

SPHALERITE AND SILICA AGGREGATION: UV-VISIBLE METHOD DEVELOPMENT

Duarte, A. C. P. and Grano, S. R.

Ian Wark Research Institute – University of South Australia – Mawson Lakes Campus – SA 5095 – Australia.
Ana.PereiraDuarte@postgrads.unisa.edu.au

Particles interactions and their subsequent aggregation or dispersion state is an important parameter related to mineral flotation, and can be measured by several methods. In the present work, the development of a methodology using UV-Visible technique to quantify sphalerite and silica aggregation is presented. Zeta potential measurements were used to predict the pH at which aggregation could be greatest. Based on this data, it was possible to define that at approximately pH 6.5, silica and sphalerite can achieve maximum aggregation. This prediction was confirmed using UV-Visible to quantify particle aggregation and it was found that approximately 43% of silica could be attached to the sphalerite surface by changing the pH of the suspension. However, this methodology needs further development due to the sphalerite dissolution products that can interfere in the absorbance measurement.

Key words: Sphalerite, Silica, Aggregation, and Zeta potential.

Area: Flotation.

INTRODUCTION

The present work is a preliminary study about particles interactions, which are an important aspect in mineral separation. This is due to the adsorption (attachment) of very fine particles onto mineral surfaces, which can affect mineral flotation amongst other industrial processes. The interactions between minerals can be studied according to the DLVO theory, which considers only electrostatic and van der Waals interactions.

It is defined in terms of energy changes that take place when particles approach one another. As a consequence, the estimation of the total energy is based on the overlap of the electric double layer (usually repulsive) and the van der Waals (usually attractive) forces. [Deryagin and Landau, 1941; Verwey and Overbeek, 1948 and Toikka *et al.*, 1997].

The phenomenon that can affect mineral stability is generally called aggregation and it can be obtained by reducing or eliminating the energy barrier (normally repulsive) that keeps particles dispersed in the solution. The principal cause of aggregation is the van der Waals attractive forces between the particles, whereas stability is a consequence of repulsive interaction between similarly charged electric double layers. The total interaction energy (V_T) is given as the summation of attractive van der Waals (V_A) and repulsive electrostatic double layer (V_R) interactions, as illustrated in equation 1 [Yotsumoto and Yoon; 1993]:

$$V_T = V_A + V_R \quad [1]$$

Although several particle interactions in mineral processing can be explained by DLVO theory, there are a large number of situations that will not fit this theory in the understanding of particle stability [Sjollem and Busscher, 1990]. In this case, one should consider other type of interactions, such as hydration, hydrophobic and steric forces, which are known collectively as “structural” forces. All these forces, together with van der Waals and electrostatic interactions, result in a modified DLVO theory.

Suspension stability or dispersibility can be studied by several methods that include optical microscopy, scattering methods, electronic counting technique and rheology, among others. The first three techniques involve, in some way, the counting of the number of particles present in a suspension and the last technique involves the correlation between viscosity and shear rate [Laskowski and Ralston, 1992]. In general, the UV-Visible technique is based on the measurement of the transmittance or absorbance of solutions contained in a transparent cell having a specific path length. Thus, the amount of light absorbed depends on the number of particles present in a solution. This technique needs a calibration plot for the suspensions without sulphide minerals prior to the aggregation test, which can be used to define the absorbance as a function of known solids concentration. As a result, the concentration of fine particles in a suspension can be determined.

OBJECTIVE

The present project is aimed at aggregation studies between colloidal silica particles and natural sphalerite using the UV-Visible technique. For this purpose, the methodology applied to quantify the amount of silica attached to zinc sulphide surfaces using light scattering methods needs to be developed.

MATERIALS AND METHODS

1. Materials

Colloidal silica with particle size of 1 micron was purchase from Fiber Optic Centre and sphalerite, from Tennessee / USA, is a natural zinc sulphide mineral with particle size ranging from 38 to 75 microns. The natural sample was prepared as followed: after grinding, the sample was wet sieved to obtain the desired size fraction and stored at room temperature. Prior to use, sphalerite was deslimed by a sequence of sonication and decantation steps to remove fine particles adhered to the surface. Silica particles were heated at 700°C for 2h and kept at room temperature prior use.

