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Pyrite flotation in the presence of galena. Study on galvanic interaction

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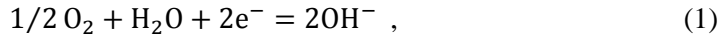
Abstract: In this investigation, galvanic interaction between galena and pyrite in flotation and its effect on floatability of pyrite were studied. Rest and mixed potential studies in the presence and absence of a collector indicated that pyrite was nobler than galena under all investigated conditions. Therefore, pyrite served as a cathode in galvanic interactions with galena. Floatability of pyrite was performed alone and as a mixture with galena in the ratios of pyrite to galena equal to 1:4, 1:1 and 4:1. The experiments were conducted with air and nitrogen. In any galvanic contact between pyrite and galena, anodic oxidation occurred on the galena surface, and hydrolysed lead species adsorbed on the pyrite surface. The investigation of the various reactions occurring on the sample surface was investigated by ethylene diamine-tetra acetic acid disodium salt (EDTA) extraction and X-ray photoelectron spectroscopy (XPS) measurements. In the presence of nitrogen, floatability of pyrite increased. The recovery of pyrite in the presence of air was 22%, while in the mixture with galena (ratio 1:4) the recovery increased to 43%. The results indicated that the presence of galena improved floatability of pyrite.

Keywords: *flotation, galena, pyrite, galvanic interaction*

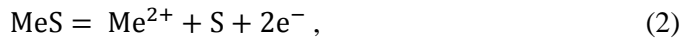
Introduction

Sulphide ores are generally concentrated by flotation. Interaction of two sulphide minerals can affect their surface properties, and thus influences their floatability. Galvanic interactions between sulphide minerals play an important role in flotation. Interaction between two sulphide minerals (or a sulphide mineral/grinding media) resulting from their electrochemical relativities is called a galvanic cell. The electrochemical reactivity of sulphide minerals is specified by their rest potential. The bigger difference between the rest potentials, the stronger galvanic interactions. Two sulphide minerals in contact with each other establish the galvanic cell where the mineral with the higher rest potential accepts electrons from the one with the lower rest potential, thus a cathodic reaction occurs on the mineral surface with higher

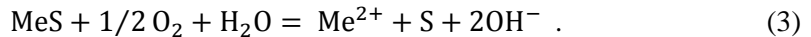
potential (Subrahmanyam and Forsberg 1993). The cathodic reduction reaction of the sulphide mineral with a higher rest potential can be represented by:



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



and the overall reaction is:



The contact between cathodic (i.e. electron acceptor) and anodic (i.e. electron donor) surfaces results in creation of a galvanic cell. Flotation slurries are composed of minerals with different electrochemical activities represented by their rest potentials. In a mixture of two sulphides, the mineral with the higher rest potential acts as the cathode, while that with the lower rest potential as the anode.

Different kinds of galvanic contact have been present for various systems of mineral mixtures affecting mineral reactivity (Rao and Finch, 1988; Pecina-Trevino et al., 2003; Moslemi et al., 2011). For example, Rao and Finch (1988) showed that the galvanic contact between pyrite and sphalerite influenced their flotation recovery. The pyrite recovery increased in the presence of sphalerite, while the recovery of sphalerite decreased in the presence of pyrite.

The galvanic reactions can take place either through local cells on a heterogeneous surface or through the Wagner-Traud mechanism (Bockris and Reddy, 1970) on a homogeneous surface (Ahmed, 1978). Ahmed (1978) found that the local cell mechanism was valid for the galena-xanthate-oxygen system. Holmes and Crundwell (1995) applied thermodynamic and kinetic parameters to quantify the galvanic interactions between copper-pyrite and galena-pyrite. They applied these parameters in the mathematical model to predict the magnitude of galvanic interaction. Their mathematical model was in a good agreement with the experimental data. Qin et al. (2015a, 2015b) studied the effect of galvanic interaction between galena and pyrite and its influence on their floatability. The results of their electrochemical tests showed that in the galvanic contact between two minerals, the pyrite acted as the cathode and the galena as the anode. The flotation recovery of galena in a mixture of galena and pyrite decreased in comparison to flotation of individual mineral particles. The zeta potential of galena changed significantly, while that of pyrite increased when two minerals were mixed together. Therefore, interaction of galena with pyrite in flotation significantly affected the flotation recovery of galena.

