# THE DISPERSION-FLOCCULATION BEHAVIOUR OF THE NATURAL RAW CLAY SAMPLES FROM OMARSKA MINE

*Ljiljana Tankosić[1,*], Svjetlana Sredić[1], Pavle Tančić[2], Zoran Nedić[3]*

[1] University of Banja Luka, Faculty of Mining Prijedor, Save Kovačevića bb,
Prijedor, Republic of Srpska, Bosnia and Herzegovina
[2] Geological Survey of Serbia, Rovinjska 12, Belgrade, Serbia
[3] University of Belgrade, Faculty of Physical Chemistry,
Studentski Trg 16, Belgrade, Serbia

**Abstract:** In present paper, studied were the dispersion-flocculation behaviour of the primary natural raw „clay samples" from Omarska mine (Republic of Srpska, Bosnia and Herzegovina). Namely, our previous results showed that during the processing of iron ore in the Omarska mine, large quantities of fine sized (<15μm) waste sludge, with relatively high Fe concentrations, were generated. Sludge samples are composed of major goethite and quartz, less clay minerals, and minor magnetite and todorokite. Selective flocculation is one of the methods that can be applied for the separation of fine class iron minerals from impurities and depends on the individual components of the sludge and their behaviour. This paper presents part of the research of the individual components of the sludge. The „clay samples" are composed of major quartz and clay minerals, which dominate over minor contents of feldspars, amphiboles, goethite and hematite. The clay minerals were identified as mostly illite-sericite which prevails over kaolinite, and with chlorites which appears only sporadically. The dispersion-flocculation behaviour was studied by settling and flocculation experiments and Zeta potential measurements. A three different dispersants (sodium-hexametaphosphate, sodium-pyrophosphate and sodium-silicate), and anionic and non-ionic polyacrylamide (PAM) flocculants were used. It was established that the best results were achieved with sodium-hexametaphosphate (1000 g/t) and anionic A100 PAM.
**Keywords:** Omarska mine, sludge, clays, dispersion-flocculation behavior.

## 1. INTRODUCTION

Clay minerals are among the most abundant in the Earth's crust. They have a wide industrial application. However, clay is often an undesirable companion for other minerals useful in other utilizations. Iron ore from Omarska mine (Republic of Srpska, Bosnia and Herzegovina) was previously assigned as limonite ore in association with clay minerals, quartz and some manganese minerals, as well [1]. XRPD, FTIR and SEM-EDS analyses were recently performed for obtaining more precise mineral determination [2]. These studies showed that primary natural mineral raw materials from this deposit are generally composed of major goethite-FeO(OH), quartz and clay minerals; in association with more or less minor contents of hematite, magnetite, feldspars, amphiboles, chloritoid, etc. Processing of ore in Omarska mine is carried out by following methods: washing, sieving, grading and magnetic concentration. The morphological and structural characteristics of limonite ore cause the production of a significant amount of small fractions, with a volume below 25 μm, in exploitation. Therefore, during the processing of iron ore in the Omarska mine, large quantities of fine sized (<15μm) waste sludge, with relatively high Fe concentrations, were generated. Our previous results showed that sludge samples are composed of major goethite and quartz, less clay minerals, and minor magnetite and todorokite [3].

Studies that we have conducted are focused on evaluation of useful minerals from hydrocyclone overflow. One of the promising methods of the concentration of useful minerals from the sludge is the application of selective flocculation as a prior stage in order to increase the efficiency of the process magnetic ore concentration [4-15]. The

---

* Corresponding author: ljiljana.tankosic@rf.unibl.org

process of selective flocculation usually consists of several sub-processes: particles dispersion, pH regulation, particle deactivation, selective adsorption of flocculant, flocs forming and conditioning, separation of flocs from non-flocculated material [16]. The selective separation of useful minerals from gangue in a complex system such as sludge, is a very complex physicochemical system, and depends on the individual components of the sludge and their behaviour [17-19].

Our earlier results of sludge testing have shown that, despite the good results regarding the stability of dispersion and flocculation, selectivity has not been achieved [20]. Therefore, our present research is focused at the physic-chemical properties of natural minerals that have been previously identified as the primary natural raw clay samples from Omarska mine [2], and their behaviour in the presence of different dispersants and flocculants. The dispersion-flocculation properties, such as: natural settling; settling with the addition of flocculant; effect of solid concentration; effect of the addition of different dispersants concentration and zeta potential variations were studied. In such way, study of the mineral composition and its connection with some properties important for the clay flocculation process, was processed.

## 2. MATERIALS AND METHODS
### 2.1. Materials

In this paper, studied was primary natural raw material sample, labeled as "clay II" [2]. It has the following mineral composition: major quartz (~50%) and clay minerals (~44%), which dominates over minor goethite (~4%), chloritoid (~2%) and hematite. The clay minerals were identified as mostly illite-sericite which prevails over kaolinite, and with chlorites which appears only sporadically. It has following chemical composition (in mass %): Fe 3.67, $SiO_2$ 54.45, $Al_2O_3$ 25.20 and LOI 4.80; and density of 2.734 (g/cm³).

All reagents used were of analytical grade, and they were prepared as solutions in distilled water. The sodium hexametaphosphate (SHMP), sodium pyrophosphate (SPP) and sodium silicate (SS) manufactured by Lach-Ner, s.r.o. (Czech Republic), were used as dispersants. As flocculant, anionic polyacrylamide (PAM) type SUPERFLOC A100, manufactured by Kemira, was used. Preparation of flocculant for all experiments was carried out in the same way according to the instructions provided by the manufacturer of reagents [21]. As pH modifier, 0.1M NaOH was used.

### 2.2. Methods
#### 2.2.1. Particle size distribution analysis

Particle size distribution of the sample was performed using Malvern analyser in the laboratory Global Research and Development, Mining and Mineral Processing, Maizières-lès-Metz, France. Data were obtained on Mastersizer 2000, at dry and wet samples.

