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SELECTIVE REDUCTION OF PbSO₄ TO PbS WITH CARBON AND FLOTATION TREATMENT OF SYNTHETIC GALENA

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Abstract: In order to recover lead from the zinc leaching residues, a new technology involving selective reduction of lead sulfate to lead sulfide with carbon followed by flotation was investigated. The reduction thermodynamics of PbSO₄ was discussed and the effects of molar ratio of C to PbSO₄, reaction temperature and time were examined by thermogravimetry (TG) and XRD. Verification tests were further carried out to prove the conclusions of thermodynamic and TG analyses, and the transformation extent could reach 86.45% under the optimal roasting conditions. The prepared galena was then subjected to micro-flotation tests, and the highest lead recovery could reach up to 75.32%.

Keywords: wastes, lead sulfate, reduction, carbon, lead sulfide, flotation

Introduction

The recovery of lead from zinc leach residues, usually containing from 5 to 20% Pb, is of interest for the zinc plants. Nowadays, more than 70% of zinc is produced from zinc sulfide concentrates by conventional roast-leach-electrowinning processes in the world (Ozverdi and Erdem, 2010; Peng et al., 2003; Rashchi et al., 2005). Therefore, significant amounts of residues are generated during this process, which may contain mainly zinc ferrite, goethite, hematite or jarosite, depending on ways of iron elimination. Meanwhile, lead in the form of PbSO₄ is reported to the leach residues (Altundogan et al., 1998; Li et al., 2012). Most of the residues have to be stockpiled resulting in serious environment problems because of their heavy metal content. Currently, the concerns over these wastes are not exclusively environmental, but economic as well. In the past years, many processes have been tested for treating these

lead sulfate bearing residues, such as flotation, flotation combined with gravity concentration, pyrometallurgy and hydrometallurgy.

In term of flotation reagents of PbSO_4 , salicylhydroxamic acid and cupferron were approved to be effective collectors (Jingyun and Jianguang, 1991; Zhu and Zhao, 1991). However, these collectors were poor in selectivity against iron compounds. Generally speaking, oxidized minerals are more difficult-to-float than their sulfide counterparts (Herrera et al., 1998; 1999). Therefore, surface modification by Na_2S or Na_2CO_3 was usually proposed to enhance its recovery (Fuerstenau et al., 1987; Herrera et al., 1998; Onal et al., 2005). However, it was still difficult to achieve a satisfactory recovery for the concentrate because the particles were extremely fine. In order to further improve this, desliming prior to flotation was proposed as a promising method (Rashchi et al., 2005). Nevertheless, the loss of lead sulfate remained unavoidable since it was partially distributed in the fine fraction.

On the other hand, the pyrometallurgical processes, such as blast furnace reduction, reverberatory and bottom blowing methods, are usually used to extract lead from the wastes, especially from the materials with lead content higher than 20% (Badanoiu and Buzatu, 2012; Peng et al., 2003; Rennerta, 2010). However, these technologies were not promising in treating the materials with a lower lead content due to the high operation cost. Chlorination and carbochlorination of PbSO_4 , which could be performed at a relatively low temperature, were also reported for the recovery of lead from the leach residue (Menad et al., 1997). Yet the generation of Cl_2 presented another potential threat for the environment. In order to avoid these problems, a variety of hydrometallurgical processes including leaching and transformation by carbonates were introduced. In the literature available, hydrochloric acid and thiourea solution were found to be widely used (Baba et al., 2011; Qin et al., 2009; Shirchinnamjil et al., 2008; Vinals et al., 1991). However, the operating environment was usually unacceptable due to the release of various noxious gases such as HCl , H_2S and AsH_3 . Generally, ammonium and sodium carbonates were usually used as transformation reagents. Gen-shou (2002) reported the preparation of tribasic lead sulfate from lead bearing ash by transformation with ammonium carbonate followed by leaching and precipitating processes. Gong et al. (1992) studied the conversion of PbSO_4 to PbCO_3 with sodium carbonate, and found that the conversion extent was improved with increasing temperature. Despite achievements made, further work was required before these technologies could be put into practice.

