

## Agglomerate flotation of fine MgO and ZnO particles at the presence of polymer and surfactant

Z. Sadowski

*Department of Chemical Engineering and Heating Equipment*

*Wrocław University of Technology*

*Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland*

*Sadowski@iic.pwr.wroc.pl*

The paper presents the experimental data with using both flocculants and surfactants for flotation and aggregation of fine particles. The work has been performed with two oxides ZnO and MgO. The conventional flotation collectors such as sodium oleate, sodium dodecyl sulphate and cetyltrimethylammonium bromide were used. The surfactant adsorbed layers were characterized by both the surfactant adsorption data and zeta potential measurements. The sedimentation experiments showed that the addition of anionic surfactant and cationic flocculant induces strong flocculation as a result of electrostatic interaction. The hydrophobic flocs and satisfied flotation conditions were created by addition of sodium dodecyl sulphate and nonionic flocculants

### 1. INTRODUCTION

Small particles aggregation and flotation are significant importance in the mineral industries. During the last two decades, various approaches to fine aggregation have been report [1-5]. Aggregation resulting from the reduction of surface charge is referred to as coagulation. Flocculation is induced by dissolved polymer molecules and it can be attributed to charge neutralization and /or interparticle bridging.

Polymers, which are soluble in water, are widely used as flocculants in mineral processing and the treatment of liquid wastes. Flocculants promote settling and aid in filtration of fine-particles suspensions. It is generally agreed that the adsorption of nonionic polymers on the mineral surface is usually

occurred through hydrogen bonding while polyelectrolytes may adsorb through a combination of electrostatic and hydrogen bonding [6].

The adsorption of surfactants at the solid-liquid interface plays an important role in ore flotation. The surfactant microstructures formed at the solid-liquid interfaces create these surfaces more hydrophobic. In the low concentration region, the adsorption of ionic surfactants onto oppositely charged mineral surfaces occurs primarily through attractive electrostatic forces.

Aggregation of fine particles was developed as shear flocculation process, where the hydrophobic particles were aggregated in a shear field [7]. Spherical oil agglomeration was also realized at the shear field conditions, where the hydrophobic fines were joined to the aggregates by the oil bridges [8].

The one of the possibility of obtaining effective agglomeration can be an interaction of classical ionic surfactants (flotation collectors) pre-adsorbed on the oxide fine particles with oppositely charged polymers (flocculants). Such interaction may lead directly to the agglomeration mechanism that combines electrostatic and hydrophobic interactions.

The competitive adsorption polymer-surfactant at the silica surface has been observed by Rachas et al. [9] and Moudgil et al. [10]. Rattanakawin has show, that anionic and nonionic flocculants show very similar behavior when added to stable dispersion of alumina particle at pH 5 [11]. The competition is governed by both the relative length of polymer chains and surfactant polar chains [12]. The surfactant molecules are also responsible for the configuration of the polymer at the solid-liquid interface [13]

Szczypta and Chibowski [14] have observed synergism in adsorption due to formation of polymer-surfactant complex. Hydrophobic flocculation arises as a result of hydrophobic interaction between hydrophobic particles and nonionic flocculant. The separation of hydrophobic flocs can be achieved using froth flotation [15].

The object of the present paper was to investigate the interaction between surfactant and polymer and effect of these interactions on aggregation and flotation of fine MgO and ZnO particles.

## 2. EXPERIMENTAL PROCEDURE

**Materials and reagents.** ZnO obtained from Huta Olawa (Poland) was used in this study. This material has an average particle size of 0.115  $\mu\text{m}$ , a BET surface area of 5.75  $\text{m}^2/\text{g}$ . MgO was purchased from Ubichem Limited, Hampshire, U.K. The BET nitrogen specific surface area of this sample was found to be 8.4  $\text{m}^2/\text{g}$ . The mean particle size of MgO was found to be 0.88  $\mu\text{m}$ .

As a surfactant, sodium dodecyl sulphate (SDS) was used. It was pure grade from BDH Chemicals. Sodium oleate (SOL), and cetyltrimethylammonium

bromide (CTAB) were also used. These reagents were purchased from Aldrich Chemicals.

The flocculants used in the study were polymer reagents obtained from Allied Colloids, Bradford, England (MAGNAFLOC 1440 cationic polymer, MAFNAFLOC E-10 anionic polymer, MAGNAFLOC 351 nonionic polymer). All reagents were used without any further purification.

