Selective Flocculation Study of Hematite in Hematite-Quartz-Kaolinite System in Presence of Ca²⁺, Mg²⁺ and Fe³⁺ Ions. Part1: Optimization of Ligand

Muhammad Ishaque Abro[1a], Abdul Jaleel Laghari[1b], Umair Aftab[1c], Sikander Ali Channa[1d], Mukesh Kumar[1e]

ABSTRACT

Separation of ultrafine hematite from quartz and kaolinite gangue minerals using selective flocculation technique is markedly affected by the state of inter mineral interaction which is governed by type and content of polyvalent metal ions. Because of the presence of polyvalent metal ions hetracoagulation of gangue minerals is widely acknowledged, thus selective flocculation of ultrafine hematite from associated gangue minerals is challenging task when their concentration is above 10 ppm. This study has shown that state of strong interaction of gangue minerals with hematite due to presence of 15 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3 ppm Fe^{3+} ions can be weakened by addition of optimal dose of Sodium Hexametaphosphate (SHMP) ligand. The optimization of ligand dose is achieved through analysis of Zeta Potential (ZP) as a function of slurry pH. It is noted that 50 ppm of SHMP is sufficient to restore the ZP of hematite, where selective dispersion of the slurry constituents are possible. Our results further showed that conventional strategy of obtaining minimum difference of ±30 mV in the ZP of hematite and gangue minerals quartz and kaolinite would not work especially in the presence of 15 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3 ppm Fe^{3+} ions. Attempts to achieve the minimum threshold difference in the ZP of the minerals will cause over dispersion.

Keywords: Hematite, Quartz, Kaolinite, SHMP, EDTA, Metal Ions.

1. INTRODUCTION

Among the well-known iron ore deposits in the Pakistan, Dilband ore deposits are mainly lean grade hematite usually consisting an intimate mixture of hematite and quartz with sufficient amount of kaolinite, calcite and fluorapatite minerals [1, 2]. At the time of exploration of Dilband iron ore deposits by Geology Survey of Pakistan (GSP) it was dreamed that ore will play vital role in the economic growth of Pakistan, and import of foreign ores for the Pakistan Steel Mills Limited (PSM) will be reduced. Keeping in view the significance of Dilband iron ore deposits, the first beneficiation study was carried out by Abro [3] in 2009. Through this study it was learnt that presence of variety of metal ions and complex mineralogy are the alarming challenges to successful selective flocculation of Dilband iron ore.

Literature pertaining to selective flocculation of hematite indicates that polymers specially corn starch and polyacrylamide adsorb preferentially on hematite surfaces provided the ore slurry is depleted from gangue activating species [4–9]. By the presence of species like Ca^{2+}, Mg^{2+} and Fe^{3+} ions, hereinafter referred as Polyvalent Metal Ions (POMI), surfaces of gangue minerals also activate themselves for the adsorption of polymer. Therefore, hetrocoagulation

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[1] Department of Metallurgy and Materials Engineering, Mehran University of Engineering and Technology, Jamshoro, Sindh, Pakistan. Email: [a]ishaque.abro@faculty.muet.edu.pk (Corresponding Author), [b]jaleel_ali2008@yahoo.com, [c]umair.aftab@faculty.muet.edu.pk, [d]sikandar.channa@faculty.muet.edu.pk, [e]mukesh.kumar@faculty.muet.edu.pk

ther selective flocculation takes place. Mechanism involved in the activation of gangue minerals due to presence of POMI is extensively studied by many researchers [10–12]. Majority of the researchers are in agreement that substantial decrease in the ZP of the gangue minerals due to presence of POMI is one of the basic reason of hetrocoagulation. Henceforth, variety of chemical reagents hereinafter referred as ligand for chelating action with POMI has been investigated.

