Effect of Ambient Conditions on Self-Heating Characteristics of a Ni-Cu Sulphide Ore

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Abstract

Self-heating characteristics of a complex nickel-copper sulphide ore stockpile containing pentlandite, chalcopyrite and pyrrhotite have been investigated through continuous monitoring of its inner temperature over a 7-month period (May to December). Variation of external weather parameters such as air temperature, dew point, wind velocity, air humidity and atmospheric pressure are reported. The inner temperature of the stockpile varied from 10.5°C to 44°C. One reason for the maximum temperature to be relatively low is related to lack of reactive surface area since amount of fines in the stockpile is limited. The inner temperatures indicated significant fluctuations due to rapid changes in ambient conditions, particularly the outside temperature, which ranged from -5°C to 32°C. Despite an apparent parallelism between these two types of temperatures, occasional occurrences of rapid decrease in the ambient temperature while the stockpile was still in a self-heating mode were notable. These rapid cooling effects on the stockpile had a retardation effect on trends of increasing inner temperatures. Regular rain showers that the stockpile area received may have also played a role in dissipation of heat, especially when the stockpile experienced a heavy rain.

The loss of pentlandite recovery due to stockpile oxidation was about 6.2% compared to 4.0% for chalcopyrite. These losses have been attributed to over-oxidation of these minerals primarily based on development of ferric hydroxy oxide species such as goethite and precipitation of hydroxides of various metal species mobilized as a result of oxidation. Interestingly, floatability of pyrrhotite has been enhanced by stockpile-oxidation. Thus, the flotation selectivity shifts in favour of pyrrhotite for the oxidation case. This behavior was attributed to metal-activation and elemental sulphur/polysulphide formation due to oxidation of the sulphide part of these sulphide minerals. Relative amounts of hydrophilic to hydrophobic species on the surfaces are responsible for observed bench scale behavior.

Keywords: Ni-Cu sulphides, stockpile oxidation/self-heating, metal losses, flotation selectivity

Introduction

The self-heating of sulphide minerals can be an operational problem and a safety hazard during the mining stage and stockpiling, which is important from the point of transportation of concentrates (Kirshenbaum, 1968; Wright et al., 1972) and storage of the iron sulphide talings and backfilling (Rosenblum et al., 1982; Chao et al., 1997; Bernier and Li, 2003).

Sudbury and Petcovich (1961) reported first series of laboratory tests with the Ni-Cu concentrates carried out for a period of about three days. They observed temperatures in the range 80 to 90°C during spontaneous heating and demonstrated that initial rate of self-heating was significantly greater with higher pyrrhotite content of the moist concentrate. Their results also indicated that formation of oxidation products slowed down the spontaneous heating tendencies of the sample. Subsequent laboratory studies were directed to better understanding and control of the self-heating of sulphide concentrates (e.g., Rosenblum and Spira, 1981; Rosenblum et al., 2001; Somot and Finch, 2010).

Investigations on stockpiles are highly limited. Chao et al (1997) reported results of measurements on O_2 absorption of iron sulphide stockpiles along with release of SO_2. The temperatures up to about 110°C were recorded. Rosenblum et al. (2001) reported the development of highly localized hot spots reaching 150°C in a chalcopyrite concentrate stockpile following a month of storage. These studies reaffirmed the importance of humidity and oxygen availability as being critical for evolution of heat.

As part of our recent work on stockpile oxidation, general observations on inner temperatures of the stockpile were reported together with some preliminary data on flotation behavior (Ozdeniz and Kelebek, 2013; Cummings et al., 2013). The objective of this manuscript is to report variation of simultaneous external conditions and possible effects that ambient conditions have on self-heating trends of the stockpile and discuss details on consequent processability through metal losses and mineral selectivity rougher-scavenger flotation.