Recently, the transformation of PbSO_4 to PbS has received considerable attention as a promising method for treating the lead bearing wastes. On the one hand, the PbS obtained is less soluble than PbSO_4 (Appelo and Postma, 2010; Pacholewska, 2004; Weijma et al., 2002; Wolthoorn et al., 2007), which lowers the risk of pollution of the heavy metal. On the other hand, it is expected that PbS generated can be recovered by some conventional techniques. Schroder et al. (2008) applied biological reduction to convert PbSO_4 in the spent car batteries to PbS which was then recovered by electrochemical processes. Karnachuk et al. (2002) studied the transformation of

$PbSO_4$ in acid mine drainage to PbS with lactate bacteria, and found that the concentration of Pb^{2+} was decreased in the solution attributed to the stable precipitation of PbS formed.

The present paper focused on conversion of $PbSO_4$ to PbS by reduction roasting with carbon powder and the flotation performance of synthetic galena was also investigated. To our knowledge, there was little related work reported. The goal was to develop a new technology to enhance lead recovery from the zinc leach residues.

Experiment

Materials

The lead sulfate was of analytical grade and argon was used as a protective gas with a purity of 99.999%. The TG curves of carbon powder are shown in Fig.1, which reveals that about 23 wt% and 90 wt% of sample would be finally lost under argon and air atmosphere, respectively. It also can be seen that about 20 wt % of the sample was decreased when the temperature was increased to 650 °C, indicating that mass loss of itself has little effect on the mass loss of the reduction reaction which occurred above the temperature.

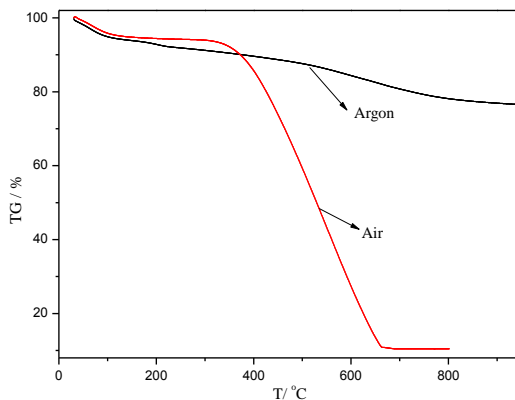


Fig.1. TG curves of the carbon powder under argon and air atmosphere

Hydrochloric acid and sodium hydroxide as pH modifiers, sodium diethyldithiocarbamate (SD) and ammonium dibutyldithiophosphate (ADD) as collectors and terpineol as frother were used in the flotation tests.

Experimental apparatus and procedure

The reaction process of $PbSO_4$ was conducted making use of a thermal analyser (NETZSCH5, STA 449 F3) and the non-isothermal tests were carried out within 900 °C at a heating rate of 10 °C/min. In the isothermal tests, sample was heated at a

heating rate of 30 °C/min to the desired temperature, and then reacted for 60 min. Samples obtained were subjected to XRD (Germany Bruker-axs D8, Cu K α) analyses.

Verification tests were carried out in a horizontal resistance furnace under argon atmosphere. About 20 g of PbSO₄ was mixed with carbon powder on different molar ratio, and then loaded into an alundum crucible with a volume of 450 cm³, which was then placed in the furnace heated. The powder samples obtained were subjected to XRD and chemical phase analyses to determine the optimal reduction conditions. The transformation extent of PbSO₄, which equals to the percentage of PbS accounting for total lead in this work. Micro-flotation was carried out in a cell with an effective volume of approximate 40 cm³ and the flotation flow sheet is shown in Fig. 2. Concentrate and bottom product, after flotation, were washed with distilled water, filtered, dried, weighed and calculated.

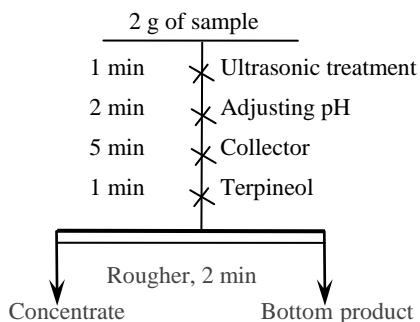
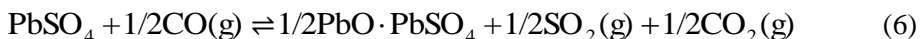
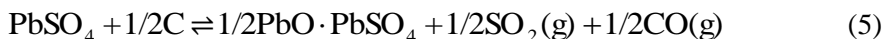
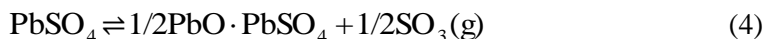
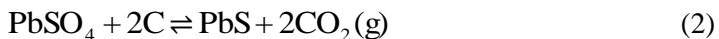
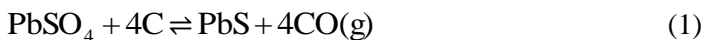
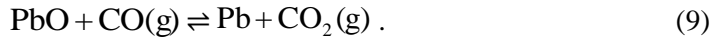
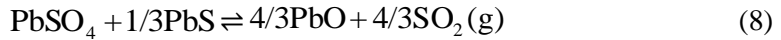
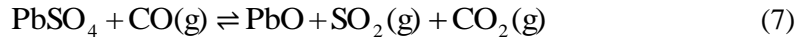