Ligands so far introduced are of five broad classes, which are: (1) Inorganic ions [NH^+_3, CN^-, F^-], (2) Polyphosphates [sodium tripolyphosphate (STP), sodium hexametaphosphate (SHMP)], (3) Aminopolycarboxylic acids [ethylenediamine-tetraacetic acid (EDTA), nitrilotriacetic acid (NTA)], (4) Organophosphates and (5) Hydroxycarboxylic acids [citric acid ($H_6C_6O_7$)]. Among these, EDTA, SHMP, STP, NTA, and citric acid (CA) are now a days commercially available ligands and are successfully applied as complexing agents for alkaline-earth POMI.

In present study the SHMP, EDTA and CA are used to chelate with 15 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3 ppm Fe^{3+} POMI present in Dilband irone ore. The optimization of ligand and its dose in present study was determined by measuring the ZP value of the minerals as a function of pH. The idea behind the approach used in the optimization of ligand through ZP value is based on widely acknowledged understanding that "Higher shift in ZP of the mineral will takes if chelating action of the ligand is strong with particular ion species" [6,8,12–14]. It is worth mentioning here that the concentration of POMI and the complexity due to presence of more than one type of PV in Dilband iron ore for which ligand optimization study was carried out is rarely reported in the literature. For this, preliminary experimentation with synthetic minerals was carried out.

2. EXPERIMENTS

2.1 Materials and Methods

Reagent grade synthetic hematite was obtained from the Sigma-Aldrich Company, whereas natural quartz and kaolinite of Nagarparker, District Thar Sindh Pakistan was obtained from Center of Geology,

University of Sindh Pakistan. The quartz and kaolinite minerals were ground and dry sieved using 25 µm sieve. The quartz and kaolinite samples of -25µm size fraction were used for the present study. The particle size distribution of samples was analyzed using Horiba Laser Scattering Particle Size Distribution Analyzer (LA-300), which is shown in Fig.1. It can be seen in Fig. 1 that 80% material of all three samples was finer than 10 µM. The X-ray diffraction patterns of the samples given in Fig.2 were obtained using D8-Bruker XRD machine from which mineral purity level was confirmed. The Merck brand ligands namely SHMP, CA, and EDTA were used, whereas Iron chloride, magnesium chloride and calcium chloride salts of analytical grade were used as a source of Fe^{3+}, Mg^{2+} and Ca^{2+} ions. Moreover, NaOH and HCl were used as pH modifiers.

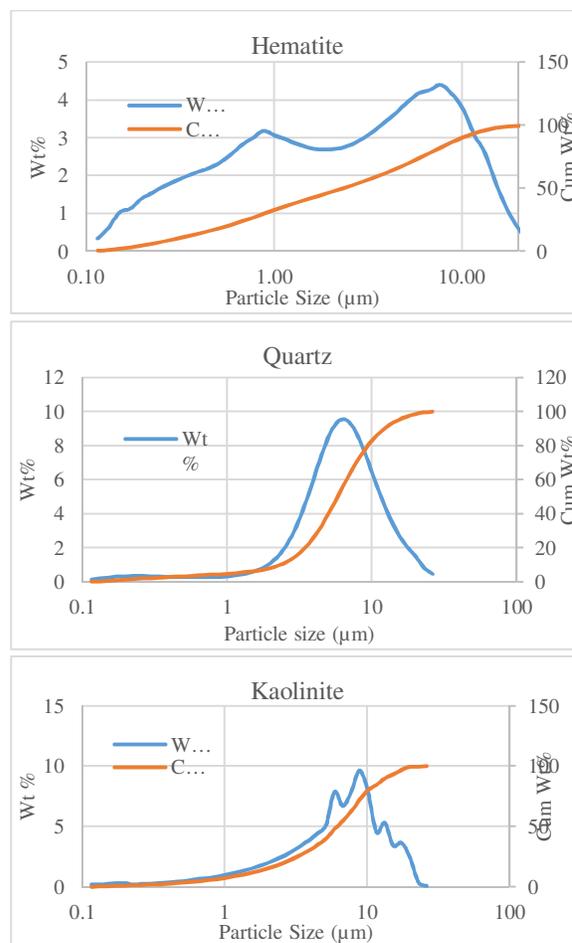Fig. 1: Particle Size Analysis of Hematite, Quartz and Kaolinite Sample

