THE INFLUENCE OF CYANIDE SALTS AND FERROUS SULPHATE ON PYRITE FLOTATION

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Abstract: The effect of cyanide salts as depressants, i.e. sodium cyanide (NaCN) and complex cyanide salts such as potassium ferricyanide (K\textsubscript{3}Fe(CN)\textsubscript{6}) and potassium ferrocyanide (K\textsubscript{4}Fe(CN)\textsubscript{6}), as well as combination of sodium cyanide with ferrous sulphate (FeSO\textsubscript{4}/NaCN) on pyrite flotation was investigated. Tests covered the frothless flotation of pyrite under different concentrations of depressants at various solution pH’s with potassium butyl xanthate (KBX) as collector. Flotation test results have shown that NaCN, and even more the combination of reagents FeSO\textsubscript{4}/NaCN are more successful in pyrite depression than complex cyanide salts, such as K\textsubscript{3}Fe(CN)\textsubscript{6} and K\textsubscript{4}Fe(CN)\textsubscript{6}. Surface characteristics of pyrite were studied using rest potential (Eh) measurements and infrared attenuated total reflecti

on spectroscopy (ATR-IR). In the presence of tested reagents in the flotation system, iron cyanide compounds and hydrated iron oxides were formed on pyrite surface. The composition of formed compounds depends not only on cyanide ions in the solution, but also on the pH of the system and solution species. These compounds, depending on the reagents used, are responsible for the resulting efficiency of the pyrite depression.

Keywords: pyrite, flotation, ferrous sulphate, cyanide salts, depression

Introduction

Pyrite, which often accompanies nonferrous metal sulphide ores, is routinely depressed at certain stages of selective flotation or extracted into a separated concentrate. In the industrial practice, pyrite is floated with xanthate as collector, whereas the commonest reagents for its depression in lead-zinc ore flotation are of cyanide type. However, cyanides are not mainly in use for pyrite depression in copper ore flotation. Depressing effect is achieved with OH\textsuperscript{−} ions at high pH, mostly with lime.

The first published data about the depressing effect of cyanide were found in 1922. From the fifties of the last century until today, various authors have assumed different
effects of cyanide on depression and explained them from different viewpoints and tried to determine the mechanisms of depression.

Some of the authors explain the pyrite depression as a result of competitive action between undissociated hydrocyanic and xanthic acids (Cook and Last, 1952), cyanide and xanthate ions (Gaudin, 1957), or as a consequence of forming a low-soluble compound at the mineral surface (Taggart, 1951; Majumdar, 1954). However, most authors associate the depression of pyrite by cyanide with the electrochemical process. Elgillani and Fuerstenau (1968) connected the electrochemical reaction with the formation of the insoluble compound Fe₄[Fe(CN)₆]₃, mainly based on thermodynamic calculations. Wang and Forssberg (1996) brought to suspicion this thermodynamic calculations and data related to the stability of iron cyanide species in the Fe-S-CN-H₂O system. The existence of insoluble iron cyanide surface species still remains uncertain. According to these authors, the chemistry of the sulphide mineral flotation with cyanide is very complex and achieved through the one or more different processes. Janetski et al. (1977) showed that the anodic oxidation of xanthate to dixanthogen is inhibited in the presence of cyanide, which may act as an inhibitor from the electrochemical reactions on the surface of the pyrite. Prestige et al. (1993) considered that the competitive adsorption of cyanide in the presence of ethyl xanthate is an important mechanism of pyrite depression. Wet et al. (1997) explained that pyrite depression is a result of the inhibition of the cathodic oxygen reduction reaction on the pyrite surface and is not caused by enhanced anodic rates. Guo et al. (2014) concluded that free cyanide significantly inhibits the electrochemical activities and decreases the mixed potential on pyrite surface which is of vital importance for the chemisorption and oxidation of xanthate.