Fig. 2. Experimental schematic of the micro-flotation

Experimental reaction mechanism

As mentioned above, the recovery of lead from zinc leach residues is of interest for the zinc plants. The present paper suggests that it should be advantageous to transform PbSO₄ to PbS. Therefore, selective reduction of PbSO₄ to PbS plays an important part in this work. The reactions that may occur are listed as follows:





The software HSC 5.0 (Outokumpu, 2002) was used to calculate the standard Gibbs free energy changes of these reactions (Fig. 3) and the equilibrium amounts of roasted products (Fig. 4). Figure 3 presents the relationship between the standard Gibbs free energy changes and temperature. It can be seen that the decomposition of $PbSO_4$ (Eq. (4)) seems to be difficult within the temperature, but the reductions of $PbSO_4$ may be feasible (Eqs. (1)-(3)) in the presence of carbon. The selective reduction of $PbSO_4$ to PbS by carbon involves direct (Eqs. (1) and (2)) and indirect (Eq. (3)) ways. The indirect process (Eq. (3)) may be most likely attributed to the minimum of the standard free energy below $700^\circ C$, but the direct reduction (Eqs. (1) and (2)) may prevail above this temperature. However, the PbS produced may further react with $PbSO_4$ (Eq. (8)) at temperature higher than $800^\circ C$. In the meantime, the reduction of $PbSO_4$ to $PbO \cdot PbSO_4$ or PbO (Eqs. (5)-(7)) seems also to be possible at the temperature higher than $500^\circ C$ and the PbO generated may be further reduced to metallic Pb (Eq. (9)). Therefore, selective transformation of $PbSO_4$ to PbS could be achieved by controlling reduction temperature.

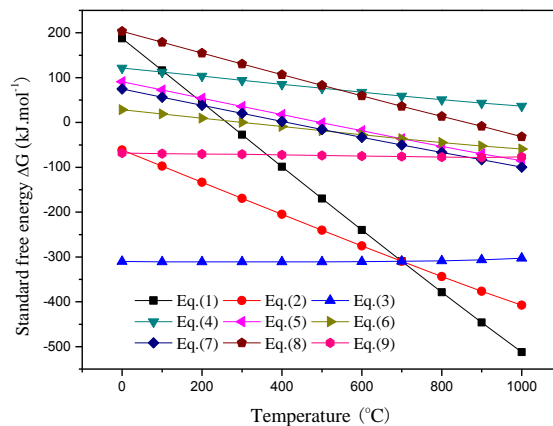


Fig. 3. Standard Gibbs free energy changes for the reduction of $PbSO_4$ in the temperature range of $0\text{--}1000^\circ C$

Figure 4 shows the equilibrium amounts of roasted products as function of carbon dosage at the temperature of $700^\circ C$ (Fig. 4(a)) and $800^\circ C$ (Fig. 4(b)). The calculations were performed in 1 kmol of $PbSO_4$ under 0.1MPa (1 atm). They reveal that the amount of PbS produced was increased as the carbon dosage was increased

from 0 to 2.1 kmol. With a further increase on carbon dosage, the amount of PbS kept a constant value. However, increasing temperature is not favorable for the transformation of PbSO_4 to PbS at carbon dosage less than 2.1 kmol, but beneficial for the formation of PbO, PbSO_4 , PbO and even metallic Pb. Accordingly, the theoretical molar ratio of C to PbSO_4 was determined to be above 2.0. In order to exactly examine the factors affecting the reduction of PbSO_4 to PbS, TG tests were performed for the related samples.

