SODIUM DITHIONITE AS A PYRITE DEPRESSANT IN GOLD ORE FLOTATION

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Abstract

Sodium dithionite ($Na_2S_2O_4$) is a widely used reducing agent to control pulp potential (Eh) and pyrite depressant in sulfide ore flotation. In this study, the pyrite depressant effect of sodium dithionite on gold ore flotation was investigated at pH 8 and pH 10.5 comparatively in terms of gold, chalcopyrite, and pyrite recoveries and grades. The presence of sodium dithionite resulted in a drop of approximately 50–70 mV in the Eh values, regardless of the studied pH values, confirming the reducing effect of sodium dithionite. The effects of sodium dithionite on gold and chalcopyrite grades and recoveries were quite limited, especially at pH 10.5. At pH 8, the utilization of sodium dithionite slightly decreased gold and chalcopyrite recovery and grades, while the decrease in pyrite recovery and grades was remarkable. Both pyrite recovery and grade were reduced from 79.5% to 54.7% and 15.3% to 10.7% by the utilization of sodium dithionite at pH 8. In conclusion, it is considered that the selective flotation of gold and chalcopyrite from pyrite can be achieved at a lower pH accompanied by a slightly reduced Eh by the utilization of sodium dithionite.

ALTIN CEVHERİ FLOTASYONUNDA BİR PİRİT BASTIRICI OLARAK SODYUM DİTİYONİT

Anahtar Kelimeler
Flotasyon
Altın
Kalkopirit
Pirit
Sodyum dityionit

Öz

Sodyum dityionit ($Na_2S_2O_4$) sülfürlü cevherlerin flotasyonunda pülp potansiyelini (Eh) düşürmek ve pirit bastırmak için yaygın olarak kullanılan bir indirgeyicidir. Bu çalışmada sodium dityonitin altın cevheri flotasyonunda pirit bastırıcı etkisi pH 8 ve 10,5'ta altın, kalkopirit ve pirit verim ve tenörleri açısından karşılaştırılmalı olarak incelenmiştir. Sodyum dityionitin varlığı, etkisi incelenen pH değerlerinden bağımsız olarak Eh değerlerinde, 50-70 mV bir düşüşe neden olmuştur. Bu da sodyum ditionitin indirgeyici etkisine işaret etmektedir. Sodyum dityonitin altın ve kalkopiritin verim ve tenörleri üzerindeki etkisi özellikle pH 10,5'ta oldukça sınırlıdır. Buna karşın, sodyum dityionit pH 8'de altın ve kalkopirit verim ve tenörlerini az miktarda düşürürken, pirit verim ve tenörü üzerinde dikkat çekiçi bir düşüş sağlamıştır. Sodyum dityionitin pH 8'deki kullanımı sonucunda pirit verimi %79,5'ten %54,7'ye düşerken, pirit tenörü %15,3'ten %10,7'ye gerilemiştir. Sonuç olarak, sodyum dityionit kullanımı ile altın ve kalkopiritin, pirit seçimli olarak yüzdürülmesinin daha düşük pH değerinde, Eh değerinin bir miktar azaltılarak elde edilebileceği düşünülmektedir.

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1. Introduction

Gold can occur in ores with a wide range of minerals, mainly in native form to a lesser degree as metal alloys, within iron and base metal sulfides, silicates, carbonates, and oxide minerals (O'Connor and Dunne, 1994). Sulfide ores account for a significant portion of gold production today, and flotation is a well-accepted method to process these ores because it is selective, flexible, and cost-effective (Klimpel, 1997; Teague, Van Deventer, and Swaminathan, 1999).

It is well known that naturally occurring gold can easily be floated with little or no collector addition in a wide pH range (Aksoy and Yarar, 1989; Allan and Woodcock, 2001; Forrest, Yan, and Dunne, 2001; Oluklulu, Gökçen, Bozkurt, and Ucbaş, 2019). However, gold ores are commonly found with a wide range of sulfide minerals, which affects flotation performance significantly (Klimpel, 1999). Differential flotation of gold from these types of ores usually involves unique applications that strongly depend on the ore mineralogy (Bulatovic, 1997; Dunne, 2016).

