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EFFECT OF PH CONDITIONS ON GOETHITE BEHAVIOR IN THE PRESENCE/ABSENCE OF DIFFERENT DISPERSANTS

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Abstract: Dispersion and settling behavior of goethite has been studied and effect of pH values on surface properties of goethite particles with /without dispersants has been discussed. A prerequisite for the successful flocculation is the stabilization of the system which is achieved by the good dispersion of particles. The effect of pH, sodium silicate (Na_2SiO_3), sodium hexametaphosphate ($Na_6P_6O_{18}$) and sodium pyrophosphate ($Na_4P_2O_7$), on the surface charges of goethite was studied. The IEP of natural goethite was found by measuring zeta potential at pH value of 6.6. With the use of sodium silicate the IEP of goethite moves to pH 4.95. An IEP could not be detected when the poly-phosphates were used and the surface charge is negative from pH 2 to pH 12. The relatively high zeta potential values indicate a fairly stable dispersion, especially when the sodium hexametaphosphate were used as dispersant.

Keywords: goethite, dispersion, pH value, zeta potential, IEP.

1. INTRODUCTION

Goethite, α-$Fe^{3+}O(OH)$ is one of the most abundant iron-bearing mineral. Although goethite is very widespread, it is often part of the low grade iron ore with fine mineral particles (below 20 µm). Besides, fine iron ores in general contain clays, quartz and other minerals as gangue material and many factors affect the recovery of valuable minerals from their ores.

Conventional processing of iron ores includes: washing, sieving, classing, gravity and magnetic concentration. Beneficiation of fine and ultrafine mineral particles is one of the most important problem for the mineral processing industry because classical techniques are not successful in the case of these fine-grained complex systems. Flotation and selective flocculation techniques have been found to show great potential to solving this problem, whose success is highly dependent on the physical, chemical and mineralogical properties of constituent minerals. [1–10].

A stable dispersion of mineral particles is the precondition for the selective flocculation. Dispersion stability of mineral particles is dependent by the surface charges of present particles. The higher surface charge causes the higher repulsive forces between particles and thus better particle dispersion.

Some of the ways to achieve stable dispersion are based on the adjustment of pH, solid concentration, stirring condition and selection of the most effective dispersant. [11]. Dispersants are used to prevent fine particles from aggregating. Interaction between a particular mineral and the dispersant is a basic parameter which determines the efficiency of separation of the mineral.

The choice of a dispersant is an important parameter in stabilizing the dispersion. Sodium hexametaphosphate (SHMP), sodium pyrophosphate (SPP) and sodium silicate (SS) were used as dispersants for stabilizing the dispersion in many cases. A review of the literature shows that the results are different in terms of the selectivity of certain dispersants). Some authors pointed to a better effect of silicate in the case of sludges containing hematite and kaolinite, others to a better efficiency of SPP compared to SS for montmorillonite and illite, etc. [12,13].

Dispersion and settling behavior of natural goethite has been studied and the effect of pH values on surface properties of goethite particles with /without dispersants has been discussed in this paper. Sodium silicate (Na_2SiO_3), sodium hexametaphosphate ($Na_6P_6O_{18}$) and sodium pyrophosphate ($Na_4P_2O_7$) were used as dispersants (Figure 1).

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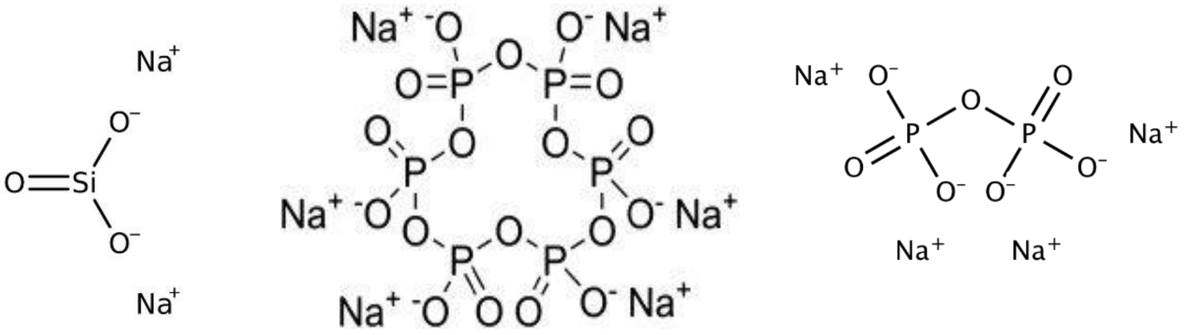


a) b) c)