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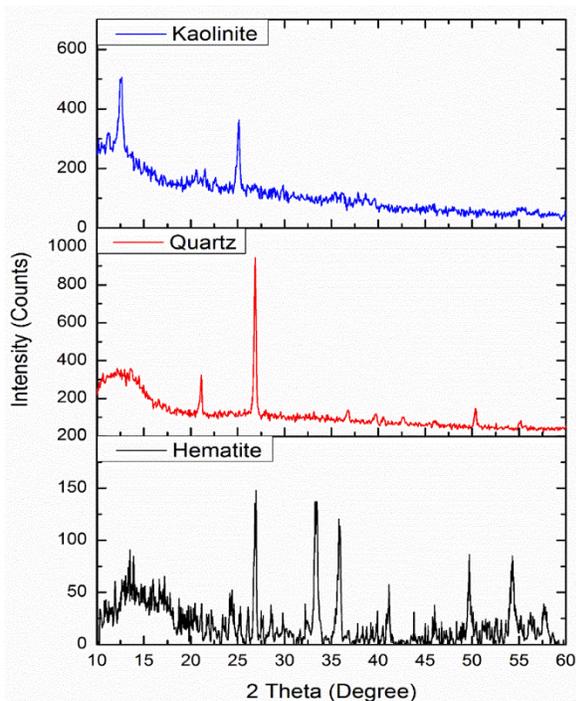
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Fig. 2: XRD Analysis of Hematite, Quartz and Kaolinite

2.2 Preparation of pH Modifiers, Metal Ions and Dispersants Solutions

One molar solution of NaOH and HCl were prepared in de ionized water. The solutions were used to modify the pH of the mineral slurry. Calcium chloride, magnesium chloride and iron chloride salts were dissolved in deionized (DI) water to prepare the Ca^{2+}, Mg^{2+} and Fe^{3+} ion solutions of 200 ppm each. These solutions were added to mineral slurry as and when required. The concentration of prepared metal ion solutions was confirmed on atomic absorption spectrometer. Similarly, stoichiometrically calculated mass of SHMP, EDTA and CA salts were dissolved in DI water to prepare 1000 ppm ligands solutions.

2.3 Zeta Potential (ZP) Measurement of Minerals

The interaction of ligands with POMI was studied by measuring ZP of the minerals using Malvern Nano Zetasizer (Nano ZS90). For this 0.1 g mineral sample was diluted in 250 ml deionized (DI) water and agitated mechanically for 5 min at 200 rpm. Addition of POMI and adjustment of pH as and when required further enhanced the condition time to 15 min. The

ligands were added before the adjustment of pH and the sample conditioning time was extended up to 20-25 min. Once the sample was ready, then it was transferred to cuvette using the syringe. Three samples for every pH and POMI content were run to record ZP.

3. RESULTS AND DISCUSSION

More than 1000 ZP tests were conducted at different combinations of pH, POMI and ligand. The ZP of each mineral in different conditions is given below.

3.1 ZP of Minerals in Absence of POMI

In absence of POMI the ZP of hematite, quartz and kaolinite at different pH is shown in Fig. 3 which indicates that with increasing the pH the ZP of all three minerals gradually shifts to negative value. For instance at pH 6 the ZP of hematite, kaolinite and quartz was -20 mV, -30 mV and -35 mV, whereas at 10.5 pH the ZP of hematite, kaolinite and quartz was -30 mV, -48 mV and -70 mV respectively. The ZP trend of hematite, kaolinite and quartz minerals illustrated in Fig.3 is in agreement with majority of the researchers [15–18], however there is slight deviation in the ZP values which is due to many factors. The substantial difference between the ZP of hematite and quartz at alkaline condition is the reason due to which the selective flocculation of hematite is widely reported at 10 to 11 pH.