#### 2.2.2. Settling dispersion and flocculation experiments

The natural settling, and settling with the addition of dispersant and flocculant, were determined. Also, different solid/liquid relationships (marked as S:L) of: 1:7; 1:9.7; and 1:19.7; at the same conditions were used. For settling, graduated glass cylinder with volume of 100 ml was used. The flocculation experiments were performed at a pulp density with three different solid/liquid ratios (i.e.: 1:7; 1:9.7; and 1:19.7). All of the tests were performed at the pH=7, which is average pH value in real conditions.

For the tests of selectivity, the following was used: (i) Beaker of 1000 ml volume for better visualization of the dispersion; (ii) 69 g of dry sample in 500 ml of distilled water for the experiment (which is adequate to the simulation of natural industrial conditions); (iii) 30 and 50 g/t of flocculant A100; and (iv) 50, 100, 200 and 1000 g/t of dispersants SHMP and SPP; and 300, 500 and 1000 g/t of SS. The effect of different dispersants on the stabilization of system was studied by conducting the dispersion tests in 1000 ml graduated glass cylinder. Suspension of 12.5 % solids by wt. was mixed for 2 minutes, while maintaining the pH value at 10.5. Desired dispersant dose was added to the suspension, mixed for five minutes, and left to settle. It was separated float from sink, after ten minutes, and they were both dried at 105° C in oven. After weighing the sediment material, elemental analysis was performed.

For flocculation tests, sample was mixed for two minutes. After adjusting pH value at 10.5, the suspension continued to mix for two minutes, and then dispersant was added. The suspension has been mixed up for another five minutes. After addition of flocculant, sample was mixed for five minutes, and left to settle for one minute, separated float from sink, and dried both of them at 105° C in oven. After weighing the sediment material, elemental analysis was performed.

2.2.3. Zeta potential measurements

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 Universidad Federal de Minas Gerais, Belo Horizonte, Brazil. The measurements were carried out according to the following procedure: samples were classified through the sedimentation in test tubes of 250 ml, with a mineral concentration of 80 mg/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. Before each test, completely opened Zeta Meter cell was first washed intensively with tap water, and after that 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.

3. RESULTS AND DISCUSSION
*3.1. Particle size distribution analyzis*

The particle diameter in the clay sample has a significant effect on the flocculation process. According to the particle size of the solid phase, the suspensions can be divided into large and medium-sized (particles larger than 300-500 μm); fine-grained (particles smaller than 300-500 μm); and fine sludges (particles smaller than 5-10 μm). The boundary between the suspension and the colloid ranges from 0.1 to 1.0 μm [22]

The result of particle size distribution analyses of the clay sample is given in Figure 1. It is clearly seen that the highest mass percentage (about 50%) belongs to the finest classes, i.e. to those below 8 μm. Furthermore, almost 80% of the sample belongs to the classes below 25 μm. These data indicate that the clay is in a stable suspension, and the solid phase is in a dispersed state under the influence of molecular forces. As clay minerals mainly appear as fine and ultra-fine particles with strong intermolecular forces that overcome the force of gravity, it is necessary to accomplish the consolidation (flocculation) to separate the phases.
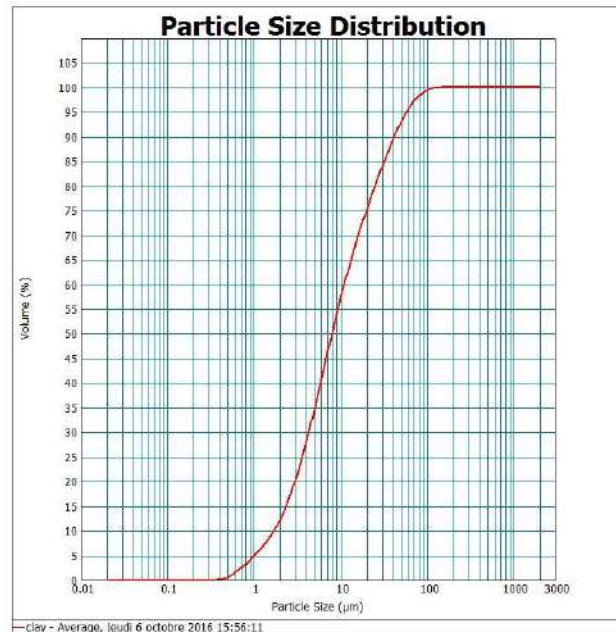


*Figure 1. Particle size distribution of clay*

*3.2. Settling, disspersion and flocculation studies*

Based on the previously done experiments of sludge settling [20], it can be concluded that, despite some differences of the behavior of individual phases, these are not sufficient enough to achieve selective PAM activity under studied conditions. The mineralogical heterogeneity of the sludge makes complex dispersion system, in which one of the basic parameters for the selective flocculation process is dispersive and flocculating behavior of the individual components of the system.

The main goal of initial settling, dispersion and flocculation studies was to obtain the behavior of natural clay sample, as one of the important components of the system with different S/L ratios with different dispersants, and with or without flocculant, as well.

These experiments aim to demonstrate the possible impact of the different input parameters on the behavior of settling rate: naturally and also in the presence of the different dispersants and flocculants. Furthermore, effect of solid concentration was examined by using different ratios of solid/liquid. In such manner, it was tried to define behaviors of clay sample.

3.2.1. Natural settling with different S/L ratio

As it is well known, forms for calculating the grain fall rate cannot accurately determine the rate of

precipitation, due to the defects in the correct values for correction coefficients that take into account the irregular shape of the grain; the change in fluid density; and in particular, the questions related to the flocculation or dispersion of the smallest classes resulting from the charge of the grain or Braun's motion.