Figure 1. Structures of the used dispersants: a) Sodium silicate (Na_2SiO_3), b) sodium hexametaphosphate ($Na_6P_6O_{18}$), c) sodium pyrophosphate ($Na_4P_2O_7$)

2. MATERIALS AND METHODS

2.1. Materials

Natural goethite from Omarska mine (Bosnia and Herzegovina) was handpicked. X-ray powder diffraction (XRPD), Fourier Transform Infrared (FTIR) spectroscopy and Scanning Electron Microscope with Energy Dispersive Spectrometry (SEM-EDS) analysis showed that the “limonite ore” samples are composed of major goethite which dominate over hematite, and with minor contents of magnetite, quartz and clay minerals [14]. It has the following chemical composition (in mass %): Fe 57.16, SiO_2 4.44, Al_2O_3 0.59, Mn 1.18 and LOI 10.86; and density of 3,940 (g/cm^3).

The sample was grounded several times in a laboratory disk mill, dried and sieved through a 25 µm sieve. A particle size analysis showed that the highest mass percentage belongs to the fine classes (d_{80} = 15 µm).

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 pH modifier, 0.1M NaOH and 0.1M HCl were used.

2.2. Settling and dispersion experiments

The natural settling at different pH values, and settling with the addition of three different inorganic dispersants were determined. For settling, graduated glass cylinder with volume of 100 ml was used.

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 five minutes, and left to settle. Float from sink was separated, after ten minutes, and then dried at 105^o C in the oven. After weighing the sediment material, elemental analysis was performed.

For the settling rate tests we use 100 ml graduated glass cylinder. Suspension of 5 % solids was mixed for 2 minutes adjusted with necessary pH of water (depending on the pH value of the tests, the adjustment is made by adding HCl or NaOH). The dispersant is added at a certain concentration and the suspension is mixed for another five minutes. After that, the deposition time was measured and based on that, the deposition rate curves were drawn.

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, the 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. Settling and disspersion studies

In solid-liquid systems, the settling velocity of the solids depend on size and shape of the grain, the fluid and grain density, charge density, etc. In many industrial processes it is necessary to produce more rapid settling of fine particles by using flocculation technique. A prerequisite for successful flocculation is good particle dispersion.

These experiments aim to demonstrate the possible impact of the different input parameters on the behavior of settling velocity of goethite: naturally and also in the presence of the inorganic different dispersants.

3.1.1. The settling behavior of goethite at different pH

The stability of the goethite suspension without dispersants strongly depends on the pH value. This is clearly seen from Figure 2, where they are shown natural settling curves of goethite at different pH values. Van der Waals interactions depend on polarity and polarizability of particles and media. Depending on the pH of the solution, the hydroxyl surface of goethite can be positively, negatively, or neutrally charged. Goethite particles do not precipitate at either pH 4 or pH 10, because of increasing of surface charge causing the repulsive forces. At condition of neutral pH, the dispersion is unstable, because there are no reflective forces present among the particles and precipitation occurs.

