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ELECTROCHEMICAL DISSOLUTION OF SYNTHETIC HEAZLEWOODITE (Ni₃S₂)

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The aim of the study was to examine the dissolution kinetics of synthetic heazlewoodite and the formation of elemental sulfur by electrochemical methods. Anodic polarisation curves, potentiostatic measurements and cyclic voltammetry were carried out in 1 N sulfuric acid at temperature 25°C. The anodic dissolution of heazlewoodite proceeds in two stages. At potentials below 600 mV vs. SCE heazlewoodite is only converted to higher sulfides such as millerite NiS. At higher potential the reaction products dissolve forming first other sulfides and elemental sulfur and later other sulfides, elemental sulfur and sulfate. The percentage of sulfides in the reaction products was high even at high potentials. The formation of elemental sulfur was not seen to hinder dissolution of the sulfide. The part of sulfur oxidized to sulfate increased with increasing potential. Up to 900 mV only elemental sulfur was formed, at 1000 mV 10% of sulfur was oxidized to sulfate and at 1600 mV 90% of the sulfur was sulfate.

keywords: Nickel sulfide, dissolution, reaction mechanism, sulfur formation

1. INTRODUCTION

Nickel is a transition element that exhibits a mixture of ferrous and nonferrous metal properties. Nickel forms several natural sulfides of which heazlewoodite (Ni_3S_2) is the most nickel-rich compound. The other stable compounds found in sulfide ores are godlevskite (Ni_7S_6) , millerite (NiS), polydymite (Ni_3S_4) and vaesite (NiS_2) . The bulk of the nickel comes from laterites where the principal ore minerals are

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nickeliferous limonite (Fe,Ni)O(OH) and garnierite (a hydrous nickel silicate), or magmatic sulfide deposits where the principal ore mineral is pentlandite $(Ni,Fe)_9S_8$ (Kuck, 2010). Heazlewoodite is sometimes found in nickel ores but it is a main component in smelted nickel matte (Muir et al., 2006; Palant et al., 2008).

Mineral sulfides are non-stoichiometric and they contain impurities. Therefore they have crystal defects that affect sulfide electrical properties. Heazlewoodite is a metallic conductor. This is based on the location of d-electrons that do not participate in the formation of chemical bonds. In sulfide minerals, sulfur occurs at its lowest oxidation state, -2. The metals have usually oxidation state +2. In several compounds the electroneutrality would not be fulfilled if there were not anion-anion bonds that decrease the net oxidation state of anions or cation-cation bonds that decrease the oxidation level of cations (Vaughan et al., 1978).

The usual hydrometallurgical route for the extraction of metals from sulfides requires oxidation of sulfur in the compound to either elemental sulfur or sulfate. Oxidation of sulfur to higher oxidatlin states (0, +2, +4 and +6) can occur if the redoxpotential of the oxidant in solution, e.g. O_2 , Fe³⁺, is higher than the equilibrium potential of the sulfide. Basing on leaching studies of natural and synthetic heazlewoodite and nickel converter matte, the dissolution of heazlewoodite proceeds in two stages (Buckley et al., 1991; Ghali et al., 1981; Laig-Hörstebrock, 1969; Power, 1982; Price et al., 1982). In the first stage nickel is released from the sulfide structure and a reaction product layer forms. In this reaction product layer the ratio of metal atoms to sulfur atoms is less than the 1.5 of heazlewoodite. This is also known as conversion of heaxlewoodite to higher sulfides. Heazlewoodite dissolves in the first stage after reaction (1) releasing nickel ions

$$Ni_{3}S_{2} \rightarrow xNi^{2+} + Ni_{3-x}S_{2} + (2x)e^{-}$$
 (1)

In the second stage the reaction product layer dissolves after reactions (2)-(4) depending on the oxidation potential and pH

$$Ni_{3-x}S_2 + 8H_2O \rightarrow (3-x)Ni^{2+} + 2HSO_4^- + 14H^+ + (18-2x)e^-,$$
(3)

$$Ni_{3-x}S_2 + 8H_2O \to (3-x)Ni^{2+} + 2SO_4^{2-} + 16H^+ + (18-2x)e^-.$$
(4)