At the beginning of precipitation, in diluted pulp, and under free fall conditions, deposition rate is relatively large and constant. The critical rate ($V_{av}$) in this paper is calculated as: $V_{av} = H/t_{cr}$ (mm/min); where H is height of the clear zone during critical time (in mm), and $t_{cr}$ is deposition time required to achieve a critical deposition point (in minutes).

In Figure 2, natural settling curves of clay with different ratios of S:L are shown. Generally, there is no big difference in settling behaviour between these three different solid/liquid ratios. Also, samples with smallest solid/liquid ratios have the highest settling rates, which is in accordance with some other studies [20,23].

### 3.2.2. Settling with different S/L ratios with additional flocculant A100

In Figure 3, settling curves with different ratios of S/L and with additional anionic flocculant A100 are shown. In all three different ratios, settling starts fast, only after 30 seconds from the beginning, regardless of the S/L ratio. However, by comparison with natural settling (Fig.2), it can be clearly seen that the settling rate is obviously improved with additional flocculant.
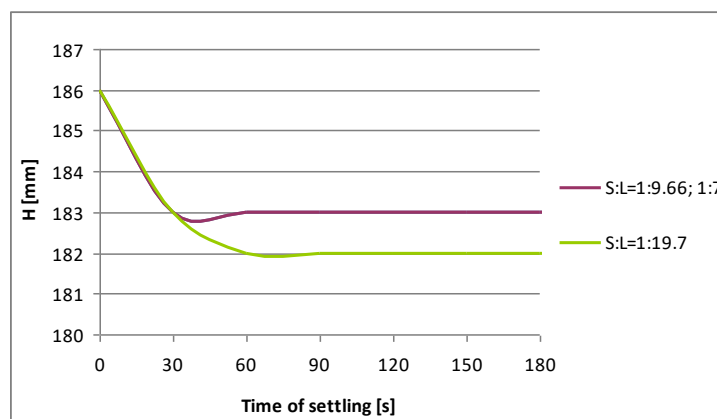


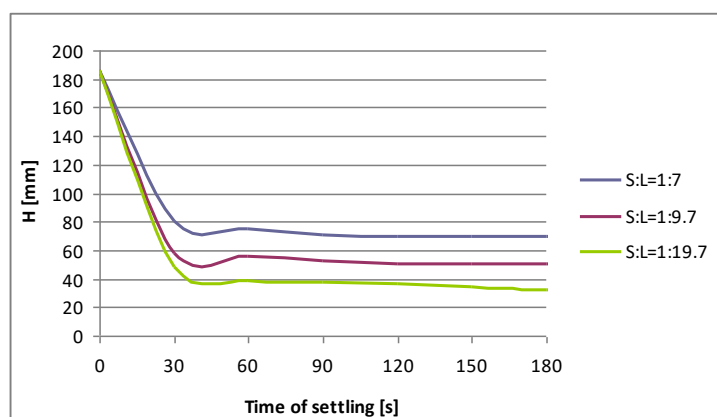*Figure 2. Natural settling of clay with different solid/liquid ratios*



*Figure 3. Flocculation settling of clay with different solid/liquid ratios*

Influence of the solid/liquid ratio is shown by comparison of critical settling rate as well as comparison of hindered settling rate. Critical and hindered settling rate of clay sample are shown in Table 1. From these, it can be clearly seen that in the case of natural settling, there are no significant differences in critical settling rates, regardless of the S/L ratios. With the addition of the flocculant, these rates increases significantly with the increase of the liquid component in both of the samples. Furthermore, the differences in critical settling rates between samples in the presence of the flocculant

are also obvious. Obviously, the effect of flocculant in the heterogeneous system depends both on the mineral composition and the S/L ratio. Effect of solid/liquid ratio on settling rate was confirmed by the results of hindered settling rate which was calculated according to Richardson-Zaki equation [23]. This equation describes a method of calculating the sedimentation rate in a liquid-solid system as a function of the free falling rate of a single particle and the concentration of particles. From the Table 1, it can be seen that samples with smallest solid/liquid ratios have a highest settling rates in both cases.

*Table 1. Critical and hindered settling rate (mm/s) of clay.*

| S:L (% of Solid) | Clay | | | |
|---|---|---|---|---|
| | natural settling | settling with flocculant | terminal settling | hindered settling |
| 1:7 (12.5) | 0.075 | 3.03 | 0.059 | 0.026 |
| 1:9.7 (9.4) | 0.075 | 3.65 | 0.059 | 0.049 |
| 1:19.7 (4.8) | 0.070 | 4,17 | 0.059 | 0.054 |

### 3.2.3. Dispersion studies

An important step in the selective flocculation process is to achieve a stable dispersion of mineral particles. Dispersants are used to prevent fine particles from aggregating. The choice of a dispersant is an important parameter in stabilizing the dispersion. Much of the work on selective flocculation was carried out in the presence of inorganic dispersants, like SS, SHMP and SPP.

