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Flotation of copper-bearing shale at different pH values of solutions and sodium chloride concentrations

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Abstract: Flotation of copper-bearing shale in aqueous solutions of NaCl at their different pH values was investigated. The tests were carried out in a laboratory flotation machine. The pH range was between 5 and 10 while NaCl concentrations were 0.5M, 1.0M and 2.0M. It was observed that the flotation recovery of the copper shale was increasing with the increase of pH and concentration of the salt solution. On the basis of thermodynamic and hydrodynamic considerations it was postulated that the increasing surface tension was responsible for better shale flotation observed with increasing salt concentration. The observed improved shale flotation caused by increasing pH is most likely due to changes in the properties of the thin film between particle and bubble including mosaic structure of water on the surface of shale. It was shown that the zeta potential of shale particles, zeta potential of air bubbles, solution surface tension, and shale hydrophobicity were not responsible for the increasing with pH recoveries.

Keywords: shale, salt flotation, zeta potential, surface tension, hydrodynamics, entrainment, thin films

1. Introduction

In the mineral processing industry, it is common to use salty mine or sea waters (Drzymala, 2007; Laskowski and Castro, 2014; Laskowski and Castro, 2015; Castro, 2018). Salt flotation can be also carried out at salt saturated aqueous solutions (Ratajczak and Drzymala, 2003). The presence of dissolved salt usually increases both the rate and final efficiency of flotation (Paulson and Pugh, 1996; Pugh et al., 1997; Kurniawan et al., 2011; Ozdemir, 2013; Laskowski and Castro, 2015; Zhang, 2015).

During flotation of copper-bearing shale in the presence of NaCl, an increase in recovery is observed with an increase of salt concentration in the solution (Smolska and Ratajczak, 2017; Kuklinska and Ratajczak, 2016; Ratajczak et al., 2020). A similar effect of increasing flotation of copper-bearing shale is observed for other aqueous salt solutions, including Na_2SO_4 and KCl (Kuklinska and Ratajczak, 2016; Smolska and Ratajczak, 2017; Kosinski and Ratajczak, 2021). The improved flotation is mostly due to increased surface tension of water (Ratajczak and Drzymala, 2003; Drzymala, 2007; Smolska and Ratajczak, 2017; Ratajczak, 2017). However, there are exceptions, for instance KPF_6 decreases water surface tension and makes shale flotation worse (Lipniarski et al., 2015; Smolska and Ratajczak, 2017).

In most works involving shale flotation the regulation of aqueous solution pH is not taken into account. Instead, flotation tests are carried out at natural pH. Exceptions are the works of Pazik et al. (2016), Swebodzinska and Kowalczuk (2016), and Kiedracha and Drzymala (2016). According to Pazik et al. (2016) the flotation of copper-bearing shale in industrial process water does not depend on pH. Similar conclusion was reached by Swebodzinska and Kowalczuk (2016). They found that flotation of shale in water and in the presence of frother is not influenced by pH, while Kiedracha and Drzymala (2016), by conducting frother flotation of shale using α-terpineol and methylisobutylcarbinol, found no role of pH of the aqueous solution in the increase of shale flotation yields.

Other than shale flotation systems are also sensitive to pH and salt concentration. For instance, Castro (2018) noted that regulation of the distilled water pH, 0.5M NaCl and seawater affects chalcocite flotation in the presence of isopropylxanthate or amyl alcohol as the flotation reagents. An increase in

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chalcocite flotation was noted in the pH range of 6-9, and its decrease above pH 9. In addition, it was noted that the flotation carried out in distilled water was better in relation to 0.5M NaCl solution and sea water. Similar results were obtained by Castro (2018) during molybdenite cleaning flotation, where it was noticed that when the pH increased above pH 9, molybdenum flotation carried out in sea water in the presence of flotation reagents deteriorated. Thus, depending on the flotation system, the influence of pH on salt flotation of mineral substances may be different. This paper investigates the flotation of copper-bearing shale regulated with pH and sodium chloride without the presence of other flotation reagents.

Our preliminary flotation tests involving copper-bearing shale indicated that the conclusion of other authors saying that its flotation is independent of pH is not precise. Therefore, a series of tests was carried out involving flotation of copper-bearing shale in the presence of NaCl and varying pH values. The results of the tests were subsequently presented and analysed in the light of our own and literature flotation data.