The aim of this work was to determine the galvanic interaction between galena and pyrite under different conditions and to show its effect on flotation. Floatability of

pyrite was performed alone and as a mixture with galena with ratios of 1:4, 1:1 and 4:1 in the presence of either nitrogen or air.

Materials and methods

Materials

Galena and pyrite samples were obtained from Nakhlak Mine, Iran and Ghale Zari Mine, Iran, respectively. The samples were crushed by using a roll crusher. The fraction size of +0.6 to 2.0 mm was collected for analysis and experiments. The homogenized sample was then closed in polyethylene bags. The chemical composition of these samples analysed by XRF is shown in Table 1.

Table 1. Chemical composition of galena and pyrite

| Minerals | Elements present (wt.%) | | | | | | | | |
|----------|-------------------------|------|------|-------|-------|------|-------|------------------|-------|
| | Pb | Zn | Cu | Fe | Mn | CaO | S | SiO ₂ | MgO |
| Galena | 85.73 | 0.47 | 0.03 | 0.15 | 0.013 | 0.59 | 12.85 | 0.13 | 0.036 |
| Pyrite | 0.12 | 0.51 | 0.46 | 45.05 | 0.03 | 0.71 | 52.72 | 0.27 | 0.12 |

Sodium isopropyl xanthate (SIPX, AR grade) was used as a collector, while MIBC (methyl isobutyl carbinol, AR grade) as a frother. A solution of sodium hydroxide (AR grade) was added to adjust pH during grinding and flotation. High purity nitrogen and air as gases as well as deionized water were used in all experiments.

Grinding and flotation

Either galena and pyrite alone or their mixture was mixed together with 1 dm³ of water and ground with 3 kg of balls in a ceramic mill for 15 min so that 90 wt.% of the particles present were less than 150 µm in the diameter. The pH during grinding was adjusted at 9 by pH titration through the continuous addition of sodium hydroxide solution. Samples for EDTA extractions were obtained from the chamber after grinding.

To investigate the galvanic interactions between galena and pyrite, galena with the particle size of -75+44 µm, pyrite with the particle size of -150+75 µm and water were mixed together in a 100 cm³. Then, the pulp was transferred to a 1 dm³ Denver flotation cell, and the pH was adjusted to 9 by adding sodium hydroxide solution. A collector (200 g/Mg SIPX) and a frother (10 g/Mg MIBC) were added during conditioning for 10 min. Then, the samples for EDTA extractions and XPS measurement were taken. Four flotation concentrates were collected during 0.5, 2.0, 4.0 and 8.0 min. The flotation froth was scraped every 10 s. The gas flow rate was 4 dm³/min.

Electrochemical equipment

The electrochemical studies were carried out using an Autolab potentiostat/galvanostat model PG STAT30 with GPES software. The traditional three-electrode system consisted of the working, counter (Platinum electrode) and reference (Ag/AgCl electrode) electrodes. The samples of galena and pyrite were cut into a size of 5x5 mm² and fill in a Teflon tube with a brass disc fitting at the bottom to create the mineral electrodes (Fig. 1). A copper wire was used for connecting the electrode to the digital voltmeter. This wire passed through a plastic tube and was connected to the polished surface of sample. Finally, the sample was placed in a Teflon tube. A brass button connector was attached to the surface of highly pure specimen of the mineral by applying “Electrodag”, a highly conductive paint. An electrical connection was soldered to the top of the brass rod for connecting to the voltmeter. All potential values were quoted with respect to a standard hydrogen electrode (SHE). Prior to each experiment, the electrode surface was polished gently by a 600 grade sand paper, washed with the milli-Q water, and it was not refreshed during grinding.

