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# A STUDY ON THE ZETA POTENTIAL OF GOETHITE, QUARTZ AND CLAY MINERALS DEPENDING ON pH AND THE PRESENCE OF INORGANIC DISPERSANTS

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**Abstract:** The knowledge of zeta potential is a very useful indicator of the stability of dispersed systems. This is especially important in many industrial processes, such as e.g. mineral processing, purification of water and many others. This article deals with the investigation of the electrokinetic behavior of goethite, quartz and clay minerals depending on pH and the presence of inorganic dispersants: sodiumhexamethaphosphate (SHMP), sodiumpyrophosphate (SPP) and sodium silicate (SS). All studies are conducted on natural samples, taken from Omarska iron mine (Bosnia and Herzegovina) by measuring the zeta potential. From the experimental results, it was found that the increase of the suspension pH resulted in an increase in the negative charge of all three tested samples. The clay did not show any isoelectric point (IEP). Quartz showed isoelectric points at pH about 2.6 and close to 2 in the absence and presence of sodium silicate in suspensions, respectively. Goethite showed isoelectric points at pH 6.7 and 4.95 in the absence and presence of sodium silicate in suspensions, respectively. An IEP could not be detected when the SHMP and SPP were used and the surface charge is negative from pH 2 to pH 12 in all tested samples. The addition of SHMP provided the highest negative zeta potential, i.e. the most stable dispersion, in all three tested samples.

**Keywords**: zeta potential, isoelectric point, goethite, quartz, clay, inorganic dispersants.

## 1. INTRODUCTION

Dispersion systems are encountered in a wide range of applications, such as mineral processing, water purification, pharmaceutical and cosmetic industry, catalytic processes, soil characterization etc. [1-3]. Dispersion stability is important, regardless of whether it is necessary to maintain a stable dispersion over a longer period or whether it is necessary to destabilize the system and accelerate sedimentation. The knowledge of zeta potential is a very useful indicator of the stability of dispersed systems. Zeta potential (ζ) is the potential difference between the surface of a solid particle immersed in a conducting liquid (e.g. water) and the surrounding liquid. It is related to the surface charge. The surface charge is strongly dependent on the pH value. The magnitude of zeta potential is one of the fundamental parameters known to affect stability. From a plot of zeta potential as a function of pH, a number of important data can be noted. Isoelectric point (IEP) represents condition when value of zeta potential is zero. At such conditions, the dispersion is unstable, and there are no reflective forces present among the particles. A higher zeta potential (>30 mV) produces a stable dispersion. The sign and magnitude of the zeta potential can be changed by the addition of some surface-active substances, called dispersants [4,5].

This study is focused on the influence of dispersants on the dispersion stability of natural minerals that are present in the processing of fine iron minerals. The beneficiation of iron ore frequently involves processing ultrafine materials, particularly limonite (goethite)-rich samples, where effective mineral liberation occurs at particle sizes below 50 µm. Such fine particle size requires advanced processing techniques because a significant fraction of iron is inevitably lost into slimes during crushing, washing, and desliming stages. These losses diminish overall iron recovery, despite efficient downstream concentration processes [6]. Traditional magnetic separation methods often prove ineffective for ultrafine slimes due to the fine nature of particles and their strong associations with gangue minerals such as clays and quartz. Surface-driven beneficiation techniques, particularly selective flocculation, have thus gained prominence as promising alternatives. However, these techniques remain inherently complex and highly sensitive to a suite of physicochemical parameters including surface chemistry, pH, reagent type, ionic strength, and electrical double-layer characteristics—all of which critically influence suspension stability and process efficiency.

Dispersants have emerged as essential reagents in enhancing flocculation selectivity. Inorganic dispersants such as sodium hexametaphosphate (SHMP), sodium silicate (SS), and sodium pyrophosphate (SPP) are known to inhibit aggregation of gangue minerals by increasing surface charge and colloidal stability, thereby allowing more precise control of flocculation targeting iron-bearing particles [7-11]. For instance, recent studies demonstrate that adding SHMP at 25 mg/L and pH 10 markedly improves separation efficiency when combined with selective flocculants such as starch or polyacrylamides [12]. Similarly, citric acid has proven effective for dispersing hematite fines by reducing zeta potential and reinforcing electric double-layer repulsion [13,14].