3.2 ZP of Minerals in Presence of POMI

Fig. 4 illustrates the ZP of minerals accompanied with POMI at different pH, from which it can be seen that substantial change in the trend of mineral's ZP was resulted. It can be seen in Fig. 4 that at pH 6 and 10.5 the ZP of hematite and quartz were approximately equal to 10 mv. In contrast, the ZP of kaolinite at 6 pH was -10 mv and at 10.5 pH was 0 mv respectively. The difference between the ZP of hematite and quartz at pH 6, 8 and 10.5 was marginally less than 5 mv, whereas about 20 mv was the difference between ZP of hematite and kaolinite throughout the acidic and alkaline conditions. Fig. 5 illustrates the extent to which the POMI has shifted the ZP of the minerals at pH 6, 8 and 10.5 by the additions of POMI. Fig. 5 indicates that maximum shift in the ZP of hematite by

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addition of POMI was in acidic (*i.e.* at pH 6) as compared to alkaline conditions (i.e at pH 8 and 10). In contrast, the shift in ZP of quartz and kaolinite was substantially higher in alkaline as compared to acidic condition. From this, it can be deduced that adsorption of POMI in acidic conditions is higher on hematite surfaces, whereas in alkaline conditions it is higher on the quartz and kaolinite minerals.
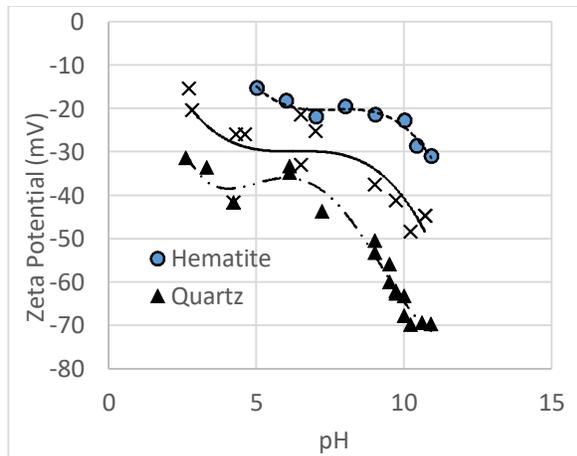

Fig. 3: ZP of Hematite, Quartz, and Kaolinite in Absence of POMI as a function of pH

The detrimental level of the POMI on the ZP of the minerals illustrated in Figs. 4-5 clearly explain the reason of hetraflocculation rather than selective flocculation of hematite when the variety of POMI are present in the ore slurry. It is quite interesting to see that at pH 10.5 where the selective adsorption of natural polymers (NP) on hematite in absence of POMI is widely reported, the ZP of the quartz and kaolinite is marginally equal to ZP of hematite in presence of POMI. Henceforth, selectivity of NP for hematite diminishes and it adsorbs on quartz and kaolinite minerals as well.

3.3 Optimization of Ligands

Ligands are normally added to chelate with POMI in order to make their complexes which do not interact with the mineral surfaces. The chelating action of the ligands in present study was observed from the shift of mineral's ZP. The anticipation was that chelating action of ligands with POMI present in the system is said to be stronger if the shift of the mineral's ZP is higher. The influence of SHMP, CA and EDTA
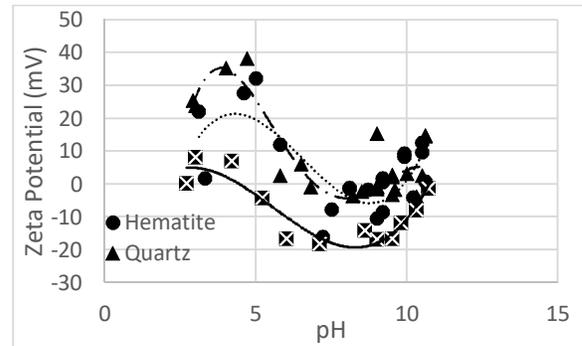