**Zeta potential measurements.** Zeta potential measurements were conducted by means of Zeta Potential NICOMP380 ZLS Zetameter. The average zeta potential relieved on three series was taken as results. The ionic strength was maintained at  $10^{-3}$ M using NaCl. The isoelectric points are located at pH= 7.1 and pH=11.2 for ZnO and MgO respectively. These values are conformable with the literature data [16].

**Adsorption study.** Adsorption isotherms of were determined in the following manner. A suspension containing 0.5 g of solid in 50 ml of surfactant solution was taken at natural pH (ZnO – pH 7.3-7.5 and MgO - pH 10.8-11.2) and shaken for a definite time (8 h) to attain the adsorption equilibrium. Then the suspension was centrifuged and a supernatant was analyzed for remaining surfactant. The colorimetric methods [17] were used to the residual surfactant concentration determination.

**Stability of suspensions.** Stability or flocculation was investigated by simple sedimentation measurement using an Andreasen pipette. The suspension proved to be stable, i.e. no decrease of the mass of taken sample, with out of both surfactant and polymer. The initial concentration of suspension in these experiments was  $1.25\text{g}/\text{dcm}^3$ .

**Flotation experiment.** Column flotation experiments were carried out in a glass column of 4.2 cm in diameter and 56 cm in height, fitted with a fine particles at the bottom. A stirrer bar magnet operated on the bottom during flotation. A suspension of hydrophobic fines was prepared in a beaker and pumped to the column. The flocculant solution was led in the column at an opposite side. Compressed air was introduced into the column through the glass porous membrane.

### 3. RESULTS AND DISCUSSION

Although the properties of both surfactants and polymers and their interaction in the bulk solution are reasonably well understood [18], the self-assembly adsorption of surfactant and polymers at the solid-liquid interface is still a much developing area. The interactions between mineral particles in the

presence of both polymer and surfactant molecules are complex. These interactions have a place both within and between the adsorbed layers at the mineral-solution interface. The polymers have been found to interact with surfactants in a variety of ways:

- hydrophobic interaction between the polymer backbone and the hydrophobic part of surfactant molecule.
- electrostatic interaction between the surfactant head group and polyelectrolyte groups of oppositely charged.

Changes in zeta potential on the addition of surfactants can be used to predict the behavior of the mineral suspension. The zeta potentials of investigated powders in the presence of different concentrations of surfactants are shown in Figs. 1A and 1B. In the electrophoresis measurements the pH was maintained at pH 7.5 and pH 11.2 for ZnO and MgO respectively.

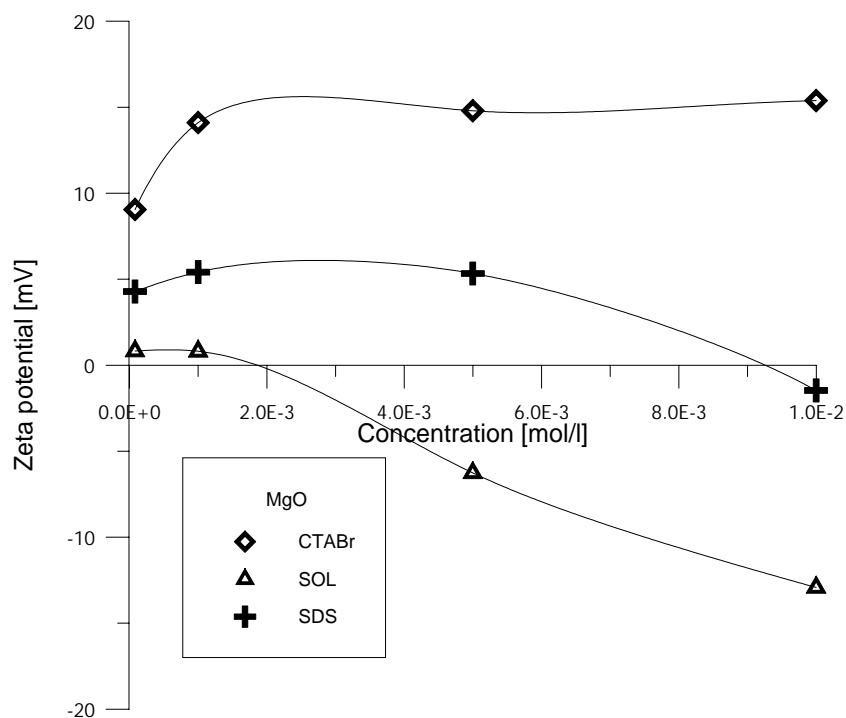


Fig. 1A. The effect of surfactant concentrations on zeta potential of MgO particles