Despite the recognized importance of zeta potential in governing mineral interactions, data on natural ore systems remain scarce. Therefore, this study investigates the zeta potential behavior of goethite, quartz, and clay minerals under variable pH conditions, both with and without inorganic dispersants. Samples originate from the Omarska iron mine (Bosnia and Herzegovina). The findings aim to inform improved strategies for iron recovery from tailings and to promote sustainable sludge re-utilization. In this context, detailed investigations were performed on goethite, quartz, and clay as the primary constituents of limonitic sludge, with particular emphasis on their response to specific conditions and reagents to better interpret the sludge behavior.

## 2. MATERIALS AND METHODS

### 1.1. Materials

The study utilized natural mineral samples labeled “goethite”, “quartz”, and “clay”. All the samples are  hand picked from drill holes at the “Buvač” open pit by the geological service of the “Omarska” mine and ground to a particle size of -25 µm at the Global Research and Development, Mining and Mineral Processing laboratory in Maizières-lès-Metz, France. Sample preparation involved drying, crushing, grinding, size classification, and homogenization. Previously, a detailed mineralogical and physicochemical characterization of the samples was carried out using X-ray powder diffraction (XRPD), Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope with Energy Dispersive Spectrometry(SEM-EDS) [15]. Basic physicochemical characteristics were given in Table 1.

***Table 1.*** *Basic physicochemical characteristics of goethite, clay, and quartz*

| Sample | Fe (%) | $SiO_2$ (%) | $Al_2O_3$ (%) | Mn (%) | $Na_2O$ (%) | $K_2O$ (%) | L.O.I(%) | Density (gcm$^{-3}$) |
|---|---|---|---|---|---|---|---|---|
| Goethite | 57,16 | 4,44 | 0,59 | 1,18 | 0,009 | 0,033 | 10,86 | 3,940 |
| Clay | 4,48 | 69,90 | 14,50 | 0,07 | 0,356 | 2,420 | 4,80 | 2,734 |
| Quartz | 0,74 | 92,90 | 3,28 | 0,00 | 0,079 | 0,506 | 1,62 | 2,663 |

Major mineral compositions of the natural samples were given in Table 2.

***Table 2.*** *Major mineral compositions of the natural samples labeled as goethite, quartz and clay*

| Sample | Major mineral composition |
|---|---|
| “Goethite” | Goethite (~86%) which dominate over hematite (~10%) and with minor contents of quartz (~4%). |
| “Quartz” | Quartz (~93%) which dominates over illite-sericite (~6%) and with minor contents of hematite (~1%). |
| “Clay” | Quartz (~50%) and clay minerals (~44%) which dominates over minor goethite (~4%), chloritoid (~2%) and hematite. |

All reagents used were of analytical grade, and they were prepared as solutions in distilled water. The sodium hexametaphosphate - $Na_6P_6O_{18}$ (SHMP), sodium pyrophosphate - $Na_4P_2O_7$ (SPP) and sodium silicate - $Na_2SiO_3$ (SS), manufactured by Lach-Ner, s.r.o. (Czech Republic), were used as dispersants. As pH modifier, 0.1M NaOH and 0.1M HCl were used.

### 1.2. Zeta Potential Studies

Surface charge behavior was investigated by measuring electrophoretic mobility and calculating zeta potential over a pH range of 2 to 12, both in the absence and presence of dispersants.

– The zeta potential measurements were performed using a ZM3-D-G meter, Zeta Meter system 3.0+, with direct video imaging from Zeta Meter, Inc, USA, at Universidade Federal de Minas Gerais (UFMG), Brazil.

To guarantee the quality of the measurements the samples were classified through the sedimentation in test tubes of 250mL with a mineral concentration of 80mg/L to reach a particle size below 10 µm. Distilled water was used during the sedimentation procedure with the natural minerals and the dispersant reagents solutions were used for the remaining sedimentation tests. The pH of the mineral suspensions with or without dispersant reagents was adjusted at the beginning of the sedimentation procedure.