Fig. 4: ZP of Hematite, Quartz, and Kaolinite in Presence of POMI as a function of pH
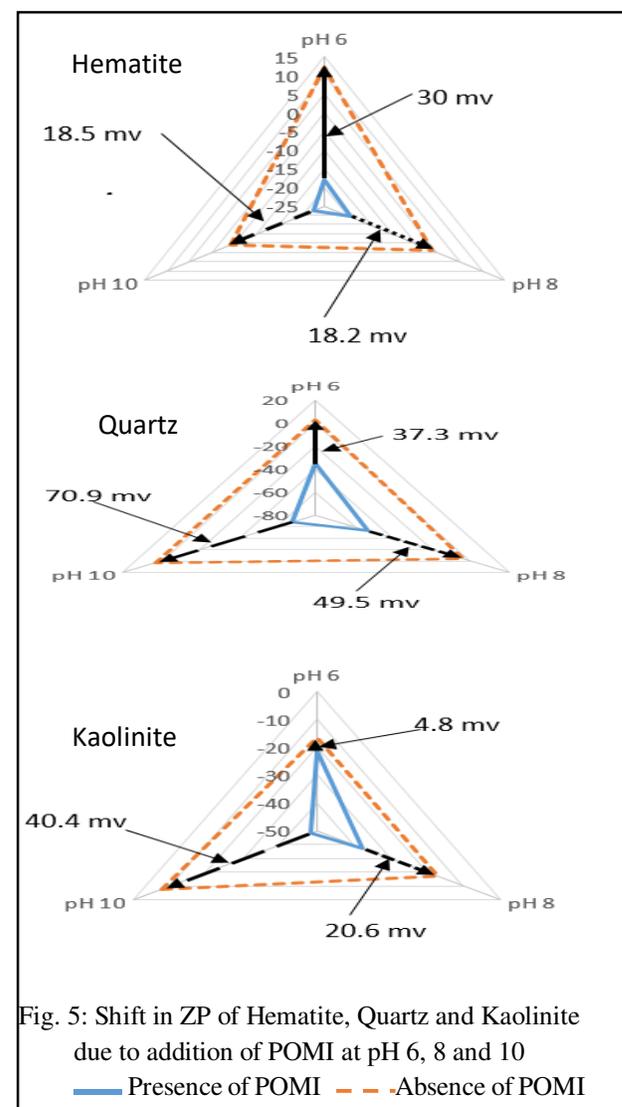

Fig. 5: Shift in ZP of Hematite, Quartz and Kaolinite due to addition of POMI at pH 6, 8 and 10
—— Presence of POMI – – –Absence of POMI
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addition on ZP of hematite quartz and kaolinite slurries containing 10 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3

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ppm Fe^{3+} ions at 10.5 pH is shown in Figs. 6-8 respectively. It can be seen in Figs. 6-8 that with increasing the concentration of SHMP, CA and EDTA the ZP of the minerals continuously shifted to negative potential and reached to maximum when the ligands concentration reached to 1000 ppm. Above the 1000 ppm the ZP of the minerals reverse back.

The ZP of the minerals at 10 ppm, 100 ppm and 1000 ppm of SHMP, CA and EDTA is given in Table 1 from which it can be seen that with marginal difference the ZP of the each mineral followed reverse trend to the ZP of the minerals noted in absence of the POMI at