2. Methods

2.1. Sample characterization

The sphalerite sample was chemically analysed with Inductively Coupled Plasma Mass Spectroscopy (ICP) and its elemental composition is shown in Table 01.

Table 01. Chemical composition for sphalerite samples using ICP technique.

Sample/%	SiO ₂	Al ₂ O ₃	Zn	Fe	Cu	Pb	S
Sph	0.88	0.17	65.3	0.34	0.08	0.065	32.4

Electrophoretic mobilities (zeta potential measurements) of sphalerite particles were conducted using the Electroacoustic technique (AcoustoSizer) and their size range was confirmed using the Malvern Mastersizer. Zeta potential measurements were carried out using a solution of 10⁻³M NaCl, as an indifferent electrolyte, and NaOH and HCl solutions were used to adjust the pH during the experiment.

2.2. Aggregation test

The amount of silica attached to the sphalerite surfaces was determined using UV-Visible Spectroscopy technique, which is an indirect method for measuring number of particles (or concentration) in a suspension. A calibration plot for the silica suspension was determined as a function of concentration, and particle stability as a function of pH using a solution of 10⁻³M of NaCl.

For aggregation studies, 25 mL of a suspension of silica (0.1%; 0.025 g SiO₂) was added to a 100 mL suspension of sphalerite in NaCl 10⁻³M (1:10), at a certain pH, and the system was stirred for 30 min. Following this, the sphalerite samples were allowed to settle and an aliquot of the suspension was taken to measure the absorbance. Prior to the absorbance determination, the aliquot was acidified with H₂SO₄ (pH<1) to remove the oxidation products from the solution, so it was possible to measure the decrease in silica concentration. Figure 01 shows the diagram for the complete aggregation experiment.

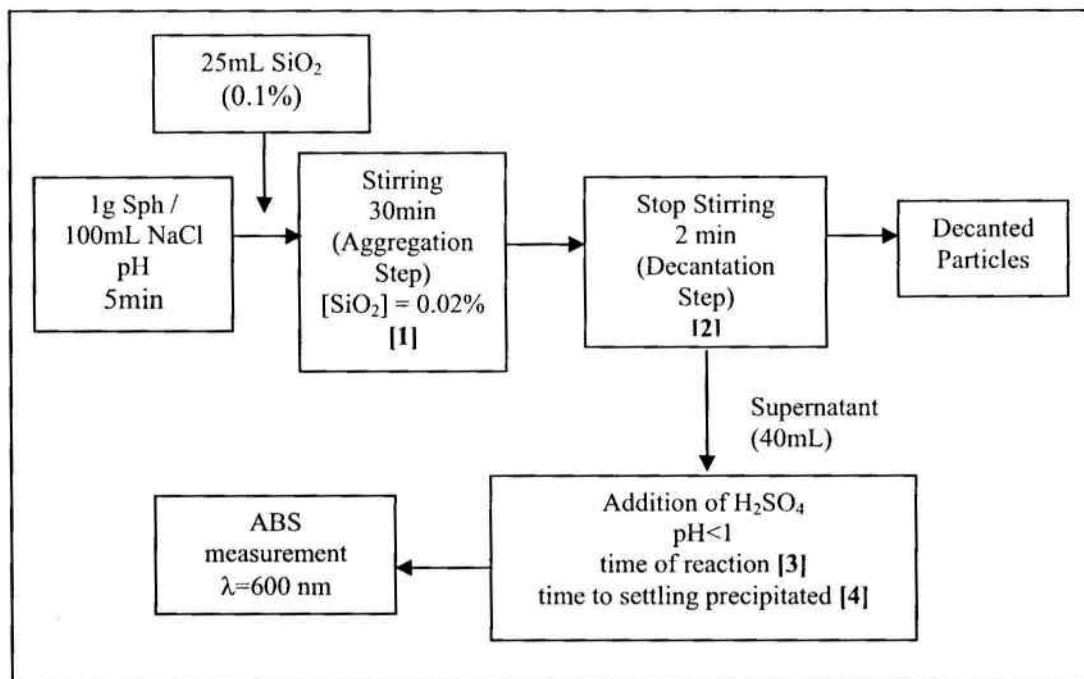


Figure 01. Schematic presentation for aggregation test: Step 1 is the aggregation test, which was carried out for 30 min after addition of SiO_2 suspension (0.1%) to sphalerite suspension in $\text{NaCl } 10^{-3}\text{M}$. In step 2, the sphalerite particles were allowed to settle for 2 min before taking an aliquot. Steps 3 and 4 are, respectively, the supernatant reaction with H_2SO_4 (25%) and the time to allow the precipitate to settle prior to the absorbance measurement.