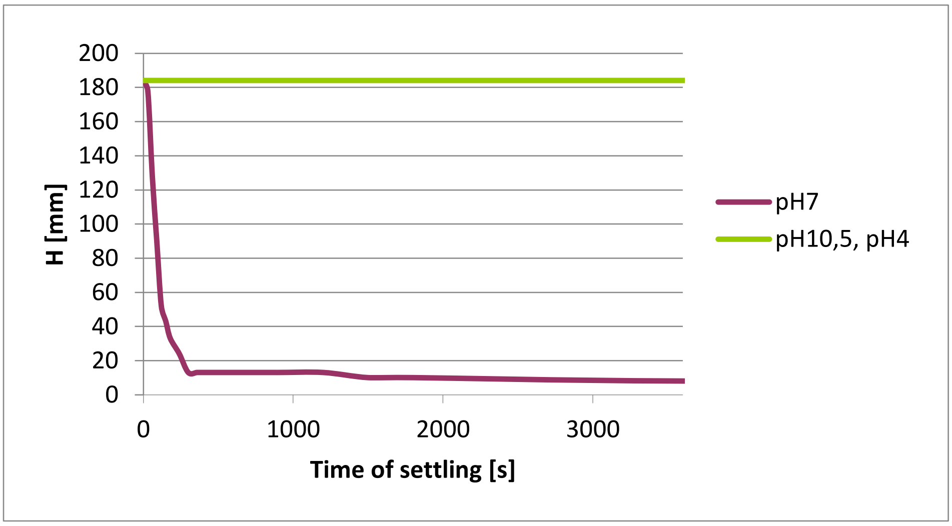


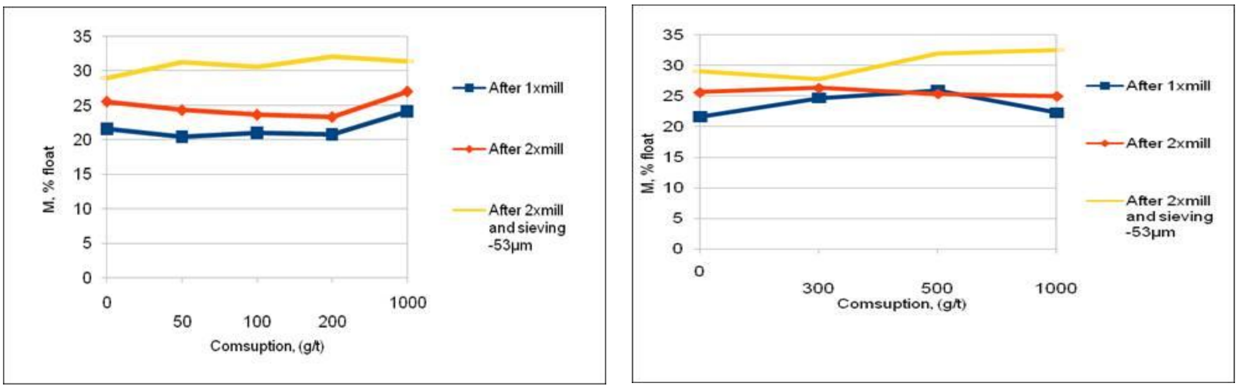
Figure 2. Natural settling of goethite at different pH values

3.1.2. Dispersion studies – influence of the type and dosage of dispersants

The choice of a dispersant is an important parameter in stabilizing the dispersion. In this paper, 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 for these experiments. Initially, dispersion behavior was tested by monitoring the weight distribution and elemental composition in floating and sinking part. There is no big difference between SHMP and SS in the amount of sinking and floating part at experimental conditions. The results of the distribution of masses after one or two grinding and elemental composition between sinking and floating part are presented in Figure 3 a) and b), and Table 1. It can be seen from Figure 3 that the best results are achieved with the highest dose of dispersant (1000 g/t). In general, they are not large percentages of mass in the floating part. The distribution of the elements is similar in both parts and the Fe content in the floating part is only slightly increased.

The effect of different dispersants on the stabilization of goethite dispersion was studied by conducting settling tests at pH 7. These are the conditions when the dispersion of goethite in the absence of dispersants is unstable (Figure 2). It is obvious (Figure 4) that the addition of dispersant causes an increase in dispersion stability in all three cases.



a) *b)*

Figure 3. a) Goethite with SHMP b) Goethite with SS

Table 1. Elemental composition of goethite (in %) in presence of SHMP and SS (in g/t) as dispersants (distribution by float/sink).

Element		SHMP				SS		
		50	100	200	1000	300	500	1000
Fe	Float	57.07	57.42	57.4	57.29	57.2	57.55	56.72
	Sink	56.58	56.62	56.14	56.06	56.64	56.42	56.26
	Total	57.16	57.16	57.16	57.16	57.16	57.16	57.16
SiO_2	Float	3.03	3.04	3.09	3.01	3.44	3.18	3.33
	Sink	5.23	5.22	5.17	5.16	5.09	5.26	5.31
	Total	4.44	4.44	4.44	4.44	4.44	4.44	4.44
Al_2O_3	Float	0.74	0.73	0.73	0.72	0.77	0.72	0.73
	Sink	0.58	0.57	0.56	0.57	0.59	0.57	0.61
	Total	0.59	0.59	0.59	0.59	0.59	0.59	0.59
Mn	Float	1.49	1.5	1.49	1.45	1.47	1.5	1.48
	Sink	1.18	1.17	1.16	1.16	1.21	1.16	1.16
	Total	1.18	1.18	1.18	1.18	1.18	1.18	1.18
LOI	Float	10.79	10.8	10.69	10.74	10.92	11.04	10.81
	Sink	11.02	10.9	10.93	10.95	10.94	10.93	10.8
	Total	10.86	10.86	10.86	10.86	10.86	10.86	10.86