According to above-mentioned theories, it is obvious that there is no generally accepted standpoint about the mechanism by which the pyrite is depressed with cyanides. In this field of research, there are still a lot of uncertainties and this issue remains a subject of further studies and discussion. Furthermore, present trends are focused to reduce the consumption of cyanides in industrial practice or to replace them with other reagents, primarily because of its toxicity and related environmental issues. Sulphur-oxy depressants in the form of sulphite, bisulphite, meta bisulphite or sulphur dioxide, as well as organic depressants like quebrach, tannins, ethylene diamine tetraacetic acid and, in recent years, natural polysaccharides such as dextrin, starch or guar gum, are used for pyrite depression (Rath et al., 2000; Khmeleva et al., 2002; Lopez Valdivieso et al., 2004; Bicak et al., 2007; Bulut et al., 2011). Consequently, it seems that cyanides became unattractive as pyrite depressant for researchers in last decades, dominantly considering the non-cyanide depression. However, examples of successful non-cyanide depression of pyrite are found mostly in investigation stages. These reagents have limited applications in the industrial practice, primary in flotation of sulphide lead-zinc ores. Presently, the cyanides (usually NaCN) are commonly used in selective flotation of lead minerals as depressants of zinc minerals, regularly in combination with ZnSO₄, particularly in the industrial practice of sulphide lead-zinc.
ores flotation. Cyanides indirectly achieve a depressing effect on pyrite, pyrrhotite and arsenopyrite, which are regularly present in these ores, especially pyrite.

This paper evaluates the influence of cyanides on pyrite depression using different types of cyanide salts and combination of reagents FeSO$_4$/NaCN. In this way, the primary scope was to investigate indirectly the depressing effect of combinations of reagents FeSO$_4$/NaCN on pyrite, which can be also successfully used in the selective flotation of lead minerals to depress zinc minerals (Pavlica et al., 2011). In addition to determining the flotation of pyrite in the presence of these reagents, attention was given to determine the effects and reactions products formed at pyrite surface under the depressing conditions in solutions of different pH's.

**Experimental**

**Mineral and reagents**

Natural pyrite mineral separated from the sulfide lead/zinc deposit in Serbia was used as a sample in the tests. Pyrite sample was manually crushed, ground in a porcelain mortar and screened to the necessary size fractions for tests. Size class – 0.210+0.149 mm was used for flotation tests, while for infrared spectrophotometry the sample was additionally grinded to 100% – 0.020 mm. Specific surface area of samples, determined on a Coulter Multisizer, were 0.133 and 0.062 m$^2$/g, respectively.

Pyrite sample had a density of 4.99 g/cm$^3$ and contained 51.3% S and 46.9%Fe. The contents of impurities were as follows: 0.73% SiO$_2$, Al, Mg and Pb between 0.02-0.08%; Zn, Ag and Au less than 0.002%; Cu, As, Sb, V, Mo and Cd in traces. Insoluble residue was 0.912%.

The reagents used in the tests were of analytical grade. Tests were performed in distilled water. All reagents solutions were prepared daily. Solution pH’s were regulated by CaO, Na$_2$CO$_3$ and H$_2$SO$_4$. Potassium butylxanthate (KBX) was used as collector, while sodium cyanide (NaCN), ferrous sulphate (FeSO$_4$) and complex cyanide salts, such as potassium ferricyanide (K$_3$Fe(CN)$_6$) and potassium ferrocyanide (K$_4$Fe(CN)$_6$) were used as depressants.

**Methods and procedures**

Pyrite flotation was performed in a modified Hallimond tube. One gram of freshly ground mineral to size fraction – 0.210+0.149 mm was floated for 4 minutes at air flow rate of 10 cm$^3$ per minute. Prior to flotation, the mineral was manually conditioned in a 90 cm$^3$flask in the solution with previously adjusted pH and appropriate reagents. After the addition of each reagent, i.e. cyanide or xanthate, conditioning time was one minute, or two minutes when FeSO$_4$ was added.

