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APPLICATION OF THE METHOD OF FOCCULATION AND SELECTIVE FLOCCULATION METHODS IN THE TREATMENT OF INDUSTRIAL SLUDGE FROM THE IRON ORE CONCENTRATION PROCESS

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Abstract: The paper presents research on the use of flocculation and selective flocculation methods in the treatment of industrial sludge, generated in the processing of iron ore minerals. The large quantity of fine sized sludge disposed as final waste still contains a relatively high concentration of iron minerals, as well as quartz and clay minerals, as tailings. It is both an environmental and an economic problem. In both cases it is useful to use flocculants to accelerate settling of fine particles. The action of flocculants, which accelerate settling, can be selective or non-selective. The research was aimed at determining the conditions under which selectivity can be achieved when using some commercial flocculants.

Key words: industrial sludge, iron ore processing, flocculation, selective flocculation,environment

1. INTRODUCTION

Iron ore is one of the most important minerals of the global economy. High-quality concentrates can only be obtained from relatively rich ores by the usual methods of magnetic and gravity separation In the future, which is already beginning, because the rich iron ore in lithosphere is almost exhausted, it will be necessary to process lower quality ores, which will require the application of more complex, new and expensive concentration procedures. Exploitation of ores of lower quality and more complex structural and textural characteristics and their crushing and classification lead to the creation of a large amount of the smallest classes of ore that are currently discarded, because the techniques for obtaining useful products are not adequate enough. The disposal of this material in the form of industrial sludge in landfills degrades the environment and endangers fertile soil. By using flocculants, it is possible to accelerate the settling of small particles, the clarification of water and increase the efficiency of magnetic separation [1-4]. Technological progress is based on science and sustainable development of the mining industry, rational use of mineral raw materials and efficient use of resources. In the last few decades, in the mineral processing, extensive and varied tests were carried out in the field of flocculation and especially selective flocculation,wich is one of the most promising techniques for removing gangue from fine iron ores.[5-8]. Fine iron ores most often contain clay, silica, and other minerals as accompanying minerals. The selective separation of useful from accompanying minerals in a complex system such as sludge, is difficult in any case, and depends on the individual components of the sludge and their behavior. Sludge generated by the processing of iron ore in the iron mine located in Omarska (Republic of Srpska, Bosnia and Herzegovina) is an example of a complex system composed of fine particles of limonite ore with admixtures of quartz and clay [9] . The iron ore deposit “Omarska” (Bosnia and Herzegovina) is located in the northeast part of the “Sana paleozoic”, or the Ljubija metalogenetic region, and in the Omarska-Prijedor field between the cities of Prijedor and Banja Luka.

The main goal of this work was to present all the previous research that is necessary to be done in order to determine the possibility of applying selective flocculation - on the example of sludge from the studied iron mine tailing deposits.. The first step was a detailed mineralogical and chemical characterization of the sludge, then of the individual components of the sludge, and then of other parameters important for the selective action of flocculants (particle size distribution and flocculation behavior properties). The flocculation behavior properties include the examinations of the influence of pH value, type and concentration of dispersant, and type and concentration of flocculant, effect of solid concentration). All tests were performed both on sludge and on individual components using the same methods.

Due to the extensiveness of the results, this article provides an overview of all the research and references where detailed results can be found.

2. MATERIALS

The research included the following samples:

– a sample of sludge with a size of 25 µm, which was taken as overflow of the hydrocyclone (batteries 2 and 4) at the “Omarska” mine Arcelor-Mittal Priijedor facility, by properly cutting the jet every twenty minutes in the amount of ½ l. Only flocculation and sedimentation tests were performed on this sample because reagent adsorption test methods require pure mineral samples,

– a sample of goethite, clay and quartz was taken from the boreholes of opet pit “Buvač”, by the geological service of the “Omarska” mine Arcelor-Mittal Company Prijedor and reduced to a size of -25 µm. Chemical and granulometric composition, moisture, density and mineralogical analyzes were determined on all samples prepared for testing.