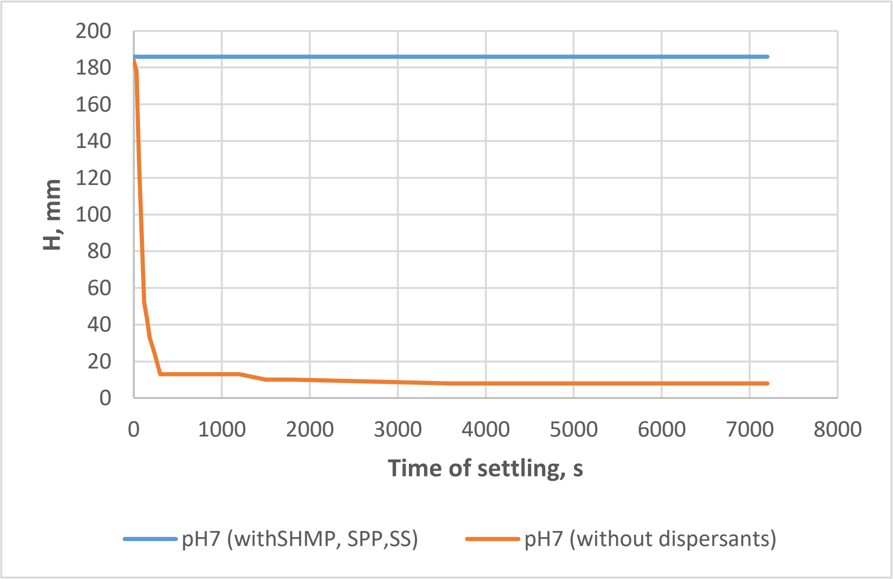


Figure 4. Settling behavior of goethite at pH 7 value, with/without dispersants

3.2. Zeta potential study

The zeta-potential for natural mineral raw sample of goethite is shown at Figure 5 Zeta (ζ) potential is a measure of the magnitude of the electrostatic or charge repulsion/attraction between particles. It is one of the most important parameters known to affect stability of the dispersion. The higher ζ-potentials absolute value produce a well-dispersed suspension. Isoelectric point (IEP) represents condition when value of zeta potential is zero. The particles with an IEP <pH7have acidic character while those with an IEP >pH are basic.

The zeta potential curve of natural goethite particles without dispersant vary from+28.7 mV at pH7 to – 28.14 mV at pH 10, with the IEPs at pH=6.7 values. Generally, the isoelectric point of natural minerals varies, depending upon the association of gangues [15].

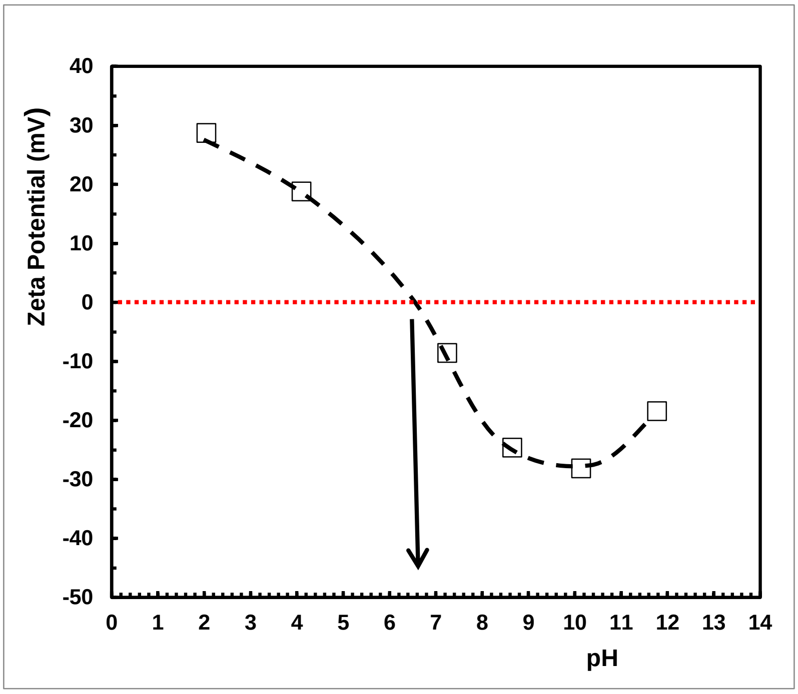


Figure 5. The zeta potential of goethite

The magnitude of the zeta potential is maximized at pH=2 and pH=10 value throughout investigated pH that correspond with settling behavior of goethite that is shown in Figure 2, because a higher zeta potential produces a stable dispersion. At pH 7 fast settling of goethite particles occurred. As a rule, ± 30 mV is taken as the limit value of the zeta potential required for dispersion stability. Namely, at that condition, the electrostatic repulsion between particles is typically strong enough to prevent particles attraction. In acidic and alkaline medium, which is farther from the IEP, the dispersion is stable and no deposition occurs.