Materials, methods and procedures
Ore Stockpile

The ore in the stockpile consists of a minus 6 inch product from surface crushing operations, which has been blended with some run-of-mine ore. Before and after monitoring, this experimental stockpile was sampled for evaluation in the laboratory.
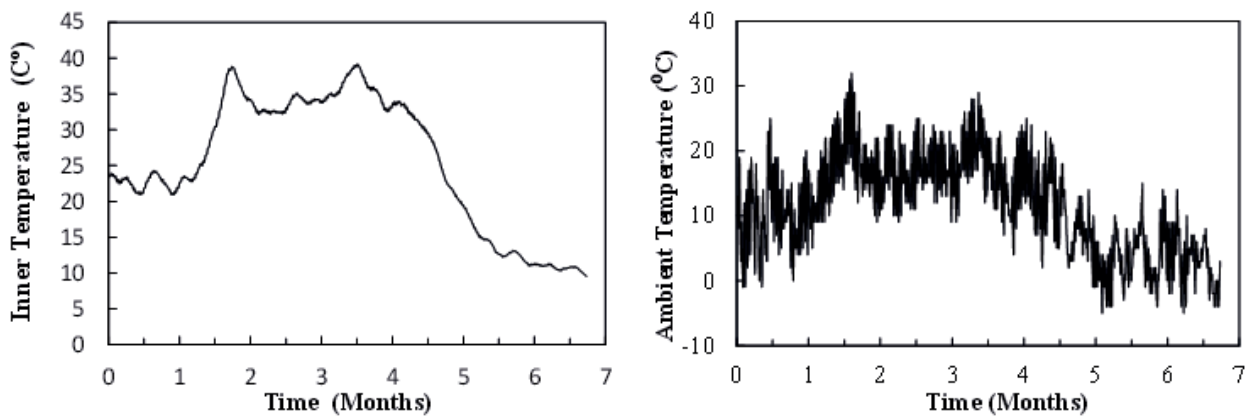
Fig. 1. Typical variation of the inner stockpile temperature (a – left) and ambient temperature (b – right) with time

Rys. 1. Typowe zmiany temperatury wewnatrz składowiska (a – lewy) i (b – prawa) temperatury otoczenia

Experimental set up and variables monitored

The stockpile was formed in a mine site in the Sudbury area in a triangular prism shape (9 m L, 6 m W and 3 m H). The inner temperature data of the stockpile were collected through temperature sensors positioned at two levels inside the stockpile. The sensors were connected to the data logger, through which the data were recorded hourly onto a laptop computer between the dates May 7th and December 2nd. In addition, various parameters related to air conditions, i.e. ambient temperature, humidity, sky condition/precipitation, dew point, atmospheric pressure, wind speed, and sky conditions were also continuously monitored.

Ore samples and flotation testing

The head grades were 2.45% Ni, 1.5% Cu, and 13% S (sampled before stockpiling) and 3.14% Ni, 1.68% Cu and 15.8% S (after stockpiling). The samples were ground to about 55 minus 74 μm. The reagents used included isobutyl xanthate as a collector (45 g/tonne) and Dow Froth 250 as a frother (35 g/tonne). Initial pH value was 9.2 (with lime). Further details on experimental details have been reported elsewhere (Ozdeniz and Kelebek, 2013).

Results and discussion
Variation of inner and outside temperatures

Variation of the inner temperatures in the stockpile is given in Fig. 1a along with variation of ambient temperature in Fig. 1b. As can be noted, there are significant fluctuations with time in both cases. There are two primary peaks in the inner temperatures; one occurring after 52 days and the other after 103 days. The initial temperatures of 22–25°C steadily increased up to 40°C, which is clearly attributable to self-heating of the

stockpile. Subsequently, the inner temperatures came down to a lower range of 33–35°C for about 1.5 months, during which a minor peak was developed. During this period, it also seems that the stockpile slowly acquired another self-heating trend, which peaked around 40°C once more, corresponding to the 103th days. Following this peak, the stockpile entered into a cooling mode around mid-September. As can be noted from Figure 1b, this cooling period coincides with declining ambient temperatures. In general, time profile of the ambient temperature has a significant resemblance to that of the stockpile inner temperature. Maximum values of 40–44°C recorded for the inner temperatures are relatively low compared to data reported on another sulphide stockpile rich in iron sulphides (i.e., process waste in finer state), which reached an inner temperature of about 110°C (Chao et al., 1997). The ambient temperature in this particular work was relatively constant 23–24°C compared to a much wider range experienced in the current case (i.e., -5 to 10.5°C). Apart from a significant difference in reactive surface areas, it may also be that the ore stockpile studied in the current work was never able to demonstrate its full potential for self-heating mode due to interruptive cycles of downward ambient temperatures.

