

# Studies of Grinding Media Corrosion from Galvanic Interaction on Galena Flotation

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## Abstract

This study has been done to determine the galvanic interaction between five types of grinding media (mild steel, cast iron, 10% chromium, 20% chromium, and ceramic media) and galena, *in situ* of the mill. The ceramic media has a significantly not galvanic interaction with galena and high chromium media has a significantly weaker galvanic interaction with galena, and produces a very much lower amount of oxidize iron species in the mill discharge than mild steel medium. The investigation of the various reactions occurring on the galena surface was investigated by ethylene diamine-tetra acetic acid disodium salt (EDTA) extraction and X-ray photoelectron spectroscopy (XPS) measurements. The floatability of galena is dependent on the galvanic current between grinding media and galena during grinding because the current is relative to the amount of iron oxidation species and the reduction rate on galena. Iron oxidation species depressed galena flotation. The optimum galena flotation was achieved by selecting grinding conditions that enabled iron oxidation to be controlled.

## Keywords

Flotation, Galena, Galvanic Interaction, Grinding Media

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## 1. Introduction

Galvanic interactions between sulphide minerals and steel grinding media increased iron levels and resulted in the formation of iron hydroxides [1]. The amount of iron oxidation species from grinding media is linked with the difference in the electrochemical reactivity between minerals and media [2]. During galvanic contact between galena and a steel grinding medium, oxidation of steel grinding media increased in the presence of galena [3]. It has been widely accepted that the grinding condition has a large effect on the flotation of sulphide minerals. During grinding, galvanic interaction and galvanic contact are created between minerals and grinding media. The interaction between two sulphide minerals resulting from their electrochemical reactivities is called galvanic.

Such interactions occur whenever two or more sulphide minerals (or a sulphide mineral/grinding media) are in contact. The electrochemical reactivity is indicated by the rest potential of the sulphide mineral, *i.e.* the higher the rest potential, the nobler it is and the less active in thermodynamic sense. Two sulphide minerals in contact with each other establish a galvanic cell where the mineral with the higher rest potential draws electrons from the one with a lower rest potential thus undergoing a cathodic reduction [4]. The cathodic reduction reaction can be represented by:



while the anodic oxidation of the sulphide mineral with a lower rest potential is given by:



The overall reaction is:



A less electrochemically active steel media, such as stainless steel and high chromium media, may give better grades and/or higher recoveries of sulphide minerals [5] [6].

Peng and Grano [7] [8] found that iron contamination from grinding media played a dominant role in depressing galena. The grinding conditions had a more pronounced effect on fine galena flotation [9]. This effect is attributed to a number of chemical mechanisms during grinding including Eh change, iron hydroxide coating on surfaces, oxygen reduction, precipitation from solution and galvanic coupling [10].

Grinding media type is a critical factor in determining the chemistry of the flotation feed pulp [11]. One of the more recently proposed models of media and mineral effects in flotation is galvanic interaction (electron transfer) between minerals and media [12]. Studies on industrial circuits also showed the depression of sulphide flotation after milling in a steel mill possibly due to the coatings of iron oxidation products [6] [13]. Guy and Trahar observed that galena flotation using thiol collectors was faster following autogenous grinding or grinding with stainless steel than that following grinding with mild steel media [14]. Learmont and Iwasaki Rey and Formanek, Thornton, Cases [15]-[18] made the same observation. Guy and Trahar attributed the promoting effect of stainless and autogenous media on galena flotation to two mechanisms:

1) Maintaining a high pulp potential. This followed work by a number of authors who identified that galena flotation was strongly potential-related [19] [20].

2) Collectorless flotation of galena, being strongest after grinding with stainless steel or ceramic media, was attributed to oxidation of the galena surface leading to formation of hydrophobic elemental sulphur.

Learmont and Iwasaki attributed the formation of oxidation products or iron on the galena surface to the use of mild steel [15]. Petruk and Hughson attributed their contradictory result to the high content of pyrite in the ore used, resulting in reducing conditions similar to those which would result from use of mild steel media [21]. The type of grinding media used can have an important effect on flotation.

## 2. Experimental

### 2.1. Material and Reagents

Galena mineral sample was obtained from Nakhlak Mine, Iran. The chemical composition of this sample analysed by XRF is shown in **Table 1**. The sample was crushed through a rolls crusher. The size fraction of +0.6 to 2.0 mm was collected for analysis and experiments. The homogenized sample was then sealed in polyethylene bags.

Five types of grinding media were used as grinding media and supplied from Pars Metal Co., Iran. They are included mild steel, cast iron, 10% chromium, 20% chromium and ceramic.