It is well known that surface properties of metal oxides in water medium depends on pH value. In the case of oxide minerals, H^+ and OH^- ions are the principal potential determining ions, and they interact with water and produce surface hydroxyls (MOH_2^+,MOH , MO^-). According to the zeta potential measurements observed, there is a development of a net particle negative surface charge as a function of increasing pH.

After interacting with dispersants, the changes in zeta potential of goethite surface were obvious, indicating that the all dispersants did interact with the goethite surface. The zeta potential measurements detected the effect of the three inorganic dispersants: sodium-hexametaphosphate (SHMP), sodium-pyrophosphate (SPP) and sodium-silicate (SS) on the surface charge of goethite (Figure 6, Table 2).

From Figure 6 and Table 2 it is evident that different dispersants have different effects on the surface charge of goethite.

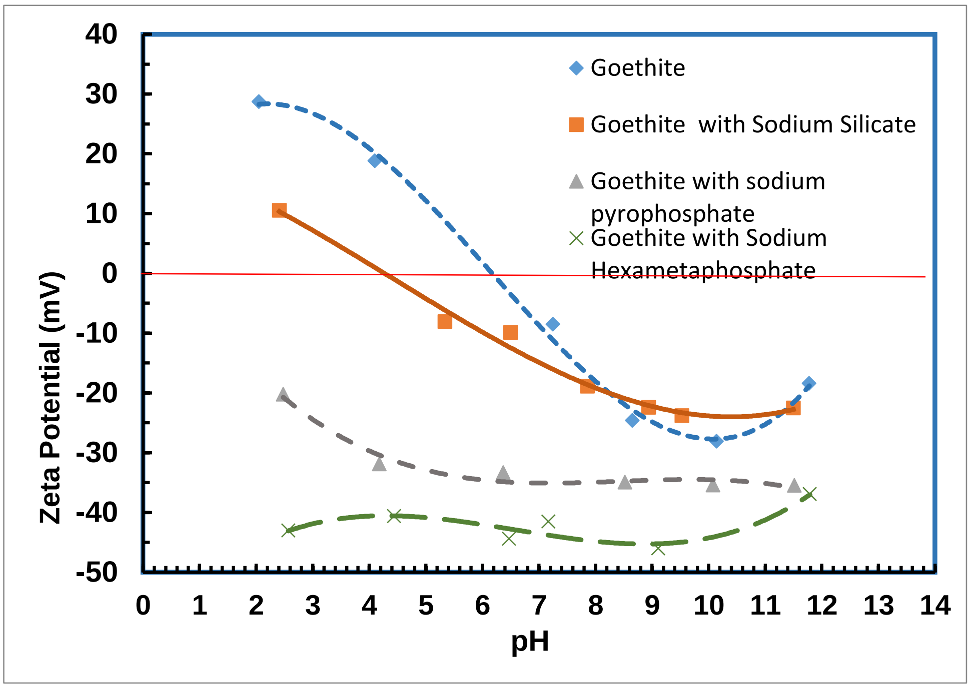


Figure 6. Zeta potential of the goethite samples in absence/presence of different dispersants

Table 2. Zeta potential of natural goethite with/without inorganic dispersants

Goethite with distilled water		**Goethite with sodium silicate**		**Goethite with sodium hexametaphosphate**		**Goethite with sodium pyrophosphate**	
pH	Zeta potential (mV)	pH	Zeta potential (mV)	pH	Zeta potential (mV)	pH	Zeta potential (mV)
2.05	28.7	2.41	10.5	2.57	-43.0	2.48	-20.2
4.10	18.8	5.34	-8.1	4.44	-40.6	4.18	-31.9
7.25	-8.5	6.50	-9.9	6.47	-44.4	6.37	-33.3
8.65	-24.6	7.86	-18.9	7.17	-41.5	8.52	-34.9
10.14	-28.1	8.94	-22.4	9.11	-46.0	10.08	-35.4
11.78	-18.4	9.53	-23.8	11.79	-36.9	11.52	-35.5

The behavior of goethite in the presence of sodium silicate indicates predominantly electrostatic forces since in the acidic environment the surface of the goethite becomes more electronegative, the IEP shifts from pH 6.7 to pH 4.95, which means that the surface of the getite will decrease in positive charge. The magnitude of the zeta potential decreases with increasing pH.