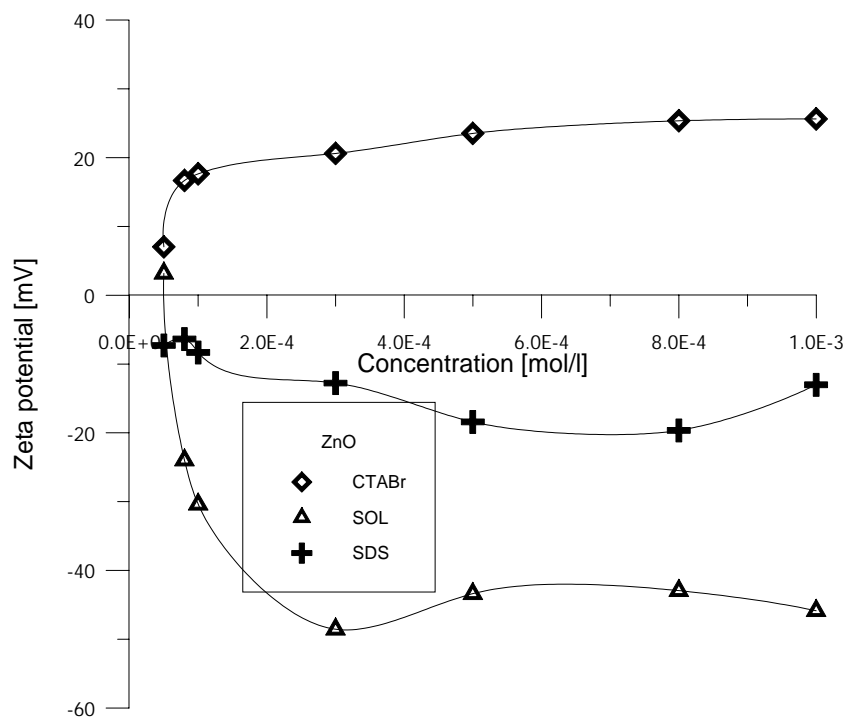


Fig. 1B. The effect of surfactant concentrations on zeta potential of ZnO particles

As a consequence to the cationic surfactant addition, the positive values of zeta potential increase for both oxides. It is interesting to note that ZnO has got negative zeta potential at the low cationic surfactant concentration ( $5 \cdot 10^{-5}$  M). The addition of sodium oleate causes the increase of negative values of both oxides. In the case of SDS zeta potentials of oxides were positive at the low concentration and become negative in the high concentration range.

The surfactant adsorption isotherms onto the surface of investigated oxides at the natural pH are presented at Figure 2 A, B and C. The adsorption of surfactants on to the polar surfaces can occur by specific electrostatic interactions in which the surface is converted from hydrophilic surface to a hydrophobic surface by the orientation of surfactant molecules. The isotherms for magnesium oxide exhibit high affinity behavior. Adsorption of ionic surfactants on to polar surface can be affected by pH. For this reason the adsorption experiments were realized at the vicinity of pH 7.5 for ZnO and pH 11.2 for MgO.