The formation of the reaction product layer can hinder the dissolution of the sulfide. This is due to slower transfer of oxidant and metal ions through the reaction product layer. The formation of the reaction product layer according to reaction (1) begins at potentials 200 to 0 mV vs. SCE (Buckley and Woods, 1991; Laig-Hörstebrock, 1969; Power, 1982; Wong et al., 2001). The reaction product layer can dissolve chemically, which indicates that the chemical bonds in the reaction product are weaker then in normal sulfide (Power, 1982). The reaction product layer breaks

down at potentials 500-800 mV vs. SCE (Ghali et al., 1981; Price and Davenport, 1982). The formation of the reaction product layer has been considered as a region of semipassivation as Ni²⁺ slowly diffuses from the sulfide lattice to form a series of increasingly sulfur-rich nickel sulfides (Muir and Ho, 2006). Formation of NiS and Ni²⁺ has also been related to oxidation peaks at 900 mV and 1100 mV vs. SCE, respectively (Wong and Tian et al., 2001). Formation of elemental sulfur has been the cause of decrease of current at potentials above 1100-1200 mV. Complete dissolution of the sulfides requires potentials above 1500 mV (Muir and Ho, 2006). Analysis of activation energies in perchloric acid shows that at potentials below 100-200 mV vs. SCE the dissolution is controlled by charge transfer or chemical step and at potentials above 800-900 mV the dissolution becomes mass transfer controlled. A mixed control prevails at potentials 200-800 mV vs. SCE (Knuutila, 1988).

Heazlewoodite has been used as model compound to study the electrochemical leaching of nickel from sulfide minerals. During chemical or electrochemical dissolution of sulfide minerals, sulfur may remain in amorphous form enveloping gradually the dissolving particles. Then, the dissolution is hindered and the diffusion of ions through the amorphous sulfur layer finally ceases. Sulfur may also be oxidized to sulfate, which increases the consumption of reagents or energy. In this paper the dissolution kinetics and sulfur formation as a function of oxidation potential have been studied.

2. EXPERIMENTAL

Heazlewoodite was synthetized in vacuum quartz ampoules as described by Vaughan and Craig, 1978. The materials were 10 μ m nickel powder with minimum 99.5% purity (Merck 12277) and sulfur powder (JT Baker 0335). The theoretical composition of the ampoule charge was 60.0031 wt. percent of Ni and 39.9969 wt. percent of S. Nickel powder was pressed to 3 cm² round pieces using 8 ton hydraulic press and treated at 500°C in hydrogen atmosphere for one hour. Sulfur was pressed to 1 cm² pieces using hand press. The mineral synthesis was done at 400°C for three days, slowly raised (50°C / 12 hours) to 700°C, followed by treatment at 700°C for another three days and slow cooling (30°C/12 hours) to room temperature. The synthesized mineral was characterized by chemical analysis and XRD. The Ni₃S₂ sample contained 70.4 wt. percent of Ni and 29.6% of S and corresponds to 56.5 wt. percent of Ni. The sulfide is slightly metal-deficient. No other phases than Ni₃S₂ were detected.

The experiments were carried out in a three-electrode cell with electrolyte volume of 800 cm³ (Fig. 1). The counter electrode was a platinum sheet with dimensions of 20 mm x15 mm. The electrode potential was measured using Haber-Luggin capillary and liquid junction. The reference electrode was Radiometer type K401 saturated calomel

electrode (SCE). The SCE was put in Agar-Agar gel in a separate beaker to protect the electrode. All the measured potentials in this paper are presented in the SCE scale, i.e. +242 mV vs. SHE.



Fig. 1. Electrochemical test cell. 1 – Sulfide sample, 2 – Gas purging, 3 – Magnetic stirrer,
4 – Luggin capillary, 5 – Counter electrode,
6 – Reference electrode, 7 – Protecting gel

Fig. 2. The sample mounting. 1 – Epoxy resin,
2 - Copper backing plate, 3 – Graphite or silver glue, 4 - Sulfide sample

Pieces of synthetic heazlewoodite were attached with graphite glue to copper backing plate and mounted in non-conductive epoxy resin (Fig. 2). The use of threaded copper backing plate allowed removal of the current conducting wire from the sample for XRD and SEM analyses.