An IEP could not be detected when the polyphosphates (SHMP and SPP) were used and the surface charge is negative from pH 2 to pH 12. A significant decrease in the positive charge of the goethite in the presence of polyphosphate may be caused by hemisorption at the positive sites of the goethite enhanced by the steric effect of polyphosphate anions. It can be noticed that goethite particles in presence of SHMP, show a variation of zeta potential as a function of pH in the range from about -36.9 to -46.0 mV, in presence of SPP from about -20.2 to -35.5 mV, and in presence of SS from about -8.1 to -23.8mV. The presence of SHMP causes significant increase of negative zeta potential magnitudes, from -28.1 mV (without SHMP) to -46mV (with SHMP), at pH=9-10. Having in mind the rule that a zeta potential of at least 30mV is required for the stability of the suspension, it can be said that SHMP and SPP have a more significant effect on the stability of the goethite dispersion compared with sodium silicate. It is observed that, of all the dispersants addition, sodium hexametaphosphate gives the maximum value of zeta potentials. It is about -46 mV at pH 10, which is most suitable for obtaining well dispersed goethite particles.

All of three used dispersants cause changes in the goethite surface, as shown by the results of the zeta potential measurements. The zeta potentials of the natural goethite are lower than that with dispersants. At pH value 7 (near IEP), zeta potential of goethite in presence SHMP, SPP and SS were –44.4mV, -33.3 mV and -18.9 mV, respectively.

This explains the results of the settling experiments showing a stable dispersion at that pH value when different dispersants were used. In the absence of dispersants, goethite particles precipitate rapidly at the same pH value.

4. CONCLUSION

Dispersion and settling behavior of goethite has been studied and effect of pH values on surface properties of goethite particles with /without dispersants has been discussed. A prerequisite for the successful flocculation is the stabilization of the system which is achieved by the good dispersion of particles. The effect of pH, sodium silicate (Na_2SiO_3), sodium hexametaphosphate ($Na_6P_6O_{18}$) and sodium pyrophosphate ($Na_4P_2O_7$), on the surface charges of goethite was studied.

The results have shown that the dispersion stability of the investigated goethite sample is affected by the pH modification and the presence of dispersants.

The settling - dispersion tests at pH=7 show that all of the used dispersants cause the stable dispersion of the goethite. At pH 7 fast settling of goethite particles occurred in absence of dispersants, while in the presence of dispersants deposition is completely absent. All of the used dispersants disperse well goethite at pH7.

The settling - dispersion test results are well correlated with zeta potential measurements.

It can be assumed that the interaction of silicate with goethite is predominantly electrostatic.

The presence of the poly-phosphates causes significant increase of negative zeta potential magnitudes also in the alkaline medium indicated combination electrostatic, steric or electrosteric interactions.

The higher dispersive stability can be expected by using 1000g / t SHMP at a pH 9–10.

5. ACKNOWLEDGMENTS

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УТИЦАЈ УСЛОВА pH НА ПОНАШАЊЕ МИНЕРАЛА ГЕТИТА У ПРИСУСТВУ / ОДСУСТВУ РАЗЛИЧИТИХ ДИСПЕРЗАНАТА

Сажетак: Испитано је понашање гоетита приликом дисперзије и таложења и дискутовано је о утицају pH вриједности на површинске особине честица са и без дисперзанта. Предуслов успјешне флокулације је стабилизација система која се постиже добром дисперзијом честица. Изучаван је утицај pH вриједности, натријум-силиката (Na_2SiO_3), натријум-хексаметафосфата ($Na_6P_6O_{18}$) и натријум-пирофосфата ($Na_4P_2O_7$), на површинско наелектрисање честица гетита. Одређена је изоелектрична тачка (IEP) природног гоетита при pH вриједности од 6,6, мјерењем зета потенцијала. Употребом натријум-силиката као дисперзанта, IEP гетита се помјера на pH 4,95. Када су коришћени полифосфати као дисперзанти површински набој је негативан у цијелом испитиваном подручју (pH 2–12). Релативно високе вриједности зета потенцијала указују на прилично стабилну дисперзију, нарочито када се као дисперзант користи натријум-хексаметафосфат.

Кључне речи: гетит, дисперзија, pH вриједност, зета потенцијал, IEP.

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