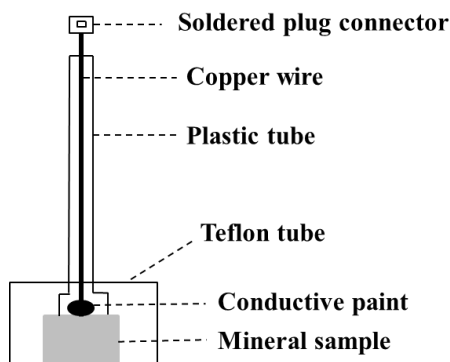


Fig. 1. Schematic diagram of mineral electrode

EDTA extraction technique

An EDTA extraction technique was employed to determine the amount of oxidized iron species from either minerals or grinding media to determine the extent of their oxidation. The EDTA solution of 0.1 M was made up and a sodium hydroxide solution was used to adjust pH equal to 7.5. The EDTA solution was continuously purged with nitrogen for more than 30 minutes prior to EDTA extraction experiments to eliminate oxygen in both the solution and atmosphere.

A weighed sample of slurry (about 10 cm³) collected from the grinding chamber was first purged by nitrogen for 10 min, and then filtered through a 0.45 μm Whatman filter. Following this, the filter cake was added to more than 100 cm³ of the prepared EDTA solution. The filter cake was leached by EDTA for 10 min, while nitrogen was continuously purged throughout. Finally, the EDTA extracted slurry was filtered

through the 0.45 μ m Whatman filter. The two filtrates were weighed and analysed by atomic absorption spectrometry (AAS), and the solid was dried and weighed to calculate the mass of metal oxidation species. Table 2 shows the amount of extracted iron from galena and pyrite.

Table 2. Amount of extracted iron from galena and pyrite surfaces

| Mineral | Extracted Fe (ppm) |
|---------|--------------------|
| Galena | < 0.5 |
| Pyrite | 0.9 |

In single mineral tests, a sample of 2 g was conditioned during 10 min, and the mineral was then filtered. The EDTA solution of 0.1 M was prepared and a sodium hydroxide solution was used to adjust pH to 7.5. The EDTA solution was continuously purged with nitrogen for more than 30 min prior to EDTA extraction experiments to eliminate oxygen in both the solution and atmosphere. The filter cake was added to 100 cm³ of the prepared EDTA solution (0.1 M) and conditioned during 10 min. In the mineral mixture tests (mixture of 2 g with different ratios of each mineral: 20% galena and 80% pyrite, 50% galena and 50% pyrite and 80% galena and 20% pyrite), the conditioning stages were the same as those described for single minerals, except that the minerals were physically separated before the conditioning with the EDTA solution. For this purpose, two easily separable sizes were used (-75+44 μ m galena and -150+75 μ m pyrite). Finally, they were chemically analysed for metal ions by atomic absorption spectrometry. The tests were performed three times and the average values were reported.

X-ray photoelectron spectroscopy

The species on the surface of minerals for different mixtures of galena and pyrite were measured by X-ray photoelectron spectroscopy. The XPS system used in this study was available at the Sharif University of Technology. XPS measurements were carried out with a Perkin-Elmer Physical Electronics Division (PHI) 5100 spectrometer with a Mg K α X-ray source (1253 eV) operating at 300 W over the Mg anode.

Results and discussion

Electrochemical studies

The open circuit potential (OCP) of single and mixed electrodes, as one of the important electrochemical properties, was monitored under different conditions. The rest potential values measured with galena and pyrite electrodes are shown in Figs. 2 and 3. With respect to the rest potential values, pyrite was found to be nobler than galena in the presence and absence of a collector. Therefore, the anodic reaction of pyrite electrode may be weakened while galena and pyrite are in contact.