The dispersion studies were carried out with different inorganic reagents: sodium hexametaphosphate (SHMP), sodium-pyrophosphate (SPP) and sodium-silicate (SS) with dosage of SHMP and SPP of 50, 100, 200 and 1000 g/t; and 300, 500 and 1000 g/t of SS. Due to the similarity of the preliminary results between dispersants SHMP and SPP, we decided to use dispersant SHMP. Initially, dispersion behavior was tested by monitoring the weight distribution and elemental composition in floating and sinking part. Out of two other reagents studied, it can be seen that there is no big difference between SHMP and SS in amount of sinking and floating part. The results of the distribution of masses after one or two grinding and elemental composition between sinking and floating part are presented in Figure 4 a) and b), and Table 2.
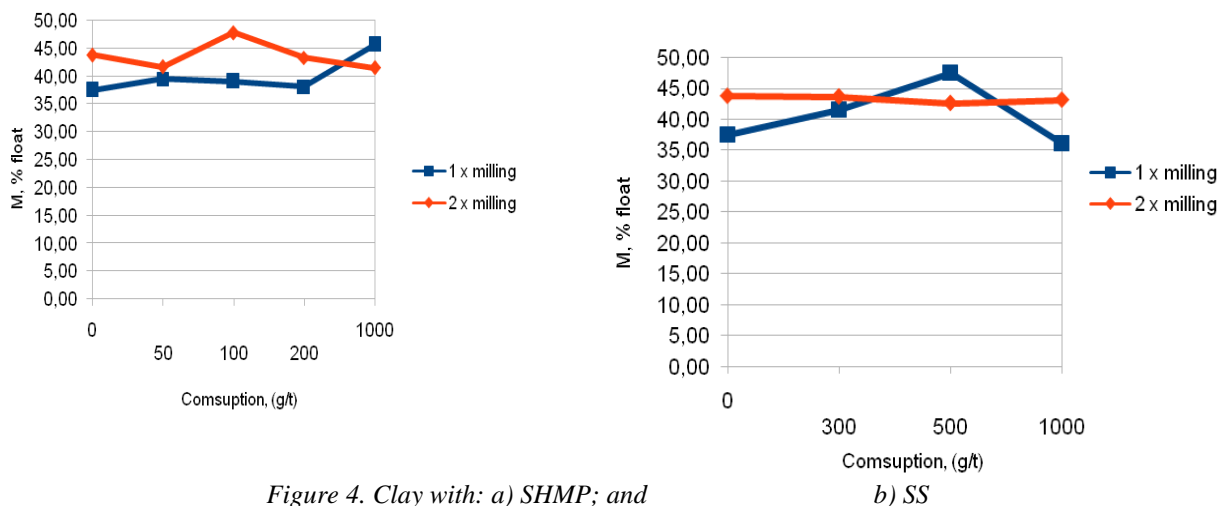


*Figure 4. Clay with: a) SHMP; and          b) SS*

*Table 2. Elemental composition of clay (in %) in presence of SHMP and SS (in g/t) as dispersants.*

| Element | | SHMP | | | | SS | | |
|---|---|---|---|---|---|---|---|---|
| | | 50 | 100 | 200 | 1000 | 300 | 500 | 1000 |
| $SiO_2$ | Float | 79.3 | 61.5 | 61.7 | 61.6 | 62.9 | 32.0 | 62.40 |
| | Sink | 62.0 | 75.5 | 76.2 | 76.1 | 75.9 | 77.0 | 76.60 |
| $Al_2O_3$ | Float | 9.67 | 20.0 | 19.75 | 19.6 | 19.3 | 19.65 | 19.5 |

| Element | | SHMP | | | | SS | | |
|---|---|---|---|---|---|---|---|---|
| | | 50 | 100 | 200 | 1000 | 300 | 500 | 1000 |
| | Sink | 19.75 | 10.3 | 9.65 | 9.85 | 9.64 | 9.13 | 9.54 |
| Fe | Float | 4.26 | 4.11 | 4.15 | 4.18 | 4.19 | 4.20 | 4.17 |
| | Sink | 4.17 | 4.27 | 4.26 | 4.29 | 4.24 | 4.34 | 4.26 |
| Na₂O | Float | 0.293 | 0.711 | 0.689 | 0.741 | 0.703 | 0.726 | 0.761 |
| | Sink | 0.72 | 0.318 | 0.30 | 0.311 | 0.293 | 0.281 | 0.294 |
| K₂O | Float | 1.66 | 3.24 | 3.22 | 3.19 | 3.15 | 3.19 | 3.17 |
| | Sink | 3.2 | 1.755 | 1.65 | 1.68 | 1.655 | 1.656 | 1.63 |
| MgO | Float | 0.39 | 0.77 | 0.78. | 0.78 | 0.74 | 0.75 | 0.75 |
| | Sink | 0.76 | 0.43 | 0.41 | 0.40 | 0.39 | 0.37 | 0.38 |
| CaO | Float | 0.21 | 0.31 | 0.31 | 0.32 | 0.30. | 0.29 | 0.30 |
| | Sink | 0.31 | 0.23 | 0.21 | 0.22 | 0.21 | 0.21 | 0.21 |
| TiO₂ | Float | 0,78 | 0.95 | 0.95 | 0.94 | 0.96 | 0.96 | 0.95 |
| | Sink | 0,96 | 0.77 | 0.76 | 0.77 | 0.75 | 0.75 | 0.76 |
| LOI | Float | 4,07 | 6.01 | 6.0 | 5.98 | 5.08 | 5.85 | 5.78 |
| | Sink | 5,92 | 4.19 | 4.02 | 4.01 | 3.85 | 3.77 | 3.87 |

### 3.2.4. Flocculation studies

The flocculant was selected on the basis of the earlier initial flocculation study of the sludge from Omarska mine [20]. In this Chapter, it was tested the influence of different consumption of the flocculant on flocculation behavior of clay, as one of the individual component of the sludge. Initially, flocculation behavior was tested by monitoring the weight distribution and the elemental composition in floating and sinking part. The results of the distribution of masses after one or two grinding and elemental composition between sinking and floating part are presented in Figs 5 and 6, and Table 3.