Sodium isopropyl xanthate (SIPX, AR grade) used as the collector, while MIBC (Methyl Isobutyl Carbonil, AR grade) was employed as the frother in the experiments. A solution of sodium hydroxide (AR grade) was added to maintain the pH at the targeted value during grinding and floatation. High purity nitrogen, air and industrial oxygen and deionised water was used in all experiments.

### 2.2. Mineral Grinding and Flotation

A sample of galena (300 g) was combined with 1 liter of water and ground with 3 kg of balls in the Denver mill

**Table 1.** Chemical composition of galena.

Element	Pb	Zn	Cu	Fe	Mn	CaO	S	SiO <sub>2</sub>	MgO
wt%	50.5	0.42	0.03	0.35	0.03	1.58	20.6	4.8	2.06

for 15 min so that 90 wt% of the particles present were less than 100  $\mu\text{m}$  in diameter. The pH during grinding was controlled to the set point of 9 by pH titration through the continuous addition of sodium hydroxide solution. Samples for EDTA extractions and XPS analyses were obtained from the cell at the completion of grinding.

After grinding, the pulp was transferred to a 1 liter flotation cell, the pH in the floatation stage was also maintained at 9 by adding sodium hydroxide solution. A collector and a frother were added in turn (200 g/t SIPX and 100 g/t MIBC, respectively) during conditioning for 4 min. Four floatation concentrates were collected after cumulative times of 0.5, 2.0, 4.0 and 8.0 min at an air flow rate of 4 l/min. The floatation froth was scraped every 10 s.

The floatation maximum recovery,  $R_{\text{max}}$ , and the floatation rate constant,  $k$ , were calculated by fitting the experimental data to the first order rate equation [22]:

$$R = R_{\text{max}} (1 - e^{-kt}) \quad (4)$$

where  $R$  is the cumulative floatation recovery at time,  $t$ .

### 2.3. EDTA Extraction Technique

An EDTA extraction technique was employed to determine the amount of oxidized iron species from minerals or grinding media to determine the extent of their oxidation. A 3 wt% solution of AR grade ethylene diamine-tetra acetic acid disodium salt (EDTA) was made up and a sodium hydroxide solution was used to adjust the pH to 7.5. The EDTA solution was continuously purged with nitrogen for more than 1 h prior to EDTA extraction experiments to eliminate oxygen in both the solution and atmosphere.

A weighed sample of slurry (about 10 ml) collected in the cell was first purged by nitrogen for 10 min, and then filtered through a 0.45  $\mu\text{m}$  Whatman filter. Following this, the filter cake was added to more than 100 ml of the prepared EDTA solution while nitrogen purging in a magnetically stirred vessel. The filter cake was leached by EDTA for 10 min while nitrogen was continuously purged throughout. Finally, the EDTA extracted slurry was filtered through a 0.45  $\mu\text{m}$  Whatman filter. The two filtrates were weighed and analysed by AAS, and the solid was dried and weighed to calculate the mass of metal oxidation species.

### 2.4. X-Ray Photoelectron Spectroscopy

Samples of mill discharge were analysed by XPS. The species on the surface of galena after different grinding were examined by X-ray photoelectron spectroscopy. XPS system used in this study is available at Sharif University of Technology, XPS measurements were carried out with a Perkin-Elmer Physical Electronics Division (PHI) 5100 spectrometer with a Mg  $K\alpha$  X-ray source (1253 eV) operating at 300 W over the Mg anode.

## 3. Results

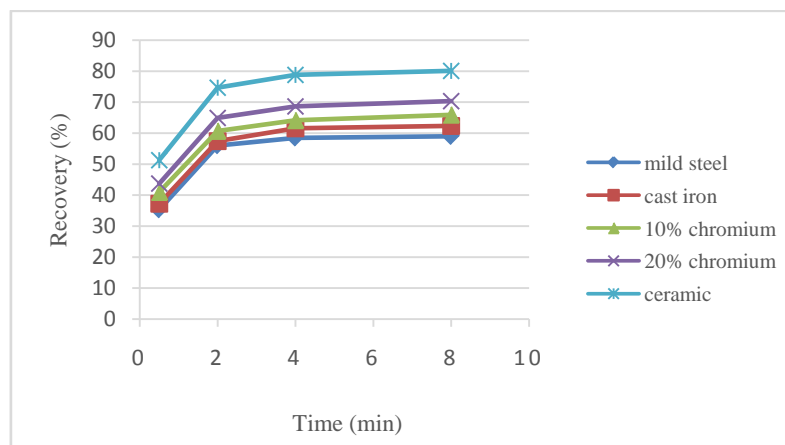
### 3.1. Effect of Grinding Media on Galena Flotation

#### 3.1.1. Galena Flotation

The influence of five types of grinding media (mild steel, 10% chromium, 20% chromium, cast iron and ceramic media) on galena flotation behavior (purged with air) is shown in **Figure 1**. It can be seen that ceramic grinding medium produced maximum galena recovery and mild steel grinding media produced minimum galena recovery.