Variation of dewpoint temperature and humidity

The dewpoint temperature is known as the temperature, below which this condensation occurs at a constant barometric pressure. As it is related to relative humidity and air temperature, it has also been monitored during the self-heating of the stockpile. Variation of dewpoint temperatures as a function of time is shown in Fig. 2a. As can be not-
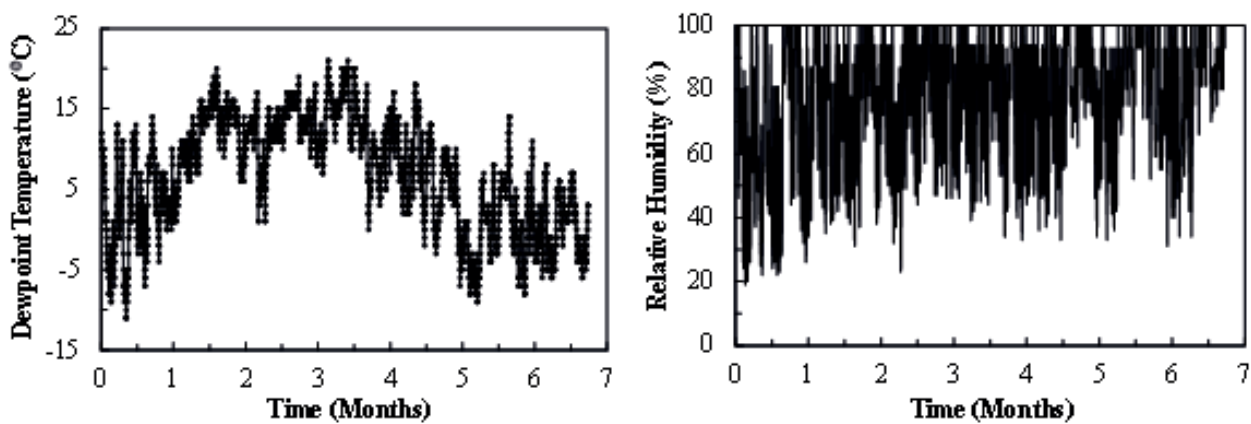
Fig. 2. Variation of the dewpoint temperature (a – left) and relative humidity (b – right) with time

Rys. 2. Zmiana temperatury punktu rosy (a – z lewej) i wilgotności względnej (b – z prawej)

ed, data fluctuations are also common to this case, perhaps to a lesser degree compared to the case of ambient temperatures. It can be noted that there is a reasonable degree of parallelism between dew point and air temperature variation. The trends of the dew point are similar to that of the stockpile inner temperature, especially in relation to timing of the primary peaks.

Variation of the relative humidity recorded during the monitoring period of stockpile is shown in Fig. 2b. It is known that relative humidity affects self-heating characteristics of sulphide minerals. Rosenblum and Spira (1981) reported that when the moisture content was around 3%, self-heating rate of an iron sulphide rich tailing was at its maximum level of 6°C/hour. Bone-dry conditions and a moisture content higher than 26% resulted in no heat generation. Earlier, Sudbury and Petcovich (1961) observed that moisture contents up to 9% significantly increased the period of self-heating of a Ni-Cu concentrate. These studies involved laboratory-conditions, typically with one variable at a time. In the current investigation, the humidity values cover a wide range from 19% to 100% with frequent fluctuations, which reflect dynamic changes in weather conditions. Great majority of the humidity data are outside of the sensitive range reported in the previous studies. Thus, the role of humidity in the current work is expected to be small, if not negligible. Periodic local showers also taking place are more likely to have a direct impact on moisture levels of the stockpile.