*Table 3. Elemental composition of clay (in %) in presence of anionic flocculant A100, and SHMP and SS (in g/t) as dispersants.*

| Element | | A100(SHMP, 1000) | | | A100(SS, 1000) | | |
|---|---|---|---|---|---|---|---|
| | | 30 | 50 | 100 | 30 | 50 | 100 |
| SiO₂ | Float | 57.4 | 57.3 | 47.90 | 51.5 | 50.20 | 46.0 |
| | Sink | 71.2 | 71.30 | 71.40 | 71.80 | 71.20 | 71.3 |
| Al₂O₃ | Float | 19.75 | 19.80 | 22.3 | 22.40 | 19.95 | 19.5 |
| | Sink | 13.45 | 13.70 | 14.10 | 13.15 | 13.70 | 14.3 |
| FeO | Float | 1.57 | 1.58 | - | - | - | - |
| | Sink | 1.75 | 1.80 | - | 1.62 | 1.80 | - |
| Fe | Float | 5.98 | 5.68 | 6.95 | 6.22 | 6.78 | 7.04 |
| | Sink | 4.12 | 4.11 | 4.26 | 4.11 | 4.20 | 4.27 |
| Na₂O | Float | 1.21 | 1.335 | 3.06 | 2.52 | 3.50 | 6.10 |
| | Sink | 0.402 | 0.489 | 0.425 | 0.483 | 0.426 | 0.422 |
| K₂O | Float | 3.09 | 3.07 | 3.43 | 3.45 | 3.12 | 3.12 |
| | Sink | 2.21 | 2.24 | 2.40 | 2.22 | 2.30 | 2.43 |
| MgO | Float | 0.80 | 0.81 | 0.98 | 0.96 | 0.88 | 0.84 |
| | Sink | 0.54 | 0.54 | 0.57 | 0.55 | 0.57 | 0.58 |
| CaO | Float | 0.43 | 0.44 | 0.76 | 0.44 | 0.54 | 0.75 |
| | Sink | 0.23 | 0.30 | 0.24 | 0.23 | 0.24 | 0.25 |
| TiO₂ | Float | 0.99 | 0.95 | 1.11 | 1.07 | 1.03 | 1.0 |
| | Sink | 0.83 | 0.84 | 0.84 | 0.82 | 0.85 | 0.85 |
| LOI | Float | 6.88 | 6.51 | 8.86 | 8.45 | 9.67 | - |
| | Sink | 4.55 | 4.42 | 4.55 | 4.46 | 4.66 | 4.56 |
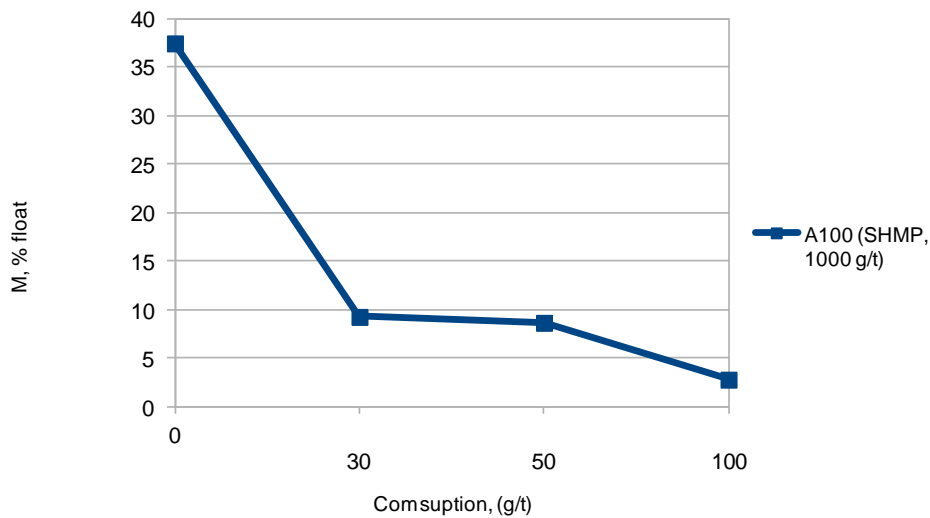
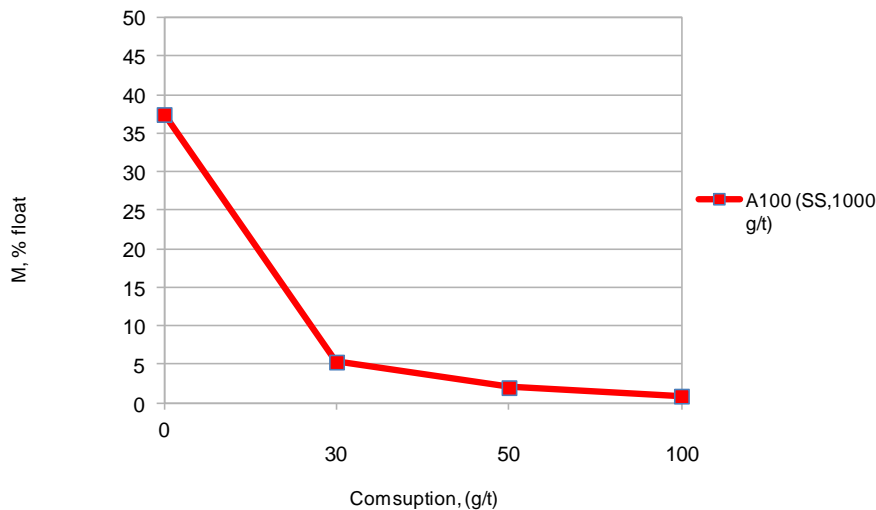*Figure 5. Clay with flocculant A100 and SHMP (1000 g/t)*



*Figure 6. Clay with flocculant A100 and SS (1000 g/t)*

According to the results, increase the flocculant consumption causes an increase in sink part. The best results were achieved with 100 g/t consumption of flocculant.

### 3.3. Zeta potential study

The surface charge characteristics are essential in order to understand the dispersion-flocculation behavior of the mineral particles. In order to better understand dispersion behavior of the clay particles, in this Chapter results of zeta potential ($\zeta$-potential) measurements were analyzed, as for the clay itself, as well as for the clay in the presence of the different surfactants. This study was done by measuring of zeta potential in the various combinations of absence/presence of the three dispersants: sodium-hexametaphosphate (SHMP), sodium-pyrophosphate (SPP), sodium-silicate (SS); and also in the absence/presence of anionic polyacrylamide A100 (PAM) flocculant, as well.