The reagents dosages were as follows:
– 27.6 mg/L for the SHMP and SPP
– 138 mg/L for the SS.

Detailed steps for performing the measurements:
– weighing of minerals;
– preparation of reagent solutions;
– adjustment of the pH of the solutions in a beaker of 1 liter;
– introduction of 200mL of the solution into the 250mL test tube;
– placing the mineral in the test tube;
– agitation of the suspension with a glass stick;
– closing the test tube with a PVC film;
– sedimentation for two hours;
– removal of the suspension with a pipette for filling the Zeta Meter cell;
– particle counting (mean of 20 particles for each measurement of zeta potential, with a minimum counting of 10 particles)

Before each test, the completely opened Zeta Meter cell was washed intensively with tap water and then with distilled water. Before each measurement the platinum and the molybdenum electrodes were washed with distilled water. The voltage used in the test was always the highest possible voltage that did not generate vortex due to the heating of the suspension during the measurements.

## 2. RESULTS AND DISCUSSION

Electrokinetic (zeta) potential (ζ-potential; hereinafter mostly as ZP) measurements were to assess surface charge behavior in the presence and absence of dispersants. The electrokinetic behavior of mineral surfaces plays a critical role in determining interparticle interactions, dispersion stability, and the efficiency of surface-active separation processes such as selective flocculation. It is well known that metal oxides in aqueous solutions typically become hydrated. The amphoteric behavior of metal oxides allows the oxide particles to develop electrical charges that are either positive (when they receive protons) or negative (when they release protons), which is highly dependent on the pH value. Generally, under acidic condition the oxide surfaces becomes positively charged due to protonation of surface hydroxyl groups, whereas under alkaline conditions the oxide surfaces becomes negatively charged by deprotonation of -OH oxygen.

### 3.1. Zeta potential of natural "goethite", "quartz", and "clay" samples as a function of pH

This section presents and analyzes the results of zeta potential measurements for "goethite", "quartz", and "clay" minerals under various pH conditions, as shown in Figure 2. The ZP of "goethite" changed from positive (28.8 mV) at pH 2.1 to negative (-28.1 mV) at pH 10.1 and IEP was observed at pH 6.6, aligning with values reported in the literature for iron oxyhydroxides [16, 17]. The ZP of "quartz" changed from positive (6.5 mV) at pH 2.1 to negative (-29.1 mV) at pH 10.1 and IEP was observed at pH 2.6. As shown in the diagram (Fig.1), the surface of "quartz" is positively charged only at strongly acidic conditions (pH < 3). "Clay" demonstrated negative surface charge throughout the tested range, with variability depending on specific composition, but generally maintained negative values above pH 4. In general, the zeta potential curves of "clay" resemble those observed for "quartz" under similar dispersant conditions. Across all tested pH values, the clay exhibited persistent negative surface charges, with increasing negativity above pH 6. In the absence of dispersants, the zeta potential of "clay" ranged between approximately –7 to –33mV across the pH range 2–12. Notably, no isoelectric point (IEP) was observed, confirming the persistent anionic nature of "clay" mineral surfaces under the experimental conditions. Based on the zeta potential measurement, the interaction between "goethite" and the two other minerals at acidic conditions can be predicted. At this conditions, "quartz" and "clay" were both negatively charged, while "goethite" was positively charged. Therefore, electrostatic attraction is expected between goethite and the other two samples due to dissimilar surface. On the contrary, no strong electrostatic attraction is expected at pH 10.1 due to similar surface charges of all three tested samples.

### 3.2. Zeta potential of natural "goethite", "quartz", and "clay" samples in the presence of sodiumhexamethaphosphate

Zeta potential of natural "goethite", "quartz", and "clay" samples in the presence of SHMP as dispersant are shown in Fig.2.

