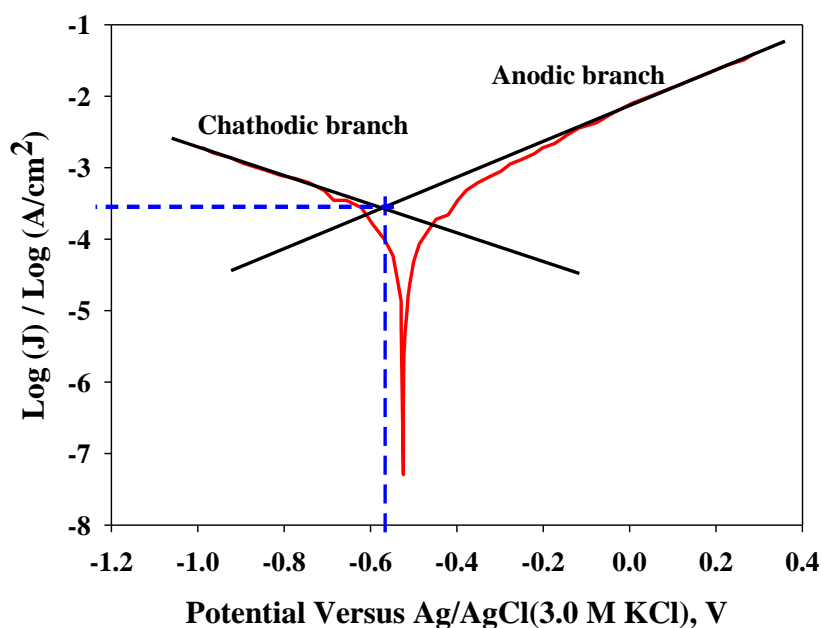


Fig. 2. Tafel extrapolation curves were measured with scan rate of 0.050 (V/s) for steel ball at pH between 7-7.5, solid percentage of 35%, for a grinding time of 15 min, and rotation speed of 75 rpm.

Table 6. The mass losses of steel balls through total wear and corrosive wear in grinding process

Run	Experiments conditions	m_{wear} (g)	m_{corr} (g)	$\frac{m_{corr}}{m_{wear}}$ (%)
1	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: low alloy steel (10 kg)	0.0045	0.00137	30.22
2	water type: tap, pH: 7, percent solid: 55 , grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: low alloy steel (10 kg)	0.0029	0.00068	23.45
3	water type: tap, pH: 10 , percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: low alloy steel (10 kg)	0.0031	0.00085	27.42
4	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore B and ball type: low alloy (10 kg)	0.0049	0.00146	29.79
5	water type: tap, pH: 7, percent solid: 35, grinding time: 90 min , mill speed: 75 rpm, ore A and ball type: low alloy steel (10 kg)	0.0064	0.00216	33.75
6	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 85 rpm , ore A and ball type: low alloy steel (10 kg)	0.0052	0.00164	31.54
7	water type: distilled , pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: low alloy steel (10 kg)	0.0027	0.00074	27.41
8	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: low alloy steel (15 kg)	0.0047	0.00132	28.08
9	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore A and ball type: High steel (10 kg)	0.0024	0.00045	18.75
10	water type: tap, pH: 7, percent solid: 35, grinding time: 60 min, mill speed: 75 rpm, ore B and ball type: High steel (10 kg)	0.0033	0.00087	26.36

As shown in Tables 5 and 6, the amount of EDTA extractable iron (corrosion products) and ball losses reduced with increase in solid percentage, pulp pH, change of ball composition and metallurgical properties. Beside, with changes in solid percentage from 30 to 55 and pH from 7 to 10, as well as change of ball type from low alloy to high carbon chromium steel, the mass loss of balls reduced by half. The reduction of mass losses with change of solid content is attributed to the fact that as the feed solids percentage increased, the pulp viscosity increased as well, which affected the abrasion rate. At higher pulp viscosity, the motion of the balls and the sulphide samples were reduced. If the pulp viscosity was too high, the balls and the sulphide samples would be stuck on the ball mills shell, significantly reducing the abrasion rate. Another reason is that at lower feed solids percentage, more oxygen will be dissolved in the slurry of inside mill, which increase the corrosion of steel balls.

As earlier mentioned, the decrease of mass losses at the higher pH may be due to the formation of passive ferric oxide at high pH, which reduces corrosive wear of balls.

It was also observed that when the mill rotation speed was increased from 75 to 85 rpm, the mass losses of balls increased. This may be attributed to the motion of the ball from sliding to cascading [31]. Meanwhile, it is clear that with increase in grinding time and change of water type from distilled water to tap water, the losses of steel balls increased.

In addition, it can be concluded from Table 6 that the contribution of corrosion mechanism to total wear of steel balls in grinding a sulphide ore is averagely 27.68%.

4. Conclusion

A series of grinding experiments using a specially designed ball mill were carried out in order to investigate the influence of grinding chemistry on the mass losses of steel ball, as well as to study the corrosion mechanism

contribution to the mass losses of balls in grinding of Sarcheshmeh copper sulphide ore. The results implied that:

1. Solutions with higher pH and solid content produced less mass losses.

2. The wear rate and corrosion products increased with gas changes from nitrogen to air to oxygen. This could be attributed to the fact that oxygen purging increased the dissolved oxygen content, which led to an oxidizing grinding environment, while nitrogen purging significantly removed oxygen from the grinding atmosphere and dissolved oxygen in the slurry. This resulted in a significantly oxidizing environment and effectively increased metal loss.

3. Water chemistry affected the corrosion of balls and consequently resulted to further mass losses.

4. The low alloy steel balls wear were majorly due to the composition and metallurgical properties of steel balls.

5. The corrosion mechanism formed 26.68% of the total wear balls and the remaining abrasion and impact were formed in ball grinding of sulphide ores.

6. It was estimated that 73.51% of corrosion products were derived from the oxidation of steel balls in ball mills.

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