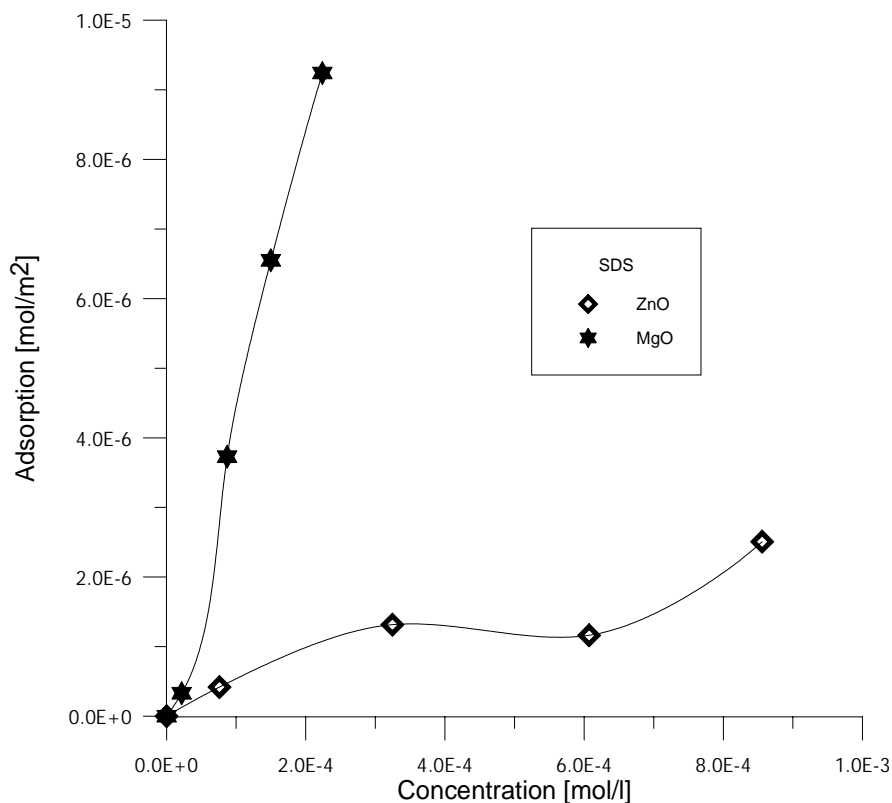


Fig. 2A. Adsorption isotherms of sodium dodecyl sulphate onto the oxides particles

The effects of surfactant concentrations on the stability of oxide suspension at natural pH (at the vicinity of pH=7.5 for ZnO suspension and pH=11.2 for MgO suspension) are presented in Figure 3A and Figure 3B. All the curves at Fig 3A indicated that some hydrophobic coagulation has occurred. In the case of MgO, the curve for CTAB is perfectly horizontal. Apparently, the hydrophobic coagulation occurred only in the sodium oleate present. MgO covered with SDS becomes unstable at the low surfactant concentration.

The dissolution behavior of MgO is not similar to ZnO. The solubility constant for ZnO equals, it is  $-16.83$  for MgO  $-9.2$  [19]. Therefore the magnesium ion concentration in the suspension must be higher compare to the zinc ions concentration in the ZnO suspension. The bulk precipitation of magnesium dodecyl sulphate seems to occur immediately after the surfactant addition. The precipitation of  $Mg(SD)_2$  may will be responsible for a low hydrophobicity of MgO surface.