The electrolyte was 1 N sulfuric acid (Merck 731) solution. All tests were done at room temperature. The electrolyte was purged with nitrogen (AGA 99.99% N_2) for two hours before the experiment and purging continued during the experiment. A magnetic stirrer was used during nitrogen purging and experiments. The corrosion potentials fluctuated, but after the five minute period the potentials were fairly constant in the range from -420 to -360 mV vs. SCE. The electrochemical experiments, which included anodic polarisation curves, cyclic voltammetry and potentiostatic measurements, were carried out with an automatic electrochemical measurement system developed at the Helsinki University of Technology, Laboratory of Corrosion and Material Chemistry (Aromaa, 1988). Metal ion contents of the electrolytes in potentiostatic leaching experiments were measured with the Perkin-Elmer 372 atom absorption spectrometer (AAS).

3. RESULTS

The anodic polarisation measurements were carried out to gain general information on dissolution characteristics of the sulfide mineral, while the cyclic voltammetry measurements gave more detailed information on reaction stages, mechanisms and behavior of sulfur. The potentiostatic leaching experiments gave more data on the kinetics of dissolution.

3.1. RESULTS

A general leaching behavior of the sulfide mineral was examined using anodic polarization measurements. Anodic sweeps were started at the corrosion potential and the samples were polarized stepwise at scan rate 20 mV/min up to gas evolution region, i.e. 2000 mV vs. SCE.

An example of the polarization curve is shown in Fig. 3. The polarization curves show three different reaction stages, i.e. two dissolution reactions of the sulfide including phase transformation (stage I) and decomposition of the sulfide to higher sulfides or to nickel and elemental sulfur (stage II and III). At the reaction stage III the oxidation of sulfur to sulfate may also occur. These reactions are followed by oxygen evolution at the anode. The reactions occur at the potential ranges of 0-500 mV (I), 700-1200 mV (II) and above 1300 mV (III), respectively. This anodic behavior agrees with the behaviour presented in literature (Buckley and Woods, 1991; Ghali et al., 1981; Muir and Ho, 2006; Power, 1982; Price and Davenport, 1982).



Fig. 3. Anodic polarisation curve of synthetic Ni₃S₂ in 1 N H₂SO₄, dE/dt = 20 mV/min. Stage I - dissolution by mineral transformations, Stage II - dissolution by oxidation of mineral sulfur to higher sulfides or elemental sulfur, and Stage III - dissolution by oxidation of sulfur to elemental sulfur or sulfate

3.2. CYCLIC VOLTAMMETRY MEASUREMENTS

The cathodic maximum potential in the cyclic voltammetry measurements was set to a constant potential of -500 mV and the anodic maximum potential was altered between +300 and +900 mV (Figs. 4 and 5). The measurements were carried out clockwise starting at the corrosion potential of the mineral. The elemental sulfur formed in anodic dissolution reaction is reduced to H_2S during the following cathodic sweep. The reduction peak can be seen in the potential range of -100 to -400 mV. The reduction peak is mostly due to reduction of elemental sulfur to hydrogen sulfide, but as side reactions can happen reductive leaching of heazlewoodite or higher sulfides (Filmer, 1981; Filmer et al., 1980). As the anodic maximum potential increases, the peak of reduction to hydrogen sulfide becomes larger. This means that at higher anodic potentials more sulfide has dissolved, even in this rapid experiment.