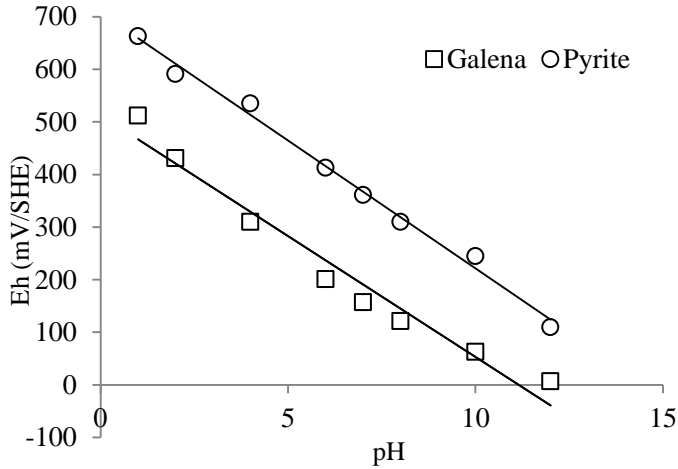


Fig. 1. Rest potential values of galena and pyrite as a function of pH

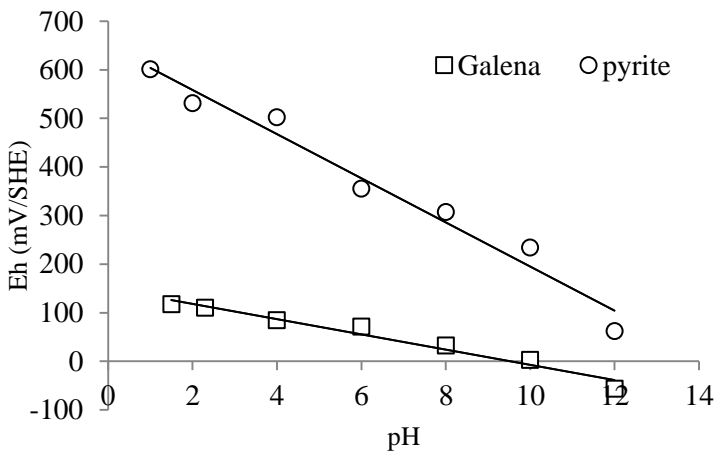


Fig. 2. Rest potential values of galena and pyrite as a function of pH in the presence of collector (250 g/Mg SIPX)

The open circuit potential (OCP) determines the role of galena and pyrite in a galvanic couple. According to the mixed potential theory (Perez, 2004), the galvanic potential should be intermediate between the potentials of anode and cathode. The measured mixed polarization of galena-pyrite couple shown in Figs. 4 and 5 is larger than the potential of galena and smaller than the potential of pyrite.

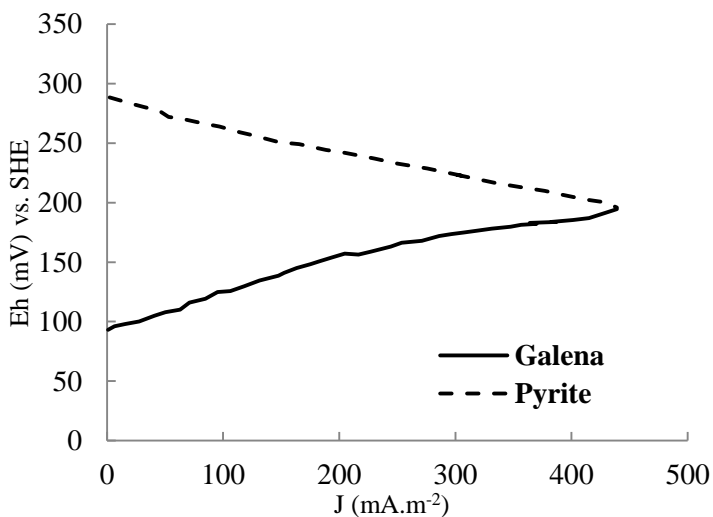


Fig. 3. Mixed potential diagram involving pyrite in contact with galena at pH = 9 (25 °C, 0.5 mol/dm³ KCl)