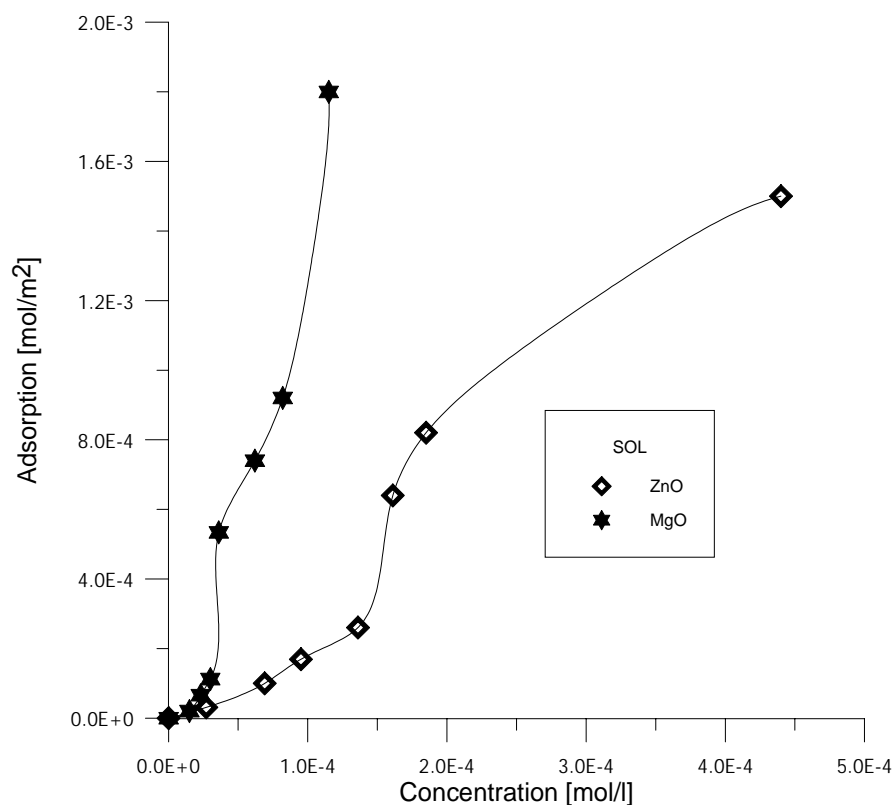


Fig. 2B. Adsorption isotherms of sodium oleate onto the oxides particles

Tab. 1. Stability of oxide suspensions in the presence of both surfactant and polymer

Reagents	ZnO		MgO	
	pH	Stability [%]	pH	Stability [%]
SOL (1 10 <sup>-4</sup> M) Magnafloc 1440 (1ppm)	7.4	2.08	11.1	42.51
SOL (1 10 <sup>-4</sup> M) Magnafloc 351 (1 ppm)	7.3	11.54	10.9	9.41
CTAB (1 10 <sup>-4</sup> M) Magnafloc 351 (1 ppm)	7.7	47.27	11.05	14.01
CTAB (1 10 <sup>-4</sup> M) Magnafloc E-10 (1 ppm)	7.4	25.93	11.0	15.33
SDS (1 10 <sup>-4</sup> M) Magnafloc 1440 (1 ppm)	7.8	1.37	11.1	51.6
SDS (1 10 <sup>-4</sup> M) Magnafloc 351 (1 ppm)	7.3	19.74	11.05	7.93

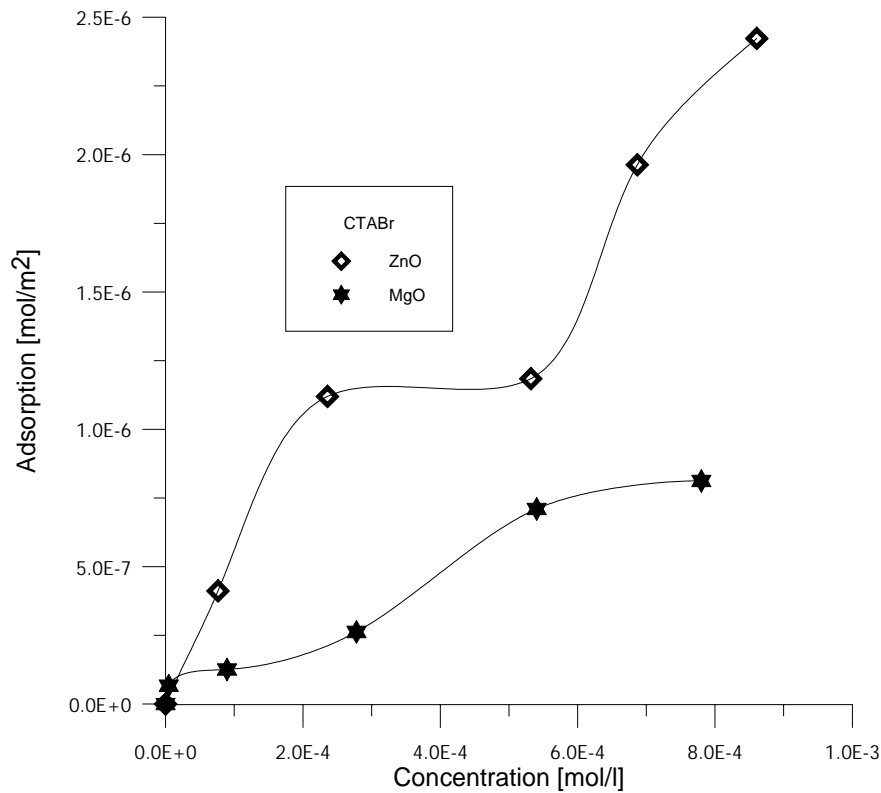


Fig. 2C. Adsorption isotherms of cetyltrimethylammonium bromide onto the oxides particles

The aggregation process realized in this work, can be divided into two steps: (1) adsorption of surfactant on the oxide particles and (b) addition of flocculants and surfactant-polymer complex creation.