Fig. 4. Cyclic voltammograms of heazlewoodite in 1 N H₂SO₄, T = 25 °C, dE/dt = 20 mV/s, second cycles, anodic max. potentials 300, 400, 500 and 600 mV



Fig. 5. Cyclic voltammograms of heazlewoodite in 1 N H₂SO₄, T = 25 °C, dE/dt = 20 mV/s, second cycles, anodic max. potentials 700, 800 and 900 mV

The charge of both anodic dissolution (q^+) and cathodic H₂S reduction reaction (q^-) is integrated from the corresponding peak areas (Figs. 4 and 5). The ratio of cathodic reduction charge of sulfur and the anodic charge of dissolution were integrated from the steady state cycles. Figure 6 shows that at low anodic maximum potentials the ratio of anodic to cathodic charges is high. At low anodic potentials the reaction products do not contain much of compounds that are reduced to hydrogen sulfide. As the anodic maximum potential increases, the ratio becomes smaller. At potentials between 600 and 700 mV the reaction product layer breaks down and elemental sulfur is formed as anodic dissolution product. At higher anodic potentials sulfur is oxidized to elemental sulfur and sulfate and the $q^+/q^-(H_2S)$ ratio is fairly constant (approximately 3).



Fig. 6. Ratio of anodic and cathodic charges calculated by integration of cyclic voltammograms. As the anodic maximum potential increases, more reaction products which can be reduced to hydrogen sulfide, are formed

3.3. POTENTIOSTATIC MEASUREMENTS

Potentiostatic leaching experiments were carried out at potential range from -200 to 1600 mV. According to the polarisation curves, several different anodic leaching reactions can be observed at this potential range. The potentiostatic tests were done for 15 minutes to 1.5 hours depending on the potential used. At lowest potentials the test times were longest.

Current densities from the potentiostatic curves at different potentials are shown in Figure 7. The times are 0 s, 60 s and 900 s. The current density at t = 0 s is determined by assuming inverse relationship of square root of current density with time. The relationship was quite well for potentials below 1400 mV. The shapes of the plots in

Figure 7 correspond good with the shape of the anodic polarization curve. The rapid decrease in current density at potentials below 600 mV supports the general trend that formation of higher sulfides leads to semi-passive state. The decrease in current density with time at 1300 mV can result from passivating sulfide formation. At higher potentials the increase in current density is due to disintegration of the sulfide and oxygen evolution. Gas evolution on sample surface was seen at this potential.



Fig. 7. Current densities from short potentiostatic tests

Even longer potentiostatic experiments were done to grow reaction product layers for analysis. In these tests the polarization times were 4 to 150 hours, again longest polarization times were used for lowest potentials. In these tests solution samples were taken for AAS analysis and the amount of dissolved nickel was determined. The reaction product layer was analyzed by cathodic reduction as in cyclic voltammogram using sweep rate 5 mV/s. The anodic charge was then calculated using the analyzed nickel concentration after Faraday's law and cathodic charge from integration of the reduction peak.

Figure 8 shows the ratio of anodic charge of the potentiostatic test and theoretical anodic charge calculated from nickel analysis. At the lowest potential (600 mV) there can be chemical dissolution in addition to the potentiostatic leaching. However at potentials of 700-900 the ratio is close to 1 indicating that all of the anodic current has been consumed in releasing of nickel. At potentials of 1100 mV and above the ratio is constant and slightly less than 1.5. The calculated charge ratio means that at potentials equal to 700-900 mV the current efficiency for nickel leaching is close to 100% but decreases to \sim 70% at 1100 mV and above. At this potential range part of the anodic current has been consumed in other reactions. According to reactions (2)-(4) this can be due to oxidation of sulfur to sulfate ions.



Fig. 8. Ratio of total anodic charge to theoretical nickel charge. At potentials of 700-900 mV the whole anodic current is consumed in nickel leaching and at potentials of 1100 mV and above part of sulfur is oxidized to sulfate



Fig. 9. Ratio of total anodic charge and theoretically calculated nickel charge to charge consumed in cathodic reduction of reaction products

By analysing the anodic charges and theoretical nickel charges vs. cathodic reduction of the reaction product layer further information on the oxidation of sulfur to sulfate was found. As shown in Fig. 9, the ratio of both anodic to cathodic charge increases at low potentials and at high potentials. At the potential range from 800 to 1200 mV the ratio is approximately 3, but little less for Ni^{2+} ratio at the higher potentials. The nickel ratio is higher than total charge ratio at low potentials and at

high potentials the ratio is vice versa. At potentials below 800 mV the high nickel ratio indicates that some of nickel has been released by chemical reactions. At potentials above 1000 mV some of the anodic charge has been consumed by other reactions than nickel dissolution.