2. Materials and methods

The copper-bearing shale, a sedimentary rock of the Zechstein age (Konopacka and Zagozdzon, 2014), originated from the Legnica-Głogow Copper District with a copper content of 2.95% in the rock, 7.25% of organic matter and a CO_2 content of 15.1% (Karwowski, 2018). Copper-bearing shale was collected from the resources of the Mineral Processing Laboratory of the Faculty of Geoengineering, Mining and Geology of the Wroclaw University of Science and Technology. The collected shale sample was crushed in the "EKO-LAB" jaw crusher, model LAB-01-65, and then ground in an Ortoalresa ball mill. Next, it was classified on a set of sieves with mesh sizes of 1.0 mm, 0.50 mm, 0.25 mm and 0.125 mm in order to obtain the required for flotation size fraction below 0.125 mm. The shale flotation tests were carried out in a Mechanobr laboratory machine in NaCl solutions at concentrations of 0.5, 1 and 2 M. Flotation time was 20 minutes. Applied sodium chloride (Stanlab®) was 99.5% pure. Distilled water was used to prepare the aqueous solutions. The pH of the solutions during flotation was adjusted with 0.1 M HCl and NaOH, and the values were controlled with an Elmetron CP-401 pH meter. Samples of 30 g of copper-bearing shales (fraction below 0.125 mm) were used for flotation. The tests were carried out in a flotation chamber with a capacity of 0.3 dm^3 and an average air flow of 4.5 dm^3/h. The flotation products were collected after 3, 8, 13, 16 and 20 minutes of the process, then washed and filtered to remove salts using a Büchner funnel. The filtered products were dried for 24 hours at 105°C and then weighed to determine the flotation mass recovery.

3. Results and discussion

Fig. 1a shows the flotation results of the tested shale at varying pH and concentration of the sodium chloride aqueous solutions. It shows that the recovery of copper-bearing shale increases both with the increase of pH and salt concentrations. In the case of 2.0M NaCl, a slight decrease is observed in the pH range above 8.

A careful comparison of the obtained shale flotation results with the literature data (Fig. 1b-e) indicates that there is always an increase of recovery with increasing pH, within the pH range of 5 and 8 and, a possible decrease in the pH range of 8 and 10. Thus, there is an agreement between our and literature data, even though our data were collected for flotation in the presence of high amounts of NaCl in solutions.

It is interesting to look now into the mechanism of the shale flotation when the pH is a variable. Flotation recover R depends on more than 100 factors (Drzymala, 2007), which can be generally grouped into thermodynamic and hydrodynamic parameters:

$$R = \text{f (thermodynamic parameters + hydrodynamic parameters)}. \quad (1)$$

In Eq.1. the hydrodynamics can be split into mico- (thin films) and macro- (mechanical carryover) hydrodynamic parameters. From a thermodynamic point of view the flotation ability can be characterized by the so-called Gibbs potential. The flotation process is more efficient when ΔG is more negative (Drzymala, 2007). The Gibbs potential of flotation can be approximated with the formula:

$$-\Delta G_{flotation} = \gamma(1\text{-}\cos\theta) \quad (2)$$

where γ is the surface tension of the aqueous solution while θ stands for contact angle. Thus, there are four main parameters responsible for flotation recovery: hydrophobicity characterized by contact angle θ, surface tension of aqueous solution γ, properties of the thin films between particle and bubble (including the pattern of surface hydration) and mechanical carryover.

According to Swebodzinska and Kowalczuk (2016), the contact angle of shale in water does not change much with pH (variation about 2-3^{o}) (Fig. 2). In fact, the contact angle even slightly decreases within pH 5 and 8, and next slightly increases between pH 8 and 12. Therefore, the contact angle is not responsible for the increase of the investigated shale flotation recovery with pH.