Variation of wind speed and atmospheric pressure

As an atmospheric event, wind can facilitate access of air into the sulphide ore stockpile, which needs oxygen to support oxidation reactions of sulphide minerals. Regardless of details of mechanisms, the oxidation reactions are highly exothermic. If its speed is too high, however, the wind can also be a medium for heat loss whenever the ambient temperature is significantly low. Wind speed variation during the monitoring period of the stockpile is given Fig. 3a. Again, substantial fluctuations are notable in the wind speed (0–45 km/h). Although a direct relationship with the self-heating characteristics is not apparent, the first maximum inner temperature appears to coincide with the minimum wind speed after about 1.5 months. Data by Chao et al. (1997) reported higher inner temperatures of up to 110°C. It is interesting to note that the wind speed in their case was very low at about 0.4 km/h. This supports the hypothesis on minimum loss of heat occurring under calm weather conditions, therefore facilitating an incubation period for propagation of heat. However, this mechanism does not seem to be repeated for the second primary peak after about 3.5 months, where the frequency of stronger winds is higher. A more effective oxygenation of the sulphide stockpile due to stronger winds supplying warmer air may have contributed to development of the second primary peak. Wright et al. (1972) observed that self-heating of a Pb-Zn sulphide concentrate stockpile was accelerated by windy conditions. It is worth noting that their stockpile had been formed at a much higher temperature (38–40°C) than the stockpile in the current case.

Atmospheric pressure is another parameter that was recorded during the monitoring period of the stockpile, which is given in Fig. 3b. It varies from 99 kPa to about 103 kPa. The period, during
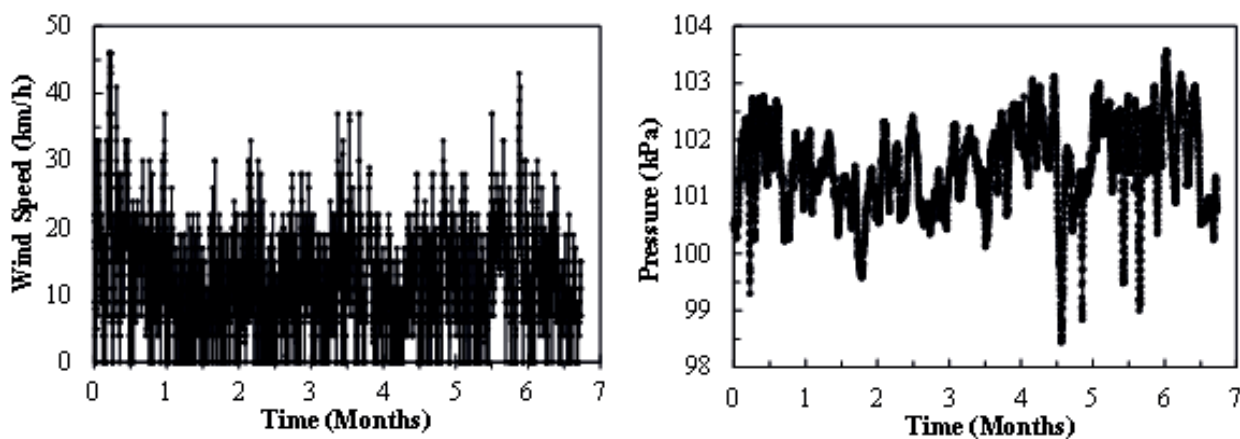
Fig. 3. Variation of wind speed (a – left) and barometric pressure (b – right) with time