3.3. XRD-ANALYSIS OF REACTION PRODUCTS

The surfaces of heazlewoodite samples were analyzed with XRD after potentiostatic leaching tests. The surfaces of fresh samples, samples left in open circuit potential, and samples polarized to potentials below 600 mV vs. SCE were greenish yellow. With microscope it was possible to see thin long cracks. When the reaction product layer disintegrates at potentials range of 600-900 mV the surface becomes black. At potentials over 1300 mV the grain boundaries of the sulfide become etched and the reaction product layers become loose.

As the sample is polarized to anodic potentials the heazlewoodite reacts to higher sulfides and when the potential is high enough, these reaction products from elemental sulfur, and finally also sulfates, are seen. Table 1 shows a compilation of XRD analyses. For a fresh untested sample only heazlewoodite was found. For an unpolarized sample left in test solution for 24 hours only heazlewoodite was seen. When the sample was polarized to the anodic direction ($\approx 200 \text{ mV}$ overpotential) several higher sulfides were detected. At potential of 600 mV elemental sulfur was seen and at potential of 1000 mV also peaks of nickel sulfate were seen. The sulfate peaks can also result from crystallization of released nickel and sulfate anions of the test electrolyte.

| Sample | Ni ₃ S ₂ | Ni ₇ S ₆ | NiS | Ni ₃ S ₄ | NiS ₂ | S ⁰ | NiSO ₄ |
|--------------|--------------------------------|--------------------------------|-----|--------------------------------|------------------|----------------|-------------------|
| Untested | х | | | | | | |
| Unpolarized | Х | | | | | | |
| E = -200 mV | Х | Х | Х | Х | Х | | |
| E = 200 mV | Х | Х | Х | Х | Х | | |
| E = 600 mV | х | х | Х | Х | Х | х | |
| E = 1000 mV | х | х | х | Х | х | х | х |
| E = 1400 mV | х | х | Х | Х | Х | х | Х |

Table 1. XRD-analysis of unreacted sample and samples polarized to constant potential for hours

4. DISCUSSION

From a phase diagram of the Ni-S system a number of intermediates could have been anticipated. From this, it is predicted that dissolution of nickel from Ni_3S_2 can proceed through the following series of phases: $Ni_3S_2 \rightarrow Ni_7S_6 \rightarrow NiS \rightarrow Ni_3S_4 \rightarrow$ NiS_2 . The anodic polarization curves (Fig. 3) showed the known behavior with three different reaction mechanisms: At low potentials up to 600 mV mineral transformation, at intermediate potentials of 700-1200 mV formation of elemental sulfur and at high potentials above 1300 mV disintegration of the sulfide with formation of elemental sulfur and sulfate. XRD analysis of reaction product layers showed all the different intermediate sulfides.

At the low potential range of mineral transformation reactions, the reaction rates are too slow for meaningful leaching. The current densities of 0.01-0.1 mA/cm² at the low potential range correspond to dissolution rate of 0.03-0.25 μ m/hour for complete dissolution to nickel and sulfur. The oxidation potential must be high enough to dissolve all the higher sulfides and form elemental sulfur in order to get useful dissolution rates. Analysis of anodic and cathodic charges suggests that elemental sulfur formation begins at approximately 800 mV vs. SCE.

The charges from potentiostatic tests show that at potentials of 900 mV and below all the anodic charge is used in nickel dissolution. At higher potentials some of the charge is consumed in other reactions. Cyclic voltammograms show that the amount of reducible species in reaction products increases with increasing potential up to about 800 mV vs. SCE. At potentials from 800 to 1400 mV the ratio of anodic charges to cathodic charges is approximately 3. The charges calculated from potentiostatic tests followed by cathodic reduction of the reaction product layer also show that at potentials of 800-1200 mV the ratio of anodic charges to cathodic charges are approximately 3. Analysis of charges consumed in potentiostatic leaching and reduction of the corresponding reaction product layers indicate that disintegration of reaction product layer begins at 1200 mV.