The orientation of polymer-surfactant complex on the particle surface would be relevant in interpreting of the stability of mineral suspensions. In order to investigate the influence of surfactant-polymer interaction on the behavior of oxide suspensions, the stability was measured. The results obtained at these series of experiments are presented at Table 1.



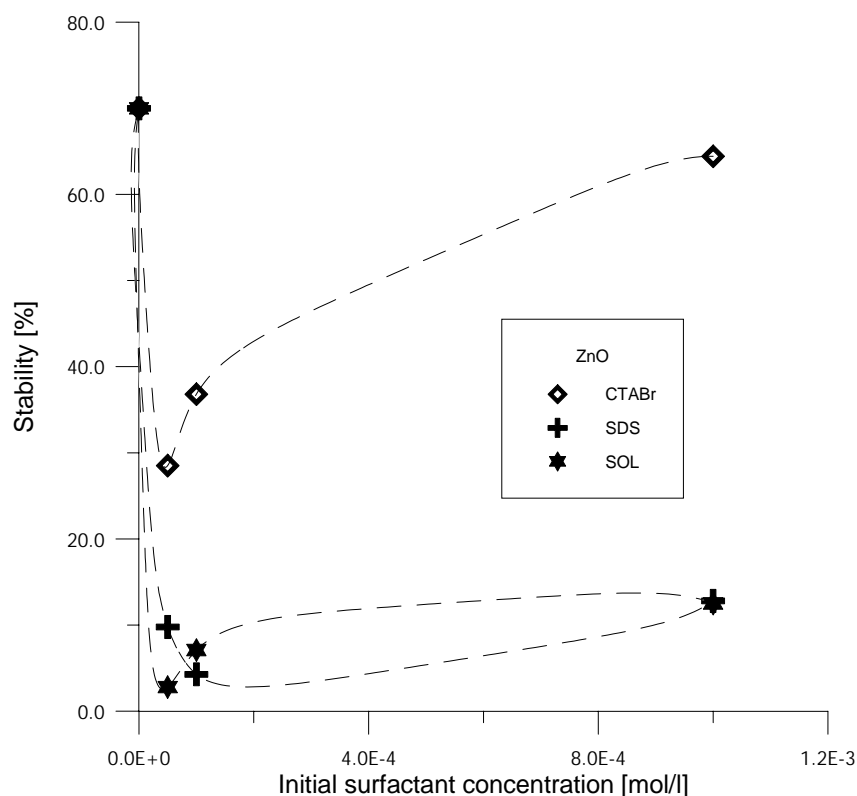


Fig. 3A. The influence of surfactant concentrations on the stability of ZnO suspension

The hydrophobic flocs flotation was examined by applying the flocs created by a surfactant-flocculant interaction. The experimental conditions were identical as used at the stability study. The selected results for sodium dodecyl sulphate (SDS) are presented in Figure 4.

A comparison of the recovery of flocs flotation for both MgO and ZnO shows that higher recovery has been obtained for zinc oxide. Such behavior can be expected on the base of the adsorption results (Figure 2A). The pre-adsorption of sodium oleate provided to the strong creation of flocs but the flotation recovery was about 10%. Also the very low recovery was obtained with the cationic surfactant (CTAB) pre-adsorption. These results suggested that in the two last cases created flocs have got the hydrophilic surface.