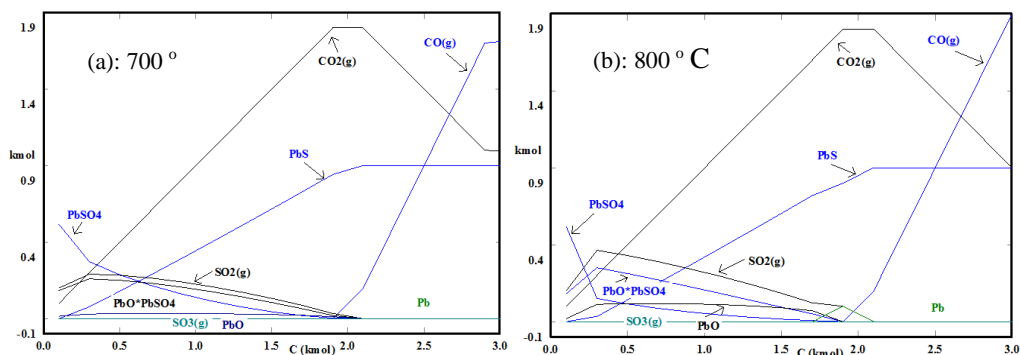


Fig. 4. Equilibrium amounts of the products as functions of carbon dosage and temperature

Results and discussion

Thermogravimetric analyses

Non-isothermal thermogravimetric tests

Figure 5 shows the TG curves (Fig. 5(a)) and derivative thermogravimetry (DTG) curves (Fig. 5(b)) with respect to temperature and different molar ratio of C to PbSO_4 . It can be seen that sample mass was slightly decreased until the temperature was increased to 650 °C. As indicated by the TG curves of carbon powder (Fig.1), this may be accounted by the mass loss of carbon powder, which had little effect on the mass loss of reduction reaction as the temperature was increased. With a further increase on temperature, mass loss continues and their maximum rates occurred at about 700 °C. Considering the results of thermodynamic analyses, the reduction of PbSO_4 to PbS may be dominant around this temperature. However, for the sample with a lower carbon dosage (curve 2), DTG curve (Fig. 5(b)) shows another rate extremum at about 800 °C. As suggested by the equations (Eqs. (7)-(9)), the formation of metallic Pb may occur at this temperature. Nevertheless, these deductions needed further confirmation. Therefore, isothermal thermogravimetric tests and XRD analyses were carried out.

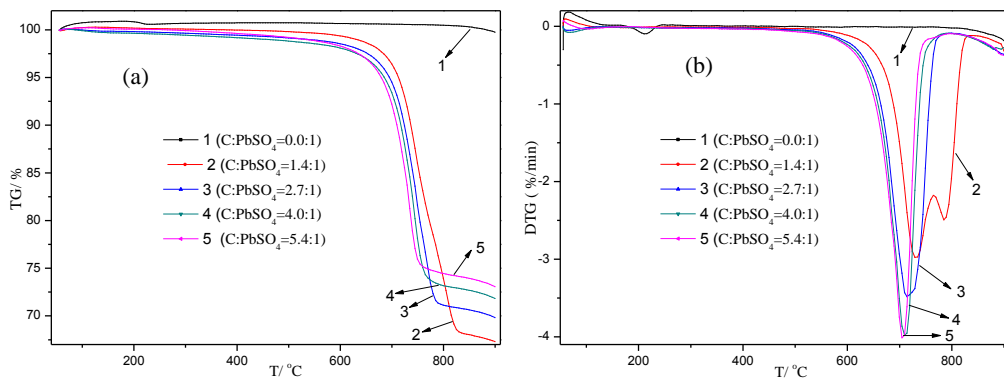


Fig. 5. TG-DTG curves of the samples with different molar ratio of C to $PbSO_4$

Isothermal thermogravimetric tests

Figure 6a presents the remaining mass as functions of time and molar ratio of C to $PbSO_4$ at 700 °C. It can be seen that the rate of mass loss was increased with increasing carbon dosage. This may be accounted by the explanation that increasing carbon dosage causes a fast de-oxidation of the $PbSO_4$. Furthermore, the reduction of $PbSO_4$ was finished within about 60 min, indicating that the transformation to PbS was highly efficient using carbon powder. The X-ray diffraction patterns of the sample obtained are shown in Fig. 6b. It can be known that the peak intensity of PbS was increased as the molar ratio of C to $PbSO_4$ was increased from 1.4 to 2.7. In the meantime, it can also be found that part of $PbSO_4$ still existed attributed to the insufficient of carbon dosage, and that small amount of metallic lead was formed ascribed to the formation of PbO (Eq. (7)) and its further reduction (Eq. (9)). However, there were no significant characteristics with a further increase on the molar ratio. Therefore, the molar ratio range of C to $PbSO_4$ was determined to be 2.7 to 4.0 as the selective reduction temperature was chosen at 700 °C.