During the tests, the following reagents were used: sodium silicate, sodium hexametaphosphate and sodium pyrophosphate (as dispersants), sodium oleate and polyacrylamide labeled Superfloc A100 (as flocculants) and pH regulators (hydrochloric acid and sodium hydroxide). All reagents used were of analytical grade, and they were prepared as solutions in distilled water.

Samples of goethite, quartz and clay are the basic components of sludge, and selective flocculation tests were performed on them individually for a more complete understanding of this process and flocculation mechanisms.

Preparation of samples included: drying, crushing, grinding, classification and homogenization.

3. METHODS

A detailed description of the used methods and test conditions is given in the cited references.

3.1.Characterization Methods

In order to precisely determine the mineral phases present and their chemical compositions, a detailed mineralogical characterization of all samples was performed using X-ray powder diffraction (XRPD), infrared spectroscopy (FTIR) and scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS). Chemical analyses were performed by wet analysis according to BAS ISO 2597-1:2012 standard for determination of iron ore [9].

3.2. Particle Size Distribution Analysis

Particle size distributions of individual raw material samples were performed using Malvern analyzer and Beaker decantation analysis[10].

In order to obtain samples of goethite, quartz and clay with a particle size of -25 µm, it was necessary to grind in several stages by using disc mill for all three samples individually. After definitive crushing of the sifted class -53+25 µm and obtaining a product - 25 µm, the sample could be considered ready for further testing.

4. ZETA POTENTIAL STUDY

The surface charge is studied by determining the electrokinetic potential, that is, the potential on the shear plane of the adsorbed layer and the mineral surface itself, by measuring the electrophoretic mobility of particles, goethite, quartz and clay under different conditions [9,11]. The same was determined only in solutions of different pH in a wide pH range of 2-12, without the presence and in the presence of flocculants and dispersants. A synonym for electrokinetic potential is zeta potential and in the literature it is often denoted by the Greek letter ς (ς potential) or Zeta potential. An important step in the selective flocculation process is to achieve stable dispersion of mineral particles. Dispersion stability of mineral particles is dependent on the zeta potential of present particles.

5. SETTLING AND FLOCCULATION STUDIES

For experimental work, reagents of the pH regulator type, mineral surface modifiers (dispersants) and flocculant type reagents, 1% polyacrylamide (PAM) and 1% sodium oleate (NaOl) were used.

Sedimentation of the tested samples and processing of the obtained data in order to determine the sedimentation of the samples was carried out according to the standard procedure described several times in the literature [1,12] in graduated cylinders with a volume of 100 ml. Also, according to the same procedure, the received data were processed.

In order to determine the selectivity of Fe minerals, it was necessary to perform studies of influence of pH value, influence of the type and concentration of dispersants, influence of the type and concentration of flocculants, effect of solid-liquid ratio (S:L) and kinetic of adsorption on individual samples.

a. Influence of pH value

A 5% solution of sodium hydroxide (NaOH) and a 1% solution of hydrochloric acid (HCl) were used to adjust the pH value. During testing in the range of pH values from 0-14, it was noticed that dispersion occurs only at pH 10.5, that is, successful flocculation of goethite with good selectivity can be expected even with the use of only flocculants A100 and NaOl at pH 10.6. Further research was focused on tests on was performed only at this pH value..

b. Type and concentration of dispersants

Inorganic compounds were used as dispersants: sodium silicate (Na_2SiO_3), sodium hexametaphosphate ($Na_6P_6O_{18}$) and sodium pyrophosphate ($Na_4P_2O_7$), which have the property of hydrating the mineral surface and binding water molecules. According to literature data in the field of selective flocculation of iron ores, quartz and clay, dispersants were used that showed the best results. Table 1 shows the names (types) and consumption of dispersants that were used for experimental tests.