Rys. 3. Zmiana prędkości wiatru (a – z lewej) i ciśnienia barometrycznego (b – z prawej) z czasem
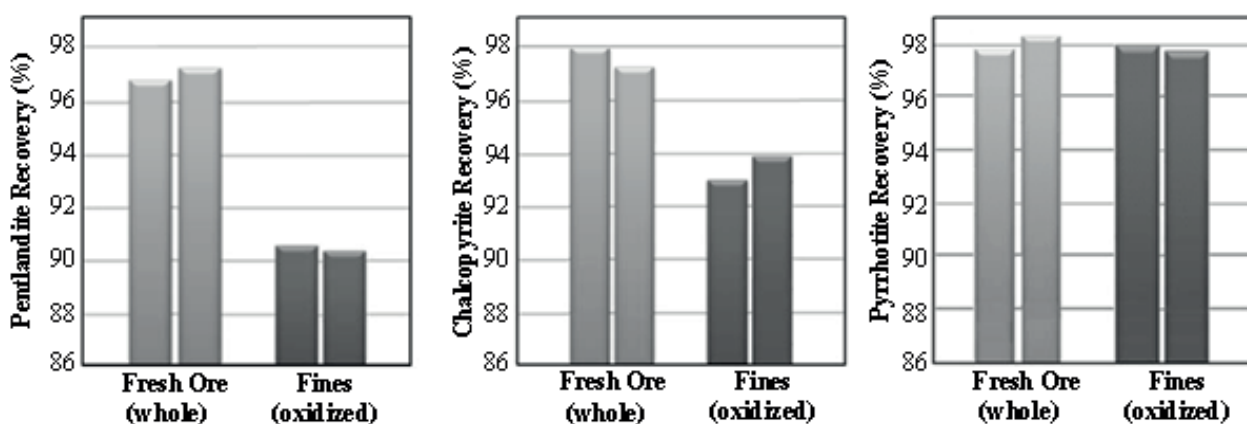

Fig. 4. Comparison of recoveries of principal minerals before and after stockpiling period

Rys. 4. Porównanie odzysku głównych minerałów przed i po okresie gromadzeniem

which primary peaks for inner temperatures were observed, appears to be somewhat associated with lower atmospheric pressures. It is plausible to think that a lower atmospheric pressure can be helpful in expansion of intermediate oxidation products within the stockpile, which may be in gaseous form. Somot and Finch (2010) pointed out that H_2S, formed as a result of non-oxidative reaction, can act as an initial fuel for self-heating. From the trends in Fig. 3b, it can also be noted that, conversely, the pressures are somewhat higher when the inner temperatures take a pattern of steady drop. This trend is especially apparent after the end of summer, despite some exceptions that mark sudden (short lived) decreases in the pressure. Considering that the stockpile has some voids due to its heterogeneity in terms of particle size and shape, natural pumping action of air (hence oxygenation of the stockpile) is expected to be more effective at higher pressures. However, during the cooling period starting in the Fall, relatively higher pres-

sure together with increasing winds (Fig. 3a) may enhance the loss of heat from the stockpile. Higher pressure can also enhance capillary suction of liquid water, potentially leading to greater degree of moisturizing of the stockpile interior periodically, which can act as a heat sink slowing down the self-heating reactions.

Sky activities expressed in terms of rainy, cloudy, sunny, foggy and snowy days indicated no apparent parallelism with inner temperatures and therefore, for the sake brevity, were excluded from this analysis.