As discussed in section 2.3, temperature plays an important part in the effective transformation of $PbSO_4$ to PbS . Figure 6c shows the effect of temperature and time on remaining mass under the maximum molar ratio (4.0) of C to $PbSO_4$. It can be seen that rate of mass loss was increased with increasing temperature, indicating that the reduction of $PbSO_4$ ran intensively at a higher temperature. The X-ray diffraction patterns of the sample obtained are shown in Fig. 6d. It was found that $PbO \cdot PbSO_4$ was formed at 650 °C, but its peak was disappeared as the temperature was increased to 700 °C. This may be attributed to the effect of mass or heat transfer (Menad et al., 1997; Szekely, 1976). With a further increase on temperature, metallic lead was formed. These results are consistent with the thermodynamic and non-isothermal thermogravimetric analyses. Accordingly, the optimal reduction temperature was determined to be 700 °C.

Based on the above analyses, the operating process parameters for the selective transformation of PbSO_4 to PbS was determined as temperature of $700\text{ }^\circ\text{C}$, molar ratio of C to PbSO_4 ranging from 2.7 to 4.0, and reaction time within 60 min.

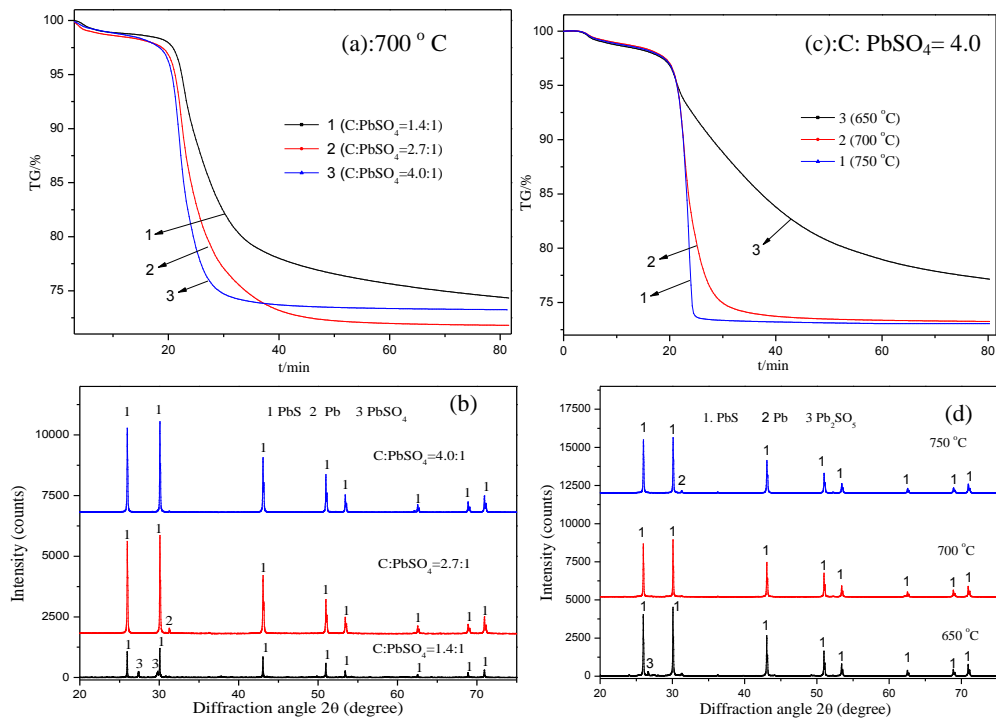


Fig. 6. Factors affecting PbSO_4 reduction under argon atmosphere and X-ray diffraction patterns of the roasted samples

Verification tests and micro-flotation tests

Verification tests were carried out at $700\text{ }^\circ\text{C}$ and the results were shown in Figs. 7 (a) and 7(b). It can be known that the highest transformation extent reached up to 86.45% under a molar ratio of 3.5 (C: PbSO_4) and a reaction time of 60 min, indicating that a sample with a higher purity was prepared.

A batch of artificial galena was prepared under the optimal roasting conditions and then micro-flotation was carried out. The flotation recovery as functions of collector concentration and pH is shown in Fig. 8. Figure 8a reveals that the artificial galena could be floated and the maximum recovery of 75.32% and 62.34% were obtained at an ADD concentration of $1.4 \cdot 10^{-4}\text{M}$ and a SD concentration of $1 \cdot 10^{-4}\text{M}$, respectively.