In most gold-chalcopyrite mineral occurrences, pyrite can be found as the most common host mineral for both gold and chalcopyrite (Chandra and Gerson, 2009; Small, Michelmore, and Grano, 2003). Differential flotation of gold and chalcopyrite from pyrite is an important issue in order to achieve economical beneficiation of gold where liberation is not a problem (Agorhom, Skinner, and Zanin, 2015). As a solution, different approaches have been suggested by the researchers to depress pyrite, including pH adjustment, pulp chemistry control, and reagent selection.

This study investigated the depressant effect of sodium dithionite on pyrite in the case of gold ore flotation. The effect of sodium dithionite was evaluated comparatively based on gold, chalcopyrite, and pyrite recoveries and grades at pH 8 and 10.5, respectively. The aim of this study was to achieve efficient pyrite depression at a relatively lower pH level to avoid excessive use of lime and its possible depression effect on gold and chalcopyrite.

2. Literature Review

In certain cases, the natural hydrophobicity of gold can also be used to achieve differential flotation of gold from pyrite. Oluklulu (2020) proposed that pyrite-selective gold flotation can be achieved by collectorless flotation to a certain extent. Yet, the use of collectors is necessary in order to obtain higher gold recoveries for many ores. Xanthates, dithiophosphates, monothiophosphates, and thionocarbamates are the most common collectors used in gold flotation and are mainly used for flotation of sulfide minerals (Allan and Woodcock, 2001; Bulatovic, 2010; Dunne, 2016). Thus, applications of these collectors make differential flotation of gold more challenging (Monte, Lins, and Oliveira, 1997). According to Nagaraj and Brinen (2001), di-p-cresyl monothiophosphate provided pyrite selective flotation in high Ag content gold ores, while Liu, Zhong, and Dai (2006) stated that they obtained selectivity by using ethoxycarbonyl thioure in porphyry copper ores.

Selective gold floatation can also be achieved by depressing the pyrite. Pyrite depression usually involves strategies such as using depressants, oxidizing agents, or the application of a higher pH (Agorhom et al., 2015). These chemicals generally depress the pyrite by inhibiting the surface adsorption of the collectors (Dunne, 2016).

The use of pH modifiers such as Na_2CO_3, NaOH, and lime is the most common application of pyrite depression in flotation. Pyrite depression at higher pH is proposed to be possible by different mechanisms, such as surface oxidation, inhibition of xanthate adsorption, and precipitation of Ca^{+2} ions on mineral surfaces (Mu, Peng, and Lauten, 2016). Nonetheless, Fuerstenau, Jameson, and Yoon (2007) showed that higher pH levels (pH > 10) are required to successfully depress the pyrite, especially in higher collector concentrations. However, a higher pH could also cause a decrease in the flotation performance of valuable metals such as gold and copper (Qiao, Ye, and Zuo, 2021). As a result, a higher pH is considered ideal for depressing pyrite, while a lower pH is favorable for auriferous pyrite ores (Chandra and Gerson, 2009).

As an alternative, oxidizing and reducing agents such as hydrogen peroxide, sodium sulfide and sulfur oxide species can be used to depress pyrite (Chander and Khan, 2000; Grano, Johnson, and Ralston, 1997; Kydros, Angelidis, and Matis, 1993; Shen, Fornasiero, and Ralston, 2001). The use of these chemicals usually involves the formation of hydrophilic sulfide species on pyrite surfaces with the aeration of the pulp (Eh reduction) in a relatively higher pH (pH > 10) range (Agorhom, Skinner, and Zanin, 2014; Mu et al., 2016). In a similar manner, Monte et al. (1997) used hydrogen peroxide for differential flotation of gold from pyrite. According to that study, hydrogen peroxide cleaned the gold surface while inhibiting collector adsorption to pyrite surfaces due to the oxidation.