Recoveries before and after oxidation in the stockpile

Sulphide ores are normally processed soon after mining stage, thus the stockpile self–heating phenomenon investigated represents an oxidation case and complicates the process. Loss of inefficiency manifests itself both in terms of the recovery and selectivity.
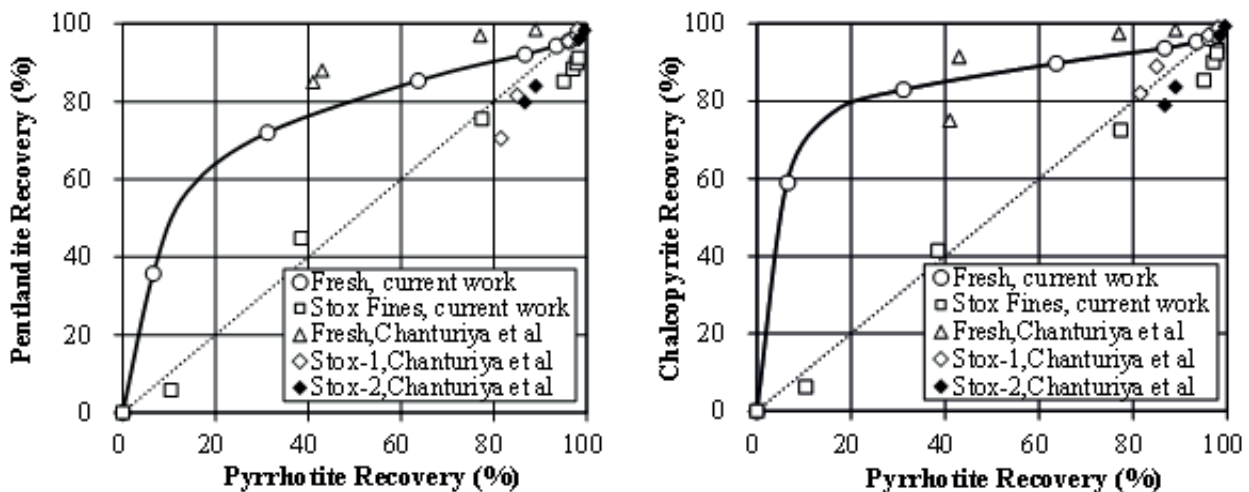
Fig. 5. Pentlandite and chalcopyrite recoveries as a function of pyrrhotite recovery
in relation to storage/stockpile oxidation of Ni-Cu sulphide ores

Rys. 5. Uzysk pentlandytu i chalkopirytu w funkcji odzysku pirohotytu w stosunku do
stopnia utleniania zasobów rud siarczkowych Ni-Cu

Fig. 4 shows a comparison of the recoveries for the three minerals before and after stockpile oxidation. The bar graphs represent data from two repeat tests. The overall recoveries of pentlandite for the fresh samples range from 96.6 to 97.1. Following the oxidation, recovery of the pentlandite in the stockpile fines decreases to a range of 90.4 to 90.8%. The corresponding recoveries of chalcopyrite in the fresh sample are a little higher at 97.9 and 97.1%, respectively. The recoveries of chalcopyrite in the oxidized fines of the stockpiled ore are 93% and 94%, respectively. These differences represent an average recovery drop of 6.2% and 4% for pentlandite and chalcopyrite, respectively. The effect that the stockpiling period had on floatability of pyrrhotite was marginal in comparison with those of pentlandite and chalcopyrite. As can be noted from Fig. 4, the average recovery level of pyrrhotite that was little over 98% before the stockpiling became little lower than 98% at the end of stockpiling period. These results are in general agreement with previously reported results on effects of stockpile oxidation on processing of Ni-Cu sulphide ores (Kelebek and Nanthakumar, 2007; Kelebek and Nanthakumar, 2012; Cummings et al., 2013). The duration of stockpiling in this previous work was much shorter at 4–6 weeks (with no monitoring for self-heating). One outcome of oxidation is mobilization of metal species that can precipitate as hydroxides on the surface of sulphides (Senior and Trahar, 1991). While this can also support self-activation, formation of highly insoluble products involving ferric hydroxy oxides such as goethite and elemental sulphur is

known (e.g., Kalinkin et al., 2000; Chanturiya et al., 2000). The extent of over-oxidation in the previous case resulted in 4.6% pentlandite recovery loss from flotation of stockpile fines. In the present case, the recovery loss of stockpile fines was greater at 6.2% due to the much longer stockpiling period. In the case of chalcopyrite, the previous work resulted in practically no loss of copper recovery from a higher grade feed compared to the case in the present work, which suffered a 4% loss due to longer period of oxidation in the stockpile.