Figure 8b discloses that pH value lower than 4.0 or higher than 10.0 will not be favorable for the flotation of artificial galena. This may be accounted by the explanation that the soluble ions at a lower pH, such as Pb^{2+} from the dissolution of Pb

compounds, were reacted with the collectors and then the precipitations were formed, but at a higher pH, the galena was oxidized and the $Pb(OH)_2$ was formed on its surface (Chernyshova and Andreev, 1997; Nowak and Laajalehto, 2000). In addition, it can be seen that the lead recovery reached about 75.0% with ADD and about 62.0% with SD in the pH range of 8.0-10.0, both of which were above 50%, indicating that the galena prepared could be recovered by flotation, and it was interesting that the ADD as collector seemed more powerful than the SD. This may be ascribed to the improvement of foam properties or occurrence of hydrophobic flocculation for the flotation of fine galena in ADD solution (Song et al., 2000; Zhang et al., 2014; Zhu et al., 1996).

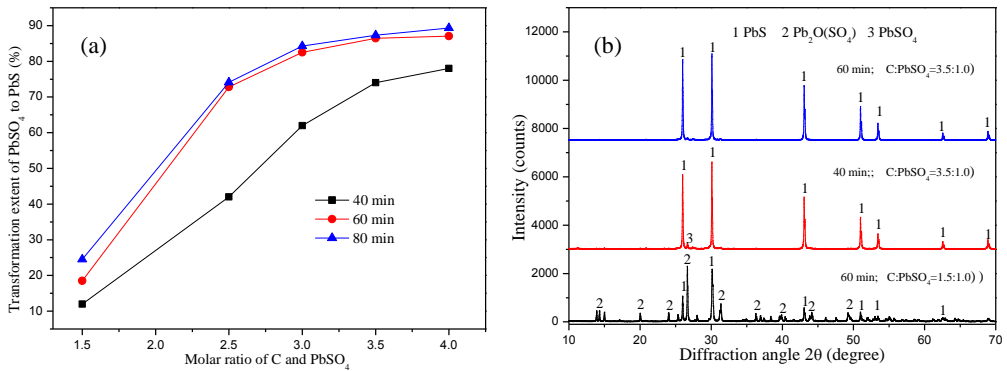


Fig. 7. The transformation extent of $PbSO_4$ to PbS and XRD patterns of the sample

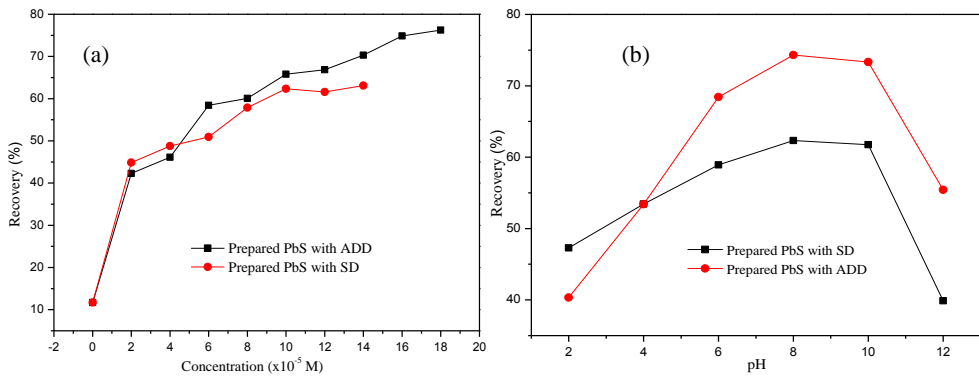


Fig. 8. Flotation performances of artificial galena (a, natural pH; b, ADD concentrations: $1.4 \cdot 10^{-4}$ M, SD: $1.4 \cdot 10^{-4}$ M; terpineol concentration: $.0.065$ M)

Conclusion

The results showed that PbSO_4 could be transformed to PbS by selective reduction roasting with carbon powder. Galena obtained could be recovered by conventional flotation technology. Accordingly, a new method to recover the PbSO_4 from the zinc leach residue was developed.

The parameters of selective transformation were established by thermogravimetric and XRD analyses as follows: temperature of 700 °C, molar ratio of C to PbSO_4 ranging from 2.7 to 4.0 and reaction time from 40 to 60 min. Results obtained by verification tests were consistent with the thermogravimetric analyses, and the transformation extent reached up to 86.45% under the optimal conditions. The samples of artificial galena were subjected to micro-flotation tests and the lead recovery of 75.32% and 62.34% were obtained with ADD and with SD, respectively.

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