Table 1. *Names and consumption of dispersants [12]*

Dispersant name/chemical formula	Consumption, g/t
Sodium hexa meta phosphate, $Na_6P_6O_{18}$ (SHMP)	50 100 200 1000
Sodium pyrophosphate, $Na_4P_2O_7$ (SPP)	50 100 200 1000
Sodium silicate, Na_2SiO_3 (SS)	300 500 1000

c. Type and concentration of flocculants

According to literature data in the field of selective flocculation of iron ores, quartz and clay, flocculants were used which, in our previous tests [13], showed the best results. The chemical connection of the selected flocculants with iron in the solution or on the surface of the mineral is achieved through a functional group, i.e. when in the OH group hydrogen or an alkali metal is replaced by a suitable ion, e.g. ferric or ferrous ion in solution or on the surface of minerals.

The types and consumption of flocculants used for experimental tests are presented in Table 2.

Table 2. *The types and consumption of flocculants*

Name of flocculant/designation/ chemical formula	Consumption, g/t
Polyacrylamide (A100, N100) (PAM)	10 30 50 100
Sodium oleate, $C_{17}H_{33}COONa$ (NaOl)	250 500 1000

d. Effect of solid-liquid ratio (S:L)

Various solid-liquid ratios (S:L) were also used in the research in order to determine the settling speed as one of the parameters for monitoring selective flocculation. Work was done with three different axes, solid: liquid:

- S:L= 1:19,66 (4,83% S)
- S:L=1:9,66 (9,38% S)
- S:L=1:7 (13% S)

The best results for all investigated samples are obtained in a diluted suspension, i.e. at S:L=1:19 [9,14,15].

e. The adsorption kinetics of flocculants on natural minerals

Adsorption capacity tests were carried out in a batch process by varying the dosage of polymer with a constant amount of adsorbents, 10 g/dm^3. A commercial anionic flocculent PAM A100 was used for the settling of fine particles of natural samples of goethite, quartz and clay minerals in this study. The pseudo-first order, pseudo-second order and intraparticle diffusion models were used to analyze experimental results in kinetic studies [16].

6. OVERVIEW OF RESULTS

6.1. Physicochemical and Mineralogical Characterization

The mineralogical and chemical analyses were recently performed for obtaining more precise mineral determination [9,17].

SEM images and EDS chemistry of the samples show heterogeneity in morphology, structure and mineral composition with predominant oxide and/or hydroxide minerals consisting mainly of iron, silicon and aluminium. Namely, goethite samples are composed of Fe minerals that dominate in relation to quartz and Al-silicates, and with a significant amount of Mn. The quartz sample consists of the main quartz that dominates over Al-silicates and Fe minerals. The clay sample consists of a higher proportion of quartz and Al-silicate, which dominate over a lower content of Fe minerals. The compositions of these natural raw materials identified and characterized in this way also agree very well and additionally explain the composition of the sludge produced during the processing of iron ore in the Omarska mine.

The XRPD and FTIR methods confirmed that goethite and quartz are the most abundant minerals in the sludge. The goethite content of the sample is approx 72.54%, quartz (13.49%), mica minerals (8.44%), chlorite minerals (2.16%) and significantly less clay minerals (about 1.26%). Using this method, it was confirmed that in a natural sample of goethite, the most abundant mineral is certainly goethite (86.28%), followed by quartz (3.5%) and hematite (10.16%). In the natural quartz sample, the presence of quartz was confirmed with 93.61%, muscovite 5.97% and hematite 0.42%. The sample that represents natural clay actually contains a very high percentage of quartz (49.71%), and mica minerals (30.94%), very little clay minerals (10.07%), chlorite minerals (2.87) and iron minerals (goethite 4.19% and hematite 0.36%).

6.2. Particle Size Distribution Analysis

The results of particle size distribution analyzes show that in limonite sludge there are the most grains below 6 µm, over 69.20%.Therefore, it is a sample with a large share of very fine grains, which confirms the reasons for the impossibility of separating rich batches of fine-grained ore with conventional technologies. the chemical composition of limonite mud by size classes clearly shows that there is a drop in Fe content compared to the input (43.43%) in classes below -18.8 + 5.9 µm (about 38%), while in class -5.9 µm we can say that there is a slight increase in Fe content (40.92%).

Particle size distribution of natural raw samples are given in Fig. 1.