Assuming that at the intermediate potential range the dissolution of heazlewoodite proceeds by reaction (2), i.e. the reaction products are nickel ions $(3xNi^{2+})$ and elemental sulfur $(2xS^0)$, the ratio of anodic nickel release to cathodic sulfide reduction to hydrogen sulfide is 1.5. At this potential range the calculated charge ratio is close to 3. This means that part of the sulfur in the reaction product layer has not been reduced or the sulfur is in form that cannot be reduced. Two main causes can explain the charge ratio: the intermediate sulfides formed at low potentials are not reacting to hydrogen sulfide and at high potentials part of the elemental sulfur has been oxidized to sulfate and that can not be reduced. By simplifying heazlewoodite dissolution reactions (2) and (4) to (5) and (6) estimations of the reaction products can be done:

$$Ni_3S_2 \to 3Ni^{2+} + 2S^0 + 6e^-$$
, (5)

$$Ni_{3}S_{2} + 8H_{2}O \rightarrow 3Ni^{2+} + 2SO_{4}^{2-} + 16H^{+} + 18e^{-}.$$
 (6)

At potentials of 700-900 mV the current efficiency of nickel is close to 100% so only formation of intermediate sulfides and elemental sulfur can happen, (reactions (1) and (5)). At higher potentials current efficiency of nickel is less than 100% and so also sulfate formation (6) happens. By using the anodic total charge q^+ (tot), anodic charge

calculated from nickel analysis $q^+(Ni^{2+})$ and cathodic reduction charge $q^-(H_2S)$, the relation between intermediate sulfide, elemental sulfur and sulfate can be calculated:

- elemental sulfur formation = $q(H_2S)$
- intermediate sulfide formation = $q^+(tot) 1.5 \cdot q^-(H_2S)$
- sulfate formation = $q^{+}(tot) \cdot [1 \eta(Ni^{2+})]$.

When calculating at potentials above 900 mV the sulfate charge is calculated first using current efficiency of nickel and intermediate sulfides and sulfur charges are calculated using the remaining total charge. The percentages of charges consumed in formation of different reaction products at different potentials are shown in Figure 10. The relative charges comply with expected behavior in that less elemental sulfur and more sulfates are formed at higher potentials. Somewhat unexpected was a high percentage of intermediate sulfides at high potentials as it was expected that sulfide disintegration with sulfate formation would be the main reaction.



Fig. 10. Percentages of reaction products calculated from measured charges. Note that no test was done at E = 1500 mV

When the formation of intermediate sulfides is excluded from the reaction products it is possible to estimate the percentages of elemental sulfur and sulfate. The ratio of elemental sulfur to sulfate decreases with increasing potential. Up to 900 mV only sulfur is formed. At 1000 mV there is 90% elemental sulfur and 10% sulfate but at 1600 mV only 10% sulfur and the rest is sulfates.

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5. CONCLUSIONS

The synthetic heazlewoodite dissolves anodically with three different reaction mechanisms as presented in literature. They were interpreted as up to 600 mV mineral transformations, at intermediate potentials of 700-1200 mV formation of elemental sulfur and at high potentials, above 1300 mV disintegration of the sulfide with formation of elemental sulfur and sulfate.

The analysis of potentiostatic tests and cyclic voltammograms revealed that the formation of reaction products is not as clear as predicted by the polarization curves. Formation of intermediate sulfides continues even at the highest potentials tested. From 30 to 75% of the charge is consumed in formation of intermediate sulfides with minimum at 1100-1200 mV. Up to 900 mV only sulfur is formed. At 1000 mV there is 90% elemental sulfur and 10% sulfates but at 1600 mV only 10% sulfur and the rest is sulfates.