Radiometer pH-meter type 61-62 was used for the rest potential measurements in an open circuit with mineral electrode as the operational and saturated calomel electrode (SCE) as the reference ones. Mineral electrode was prepared according to
standard procedure in mineral processing investigations. Experimental conditions were the same as those in the flotation tests. The electrodes were introduced into the solution and the potential was read. Final reading was recorded when the equilibrium was established. The measured values are further recalculated into Eh (SHE).

A Perkin Elmer 397 spectrophotometer with an ATR attachment was used to record reflection infrared spectra, where KRS-5 was applied as the reflection element. Sample for IR analysis was prepared by mixing of 250 mg of pure pyrite grounded to 100% – 0.020 mm with 25 cm$^3$ of distilled water. The suspension was stirred for several minutes in a magnetic mixer before pH was adjusted and depressants were added. Additional mixing followed the addition of each reagent: 8 minutes after addition of sulphate and 10 minutes after addition of cyanide. As soon as the mineral settled, the liquid phase was decanted and pyrite suspension was applied onto the reflection element. Reagent concentrations for these tests were higher than in the flotation test, because the specific surface area of the mineral in these tests was higher than in the former ones.

Infrared recording and rest potential measurements were performed in solution of selected pH without the presence of xanthate and only in the presence of depressant considering the depressants influence.

**Results and discussion**

**Flotation tests**

Flotation of pyrite was tested with and without the presence of xanthate as collector, as well as in the presence of collector and different depressants. The concentration of KBX was 10 mg/dm$^3$. Concentration of NaCN, K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ were 15 mg/dm$^3$, while the concentration of FeSO$_4$/NaCN was 5/15 mg/dm$^3$. These concentrations were adopted based on preliminary tests for determining the minimum amounts of reagents necessary to achieve maximum or minimum flotation of pyrite (Kostovic et al., 1990, 2011).

The results of pyrite flotation are presented graphically in Fig. 1 and 2 as the function of recovery and pH. First flotation tests were carried out to determine the flotation of pyrite in the absence of the collector and in the presence of the collector.

As shown in Fig.1 (curves 1 and 2), pyrite lacks natural flotation, because the mineral is not floating in neutral or basic solution without the presence of xanthate, regardless the applied pH regulator. However, when xanthate has been introduced in the flotation system (Fig. 1, curves 3 and 4), pyrite floats very well in acidic solution in the pH range up to 6 and recovery is about 95%. Flotation of pyrite is rapidly decreasing with the increase of the pH and, consequently, in the basic solution at pH from 8 up to 12, pyrite recovery falls between 17 and 30%. The flotation of pyrite was always higher in the presence of Na$_2$CO$_3$ (curve 3) as pH regulator than in the presence of CaO (curve 4). Therefore, CaO was selected as pH regulator for the following flotation tests with depressants.
The influence of cyanide salts and ferrous sulphate on pyrite flotation

Figure 1 shows the flotation of pyrite in the presence of various depressants and collector KBX.

When depressants are introduced in the flotation system, there is a relatively sharp decrease of flotation recovery in acidic pH range (pH 5–7), while in solutions of pH above 7, a decrease of pyrite recovery is not so expressive. In high basic solution of pH above 11, pyrite stopped to float, despite of applied depressants. The highest depressing effect on pyrite was demonstrated by FeSO$_4$/NaCN, since pyrite floating is discontinued at pH above 6 (curve 3). NaCN and complex cyanide salts, K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$, are less efficient in pyrite depression (Fig. 2, curves 2, 4 and 5) compared to the combination of FeSO$_4$/NaCN.

Rest potential measurements

To investigate the possible oxidizing or reducing reactions in the flotation system, the rest potential was measured in solutions of different depressants at pH 5–12.
Concentration of reagents remained the same as in the previous flotation tests. Results are illustrated graphically in Fig. 3, as a function of Eh and pH.