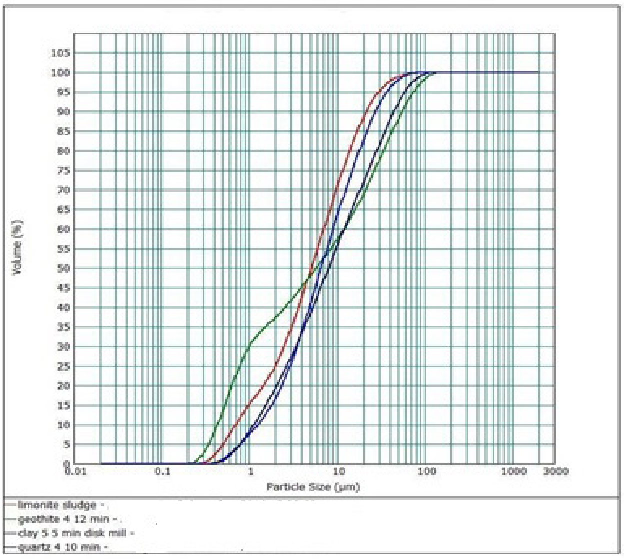

Figure 1. *Particle size distribution of limonite sludge, goethite, clay, and quartz [12]*

Detailed examinations of the particle size distribution of samples of goethite, quartz and clay, and especially of limonite sludge, were carried out with the aim of getting as close as possible to the real values of the particle size distribution of limonite sludge obtained as a definitive overflow of the two-stage classification at the Omarska plant, but also because of the importance of the particle size distribution on adsorption of reagents, flocculation rate, floc size and floc sedimentation rate. According to literature data, the most suitable for flocculation are particles in the range of 60 to 270 nm, and the tendency to flocculate decreases with increasing particle size, that is, small particles flocculate faster [2].

6.3. Zeta Potential Analysis

When it comes to the charge of the surface, that is, the electrokinetic potential, an extremely important parameter for coagulation and flocculation is the pH value at which the isoelectric point is reached, that is, the zero point of the charge, which corresponds to the electroneutrality of the mineral surface. If all particles have zero charge, the forces of electrostatic repulsion cease to act and the conditions for coagulation, flocculation and precipitation are created. Figure 2 shows the zeta potential of natural goethite, quartz and clay and sludge samples. Isoelectric point (IEP) which represents the electroneutrality of the particle was obtained at the pH values of 2.6, 6.6 and 4.5 for quartz,goethite and sludge, respectively.

This study also was done by measuring of zeta potential in the various combinations of absence/presence of dispersants, and also in the absence/presence of flocculants. After the addition of dispersants, and flocculants, the surface charge remains negative throughout all of the investigated pH values. A detailed presentation and discussion of the results are published in the cited references [9,11].

6.4. The study of adsorption kinetics

The kinetic of the adsorption polyacrylamide-based flocculant on natural minerals (goethite,quartz and clay) has been investigated at same condition of pH, temperature, adsorbent amount and adsorbate dosage. The adsorption performs very quickly in all three cases and the adsorption data with the pseudo-second-order model fit best in all three cases [16].

7. CONCLUSION

The process of flocculation is by its very nature extremely complex. This stems from the fact that the flocculation process itself consists of a series of “micro processes” that take place according to specific mechanisms, have their own process ki-