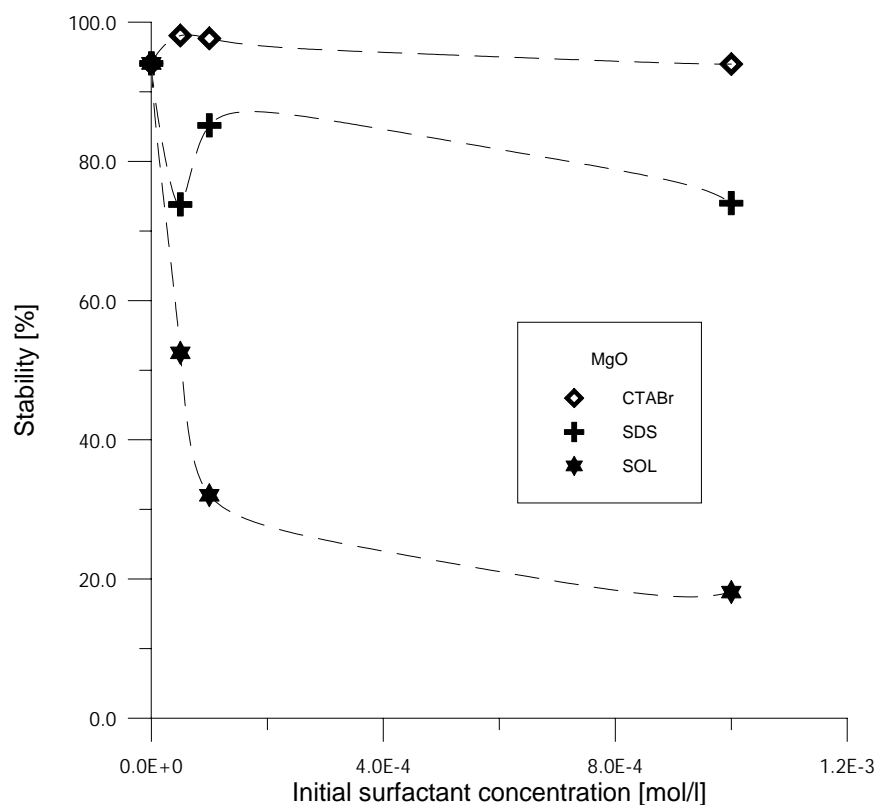


Fig. 3B. The influence of surfactant concentrations on the stability of MgO suspension

#### 4. CONCLUSIONS

A study on the polymer-surfactant interaction at the solid-liquid interface is important with a view to develop effective method to utilise fine particle. It is clearly shows that fine oxide particles were aggregated by the presence of surfactants. This is connected with a strong hydrophobic colagulation. The zeta potential of oxide particles in aqueous solution of surfactants is highly affected by the concentration of surfactants. The addition of flocculat reagents to the oxide suspensions, effects on the stabilization of these suspensions. The strong flocculation was observed when the anionic surfactants (SOL, SDS) and cationic flocculant (Magnafloc 1440) were adsorbed on the ZnO surface. In the case of MgO, the same effects were observed, when the nonionic flocculant (Magnafloc 351) was used. The good flotation recovery of flocs was obtained with anionic collector (SDS) in the presence of both cationic and nonionic flocculants.

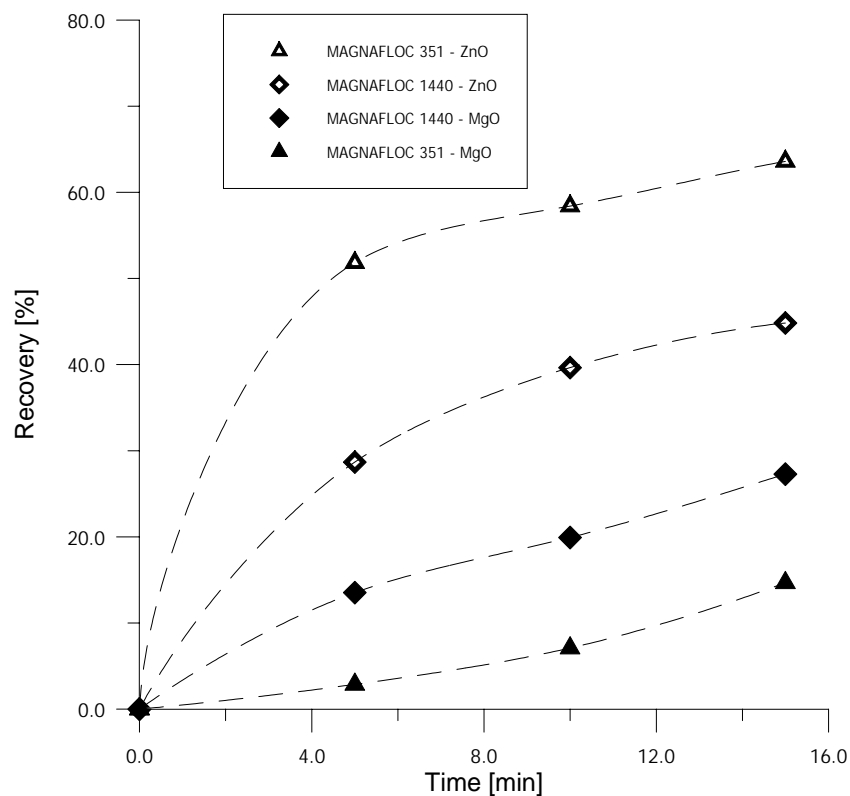


Fig. 4. Flotation recovery vs time for the hydrophobic flocs of MgO and ZnO at  $10^{-4}$  M SDS