10.5 pH. The ZP results shown in Table 1 and Fig. 6, 7 and 8 indicate that with addition of 100 ppm SHMP the % recovery in the ZP of the hematite, quartz and kaolinite was 130.39%, 63.46% and 64.87% respectively. Whereas, by the addition of 100 ppm CA the % recovery of ZP of hematite, quartz and kaolinite was 121.47%, 25.69% and 69.5% respectively. In contrast at 100 ppm EDTA the recovery in ZP of hematite, quartz and kaolinite was hardly 42.01%, 47.78% and 37.36% respectively. These results advocates that SHMP has better efficacy to chelate with 10 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3 ppm Fe^{3+} ions as compared to CA and EDTA.
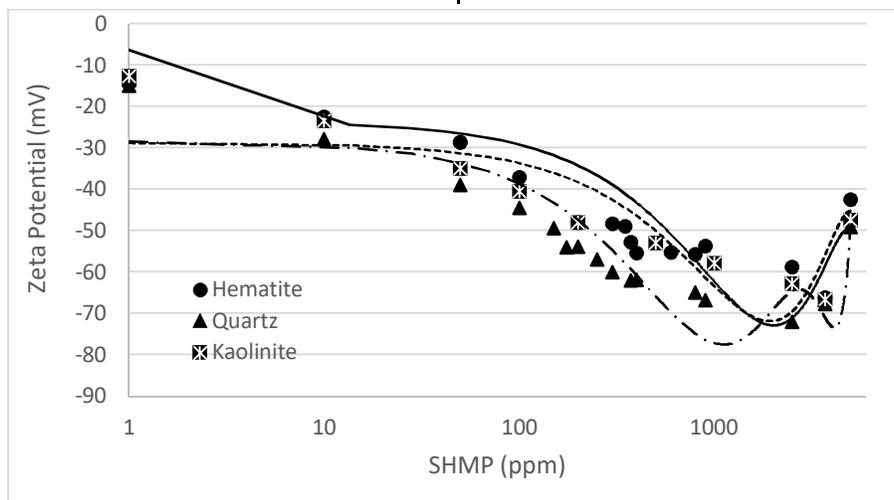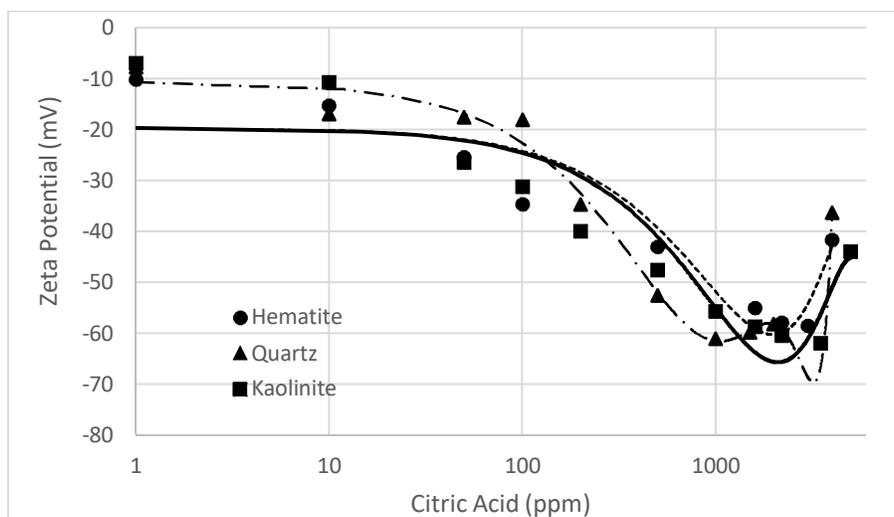