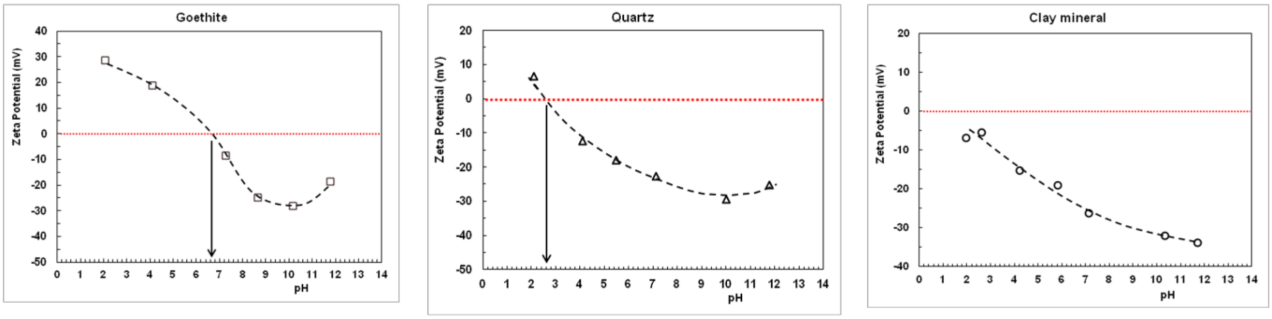

***Fig. 1.*** *Zeta potential of "goethite", "quartz" and "clay" in the absence of dispersants*

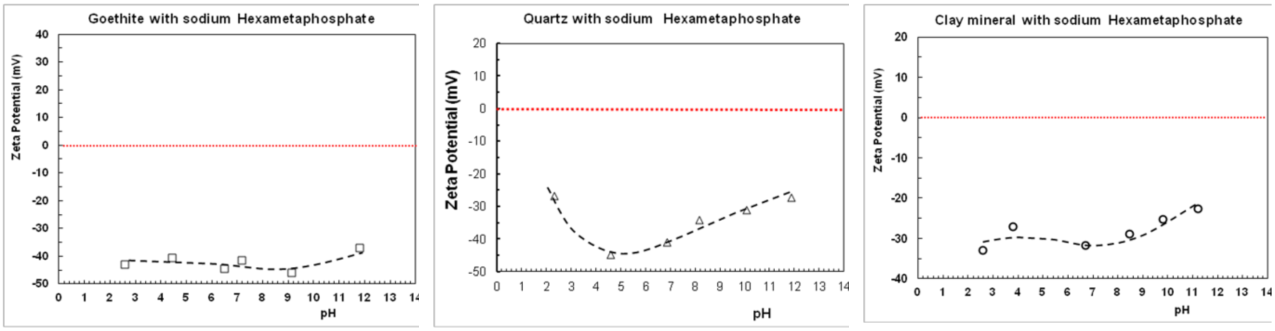

***Fig. 2.*** *Zeta potential of "goethite", "quartz" and "clay" in the presence of dispersants SHMP*

The addition of SHMP to “goethite” led to the complete suppression of the IEP, maintaining a negative zeta potential across the full pH range (2–12). This effect is attributed to the strong complexation between phosphate groups and $Fe^{3+}$ surface sites, resulting in enhanced electrostatic repulsion and improved colloidal stability [6]. Sodium hexametaphosphate (SHMP) exhibited the strongest influence on “quartz” sample, increasing the negative charge by up to 20 mV around pH 5, compared to the system without dispersant. The surface charge of “quartz” remains negative throughout the investigated pH. The addition of SHMP on “clay” led to an increase in negative surface charge of –10 to –30 mV as shown in Fig. 2. According to the results of ZP measurements, with the addition of SHMP as a dispersant, stable dispersion can be expected in the entire tested pH range.

### 3.3. Zeta potential of natural “goethite”, “quartz”, and “clay” samples in the presence of sodiumpyrophosphate

Zeta potential of natural “goethite”, “quartz”, and “clay” samples in the presence of SPP as dispersant are shown in Fig. 3. Influence of SPP on “goethite” showed a similar trend as SHMP, but with slightly less impact. It significantly increased the magnitude of the negative zeta potential, particularly under alkaline conditions (pH > 8), likely due to the adsorption of pyrophosphate anions. Sodium pyrophosphate (SPP) moderately enhanced the negative zeta potential of “quartz” throughout the measured pH range. The surface charge remains negative throughout the investigated pH as in the case of SHMP**.** The addition of SPP led to an increase “clay” sample in negative surface charge of –10 to –30 mV, as shown in Fig. 3.