RESULTS AND DISCUSSIONS

Sample characterization

Figure 02 shows the results obtained for zeta potential measurements. These results were determined as a function of pH to obtain the isoelectric point (iep) for the sphalerite sample, which facilitates the understanding of particles stabilities. This Figure also shows the zeta potential results obtained for silica samples by Subramaniam *et al.* [2003], and, as we can see, the pH_{iep} for silica particles is around 2.5.

It suggests that there are 2 regions for stability/dispersibility for the present system that should be discussed. In the first one, at pH lower than 7.0, silica can adhere to the sphalerite surface due to the reducing (or eliminating) electrostatic repulsive forces. However, maximum aggregation can be achieved at pH close to sphalerite iep, because at that point only attractive van der Waals forces are dominating particle interactions. While, the second region is dominated by repulsive forces that keep particles dispersed. It may occur at pH higher than 7.0.

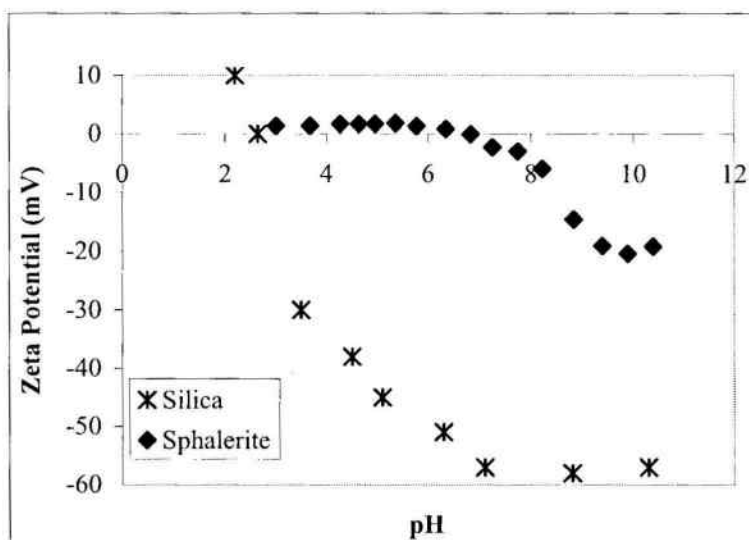


Figure 02. Zeta potential for Sphalerite (38-75 μm) and silica as a function of pH ($\text{NaCl } 10^{-3}\text{M}$).

Moignard *et al.* [1977] and Muster and Prestidge [1995] reported that the iep for sphalerite is dependent upon its state of oxidation. The pH_{iep} for unoxidised sphalerite is close to pH 2, and with an increase of oxidation it increases up to 8.5, which is the pH_{iep} for zinc hydroxide. Thus, it can be considered that the sample in this current study is partially oxidised, showing both zinc hydroxide and zinc sulphide surface groups. Moreover, zeta potential measurements at different electrolyte ionic strength (i.e. 10^{-4} and 10^{-5} M) will be conducted. This will allow us to improve our understanding in relation to the iep for sphalerite and silica samples. Zeta potential measurements at different oxidation state for sphalerite particles will be also carried out, aiming to study the effect of the oxidation on the iep values.

The results obtained for the particle size distribution and the specific surface area (SSA) for the sphalerite sample are presented in Table 02. The SSA was determined by BET technique.

Table 02. Particles size distribution and specific surface area for sphalerite particles.

Samples	D 50 (μm)	SSA (m^2g^{-1})
Sphalerite	67.0 ± 1.0	0.19 ± 0.01

The amount of colloidal silica to produce one monolayer on 1g of sphalerite is approximately 0.08 g assuming close packed spheres. This data is important to assist in our understanding about how silica particles are adsorbed onto the sphalerite surface, if it occurs as a monolayer or multiple-layers. Thus, it will be possible to study the adsorption isotherms for the present system. It is important to say that the total amount of silica particles applied to the aggregation test in the present work is equivalent to 0.30 monolayers of close packed spheres on the sphalerite surface.