Zeta ($\zeta$) potential, is electro-kinetic phenomenon on the surface of clay minerals, which affects the dispersion and the flocculation in the water suspension. It is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles, and it 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. A high $\zeta$ will produce a well-dispersed suspension and, in contrast, a low $\zeta$ results in particle association. Isoelectric point (IEP) represents condition when value of zeta potential is zero.

Zeta-potential curves for natural mineral raw sample of clay, which was previously determined [2], in absence/presence of three dispersants (SHMP, SPP and SS), are shown at Figure 7. The zeta potential curve for natural clay is similar to various curves available in the literature [24-26]. The IEP for the clay mineral, if any, is located below pH value 2. This low value for the IEP confirms an existence of a phyllosilicate (i.e. clay mineral) or a tectosilicate. According to the zeta potential measurements observed, there is a development of a net particle negative surface charge as a function of increasing pH, because electronegative $MO^-$ groups are predominant at high pH values at clay surfaces.
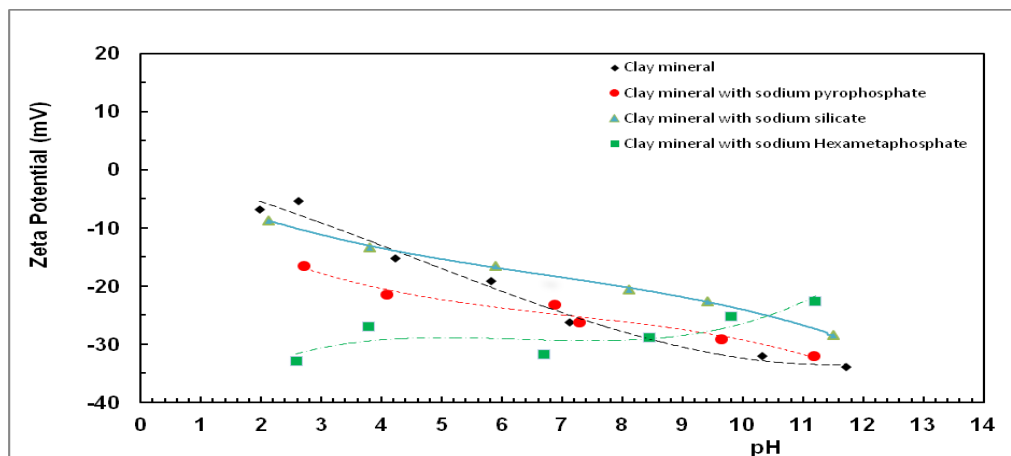


*Figure 7. Zeta potential of the clay samples in absence/presence of different dispersants*

Permanent structural charge density is always negative for clay minerals and can be attributed to Al(III) substitution for Si(IV) in the silicate structures. The charge density of the surface of the alumosilicate in aqueous solutions is due to proton adsorption and desorption reactions of the two types of surface hydroxyl groups: the silanol group, SiOH and the aluminal group (AlOH). Negative charge is caused by the ionization of weakly acid silanol groups, while positive charge arises from the protonation of the aluminol groups. So, the surface charge is dependent on Al/(Al+Si) ratio [27,28].

From Figure 7, it can be clearly seen that the surface charge remains negative throughout all of the investigated pH values, and for all of the samples, as well. This indicates a low value of the Al/(Al+Si) ratio, i.e., in our sample the Si content is dominant. These results are in accordance with the mineralogical and chemical analysis, which exhibit a high mineral content of quartz in the clay sample. The presence of SHMP and SPP causes the increase of negative zeta potential magnitudes in the pH range up to 7 (SPP) and 8.5 (SHMP), whereas the SS causes the decrease of negative zeta potential magnitudes in the pH range above 4.

According to the well-known DLVO (Derjaguin, Landau, Verwey, Overbeek) theory, the stability of the suspension of colloidal particles is determined by the balance between the electrostatic interaction and the van der Waals interaction between particles. Because the higher zeta potential produces a better dispersion, it can be concluded that the most stable conditions of the clay suspension are achieved by increasing the pH value and adding the SHMP as a dispersant. In both cases, there is an increase in the negative charge on the surface of the particles, causing their better dispersion.

The energy barrier can be eliminated by neutralization of surface charge due to the adsorption of a suitable flocculant onto the particle surface and bridging between the particles. Flocculant adsorption can be measured by changing of the zeta potential after adsorption. If the polymer is adsorbed, there is a change in the surface of the particles, and thus the change in the zeta potential. At Figure 8, zeta potential curves as a function of pH for the same studied samples in presence of anionic polyacrylamide (PAM, A100), and with/without SHMP dispersant, are shown.

It is obvious that the used anionic polyacrylamide (PAM) causes changes on the surface of tested clay sample (Figure 8). The relatively high zeta potential values of the clay sample in presence of anionic polyacrylamide (PAM) indicate a fairly stable dispersion. The further additional inclusion of a SHMP dispersant significantly reduces the zeta potential indicating favourable conditions for flocculation, particularly at pH range above 10. This means that the negative surfaces of clay are covered with polymer molecules and they have less negative surface charge than their initial conditions. As a result, the ζ-potential of solid particles is decreased throughout all of the investigated pH values, because the adsorbed