### 3.4. Zeta potential of natural “goethite”, “quartz”, and “clay” samples in the presence of sodium silicate

Zeta potential of natural “goethite”, “quartz”, and “clay” samples in the presence of SS as dispersant are shown in Fig.4.

Influence of sodium silicate (SS) on “goethite” also induced a shift toward more negative values, although its effect was less pronounced than that of SHMP or SPP. With the use of sodium silicate the IEP of “goethite” moves to pH 4.95. Sodium silicate (SS) had only a minor effect on “quartz”. Over the pH range

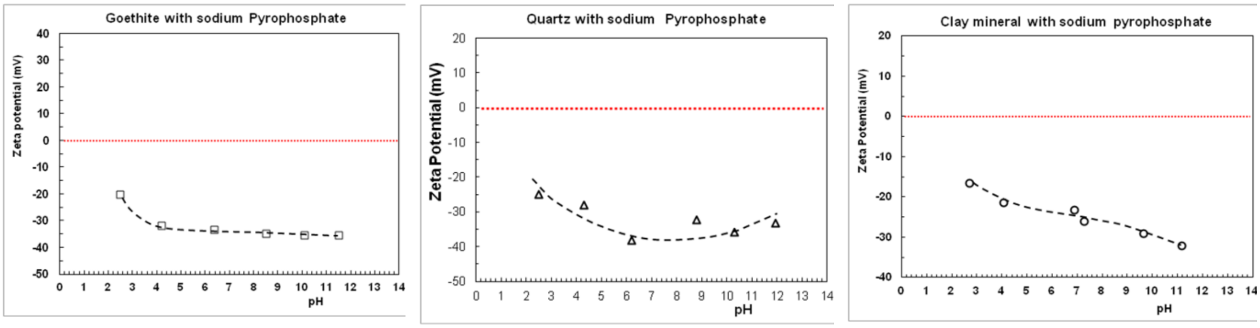

***Fig. 3.*** *Zeta potential of “goethite”, “quartz” and “clay” in the presence of dispersants SPP*

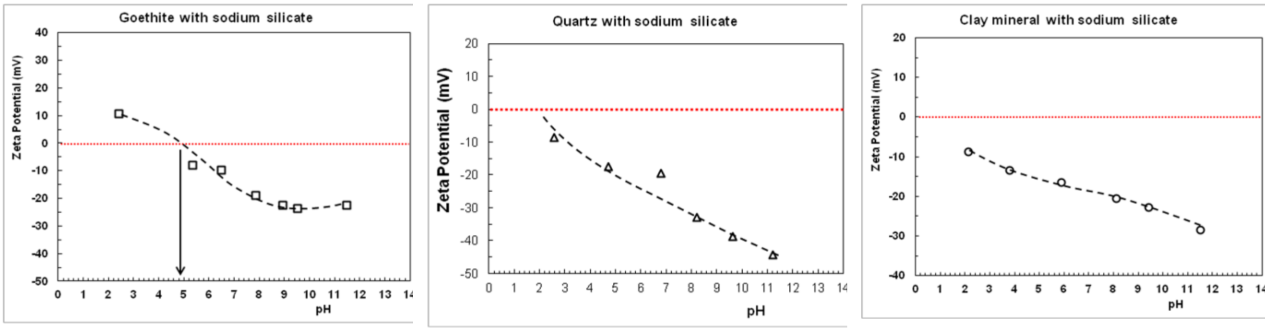

***Fig. 4.*** *Zeta potential of “goethite”, “quartz” and “clay” in the presence of dispersants SS*

from 2 to 12, a significant dispersive effect of sodium silicate on "quartz" was only observed at higher pH values. The IEP of quartz with SS could be estimated close to pH 2. Sodium silicate (SS) had a distinct effect on the "clay" sample: it reduced the negative charge, particularly under alkaline conditions.