Aggregation test

Silica particle stability and calibration plot:

Figures 03 and 04 show, respectively, the stability for 1-micron silica particles as a function of pH at a concentration of 0.5 g/L, and also the calibration plot as a function of concentration.

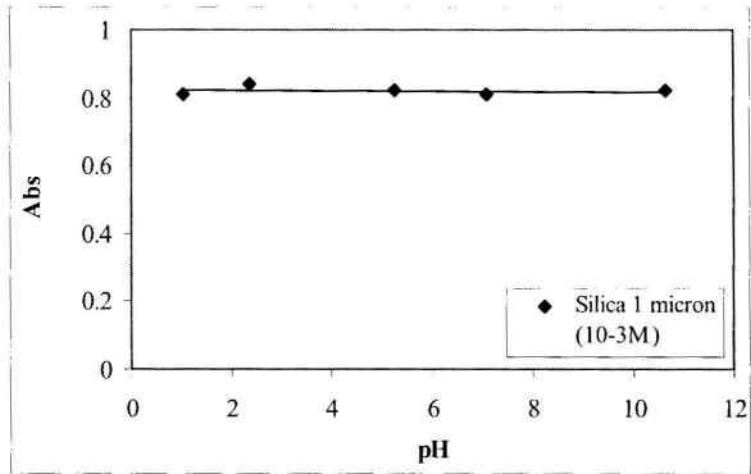


Figure 03. Silica suspension (0.5 g/L) stability as a function of pH in NaCl $10^{-3}M$.

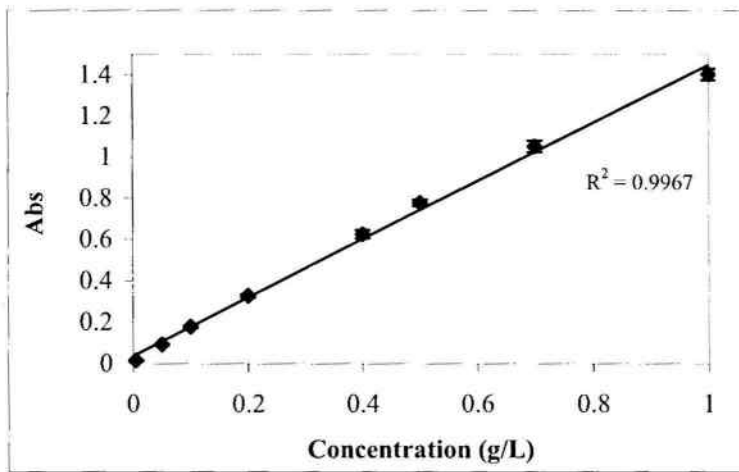


Figure 04. Calibration plot for silica suspension as a function of concentration in NaCl $10^{-3}M$ at pH 5.5.

The suspensions of silica are stable at all range of pH. Increasing the particle concentration leads to a linear increasing in absorbance. As a result, the decrease of absorbance, during aggregation experiments, can be related to the decreasing in concentration for silica in suspension and can be used as a measurement of the amount of silica attached to the sphalerite surface.

During initial experiments, it was noticed that the oxidation products derived from sphalerite surface could easily be released to the suspension, therefore increasing the absorbance. This is a limitation for the UV-Visible technique to determine the amount of silica adhered to the sphalerite surfaces, because the absorbance is strongly related to the number of particles presented in a suspension. In other words, it is necessary to develop an accurate method to measure the absorbance as a function of concentration (number of particles).

Table 03 shows the results obtained for the development of this methodology, which was carried out using a suspension of sphalerite without the addition of silica colloidal particles. The use of acid to promote the dissolution of the oxidation products, mostly like ferric hydroxide and zinc hydroxide, and the influence of reaction time, as well precipitate was allowed to settle, were noted to be important parameters in this step.

Table 03. The influence of reaction time and precipitate settling time on absorbance measurement at $\text{pH} < 1$, as shown in step 3 and 4 in Figure 1, with no gas purging.