#### 3.1.2. X-Ray Photoelectron Spectroscopy Study

The galena surface was analysed by XPS. The type of species and their atomic concentrations on galena are reported in **Table 2**.



**Figure 1.** Effect of grinding media on galena flotation as a function of time.

**Table 2.** Surface species and their atomic concentrations (%) on galena determined by XPS analysis.

Species	Binding energy (eV)	Atomic concentration of element (%)			
		Mild steel	Cast iron	10% chromium	20% chromium
Fe <sub>2p</sub>	712.0/726.0	12.1	8.1	7.3	6.9
S <sub>2p</sub>	160.5/164.2/168.8	11.7	20.4	22.7	24.1
Pb <sub>4f</sub>	137.4/138.6	7.2	11.4	10.2	13.6
O <sub>1s</sub>	531.5	69	60.1	59.8	55.4

The Fe<sub>2p</sub> spectrum shows the peak positions at 712 and 726 eV, which are attributed to iron (III) hydroxide [23].

The O<sub>1s</sub> XPS spectrum shows a peak situated at 531.5 eV which corresponds to hydroxide [24]-[26].

The S<sub>2p</sub> spectrum shows a peak situated at 160.5 eV which corresponds to sulphide in galena [25]. A shoulder at 164.2 eV and a peak at 168.8 eV are also present and indicate the presence of elemental sulphur and sulphate, respectively [26].

The Pb<sub>4f</sub> spectrum is composed of a doublet in which the lower binding energy peak is situated at 137.4 eV, attributed to lead sulphide [26]. The shoulder at 138.6 eV is attributed to lead hydroxide or lead sulphate [26].

As seen from **Table 2**, the concentration of iron hydroxide on galena surface was very high for mild steel, when 20% chromium grinding medium, the iron hydroxide was reduced significantly. The amount of oxide, hydroxide and sulphate hydrophilic species on galena surface increased with the iron percentage in grinding media. This result indicates that grinding media influence the oxidation reactions from both mineral and grinding media. 20% chromium media minimised these reactions and production of hydrophilic oxidation species (hydroxide and sulphate) on the galena surface, resulting in the highest galena recovery.

### 3.1.3. EDTA Extraction Study

Samples of the mill discharge from different grinding conditions were conditioned with EDTA solutions. The extracted amounts of iron are shown in **Table 3** together with the corresponding galena flotation recoveries at 8 min of flotation.

Mild steel medium produced more iron oxidation products than ceramic medium. The galena recoveries in **Table 3** indicate that more iron oxidation products correspond to lower galena recovery. As is shown in **Table 3**, the increased iron oxidation production could contribute to the decreased galena flotation recovery.

## 4. Discussion

After sulphide minerals or ores are wet ground with steel grinding media, iron oxide and hydroxide are observed in the mill discharge and invariably precipitated on the sulphide mineral surface, leading to an adverse influence

**Table 3.** Effect of grinding conditions on the amount of EDTA extracted iron products and their influence on galena flotation recovery.

Grinding condition (medium)	Extracted Fe (ppm)	Galena recovery (%)
Mild steel	5	59
Cast iron	2.4	62.35
10% chromium	1	65.93
20% chromium	0.5	70.34
Ceramic	N-D	80.11

on sulphide mineral flotation. A data of EDTA extractable iron in the mill discharge corresponding to galena recovery is shown in **Table 3**. It can be seen that after galena was ground with the high chromium grinding media, galena flotation recovery decreased with the amount of EDTA extractable iron in the mill discharge, in agreement with the prediction of the galvanic interaction model. Compared to 20% chromium grinding media, mild steel caused a lower galena flotation recovery, because mild steel produced more oxidized iron species.

## 5. Conclusions

The effect of type of grinding media on galena flotation was investigated. Grinding conditions had a significant effect on galena flotation. This effect was closely associated with the presence of iron oxidation species and metal deficient sulphide present on the galena surface. Iron oxidation species from grinding media played a dominant role in depressing galena flotation, whilst the presence of metal deficient sulphide improved galena flotation.

Comparison between the different types of grinding media for the same purging gas, mild steel grinding media produce the greatest amount of iron oxide species, resulting in decreased recovery of galena, while the use of ceramic grinding media does not produce iron oxidation species associated with maximum galena recovery.

In general, for the same gas purging into flotation cell, produces of iron oxidation species for difference grinding media used in this study are as follows:

Mild steel > cast iron > 10% chromium > 20% chromium > ceramic

The order shown in the above related with the amount of iron species extracted by EDTA shown in **Table 2**, which is consistent with XPS analysis.

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