## 3. CONCLUSION

The present study comprehensively investigated the electrokinetic behavior of natural minerals labeld "goethite", "quartz", and "clay" in relation to pH variation and the presence of three inorganic dispersants: sodium hexametaphosphate (SHMP), sodium pyrophosphate (SPP), and sodium silicate (SS). The results confirmed that the surface charge of all tested minerals became increasingly negative with rising pH. Without dispersants, "goethite" and "quartz" exhibited an isoelectric point (IEP) at pH 6.6 and pH 2.6, respectively while "clay" displayed consistently negative zeta potential within the pH range of 2–12.

The introduction of dispersants, particularly SHMP and SPP, led to significant shifts in zeta potential across all mineral types. SHMP was the most effective in promoting negative surface charge, eliminating the IEP of goethite and enhancing dispersion stability across the full pH range. These results suggest strong adsorption of polyphosphate anions onto mineral surfaces, indicating chemical interactions beyond simple electrostatic attraction. Sodium silicate showed a weaker effect overall, particularly in the case of clay, where it slightly reduced the negative surface charge under alkaline conditions.

Importantly, the findings demonstrate that dispersants not only increase colloidal stability but also alter surface chemistry in a way that could be exploited for selective flocculation. Under acidic conditions, where "goethite" remains positively charged and "clay" remains negatively charged, the selective adsorption of anionic flocculants onto goethite becomes feasible. This forms the basis for potential process optimization in ultrafine iron ore beneficiation, particularly for tailings recovery or sludge valorization.

These insights reinforce the role of zeta potential measurements as a valuable diagnostic tool for predicting mineral–reagent interactions, and they highlight SHMP as a particularly promising dispersant for selective flocculation strategies in complex mineral systems.

## REFERENCES

[1] Qafoku, N.P.; Van Ranst, E.; Noble, A.; Baert, G. Variable Charge Soils: Their Mineralogy, Chemistry and Management, Advances in Agronomy 2004, 84: 159-215, DOI 10.1016/S0065-2113(04)84004-5

[2] Serrano-Lotina, A.; Portela, R.; Baeza,P.; Alcolea-Rodriguez,V.; Villarroel, M.; ´Avila, P. Zeta potential as a tool for functional materials development, Catalysis Today 2023, 423, 113862. https://doi.org/10.1016/j.cattod.2022.08.004

[3] Mohanty, K.; Oliva, J.;Alfonso, P.; Sampaio, C.H.;Anticoi,H., A Comparative Study of Quartz and Potassium Feldspar Flotation Process Using Different Chemical Reagents. Minerals 2024, 14, 167. https://doi.org/10.3390/min14020167

[4] Hunter, R.J.(1993) Introduction to Modern Colloid Science. Oxford Science Publications, Oxford, UK.

[5] Kosmulski, M. The pH-dependent surface charging and the point of zero charge. J.Colloid Interface Sci. 2002,253,77-87.

[6] Kumar, R. and Mandre, N.R.. Recovery of iron from iron ore slimes by selective flocculation. *J. S. Afr. Inst. Min. Metall.* [online]. 2017, vol.117, n.4, pp.397-400. ISSN 2411-9717. https://doi.org/10.17159/2411-9717/2017/v117n4a12.

[7] Haselhuhn, S., & Kawatra, S. (2015). Role of water chemistry and dispersants in selective flocculation and dispersion of iron ore, May 2015, Minerals & Metallurgical Processing 32(2):69-77, DOI: 10.1007/BF03402423

[8] Lu J, Sun M, Yuan Z, Qi S, Tong Z, Li L, Meng Q, Innovative insight for sodium hexametaphosphate interaction with serpentine, Colloids and Surfaces A: Physicochemical and Engineering Aspects (2018), https://doi.org/10.1016/j.colsurfa.2018.09.076

[9] Liu, X.; Mäki-Arvela, P.; Aho, A.; Vajglova, Z.; Gunko, V.M.; Heinmaa, I.; Kumar, N.; Eränen, K.; Salmi, T.; Murzin, D.Y. Zeta Potential of Beta Zeolites: Influence of Structure, Acidity, pH, Temperature and Concentration. *Molecules* 2018,*23*, 946. https://doi.org/10.3390/molecules23040946