#### REFERENCES

- [1] Laskowski J.S., Ralston J., *Colloid Chemistry in Mineral Processing*, Elsevier, Amsterdam, 1992.
- [2] Elimelech M., Gregory J., Jia X., Williams R.A., *Particle Deposition and Aggregation*, Butterworth Heinemann, Oxford, 1995.
- [3] Subrahmanyam T.V., Forssberg K.S.E., *Int. J. Miner. Process.* 30, 265-286, (1990).
- [4] Rubio J, Hoberg H., *Int. J. Miner. Process.*, 37, 109-122 (1993).
- [5] Gardner K.H., Theis T.L., *J. Colloid Inter. Sci.*, 180, 162-173 (1996).
- [6] Gasbarrone P., La Mesa C., *Colloid Polymer Sci.*, 279, 1192-1199 (2001).
- [7] Warren L.J., *Transactions IMM*, 84, C99-C104 (1975).
- [8] Sadowski Z., *Powder Technology*, 80, 93-98 (1994).
- [9] Rachas I., Tadros F.Th., Taylor P., *Colloids Surfaces*, 161, 307-319 (2000).
- [10] Moudgil M.B., Prakash T.S., *Colloids Surfaces*, 133, 93-97 (1998).
- [11] Rattanakawin C., *M.S. Thesis*, The Pennsylvania State University, 1998.
- [12] Ghodbane J., Denoyel R., *Colloids Surfaces*, 127, 97-104 (1997).

- [13] Corsgrove T., Mears J.S., Thompson L., Wesley D.R., *Colloids Surfaces*, 149, 329-338 (1999).
- [14] Szczypa J., Chibowski S., *Colloids Surfaces*, 3, 393-397 (1981).
- [15] Song S., Lu S., *Proceedings of the XXI International Mineral Processing Congress, P.Massacci (Ed.)* Rome, Italy, C5-31-C5-38, 2000.
- [16] Ardizzone S., Bianchi C.L., Vercelli B., *Colloids Surfaces*, 144, 9-17 (1998).
- [17] Fowler E. W., Steel T.W., *The determination of anionic surface active agents in dilute aqueous solution*, National Institute for Metallurgy, Johannesburg, Report 443, 1968.
- [18] Langevin D., *Advances Colloid Interface Sci.*, 89-90, 467-484 (2000).
- [19] Schindler P.W., *Aquatic Chemistry*, Wiley - Interscience, New York, 1970, 196-221.

### CURRICULUM VITAE



**Zygmunt Sadowski** was born in Wroclaw in 1947. He graduated from the Faculty of Mathematics Physic and Chemistry of University of Wroclaw in 1970. In 1975 graduated from Academy of Mining and Metallurgy in Cracow. His Ph.D. was completed at September 1998 in Department of Inorganic Chemistry and Metallurgy of Rare Elements at Wroclaw University of Technology. The Ph.D. topic was “*Selective coagulation and selective flocculation of mineral suspensions*”, his supervisor was Professor Janusz S. Laskowski. He has spent three years in research at University of Nevada (Reno), Iowa State University (Ames) and University of Utah (Salt Lake City). In 1996, he changed his Department and came to Department of

Chemical Engineering and Heating Equipment. He published 44 papers and the monograph “*Hydrophobic agglomeration of mineral suspensions*” He is a science editor of *Physicochemical Problems of Mineral Processing* journal. During a period of 1994-1996, Dr. Sadowski was co-Director of NATO Advanced Study Institute – *Mineral Processing and Environment*. His research interests are related to three basic fields: behaviour of fine particle suspension, application of biogeochemistry to the mineral processing and environmental geochemistry. All the research works which he proceeds with, are connected with the fundamental problems of both colloids and interface science. His new project is connected with a biopretreatment of gold ores. A good understanding of the adhesion of both microorganism cells and fine particles to the mineral surface is a target of his research works. Also, the principles of the macromolecules (flocculent reagents) and surfactant interaction on the mineral surface are investigated. His other current interests cover such topics as spherical agglomeration, selective flocculation and fines flotation.