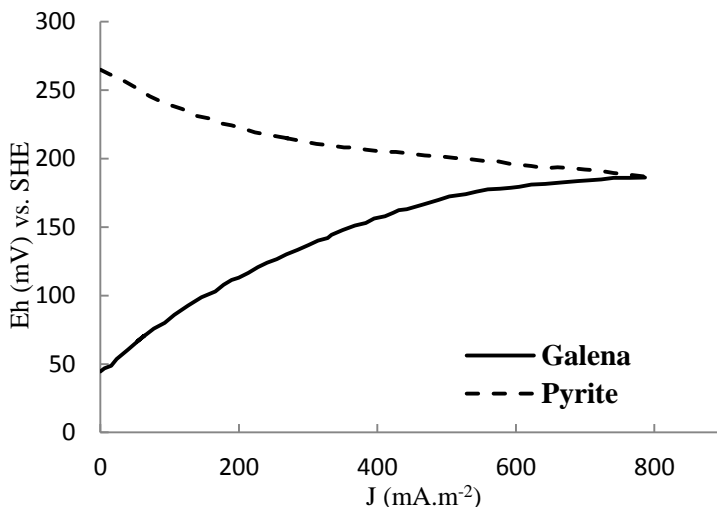


Fig. 5. Mixed potential diagram involving pyrite in contact with galena at pH = 9 (25 °C, 250 g/Mg SIPX, 0.5 mol/dm³ KCl)

The galvanic interaction between pyrite and galena belongs to a spontaneous reaction. This work only considered the oxidation reaction of the anode and the reduction reaction of the cathode. In this study pyrite acts as the cathode and the cathodic half-reaction occurring on the pyrite surface is:

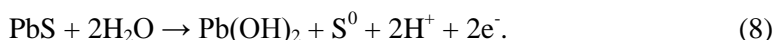
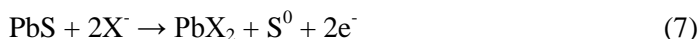


Galena acts as the anode and the anodic half-reaction is expressed as follows:



The overall reaction behaves as the oxidative dissolution of galena.

Compared with pyrite, OCP of galena is found to be lower under all conditions. Galena is electrochemically more active than pyrite, and hence serves as an anode in galvanic combination with pyrite. The following two kinds of interactions on the PbS electrode are:



Flotation of pyrite and pyrite-galena mixture

The mill product of 100 g sample comprising different proportions of pyrite and galena (20, 50 and 80% galena) was conditioned in the Denver flotation cell with xanthate as the collector and MIBC as the frother. The effect of galena and pyrite contact in the air atmosphere and nitrogen atmosphere on floatability of pyrite is shown in Figs. 6 and 7, respectively. It can be seen that the increase in galena content in the mixture from 0 to 80% resulted in the increase in the pyrite recovery from 22 to 43% in air, and from 27 to 56% in nitrogen.

The recovery of pyrite gradually increased as the amount of galena present in the mixture increased (Figs. 6 and 7). The explanation for this behaviour may be inferred from the EDTA extraction data presented in Table 3. It shows the increased concentration of lead species onto the pyrite surface as a consequence of the galvanic contact with galena.

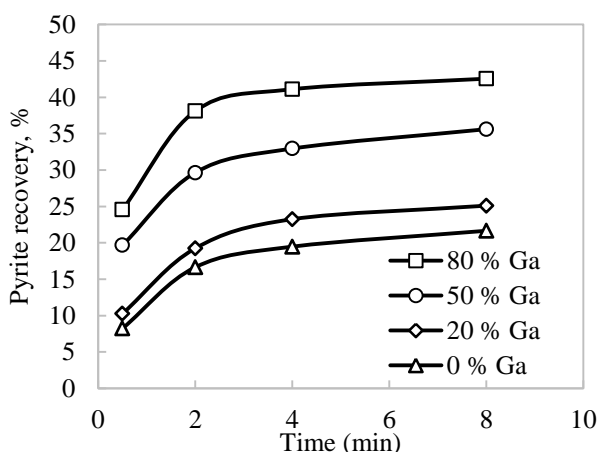


Fig. 6. Effect of galena-pyrite contact on floatability of pyrite (air atmosphere)

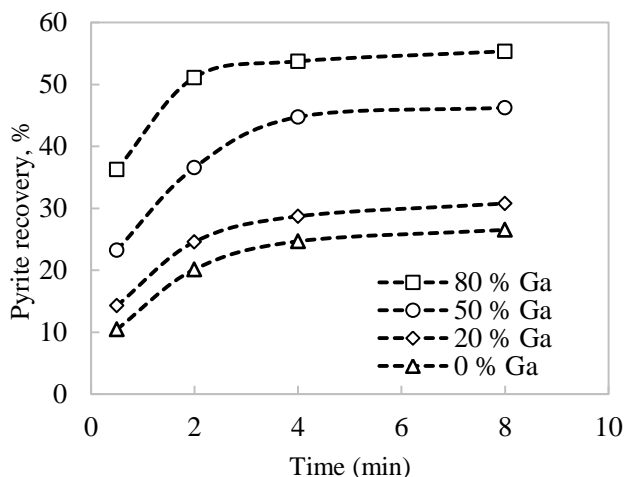


Fig. 7. Effect of galena-pyrite contact on floatability of pyrite (nitrogen atmosphere)