Fig. 6: Effect of SHMP on The ZP of Hematite, Quartz and Kaolinite at 10.5 pH

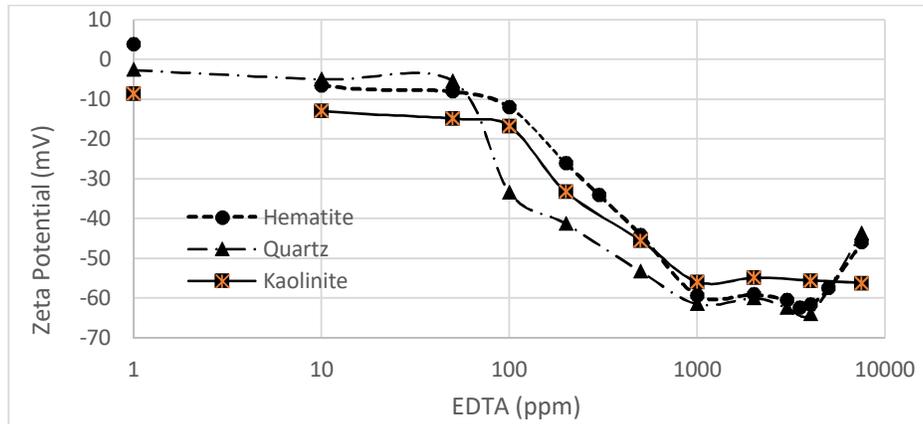Fig. 7: Effect of Ca on the ZP of Hematite, Quartz and Kaolinite at 10.5 pH

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Fig. 8: Effect of EDTA on the ZP of Hematite, Quartz and Kaolinite at 10.5 pH

Table 1: Influence of Ligands on the ZP (mV) of Minerals Containing POMI at 10.5 pH						
Ligand	SHMP					
Dose (ppm)	ZP of Hematite	% Recovery of ZP	ZP of Quartz	% Recovery of ZP	ZP of Kaolinite	% Recovery of ZP
0	7.65	-	3.16	-	-4.58	-
10	-22.33	78.63	-27.76	39.78	-23.3	52.12
100	-37.03	130.39	-44.32	63.46	-29	64.87
1000	-53.63	188.84	-66.73	95.55	-57.83	129.38
Ligand	CA					
Dose	ZP of Hematite	% Recovery of ZP	ZP of Quartz	% Recovery of ZP	ZP of Kaolinite	% Recovery of ZP
0	7.65	-	3.16	-	-4.58	-
10	-15.13	53.28	-16.83	24.06	-10.56	23.48
100	-34.55	121.47	-17.93	25.69	-31.06	69.50
1000	-52.01	183.09	-60.96	87.34	-55.56	124.31
Ligand	EDTA					
Dose	ZP of Hematite	% Recovery of ZP	ZP of Quartz	% Recovery of ZP	ZP of Kaolinite	% Recovery of ZP
0	7.65	-	3.16	-	-4.58	-
10	-6.36	22.40	-4.81	6.90	-12.95	28.85
100	-11.93	42.01	-33.35	47.78	-16.77	37.36
1000	-59.24	208.45	-61.45	87.965	-55.86	124.98
ZP at 10.5 pH in Absence of POMI	Hematite		Quartz		Kaolinite	
	-28.4		-69.8		-44.7	

4. CONCLUSIONS

Following conclusions were drawn from the effect of POMI and ligands on ZP of the minerals.

- Presence of POMI adversely affected the ZP of minerals and shrink the difference between the ZP. In absence of POMI at 10.5 pH the ZP of hematite, quartz and kaolinite was -28.4 mV, -69.8 mV and -44.7 mV. While in the presence of POMI +7.65 mV, +3.16 mV and -4.58 mV was the ZP of hematite, quartz and kaolinite respectively.

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- By the additions of SHMP, CA and EDTA the recovery in the ZP of the minerals was achieved. SHMP behaved quite effective to reproduce the ZP of minerals as compared to other two ligands.

- Throughout the concentration of ligand tested from 10pp to 1000 ppm none of the ligand produced minimum difference of ±30 mV in the ZP of hematite and gangue minerals quartz and kaolinite. Which meant that in presence of 15 ppm Ca^{2+}, 3 ppm Mg^{2+} and 3 ppm Fe^{3+} POMI it is conventionally not possible to selectively flocculate the hematite with NP. However, based on the % recovery of ZP the 10 ppm dose of SHMP can be supposed an optimal dose where quartz and kaolinite may be flocculated selectively.

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