Sodium dithionite (SD) or $Na_2S_2O_4$ is also a reducing agent that is used to control the pulp Eh in flotation applications (Bruckard, Kyriakidis, and Woodcock, 2007; Hayes, Price, Ralston, and Smith, 1987; Hintikka and Leppinen, 1995; Smith, Senior, Bruckard, and Davey, 2011). In general, the effects of SD were discussed mainly on the basis of pulp potential, and there are limited studies on the effects of sodium dithionite on sulfur flotation. Kydros et al. (1993) investigated the effects of SD on bulk flotation of an auriferous pyrite ore containing arsenopyrite in an acidic medium. It's reported that the use of SD resulted in a slight activation of pyrite at pH 4. Sui, Finch, Nesset, Kim, and Lajoie (2000) investigated the effects of dithionite ions on galena and sphalerite flotation. The authors stated that the use of SD suppresses galena oxidation and Pb activation of sphalerite surfaces, leading to selective flotation of galena from sphalerite. However, it was also reported that by using SD with xanthate, adsorption to galena surfaces is also inhibited to a certain extent. In a study by Qiao et al. (2021), the effects of sodium dithionite on pyrite and sphalerite minerals were investigated. It was concluded that $S_2O_4^{-2}$

ions originating from SD coated the pyrite surface, rendering it hydrophilic. Mhonde, Johansson, Corin, and Schreithofer (2021) studied the effects of dithionite ions on galena and chalcopyrite flotation using different types of xanthate collectors. It was determined that in the presence of dithionite ions, collector adsorption is decreased on mineral surfaces due to the decomposition of xanthates. It was also reported that flotation performance decreased in mild alkaline conditions due to the accumulation of sulfide ions on galena surfaces and the oxidation of chalcopyrite.

3. Material and Method

3.1 Material

The ore sample utilized in this study was from the Eastern Black Sea region of Turkey. It was formerly dry ground to a p_{80} size of 100 µm by a pilot-scale Loesche VRM and brought to the Eskisehir Osmangazi University Mineral Processing Laboratory. The particle size distribution of the sample is shown in Figure 1. The ore sample was then split into 1 kg batches and kept in the freezer to avoid oxidation.

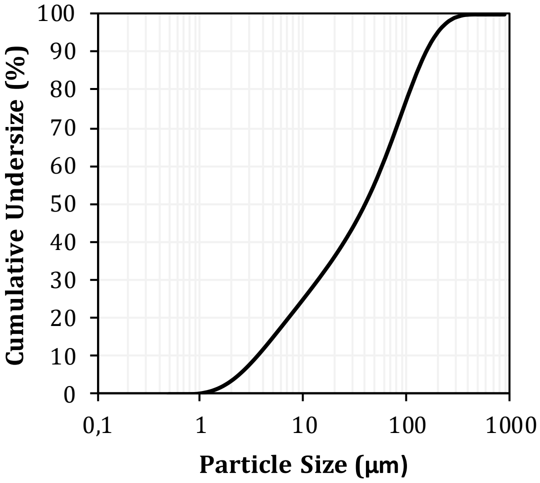

Figure 1. Particle Size Distribution of the Sample

Head assays and flotation test products was carried out using ICP-ES/ICP-MS and fire assay for gold by Bureau Veritas Commodities Canada Ltd. The head assays of the sample are represented in Table 1. Au, Cpy, Py, and S contents of the ore were 1.4 g/t, 0.2%, 5.2%, and 1.4%, respectively. Later, the Cpy and Py content was derived based on the S balance, since Cpy and Py were the main sources of S, as determined by mineralogical analyses.

Table 1. Head Assays of the Sample

Au (g/t)	Cu (%)	Fe (%)	S (%)	Cpy* (%)	Py* (%)
1.40	0.20	5.20	1.40	0.68	2.30

* Determined by balance of S

Mineralogical analyses were carried out on polished thin-sections of the ore using optical and scanning electron microscopy (Figure 2). According to these analyses, the ore can be defined as a low-grade sulfide gold ore. Sulfide mineralization consists mainly of pyrite (Py) and chalcopyrite (Cpy). In the ore, Cpy, the main Cu-bearing mineral, is present as free grains as well as at the boundaries of Py and non-opaque gang minerals. Similar to chalcopyrite, gold mainly occurs as free grains, while some are associated with pyrite and chalcopyrite. Gold grains are mostly in the 30 µm and finer size ranges. Gang mineralization is mainly dominated by quartz. Mica is also present, with moderate amounts of feldspar, carbonates, clay, and magnesium silicate minerals as well.