Table 3. Lead and iron species extracted from pyrite by EDTA

| Mineral | Condition | EDTA treatment (ppm) | | | |
|---------|------------|----------------------|----------|-----|----------|
| | | Fe | | Pb | |
| | | Air | Nitrogen | Air | Nitrogen |
| Pyrite | Single | 5.0 | 5.0 | 2.5 | 2.5 |
| | 20% galena | 4.2 | 4.0 | 10 | 18 |
| | 50% galena | 3.5 | 2.5 | 32 | 48 |
| | 80% galena | 1.6 | 1.0 | 72 | 95 |

Pyrite is nobler than galena under all conditions because the rest potential of pyrite is more anodic than galena. In any galvanic combination involving these two minerals, the preferential anodic oxidation occurring on the galena surface can be expected. The effect of the galvanic contact is related to an increased dissolution of the active mineral (galena). The metal ions hydrolyse forming either hydroxo-complexes or precipitated hydroxides, which adsorb on the mineral surface, making its hydrophilic. This model is described elsewhere (Senior and Trahar, 1991; Zhang et al., 1997).

Results presented in Table 3 show that pyrite activation by lead species (e.g. $\text{Pb}(\text{OH})^+$) is affected by the concentration of dissolved oxygen and by the galvanic contact with galena. For pyrite alone, the amount of Pb extracted by EDTA is from Pb dissolution. For pyrite and galena mixtures, adsorption of lead is higher when conditioned in nitrogen compared to air, that is, dissolved oxygen appears to play a role. The amount of lead ions adsorbed on the pyrite surface in the presence of galena (in %), is shown in Fig. 8. It can be seen that with increasing galena in the mixture, the amount of lead ions adsorbed on the pyrite surface increased. According to EDTA

extraction, the concentration of lead species onto the pyrite surface in the presence of galena increased and led to pyrite activation

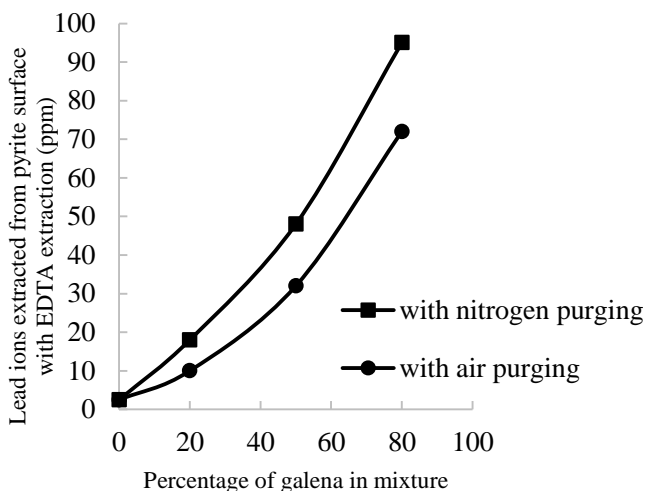


Fig. 8. The amount of lead ions adsorbed on the pyrite surface in the presence of galena

The decrease in the concentration of dissolved oxygen caused by the use of a nitrogen atmosphere weakened the galvanic interaction between galena and pyrite, which was associated with the increase in floatability of pyrite (Rao and Finch, 1988; Kydros et al., 1995, Qin et al., 2015a, 2015b). Recovery of pyrite from the galena–pyrite mixtures in the presence of nitrogen was much higher than that of pyrite alone, and even higher than that obtained from the mixture in air. It indicated that the galvanic interaction was weakened and the susceptibility to hydrophilic iron hydroxides precipitation onto the pyrite surface was reduced.