Reaction time (min) [Step 3, Figure 1]	Settling time (min) [Step 4, Figure 1]	Abs ($\lambda=600 \text{ nm}$)
15	15	0.035
	30	0.032
30	15	0.029
	30	0.027
60	15	0.032
	30	0.032
Supernatant after 30 min of stirring (aggregation step) and 2min to settle sphalerite particles (decantation step): Abs = 0.51 ($\lambda=600 \text{ nm}$)		

The addition of acid ($\text{pH} < 1$) leads to a reduction in absorbance by approximately 95%. However, this step still needs to be better developed and the intensity of the stirring could be another point of study. The time of conditioning, as shown in Table 04, is another point that needs to be explored. As we can see, the absorbance values can be reduced by at least 75% of its initial value.

Table 04. Absorbance measurement as a function of conditioning time prior and after acid addition and no gas control.

Conditioning time (min)	Abs ($\lambda=600 \text{ nm}$)	
	H_2SO_4	No H_2SO_4
5	0.003	0.02
10	0.01	0.04
40	0.04	0.16

Table 05 presents the preliminary results for silica and sphalerite aggregation as a function of pH. Although the methodology applied in the present work needs to be improved, these first results show a trend that maximum aggregation occurs at a pH close to the sphalerite iep ($\text{pH} 6.5$).

Table 05. Amount of silica attached to sphalerite surface and efficiency of aggregation as a function of pH in $\text{NaCl } 10^{-3} \text{ M}$ solution for 30 min of aggregation (step 1, Figure 1) and 2 min for settling the sphalerite particles (step 2, Figure 1).

pH	Amount Attached ($\text{mg SiO}_2 / \text{m}^2 \text{ Sph}$)	Efficiency (%)	Number of Monolayers
4.3	36.62	27.6	0.08
6.3	57.61	43.0	0.13
9.8	24.84	18.7	0.06

This result is in agreement with DLVO theory, which predicts that at a pH lower than the pH_{iep} the aggregation would be less intensity. However, maximum of aggregation would be reached at a pH close to the pH_{iep} , due to the absence of repulsive forces.

CONCLUSIONS

The zeta potential results suggest that sphalerite samples used in the current work is partially oxidised. Maximum of aggregation occurs at approximately pH 6.5, which is close to the sphalerite pH_{iep} . This is in agreement with DLVO theory that predicts at pH values close to the pH_{iep} the attractive van der Waals forces are dominant.

The UV-Visible technique provides a good quantification of silica and sphalerite aggregation, although some points still need to be improved. For an example, the methodology adjustment, prior absorbance measurement due to the dissolution products. However, even as an initial conclusion, it is possible to determine that by changing the pH of a suspension it is possible to achieve particle aggregation or dispersibility.

For the present system and under the experimental conditions applied here, silica attachment to sphalerite surface is nearly correspondent to 0.13 monolayers at the pH close to sphalerite iep.

REFERENCES

- DERYAGIN, B. V. and LANDAU, L. D. *Acta Physicochim. URSS.* 14, 633 (1941).
- LASKOWSKI, J. S. and RALSTON, J. *Colloid Chemistry in Mineral Processing.* In: *Developments in Mineral Processing.* V. 12, 428 pgs. Elsevier Science Publishers B. V. Netherlands. (1992).
- LARSON, I.; DRUMOND, C. J.; CHAN, D. Y. C and GRIESER, F. *Langmuir.* 13: 2109-2112 (1997).
- MOIGNARD, M. J.; DIXON, D. R. and HEALY, T. W. *Proc. Australas. Inst. Min. Metall.* 263:31-38 (1977).
- MUSTER, T. H., and PRESTIDGE, C. A. *Miner Eng.* 8(12): 1541-1555 (1995).
- SJOLLEMA, J. and BUSSCHER, H. J. *Colloids and Surfaces.* 47: 323 – 336. (1990).
- SUBRAMANIAM, K., VITHAYAVEROJ, V., YIACOUMI, S. and TSOURIS, C. *Journal of Colloid and Interface Science.* (Article in Press). [2003].
- TOIKKA, G., HAYES, R. A and RALSTON, J. J. *Chem. Soc., Faraday Trans.* 93(19): 3523 – 3528. (1997).
- VERWEY, E. J. W. and OVERBEEK, J. Th. G., Elsevier, Amsterdam (1948).
- YOTSUMOTO, H. and YOON, R. *Journal of Colloid and Interface Science.* 157: 426-433. (1993).