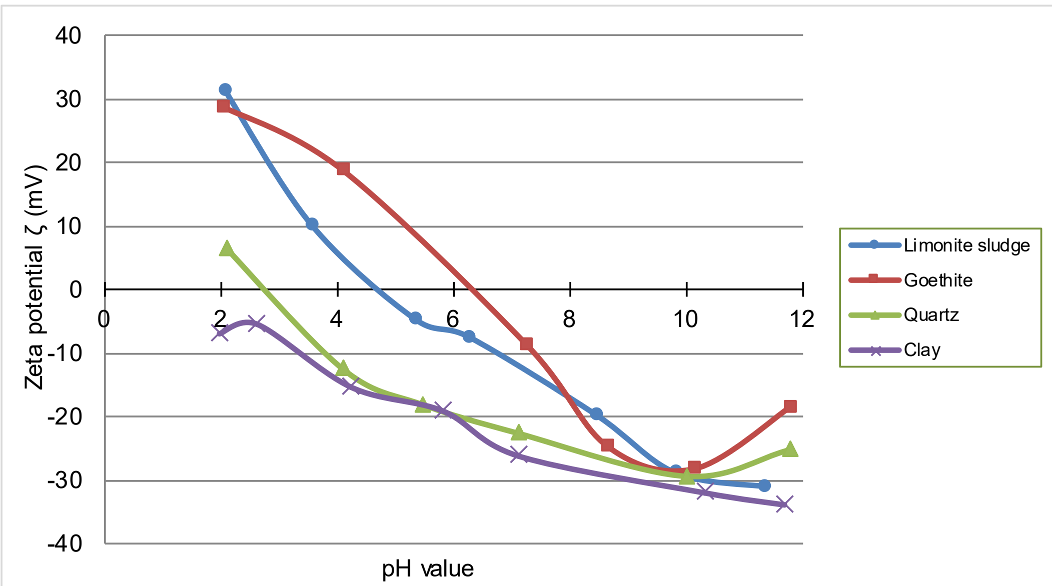

Figure 2. *Zeta potential of limonite sludge,goethite, quartz and clay as a function of pH*

netics that depend on a series of variables, and directly affect the overall flocculation kinetics, which as a whole determines the efficiency of the process. The efficiency of the process is measured by utilization per unit of time at a given product quality, or by the height of the column of clear water or sediment. When considering the flocculation mechanism, it must be emphasized whether it is heterogeneous or selective flocculation, that is, whether it is a multicomponent or at least binary suspension that is subjected to the flocculation process. Heterogeneous flocculation implies a heterogeneous suspension of solid particles of complex mineral composition that should be separated from the liquid phase and corresponds to the process of dewatering, and selective flocculation also refers to a multi-component, at least binary mixture of the dispersed phase from which it is necessary to extract a useful component in the form of a precipitated product and corresponds to the process of concentration [12].

By selective flocculation of limonite from sludge under certain conditions regarding the percentage ratio of solid and liquid phase, pH value, settling time, type and concentration of flocculants and dispersants, it is possible to achieve a satisfactory difference in settling rates, which could be used for the concentration of limonite by separating the precipitated flocs limonite from the dressing. On the other hand, previous selective flocculation of limonite would enable an increase in the kinetics of magnetic concentration of limonite from the sludge, which would make the magnetic concentration procedure possible and profitable for classes below 25 μm.

In addition to the theoretical, these tests also have a practical significance, which is reflected in the determination of the possibility of applying appropriate procedures for the preparation of the obtained concentrate or pre-concentrate from sludge and the mechanism of transfer of these results from laboratory to industrial conditions, i.e. looking at the conditions for achieving better qualitative-quantitative parameters of the overall ore preparation process limonite in industrial practice.

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METODE FOKULACIJE I SELEKTIVNE FLOKULACIJE U TRETMANU INDUSTRIJSKOG MULJA IZ PROCESA KONCENTRACIJE RUDA GVOŽĐA

Sažetak: U radu je prikazano istraživanje primjene metoda flokulacije i selektivne flokulacije u tretmanu industrijskog mulja koji nastaje pri preradi minerala željezne rude. Velika količina sitnog mulja koji se odlaže kao konačni otpad još uvijek sadrži relativno visoku koncentraciju minerala željeza, kao i minerala kvarca i gline, kao jalovine. To je i ekološki i ekonomski problem. U oba slučaja korisna je upotreba flokulanata za ubrzanje taloženja finih čestica. Djelovanje flokulanata može biti selektivno i neselektivno. Istraživanja su bila usmjerena na određivanje uslova pod kojima se može očekivati selektivnost pri korišćenju nekih komercijalnih flokulanata.

Ključne riječi: industrijski mulj, prerada željezne rude, flokulacija, selektivna flokulacija, životna sredina.

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