Results presented in Fig. 3 demonstrate a positive Eh values of pyrite in solutions with and without depressants, reaching relatively high values, up to 0.451 V (in solution of K₃Fe(CN)₆ at pH 6.6), as shown in curve 4. Furthermore, pyrite’s Eh, and consequently its flotation, decreases with the increasing pH for all concentrations and applied depressants, with the slope corresponding at about 40 – 70 mV/pH. Pyrite’s Eh values are the lowest in NaCN solution (0.116 V at pH 11.3) as observed in curve 2, and FeSO₄/NaCN solution, curve 3, which proved efficient pyrite depressants in the flotation.

In the solution with CaO (curve 1), Fe²⁺ and, in some extent FeOH⁺ ions, can be present in the solution at pH below 7, according to Pourbaix diagram for the Fe-O-H system (Takeno, 2005). The maximum flotation recovery is achieved in the flotation system with the pH below 6. At higher pH values, Fe₂O₃(s) is formed as a more stable species, in accordance to the same Pourbaix diagram. In addition, oxides of Fe(II) are formed at low potentials and Fe(III) at higher potentials (Wet and Sandenbergh, 1993).
The influence of cyanide salts and ferrous sulphate on pyrite flotation

According to Eh-pH diagram for Fe-CN-H₂O system (Adams, 1992; Wet and Sandenbergh, 1993) when cyanides are present in the solution, Fe(CN)₆³⁻ is more stable than Fe(CN)₆⁴⁻ with the respect to pH and Eh, thus confirming the higher Eh values in solution of K₃Fe(CN)₆ (curve 4) than in solution of K₄Fe(CN)₆ (curve 5). With the pH is rising above 11, the potentials are in the FeOOH stability field. This allows the assumption that a steady hydrated iron oxide can be formed on the pyrite surface in the system, irrespective of the presence of cyanide ions.

**Infrared tests**

Infrared spectra were recorded to study qualitative identification of the changes on the mineral surface and the composition of compounds that might be formed at pyrite surface under applied depressants. Concentration of reagents in all tests was as follows: 150 mg/dm³ of NaCN, 50/150 mg/dm³ of FeSO₄/NaCN and 30 mg/dm³ of K₃Fe(CN)₆ and K₄Fe(CN)₆. Tests were performed in the solutions of natural pH (from 3.4 to 5.5) and highly basic pH at 11.1. The obtained spectra are shown in Figs. 4 – 6.

Spectrum of pyrite without contact of depressants (1) in Figure 4 illustrates infrared spectra of pure pyrite, at natural pH 5.68. Fundamental lattice vibrations of pyrite below 600 cm⁻¹ are not shown (Donato et al., 1999; Gadsen, 1975), as they are out of the presented wave range.

The spectra 2–5 (Fig. 4) are resulting from the pyrite treatment with depressants in the solution of natural pH (3.4 – 3.6). It is evidently that pyrite surface significantly changes. All presented spectra show absorption bands at about 2000 cm⁻¹ as characteristic of the cyanide band vibration (Nyquist and Kagel, 1971), confirming the presence of a cyanide compound on the pyrite surface.

A sharp strong absorption bands due to the cyanide group are located between 2040 and 2070 cm⁻¹ on all spectra. These bands confirmed the presence of cyanide...
compound at pyrite surface, which probably contains Fe(CN)$_6^{4-}$ group, since characteristic absorption for ferrocyanide ion occurs at 2020 – 2130 cm$^{-1}$ (Nyquist and Kagel, 1971). Beside this, cyanide band on spectrum obtained when pyrite was treated with the combination of reagents FeSO$_4$/NaCN (Fig. 4, spectrum 3) well corresponds with cyanide band on the precipitate spectrum (Fig. 5, spectrum 1) obtained as the reaction product of FeSO$_4$ and NaCN from the aqueous solution at natural pH.