X-ray photoelectron spectroscopic study

The type of species and their atomic concentrations on the mineral surface for galena and pyrite mixtures measured by XPS are reported in Table 4. An iron (III) hydroxide layer was observed in the peak positions at 712 and 726 eV in the Fe_{2p} spectrum, both of which were characteristic of iron(III) hydroxide (Smart, 1991). Four components of oxide, hydroxide, sulphate and physically adsorbing water were observed in the O_{1s} XPS spectra at 530, 531.5, 532.2 and 533.4 eV, respectively (Buckley and Woods, 1984; Fornasiero et al., 1994). The S_{2p} spectrum showed a peak situated at 160.5 eV which corresponded to sulphide in galena (Buckley and Woods, 1984). A shoulder at 164.2 eV and a peak at 168.8 eV were also present and indicated the presence of elemental sulphur and sulphate, respectively (Fornasiero et al., 1994). The components of either lead sulphide, hydroxide or sulphate were observed in the Pb_{4f} spectra at 137.4 and 138.6 eV, respectively (Fornasiero et al., 1994). Table 4 also shows that the

concentration of Pb at the mineral surface increased with respect to the bulk concentration, as the pyrite content in the mixture decreased. The abundance of Pb on the surface was possibly as a result of transfer of Pb species onto the pyrite particle surface (Qin et al., 2015a, 2015b).

Several studies have shown that flotation of sulphide minerals is related to the surface hydrophobicity, which in turn depends on the balance of hydrophobic-to-hydrophilic surface species (Boulton et al., 2003). The XPS results show that the relative increase in the pyrite recovery at pH 9 can be attributed to lead activation of pyrite (Fuerstenau and Fuerstenau, 1982; Finkelstein, 1997, Pecina-Treviño et al., 2003). Pyrite in contact with galena led to anodic dissolution of galena with the release of Pb^{2+} ions into the solution which adsorbed onto the pyrite surface and activated it for enhanced collector adsorption. It increased the pyrite surface hydrophobicity and subsequently promoted flotation under alkaline conditions (Xu et al., 1995; Ekmekçi and Demirel, 1997; Peng et al., 2003; Qin et al., 2015a, 2015b).

Table 4. Surface species and their atomic concentrations (%) on galena determined by XPS analysis

| Species | Binding energy (ev) | Atomic concentration of element (%) | | |
|------------------|-------------------------|-------------------------------------|------------|------------|
| | | 20% galena | 50% galena | 80% galena |
| Fe _{2p} | 712.0/726.0 | 11.9 | 11.1 | 10.4 |
| S _{2p} | 160.5/164.2/168.8 | 31.9 | 33.3 | 35.1 |
| Pb _{4f} | 137.4/138.6 | 10.4 | 11.7 | 12.6 |
| O _{1s} | 530.0/531.5/532.2/533.4 | 45.8 | 43.9 | 41.9 |

Conclusions

The effect of galvanic contact between galena and pyrite on floatability of pyrite was investigated. The following conclusions can be drawn.

- The degree of galvanic interaction was associated with the difference in the mineral rest potentials. It was shown that the bigger difference is, the stronger galvanic interactions were.
- The rest potential and mixed potential studies in the presence and absence of collector indicated that pyrite was nobler than galena under investigated conditions. Therefore, pyrite served as a cathode in galvanic combination with galena.
- The pulp dissolved oxygen content and pulp oxidation potential decreased with increasing the pyrite content in the mixture. XPS studies suggested oxidation of galena and activation of pyrite.
- Increase in the pyrite flotation recovery was possibly a result of anodic dissolution of galena with the release of Pb^{2+} ions into solution which adsorbed onto the pyrite surface and activated it for enhanced collector adsorption.
- Floatability of pyrite in nitrogen was better than in air. During processing of galena-pyrite mixtures, it was likely that different dissolved oxygen levels in the

pulp were required for optimum mineral separation, depending on the relative abundance of these two minerals in the feed.

- Decrease in the concentration of dissolved oxygen caused by the use of nitrogen weakened the galvanic interaction between galena and pyrite, which resulted in increased floatability of pyrite.
- Floatability of pyrite in the mixture of galena-pyrite increased and it was related to the content of galena in the mixture.

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