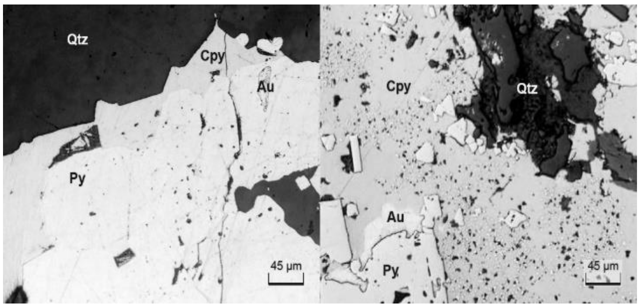

Figure 2. Polished Thin-section Images of the Ore

3.2. Method

Bench scale flotation tests were performed in a 2.5-l flotation cell using a Denver D12 flotation machine. The flotation pulp was set at 35% solids-by-weight by using tap water, and it was stirred at 1300 rpm. The air flow rate was maintained at 7 l/min by using a flow meter. The pH and the pulp potentials (Ag/AgCl) were measured throughout the flotation conditioning by using a Hach HQ40D portable meter equipped with a pH and platinum ORP electrode.

The conditioning of the pulp was carried out over 3 min. periods for a total of 9 min, including pH stabilization, pH adjustment, and the addition and conditioning of the collectors. Sodium dithionite ($Na_2S_2O_4$) from Merck was used in the flotation experiments. The effects of SD were studied at two pH levels, 8 and 10.5. In order to obtain the determined pH levels, lime was used, and SD was added to the pulp in a 1000 g/t dosage immediately after lime addition, if it was used. Potassium ethyl xanthate (PEX) and Cytec A3894 were utilized together as collectors due to their synergistic effects, as mentioned by the manufacturer (Cytec Industries, 2010). Finally, at the 10th minute, AF70 was added as a frother, and froth was scrapped following 1 min. of aeration.

Froth collection was carried out in 30 seconds intervals for a total of 7 minutes. After the flotation products were dried and weighed, they were shipped for chemical analysis. The flotation test results were evaluated based on Au, Cu, and Py recoveries and grades.

4. Results and Discussion

Throughout the flotation, the change in Eh was monitored, and the results are shown in Figure 3 for the studied conditions. The initial pH of the ore was around 6.2 with a corresponding Eh of approximately 250 mV, which stabilized at 6.5 after 3 minutes of conditioning with an Eh of 210 mV. The pH increase resulted in a decrease in Eh, as expected. After the pH adjustment, Eh values were measured as 125 mV and 25 mV at pH 8 and pH 10.5, respectively. SD utilization decreased the Eh values further around 50–70 mV in both pH 8 and pH 10.5, namely 75 mV and -45 mV, respectively. The reducing effect of SD could be attributed to the formation of dithionite ($S_2O_4^{-2}$) ions provided by the oxidation of SD (Selwyn and Tse, 2014).

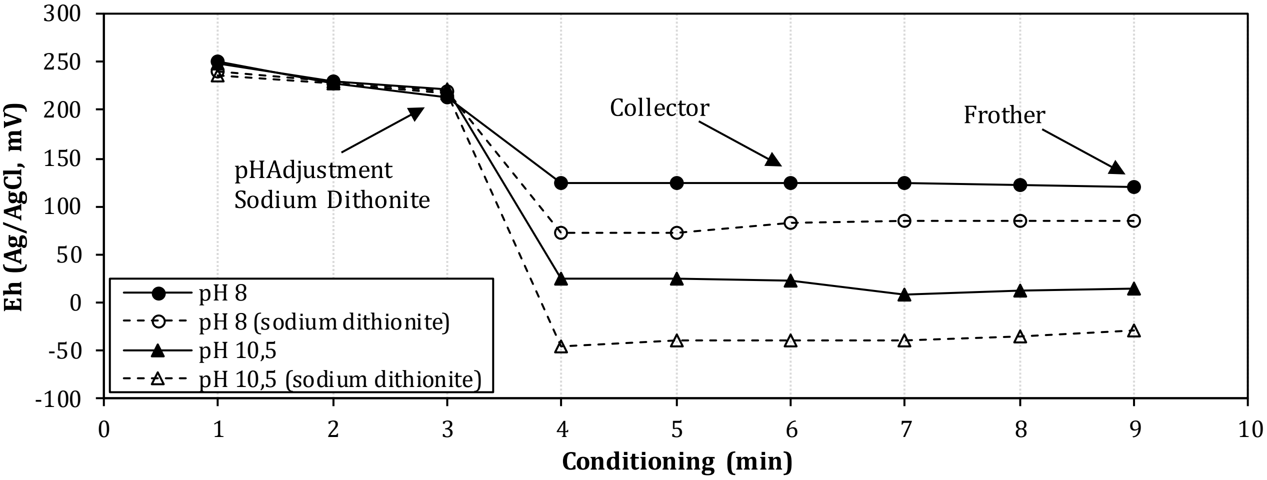

Figure 3. Change of Eh Throughout the Conditioning for pH 8 and pH 10.5, with and without SD (Oluklulu, 2020)