[10] E. Castellini, C. Berthold, D. Malferrari, F. Bernini, Sodium hexametaphosphate interaction with 2:1 clay minerals illite and montmorillon-

ite, Applied Clay Science 83–84 (2013) 162–170

[11] Raul E. Martinez, Prasesh Sharma, Andreas Kappler, Surface binding site analysis of Ca2+-homoionized clay–humic acid complexes, Journal of Colloid and Interface Science 352 (2010) 526–534

[12] E. S. Alvim & R. M. Fernandes LimaSelective Flocculation/Magnetic Separation of Ultrafine Iron Ore Particles with Corn Starch and Polyacrylamides: A Comparative Study, Pages 606-615 | Published online: 18 May 2023, https://doi.org/10.1080/08827508.2023.2214293

[13] Venugopal Tammishetti, Kaustubh Joshi, Pradip, Beena Rai and Kesri L Menaria, Beneficiation of Indian iron ore slimes using guar gum flocculant, XVII IMPC 2014, Santiago, Chile

[14] Susan Lawrence s.lawrence@latrobe.edu.au, James Grove, Peter Davies, Historical dredge mining as a significant anthropomorphic agent in river systems: A case study from south-eastern Australia, SageJournals, Volume 31, Issue 7https://doi.org/10.1177/09596836211003272, https://orcid.org/0000-0002-5452-9167,

[15] Tankosić,Lj., Tančić,P.,Sredić,S. Zoran Nedić Comparative Study of the Mineral Composition and Its Connection with Some Properties Important for the Sludge Flocculation Process-Examples from Omarska Mine, *Minerals* 2018, *8*(3), 119; https://doi.org/10.3390/min8030119

[16] Tankosić Lj. Possibility of limonite concentration of selective flocculation of sludge and sludge removal. Master’s Thesis, Faculty of Mining and Geology, University of Belgrade, Belgrade, Serbia; 2012. (In Serbian)

[17] C. Madigan, Yee-Kwong Leong, B. C. Ong, Surface and rheological properties of as-received colloidal goethite (α-FeOOH) suspensions: pH and polyethylenimine effects 2009 International Journal of Mineral Processing 93(1):41-47, DOI:10.1016/j.minpro.2009.05.005

# ИСПИТИВАЊЕ ЗЕТА ПОТЕНЦИЈАЛА МИНЕРАЛ ГЕТИТА, КВАРЦА И ГЛИНЕ У ЗАВИСНОСТИ ОД pH ВРИЈЕДНОСТИ У ПРИСУСТВУ НЕОРГАНИСКИХ ДИСПЕРЗАНАТА

**Сажетак:** Познавање зета потенцијала је веома користан индикатор стабилности дисперзних система. Ово је посебно важно у многим индустријским процесима, као што су нпр. Припрема минералних сировина, пречишћавање воде и многи други. Овај рад се бави истраживањем електрокинетичког понашања миерала гетита, кварца и глине у зависности од pH вриједности и присуства неорганских дисперзаната: натријум-хексаметафосфата (SHMP), натријум-пирофосфата (SPP) и натријум-силиката (SS). Сва истраживања су спроведена на природним узорцима, узетим из рудника гвожђа Омарска (Босна и Херцеговина) мјерењем зета потенцијала. Из експерименталних резултата утврђено је да повећање pH вриједности суспензије доводи до повећања негативног наелектрисања сва три тестирана узорка. Глина није показала изоелектричну тачку (IEP). Кварц је показао изоелектричне тачке на pH вриједности око 2.6 и близу 2 у одсуству и присуству натријум-силиката у суспензијама, респективно. Гетит је показао изоелектричне тачке на pH вриједности 6.7 и 4.95 у одсуству и присуству натријум-силиката у суспензијама, респективно. IEP није могао бити детектован када су коришћени SHMP и SPP, а површинско наелектрисање је негативно од pH 2 до pH 12 у свим тестираним узорцима. Додавање SHMP је обезбиједило највећи негативни зета потенцијал, тј. најстабилнију дисперзију, у сва три тестирана узорка.

**Кључне ријечи**: зета потенцијал, изоелектрична тачка, гетит, кварц, глина, неоргански дисперзанти.

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