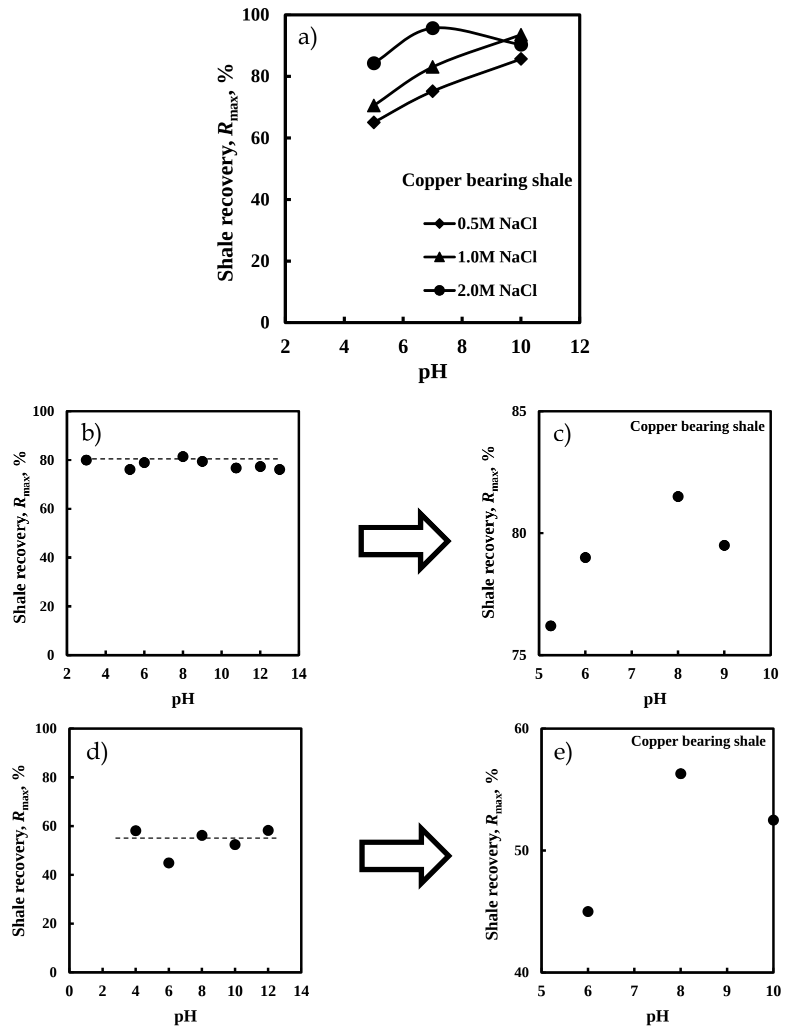

Fig. 1. Flotation yield of copper-bearing shale vs. pH and NaCl concentration; a) this work, b) Pazik et al. (2016) (no NaCl added, original data) and c) yield between pH 5 and 10, d) Swebodzinska and Kowalczuk (2016) (no NaCl added, original data) and e) between pH 5 and 10

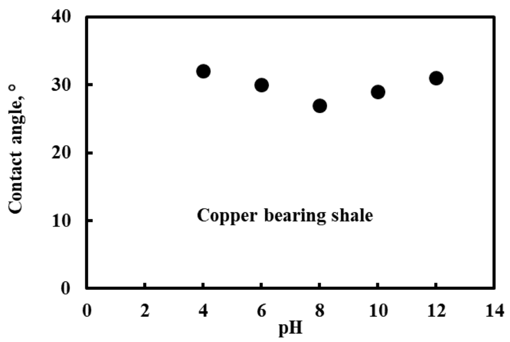

Fig. 2. Influence of pH on shale contact angle in water (Swebodzinska and Kowalczuk, 2016)

Surface tension γ, the second important factor of flotation (Eq. 2), decreases with increasing pH (Fig. 3) (Beattie et al., 2014), making the positive Gibbs potential increasingly higher, that is providing worse conditions for flotation. Thus, the decreasing surface tension is not responsible for the changes in the flotation recovery of shale with pH. It can be added that Fig. 3 shows the surface tension change with pH at very low salt concentration (10^{-2}M), where the so-called Ray-Jones effect exists (Jones and Ray, 1941; Ghosh et al., 1988; Drzymala, 2009; Beattie et al., 2014). Unfortunately, literature data on surface tension vs pH at higher NaCl concentrations most likely do not exist (Beattie et al., 2014).

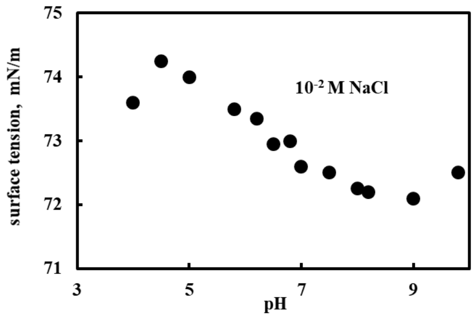

Fig. 3. Influence of pH on surface tension of NaCl aqueous solutions (Beattie et al., 2014)

It appears that the reason of the improved, with increasing pH, flotation of shale (with a possible small decrease at high pH) is of hydrodynamic nature. From the macro-hydrodynamic point of view is could be caused by an increased mechanical carryover of particles. Unfortunately, such data seem to not exist. It can be speculated this effect is not likely to occur. The remaining parameters worthwhile to consider are connected with the properties of thin films existing between particles and bubbles, which are responsible for the micro-hydrodynamics of flotation. These factors include also electric interactions between particles and bubbles and changes in the mosaic structure of the shale surface. However, the electric interaction factor can be excluded because both zeta potentials of shale (Fig. 4a) and bubbles (Fig. 4b) are more negative with increasing pH. As a result, there is an increased repulsion between particles and bubbles.