The mass pulls of the flotation concentrates corresponding to the test conditions are shown in Table 2. Mass pulls of around 11% were obtained at pH 8 in both cases with and without SD, indicating the effect of SD on mass pulls was insignificant. Increasing the pH from 8 to 10.5 resulted in a nearly twofold increase in mass pull from 11.9% to 20.7. The use of the SD increased the mass pull of the concentrate even further to 25.1%.

Table 2. Mass Pull of the Flotation Concentrates

Test Condition	Mass Pull (%)
pH 8	11.93
pH 8 SD	11.20
pH 10.5	20.65
pH 10.5 SD	25.14

The effects of SD on Au grade and recoveries for pH 8 and pH 10.5 are shown in Figure 4. In the case of pH 8, without SD, a concentrate having 9.1 g/t Au with a recovery of 77.1% was obtained. SD addition resulted in a 5% loss in recovery (72.3%) while having a similar Au grade (9.3 g/t). Although slightly higher Au recoveries were obtained at pH 10.5 compared to pH 8, Au grades decreased noticeably. At pH 10.5, a concentrate having 5.8 g/t Au with a 79.4% recovery was obtained without SD. With SD, the highest Au recovery of 81.5% was obtained with a grade of 4.6 g/t.

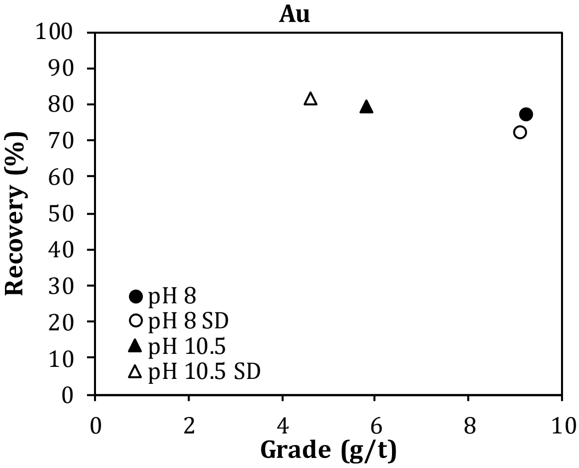

Figure 4. The Effects of SD on Au Recoveries and Grades at pH 8 and pH 10.5

The effects of SD on Cpy grade and recoveries for pH 8 and pH 10.5 are given in Figure 5. In the case of pH 8, a concentrate having 3.4% Cpy with a recovery of 63.6% was obtained. SD addition at pH 8 resulted in a slight decrease in both recovery (58.7%) and grade (3.0%). The pH increase has a limited effect on Cpy recovery while decreasing the grade significantly. A concentrate having 1.6% Cpy was obtained with a recovery of 62.6% at pH 10.5 without SD, while with SD a concentrate having 1.5% Cpy with a 65.7% recovery was obtained.