![Fig. 5. IR spectra of precipitate obtained by reaction of FeSO$_4$ and NaCN at: (1) pH 5.5 and (2) pH 11.1](image)

In the presence of depressants at highly basic pH at 11.1, some differences are evident (Fig. 6, spectra 2–5). The cyanide bands, less distinct, at 2040 cm$^{-1}$ are shown on spectra when pyrite was treated with complex cyanide salts K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ (spectra 4 and 5). It is interesting to note that cyanide bands are missing on pyrite spectra when mineral is treated with NaCN or combination of NaCN/ FeSO$_4$ at pH 11.1 (spectra 2 and 3). These spectra also are well corresponding with the spectrum of the precipitate, obtained in the reaction of FeSO$_4$ and NaCN at pH 11.1 (Fig. 5, spectrum 2).

All pyrite spectra of pyrite treated with depressants presented in Fig. 6 show several characteristic bands. First, broad band centered at about 3400 cm$^{-1}$, because of O-H stretching vibrations, and two-peak absorption bands at 2920 cm$^{-1}$ and 2850 cm$^{-1}$, also assignable to the O-H stretching frequency, may be attributed to hydrogen-bonded hydroxyl groups. Beside this, O-H bending frequency at 1660 - 1640 cm$^{-1}$ is also appeared as a consequence of hydration water (Gadsen, 1975; Rinelli et al., 1980; Rath et al., 2000; Caldeira et al., 2003). All these bands confirm the presence of hydrated forms on pyrite surface and, according to the Eh measurements, this compound may be attributable to the hydrated iron oxide FeOOH.
The influence of cyanide salts and ferrous sulphate on pyrite flotation

It is evidently that hydrophilic iron cyanide compounds at pyrite surface led to pyrite depression in the flotation system in the basic solution up to the pH 11, regardless to the applied depressants. These compounds contain some of the cyanide groups, but the exact composition remains undefined. It can be assumed that cyanide compounds are binding strongly with the pyrite surface when pyrite is treated with complex cyanide salts and consequently the compounds exist in highly basic solution, which is represented by cyanide bands that appear at spectra. However, it seems that in the case of NaCN or NaCN in combination with FeSO₄ cyanide compounds are unsteady and dissolved in highly basic solution. It can be seen that the intensities of the cyanide absorption bands at spectra are not so evident and the cyanides are not present on the pyrite surface as dominant species. In highly basic solution, hydrated iron oxide is dominant as more stable compound and leads to pyrite depression. Beside this, the cyanide compounds have relatively higher solubility than iron hydroxide, according to theirs constants of solubility products (Elgillani and Fuerstenau, 1968), providing the conditions for domination of hydroxide species on pyrite surface. All these statements are confirmed with Eh measurements, as the most Eh potentials are in the range where the formation of iron hydroxide is thermodynamically favorable.

**Conclusion**

The results obtained in this investigations show that flotation of pyrite, using xanthate as collector, is reduced in the presence of cyanide salts and/or ferrous sulphate. Therefore, all applied depressants can be classified in the following order, according
to the efficiency of reducing collection ability of pyrite in the presence of xanthate at pH 5.5-12:

$$\text{FeSO}_4/\text{NaCN} > \text{NaCN} > K_3[\text{Fe(CN)}_6] > K_4[\text{Fe(CN)}_6].$$

It is obvious that combination of reagents FeSO$_4$/NaCN provide the best depressing effect. Almost complete pyrite depression in the flotation system was noted at highly basic solution at pH>11, apart from the applied depressants and their concentrations. Based on the Eh measurements and infrared tests, hydrophilisation of pyrite surface at solutions below pH 11 in the presence of depressants is caused by the formation of the iron – cyanides compounds on the pyrite surface. These compounds are steady within a wide pH range up to about pH 11, preventing the xanthate adsorption. A composition of the formed compounds depends on cyanide and iron ions, theirs concentrations and relations in solution, and on pH. In the highly basic medium, at pH above 11, hydrated iron oxides, as the most dominant compounds are responsible for pyrite depression. Under these conditions, pyrite is completely depressed in the flotation system, independently from the applied depressants.

Acknowledgment

This paper was realized as a part of the projects financed by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Projects 33045, 33007 and 176010).

References


The influence of cyanide salts and ferrous sulphate on pyrite flotation