molecules on clay have negative charge, so measured ζ-potential values must be negative. Adsorption of polymer molecules on mineral particles is governed mainly by three types of bonding: electrostatic, hydrogen and covalent bonding, as well as their combination. Although electrostatic forces are considered to be predominant in bonding anionic PAM to metal oxides, in our example, this is not the case. It can be concluded from Figs. 7 and 8 that all clay samples without/with reagents are negatively charged within the whole investigated pH range. In part, adsorption of PAM on mineral particles is of electrostatic character, which can be seen in reducing of the zeta potential. On the other hand, there is certainly another type of bonding, probably hydrogen bonding between the polymer molecules and the hydroxylic groups on the surface of clay minerals.
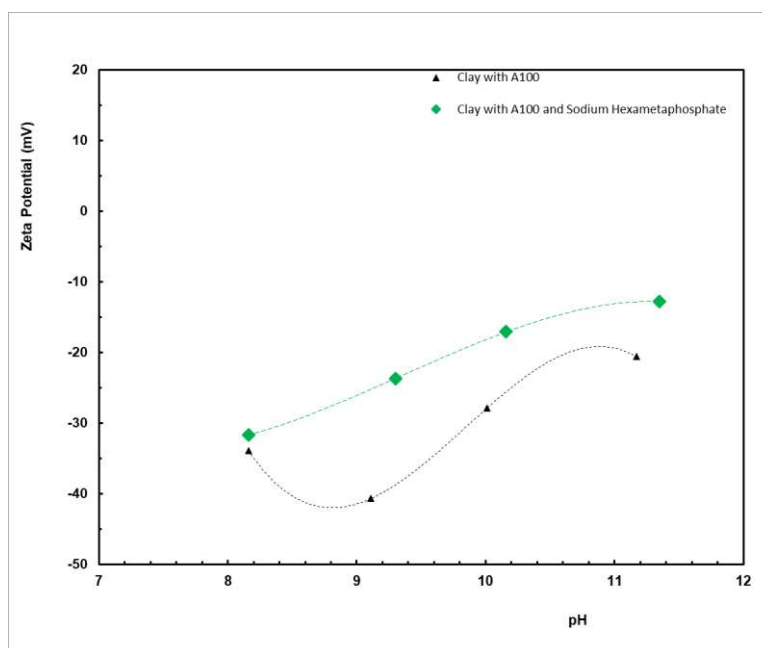


*Figure 8. Zeta potentials of clay: with PAM (A100); and with PAM (A100) and SHMP.*

## 4. CONCLUSION

The dispersion–flocculation behaviour of the clay minerals from Omarska mine, which were identified as mostly illite-sericite, was investigated. Particle size distribution analyses shown that clay samples are present as fine and ultra-fine particles. Also, similar mineral compositions are present among every size classes within the samples, which makes this system very complex for separation processes. It is obvious that majority of the visible grains are very fine or ultra-fine, with sizes less than about 10 μm.

Samples with smallest solid concentration of the clay have a highest settling rates. The settling rate is obviously improved by using anionic polyacrylamide flocculant. The effect of flocculant depends both on the mineral composition and from the S/L ratios.

The dispersion tests show that both used dispersants cause the stable dispersion of the clay with higher quartz content in the sinking part, and the best results were achieved with 1000 g/t consumption of dispersants.

According to the results of the flocculation tests, type of dispersant does not play a significant role in the distribution of masses between sinking and floating part, but consumption of flocculant does. The best results were achieved with 100 g/t consumption of flocculant.

The influence of the mineral composition of the clay on the surface charge can be seen from the zeta potential values. The surface charge remains negative throughout all of the investigated pH values. The IEP for the clay mineral, if any, is located below pH value 2. This low value for the IEP confirms an existence of a phyllosilicate (a clay mineral).

After the addition of dispersants, the surface charge remains negative throughout all of the investigated pH values, and for all samples.

The most stable conditions of the clay suspension are achieved by increasing the pH value and adding the SHMP as a dispersant. In both cases, there is an increase in the negative charge on the

surface of the particles, causing their better dispersion.

After the addition of SHMP as dispersant, and A100 as flocculant, the surface charge remains negative throughout all of the investigated pH values.

Adsorption of PAM on mineral particles has a partially electrostatic character, and partially another type of bonding, probably hydrogen bonding between the polymer molecules and the hydroxylic groups on the surface of clay minerals.

## 5. ACKNOWLEDGMENTS

## 6. REFERENCES

[1] D. Milovanović, A. Milošević, E. Salcin *Elaboration on Iron Ore Classification, Categorization, and Calculation for the Deposit of "Omarska" – Location of "Buvac",* Institute of Mining, Prijedor, Bosnia and Herzegovina, 2007 (in Serbian).

[2] Lj. Tankosić, P. Tančić, S. Sredić, Z. Nedić, V. Malbašić, *Characterization of natural raw materials in the processing of iron ore from Omarska mine,* Proceedings of International Symposium „Mining and Geology Today", Belgrade, Serbia, 2017, 316−330.

[3] Lj. Tankosić, P. Tančić, S. Sredić, Z. Nedić, *Characterization of the sludge generated during the processing of iron ore in Omarska mine,* Book of Proceedings 6th International Symposium „Mining and Environmental Protection" Vrdnik, 2017, 255−262.

[4] R. Kumar, N. R. Mandre, *Recovery of iron from iron ore slimes by selective flocculation,* The Journal of the Southern African Institute of Mining and Metallurgy 2017, 117, 397−400, doi.org/10.17159/2411-9717/2017/v117n4a12.

[5] H. A. M. Ahmed, G. M. A. Mahran, *Processing of Iron Ore Fines from Alswaween Kingdom of Saudi Arabia,* Physicochem. Probl. Miner. Process, Vol. 49−2 (2013) 419−430.

[6] E. O. Ajaka, *Recovering Fine Iron Minerals From Itakpe Iron Ore Process Tailing,* Journal of Engineering and Applied Sciences, Vol. 4−9 (2009) 17−28.

[7] G. C. Sresty, P. Somasundaran, *Selective Flocculation of Synthetic Mineral Mixtures Using Modified Polymer*s, International Journal of Mineral Processing, Vol. 6 (1980) 303−320.

[8] P. K. Weissenborn, L. J. Warren, J. G. Dunn, Optimisation of selective flocculation of ultrafine iron ore, International Journal of Mineral Processing, Vol. 42 (1994) 191−213, doi.org/10.1016/0301-7516(94)00026-3

[9] P. Somasundaran, V. Runkana, *Selective flocculation of fines,* Trans. Nonferrous Met. Soc. China2000, Vol. 10, Special Issue (2000) 8−11.