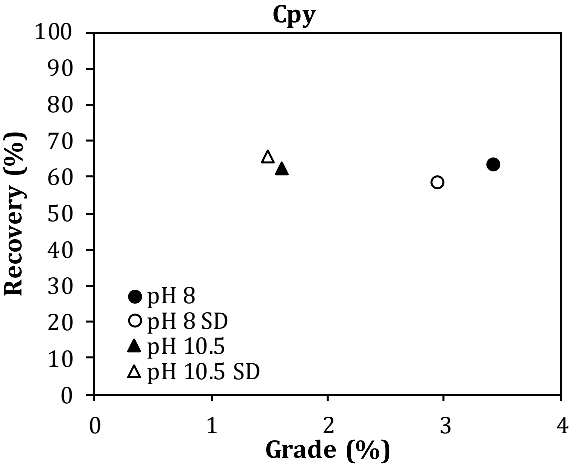

Figure 5. The Effects of SD on Cpy Recoveries and Grades at pH 8 and pH 10.5

The effects of SD on Py grade and recoveries at pH 8 and pH 10.5 are shown in Figure 6. In the case of pH 8, a concentrate having 15.3% Py with a recovery of 79.5% was obtained. Utilization of SD at pH 8 resulted in a significant decrease in both Py recovery and grade. A concentrate having 10.7% Py and 54.7% recovery was obtained. The pH increase from 8 to 10.5 resulted in a slight increase in the Py recovery while decreasing the grade remarkably. A concentrate having 8.4% Py was obtained with a recovery of 81.4% at pH 10.5 without SD. The utilization of SD did not alter the Py grade and recovery. A concentrate having 7.7% Py with a recovery of 82.8% was obtained with SD.

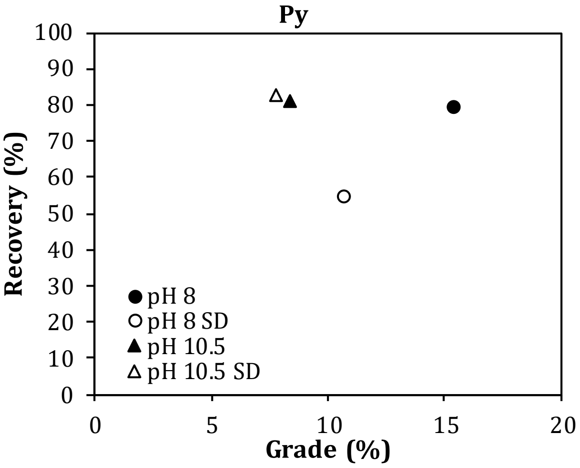

Figure 6. The Effects of SD on Py Recoveries and Grades at pH 8 and pH 10.5

A significant decrease observed in Py recovery and grade at pH 8 compared to pH 10.5 could be attributed to the depression of Py by the reduction of iron oxidation species, elemental sulphur, and the cathodic decomposition of Py (Chemilewski, Birlingmair, and Pollard, 1991). The other possible completing mechanism could be the reduced collector affinity towards Py surfaces due the lowered Eh (Prestidge, Ralston, and Smart, 1993).

As flotation results revealed, the utilization of SD as a Py depressant assisted in the achievement of Py depression at a pH of 8 without significantly altering the Au and Cpy recoveries and grades. In contrast to the traditional method of increasing pH through the use of excessive amounts of lime, the utilization of SD provided additional benefits, such as decreasing lime consumption and inhibiting the potential detrimental impacts of lime on Au flotation. The slight decrease observed in Au and Cpy recoveries could be attributed to the Au and Cpy associations with Py, as confirmed by the mineralogical analysis. The depressant effect of SD at pH 10.5 was insignificant which could be attributed to the higher mass pulls obtained and SD speciation products at this particular pH level.

6. Conclusions

In general, the utilization of the SD resulted in reduced Eh levels at the studied pH levels. Increasing the flotation pH from 8 to 10.5 resulted in higher mass pulls without significantly affecting Au, Cpy, and Py recoveries while decreasing the grades, indicating a loss in selectivity. Furthermore, utilization of SD resulted in effective Py depression at pH 8 without significantly effecting Au and Cpy recoveries and grades.

Consequently, it is considered that the selective flotation of Au and Cpy from Py can be achieved at a lower pH, accompanied by a slightly reduced Eh level, by the utilization of SD. In addition, the selective flotation accomplished at a lower pH was advantageous in terms of lower lime consumption and inhibition of the potential detrimental effects of excessive use of lime in Au flotation.

It's also important to keep in mind that, the ore samples used in this study were dry ground, which could significantly affect the pulp chemistry. Therefore, the effects of the SD should be investigated concurrently for different grinding environments as well as different SD dosages and pH levels, which is the subject of ongoing research.

Contribution of the Researchers

In this manuscript; Semih Oluklulu, contributed to the research, analysis of the results, discussion, and writing the manuscript; Volkan Bozkurt contributed to the research, discussion, and review; and Yaşar Uçbaş contributed to the supervision and review.

Conflict of Interest

No conflict of interest has been declared by the authors.

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