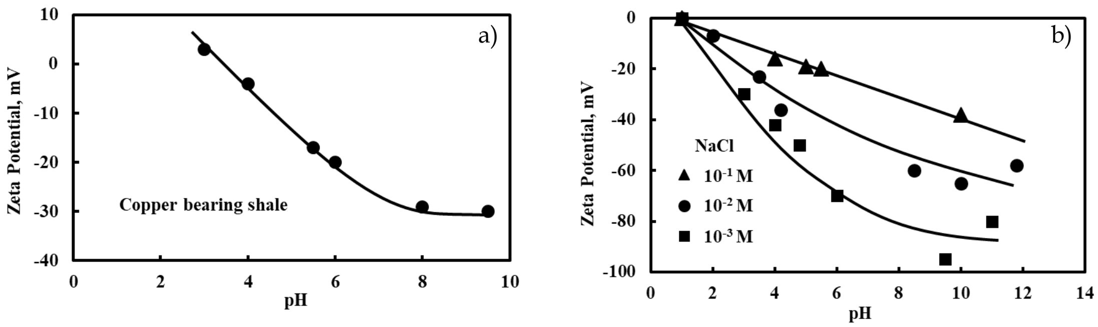

Fig. 4. (a) Zeta potential of shale as a function of pH in water (Peng et al., 2014), (b) Zeta potential of bubbles as a function of pH in NaCl salt solutions (Li and Somasundaran, 1992)

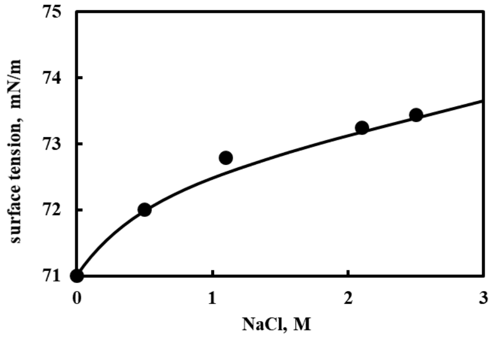

Fig. 5. Surface tension of NaCl aqueous solutions (Ghosh et al., 1988)

In the light of the presented discussion, the possible explanation of better flotation of shale with pH increase is the modification of the mosaic structure of water on the shale surface, as postulated for instance by Laskowski (Laskowski 1995, 2001; Ratajczak and Drzymala, 2003). However, it requires an appropriate verification.

In our experiments increasing addition of sodium chloride at a given pH improved flotation (Fig. 1.). It can be explanation by increasing surface tension of the NaCl solutions, as shown after Ghosh et al. (1988) in Fig. 5. and in Eq. 2.

4. Conclusions

Flotation of copper-bearing shale in aqueous solutions of sodium chloride and different pH values in the range of 5-10 was investigated. It was shown that flotation yield increases with increasing pH and with increasing salt concentration. It was proposed that improving, with increasing pH, flotation recovery is caused by changes in the properties of the thin film created between particle and bubble and/or mosaic structure of water present on the surface of shale, as it was postulated by Laskowski (1995, 2001). It was demonstrated in the paper, and summarized in Fig. 6., that the zeta potential of shale particles, zeta potential of air bubbles, hydrophobicity of shale, and surface tension of aqueous solution are not responsible for the increased recovery of shale with increasing pH.

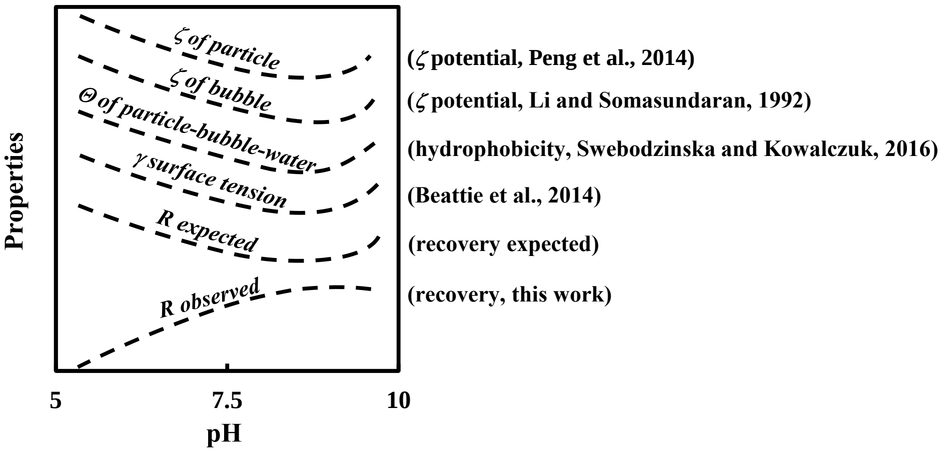

Fig. 6. Selected parameters of shale flotation as well as expected and observed response

The observed in this work better, with increasing salt concentration, shale flotation can be assigned mostly to the increasing surface tension of the aqueous solution (Eq. 2.) (Kuklinska and Ratajczak, 2016; Smolska and Ratajczak, 2017; Ratajczak, 2017; Kosinski and Ratajczak, 2021).

In order to understand better the role of pH in flotation of copper-bearing shales in water and in salt solutions, it is necessary to carry out research on hydrodynamics of shale flotation, especially the properties of thin films and particles entrainment.

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