REFERENCES

- AROMAA, J. (1988). Automatization of Electrochemical Experiments Using a Microcomputer, Lic.Tech. Thesis, Helsinki University of Technology, 115 p. (in Finish)
- BUCKLEY, A. & WOODS, R. (1991). Electrochemical and XPS studies of the surface oxidation of synthetic heazlewoodite (Ni₃S₂). Journal of Applied Electrochemistry 21: pp. 575-582.
- FILMER, A. (1981). The non-oxidative dissolution of nickel mattes in aqueous solutions. Journal of the South African Institute of Mining and Metallurgy(3): pp. 74-84.
- FILMER, A. & NICOL, M. (1980). The non-oxidative dissolution of nickel sulphides in aqueous acidic solutions. Journal of the South African Institute of Mining and Metallurgy(12): pp. 415-424.
- GHALI, E., MERIC, C. & DEROO, D. (1981). Electrodissolution de la heazlewoodite in milieu chlorhydrique. Journal of Applied Electrochemistry 11: pp. 153-163.
- KNUUTILA, K. (1988). Anodic dissolution behaviour of heazlewoodite (Ni₃S₂) in perchloric acid solution. Doctoral Thesis, Helsinki University of Technology, 72 p.
- KUCK, P. (2010). Nickel Statistics and Information. Retrieved 18.4.2010, from minerals.usgs.gov/ minerals/pubs/commodity/nickel/index.html
- LAIG-HÖRSTEBROCK, H. (1969). Electrochemisches Verhalten von Metallsulfidanoden. Dr.-Ing. Thesis, TU Berlin, p.
- MUIR, D. & HO, E. (2006). Process review and electrochemistry of nickel sulphides and nickel matters in acidic sulphate and chloride media. Transactions of the Institute of Mineral and Metallurgy C 115(2): pp. 57-65.
- PALANT, A., BRYUKVIN, V., VINETSKAYA, T. & MAKARENKOVA, T. (2008). Kinetics of Ni₃S₂ Sulfide Dissolution in Solutions of Sulfuric and Hydrochloric Acids. Russian Metallurgy (Metally)(1): pp. 22-24.
- POWER, G. (1982). The electrochemistry of nickel sulfides 2Ni₃S₂. Electrochimica Acta 27(3): pp. 359-364.
- PRICE, D. & DAVENPORT, W. (1982). Anodic reactions of Ni₃S₂, b-NiS and nickel matte. Journal of Applied Electrochemistry 12: pp. 281-290.
- VAUGHAN, D. & CRAIG, J. (1978). Mineral chemistry of metal sulfides. Cambridge, Cambridge University Press. 493 p.

WONG, J., TIAN, M., JIN, W. & HE, Y. (2001). Speciation of Sulfidic Nickel by Carbon Paste Electrode Voltammetry. Determination of Ni₃S₂ in Solid Mixtures. Electroanalysis 13(16): pp. 1355-1359.

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Przedmiotem pracy były badania kinetyki roztwarzania syntetycznego hezelwudytu oraz tworzenia się siarki w tym procesie, z zastosowanie metod elektrochemicznych. Badania prowadzone były w 1 N kwasie siarkowym, w temperaturze 25°C, metodami: potencjostatyczną, krzywych polaryzacyjnych oraz woltamperometrii cyklicznej. Roztwarzanie anodowe hezelwudytu przebiego dwustopniowo. Przy potencjałach poniżej 600 mV hezelwudyt przechodzi w siarczki o wyższej zawartości siarki, na przykład mileryt (NiS). Przy wyższych potencjałach hezelwudyt ulega roztwarzaniu, tworząc siarczki o wyższej zawartości siarki i siarkę, a następnie siarczki o wyższej zawartości siarki, siarkę i siarczany, przy czym przy wyższych potencjałach obserwowano tworzenie się większej ilości siarczków o wyższej zawartości siarki. Nie zaobserwowano negatywnego wpływu tworzenia się siarki elementarnej na przebieg procesu roztwarzania. Ilość tworzących się siarczanów wzrasta wraz ze wzrostem potencjału. Poniżej potencjału 900 mV tworzy się siarka elementarna, przy potencjałe 1000 mV 10% siarki ulega utlenieniu do siarczanów, a przy potencjałe 1600 mV do siarczanów ulega utlenieniu aż 90% siarki.

słowa kluczowe: siarczek niklu, roztwarzanie, mechanizm reakcji, tworzenie siarki