Flotation selectivity

Fig. 5 shows a comparison of recoveries of pentlandite and chalcopyrite relative to that of pyrrhotite for the fresh ore sample and the stockpile oxidized fines. As can be noted, the recoveries of pentlandite and chalcopyrite against pyrrhotite for the fines are scattered around the dotted line representing non-selectivity. This means that the surface characteristics of these three minerals in the oxidized fines become similar after about 7 months of ageing/oxidation. When the ore is fresh, keeping more or less its original form, pyrrhotite is typically less floatable than both pentlandite and chalcopyrite, respectively. Thus, under such normal circumstances, flotation selectivity is always in favour of Ni and Cu. Fig. 5 also shows some data from flotation of a Ni-Cu sulphide ore from the Norilsk region, Russia (Chanturiya et al., 2000). The authors periodically water-sprayed their samples at 45°C and studied resulting flotation behaviour under conditions of evaporation prevailing over precipitation to simulate oxidation

corresponding to 20–30 days of storage at 10–15°C. The samples used in this particular study was much higher grade with 29.3% pentlandite, 2.8% chalcopyrite and 53.9% pyrrhotite. Despite such a big difference in the origin and head grades of this ore, the mineral recoveries from the Russian ore follow the general trends of the Sudbury ore samples experiencing oxidation. The higher recoveries obtained from the Norilsk sample are related, in addition to the difference in sample characteristics, to the test procedure used, such as choice of stage retention time as well as the use of copper sulphate as activator. The difference of oxidation reportedly corresponding to about 1 month and 3 months of storage is shown through labels of "Stox-1" and "Stox-2", respectively.

When pyrrhotite is oxidized, its surface initially generates an iron-deficient surface resulting in an enrichment of sulphur at its surface (Buckley 1985). While an iron-deficient sulphur-rich surface may be sufficient to trigger a collectorless flotation behavior, its transformation to elemental sulphur or polysulphide (depending on the pH) is expected to support floatability even better. Collectorless flotation of nickel-copper sulphides are well documented in the literature for freshly ground ores (Hodgson and Agar, 1985) as well as stockpile-oxidized ores (Kelebek and Nanthakumar, 2007; Kelebek and Nanthakumar, 2012).

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Wpływ warunków otoczenia na charakterystykę samonagrzewania rudy siarczkowej Cu-Ni

Właściwości samonagrzewania złożonych siarczków niklu i miedzi na składowisku rud zawierających pentlandyt, chalkopiryt i pirotyn, zostały zbadane poprzez ciągłą obserwację temperatury wnętrza hałdy w ciągu siedmiu miesięcy (od maja do grudnia). Wzięto pod uwagę zmiany w czynnikach pogodowych panujących na zewnątrz hałdy. Uwzględniono zmiany temperatury powietrza, punktu rosy, szybkości wiatru, wilgotności powietrza i ciśnieniu atmosferycznego. Temperatura wewnątrz hałdy wahała się od 10,5°C do 44°C. Jednym z powodów relatywnie niskiej temperatury był brak reaktywnej przestrzeni. Temperatura wewnątrz hałdy wykazała znaczące wahania spowodowane gwałtownymi zmianami warunków otoczenia, w szczególności temperatury zewnętrzną, której zakres zmian sięgnął od -5°C do 32°C. Poza oczywistą zależnością między tymi dwoma temperaturami, udało się odnotować pojedyncze przypadki, gdzie temperatura otoczenia gwałtownie spadła, a proces samoogrzewania wewnątrz hałdy trwał. Gwałtowne spadki temperatur powodowały spowolnienie trendu wzrostu temperatury w hałdzie. Rozproszenie ciepła było również powodowane regularnymi opadami deszczu.

Straty odzysku pentlandytu spowodowane oksydacją wyniosły 6,2%, zaś chalkopirytu 4,0%. Straty te można przypisać nadoksydacji minerałów, która jest wynikiem powstawania składników takich jak getyt czy osad wodorotlenków metali. Co ciekawe, flotowalność pirotynu wzrosła dzięki oksydacji. Zatem selektywność flotacji zmienia się korzystnie dla pirotynu w przypadku oksydacji. Sytuacja ta jest wynikiem aktywacji metalu i formy pierwiastkowej siarki poprzez oksydację.

Słowa kluczowe: siarczki Ni-Cu, utlenianie zapasów, samonagrzewanie, straty metalu, selektywność flotacji