[10] F. F. O. Orumwense, J. C. Nwachukwu, *Flocculation studies on hematite-silica system using polymeric flocculants,* Indian Journal of Chemical Technology, Vol. 7−1 (2000) 23−29.

[11] Panda, L.; Biswal, S.K.; Tathavadkar, V. Beneficiation of Synthetic Iron Ore Kaolinite Mixture Using Selective Flocculation, *Journal of Minerals & Materials Characterization & Engineering,* Vol. 9 (2010) 973−983.

[12] T. Su, T. Chen, Y. Zhang, P. Hu, *Selective Flocculation Enhanced Magnetic Separation of Ultrafine Disseminated Magnetite Ores,* Minerals, Vol. 86−6 (2016) 1−12, doi:10.3390/min6030086

[13] M. I. Abro, A. G. Pathan, A. H. Mallah, *Selective Flocculation of Dilband Iron Ore, Pakistan,* Mehran University of Engineering & Technology, Vol. 30−2 (2011) 319−328.

[14] L. Panda, B. Das, D. S. Rao, Mishra B.K., *Selective Flocculation of Banded Hematite Quartzite (BHQ) Ores,* The Open Mineral Processing Journal, Vol. 4 (2011) 45−51.

[15] F. F. O. Orumwense, J. C. Nwachukwu, *Flocculation studies on hematite-silica system using polymeric flocculants,* Indian Journal of Chemical Technology, Vol. 7−1 (2000) 23−29.

[16] J. Drzymala, *Mineral processing, Foundations of theory and practice of minerallurgy,* Wroclaw University of Technology, 2007, 449−462

[17] R. D. Kulkarni, P. Somasundaran, *Mineralogical Heterogeneity of Ore Particles and Its Effects on Their Interfacial Characteristics,* Powder Technology, Vol. 14 (1976) 279−285.

[18] N. P. Nayak, *Mineralogical Characterization of Goethite-Lateritic Ore & its Implication on Beneficiation*, International Journal of Engineering Sciences & Research Technology, Vol. 3−11 (2014) 288−291.

[19] T. Leistner, U. A. Peuker, M. Rudolph, *How gangue particle size can affect the recovery of ultrafine and fine particles during froth flotation*, Minerals Engineering, Vol. 1−9 (2017) 109, DOI:10.1016/j.mineng.2017.02.005.

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

[21] Cytec Industries Inc, *Cytec Mining Chemicals Handbook*, 1976, 1989, 2002, 187−202, https://www.911metallurgist.com/wp-content/uploads/2017/03/2002-cytec-mining handbook 924751.pdf.

[22] S. Đ. Milošević, *Multiphase dispersion systems*, Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, 1997, 47−119 (In Serbian)

[23] Z. Shi, X. Zhou, W. Luo, Z. Liu, D.Sun, X. Zhang, *Different slurry concentration on settling effect of the iron tailings*, Advanced Materials Research, 2013, 634−638, 3325–3330.

[24] M. Kosmulski, *pH-dependent surface charging and points of zero charge. IV. Update and new approach*, Journal of Colloid and Interface Science, Vol. 337 (2009) 439–448

[25] R. E. Martinez, P. Sharma, A. Kappler, *Surface binding site analysis of Ca2+-homoionized clay–humic acid complexes*, Journal of Colloid and Interface Science, Vol. 352 (2010) 526–534

[26] M. Chorom, P. Rengasamy, *Dispersion and zeta potential of pure clays as related to net particle charge under varying pH, electrolyte concentration and cation type*, European Journal of Soil Science, Vol. 46 (1995) 657−665.

[27] K. W. Perrott, *Surface charge characteristics of amorphous aluminosilicates*, Clays and Clay Minerals, Vol. 25 (1977) 417−421.

[28] B. K. Schroth, G. Sposito, *Surface charge properties of kaolinite*, Clays and Clay Minerals, Vol. 45−1 (1997) 85−91.

༄༅

ПОНАШАЊЕ ПРИРОДНИХ УЗОРАКА ГЛИНЕ ИЗ РУДНИКА ОМАРСКА У ПРОЦЕСИМА ДИСПЕРЗИЈЕ И ФЛОКУЛАЦИЈЕ

**Сажетак:** У раду је проучавано понашање природних ровних узорака глине из Рудника Омарска (Република Српска, БиХ) у процесима дисперзије и флокулације. Приликом прераде руде гвожђа у Руднику Омарска, настаје велика количина ситнозрног отпадног муља (< 15 μm), који садржи релативно високе концентрације гвожђа. Наша ранија истраживања су показала да у минералошком саставу муља преовлађују гетит и кварц, мање минерал и глина, и, само минорно, магнетит и тодорокит. Селективна флокулација једна је од метода која може да се примијени за одвајање финих класа минерала гвожђа од примјеса, али она зависи од индивидуалних компоненти муља и њиховог понашања. ХРПД, ФТИР и СЕМ-ЕДС анализе смо користили за детаљно одређивање минералошког и хемијског састава фаза присутних у муљу. Узорци глине се првенствено састоје од кварца и минерала глина, уз много мањи садржај фелдспата, амфибола, гетита и хематита. Минерални састав глина је идентификован као углавном илитно-серицитни, који преовладава над каолинитом, са хлоритима који се јављају само спорадично. Испитивано је понашање природне глине извођењем експеримената таложења и мјерењем зета-потенцијала. Као дисперзанти су коришћени Na-хексаметафосфат, На-пирофосфат и На-силикат, а као флокуланти нејонски и анјонски полиакриламиди. Најбољи резултати су постигнути са На-хексаметафосфатом (1000г/т) и анјонским полиакриламидом.

**Кључне ријечи:** Рудник Омарска, муљ, глине, дисперзија, флокулација, понашање.

ༀ