

## Mineralogical Heterogeneity of Ore Particles and Its Effects on Their Interfacial Characteristics\*

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### SUMMARY

A significant proportion of the U.S. hematitic ores contain silica and other impurities in a very finely dispersed form. The mineralogical heterogeneity of the particle surface and sub-surface regions of such natural hematite and the effect of desliming treatments, are examined in this work using scanning electron microscopy, energy dispersive analysis of X-rays and Auger spectroscopy techniques. The implications of the observed mineralogical heterogeneity on interfacial properties such as zeta potential and adsorption, and on the validity of prior interpretations of results obtained for such properties are discussed. Specifically, the reasons for a lower isoelectric point of natural hematites than that of the synthetic hematite, and for the adsorption of anionic collectors on natural hematite above their isoelectric point, are explained on the basis of the concentration of impurities, as in this case silica and clay, in the surface region.

### INTRODUCTION

Selective adsorption of reagents on one or more minerals, in preference to others that are present in an ore, has been the basis for flotation and flocculation for beneficiation of ores. The degree of separation obtained in these processes depends essentially upon the degree of liberation of minerals during grinding. Minerals are not, however, usually fully liberated; as a result the ore particles remain heterogeneous. Under such conditions, a

knowledge of the nature of such mineralogical heterogeneity on the surface of particles, and that of the manner in which they affect the surface properties is essential for accurate elucidation of mechanisms involved in the interfacial processes.

In the past two decades, the interfacial processes, such as flotation and flocculation, have been correlated with the zeta potential of minerals. Thus, mechanisms of adsorption of surfactants have been studied by measuring the variation in zeta potential of minerals upon adsorption. While significant advance has been made along this line, particularly for synthetic minerals, confusion prevails for natural minerals with regard to the actual magnitude of the zeta potential of the mineral particles and the location of their isoelectric points. Widely differing values have often been reported by different authors for the same mineral. For example, isoelectric points ranging from 2 to 9 for various natural hematites [1, 2] and from 8 to 9.1 for synthetic hematite [2] have been reported. Such differences can arise from the natural variations in the crystal structure [3] or those produced during preparation [4].

In the case of natural minerals there can also be differences owing to the mineralogical or chemical heterogeneity of the particles either as a result of incomplete liberation, or because of the type of pretreatment, such as acid leaching, often used for cleaning the minerals. In the case of low grade iron ores, silica and clays are disseminated in a matrix of iron oxide; various ratios of silica to hematite can therefore result at the surface upon subjecting it to different treatments. With such ore particles, the measured zeta potential and isoelectric point will lie between the values for the individual minerals present in the particle surface region. The

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TABLE 1

Description of the mineral samples used and the treatments received by them

No.	Sample	Treatment received
1	½-in. hematite	Unwashed
2	½-in. hematite	Washed with distilled water several times
3	½-in. hematite	Washed with distilled water and treated with $3 \times 10^{-5}$ mole/l potassium oleate solution at pH 4
4	325/400 mesh hematite	Deslimed
5	Slimes	Obtained during preparation of sample 4
6	½-in. hematite	Ultrasonically treated

presence of a second mineral on the surface need not, however, affect the response of the original mineral to properties such as adsorption and flotation. Thus, adsorption of an anionic surfactant, for example oleate or alkylsulfate, on the siliceous hematite can have the same pH dependence as that for pure hematite (except for a difference in the total available surface area, and hence the magnitude of surfactant adsorbed in the complete pH range). However, the pH dependence of the zeta potential of it will be different from that of pure hematite or silica. Clearly, a correlation of results of electrokinetic studies with other interfacial properties for determining their mechanisms can, in such cases, yield misleading results. Such correlations are usually made using mineral samples hand-picked for impurity content. The purpose of the present study was to examine the chemical composition in the surface and sub-surface region of such a selected mineral sample, and its relation with the interfacial properties. A natural hematite sample was examined using scanning electron microscopy, low-angle X-ray analysis and Auger spectroscopy techniques before and after various pretreatments. The results obtained are correlated with the electrokinetic, titration and surfactant adsorption properties of the natural minerals.



Fig. 1. Typical scanning electron micrograph of an unwashed natural hematite sample (No. 1).



Fig. 2. Typical scanning electron micrograph of the washed natural hematite sample (No. 2).

## MATERIALS AND METHODS

Hand-picked pieces of massive natural Minnesota hematite sample (obtained from Ward's Natural Sciences Establishment) were used for this study. Chemical and X-ray analyses of the bulk sample showed it to consist of 94 wt.% hematite and the rest essentially quartz. Samples for tests were prepared by roll-crushing and sieving. The various size fractions used for the different studies are as follows: the fractions +4 mesh, 325/400 mesh and the slimes for the spectroscopic studies; the 35/65 mesh fraction for electrokinetic studies; and the 325/400 mesh fraction for adsorption and titration studies.

TABLE 2

Probe analysis of various hematite samples showing the effects of washing, desliming, and ultrasonic treatment: oxygen is excluded for calculation of the atomic percentages

Elements	Sample 1 Unwashed, at. %	Sample 2 Washed, at. %	Sample 4 Deslimed, at. %	Sample 5 Slime, at. %	Sample 6 Ultrasonically treated at. %
Fe	88.7	79.4	81.9	75.1	88.5
Si	8.4	10.3	10.6	10.5	7.7
Al	1.9	1.9	4.4	7.7	2.0
Na	—	4.1	0.5	1.5	0.7
Mg	0.9	3.4	1.7	4.9	0.9

Spectroscopic studies were conducted using unwashed, washed and ultrasonically treated samples, and slimes which resulted from the washing of 325/400 mesh hematite sample (See Table 1). Zeta potential and isoelectric point\* were determined using streaming potential [5] and microelectrophoresis [6] techniques, and point of zero charge\* was determined by titrating the mineral suspensions with acid or alkali. Adsorption capacities were determined using radioactive oleate [7].

## RESULTS AND DISCUSSION

The scanning electron micrograph of a typical region on an unwashed hematite sample (No. 1) is given in Fig. 1. The analysis showed an iron content of 88 at.%\*\* for the surface and sub-surface region (1  $\mu$ m thick), which is lower than the bulk concentration of 96%\*\*. Auger analysis of the surface region alone gave lower values in the range of 50 - 85%\*\*. Washing of the sample removed most of the slimes on its surface (see Fig. 2). A comparison of the results from the probe analysis of the unwashed and washed samples given in Table 2 shows a decrease in iron content upon washing, suggesting removal of hematite during that operation.

The heterogeneity of the surface was studied by analyzing different spots on the

same hematite particle, for example the spots E, G and H shown in Fig. 3. Probe analyses of E and G spots were similar and indicated them to consist mostly of Al and Si. Spot H, on the other hand, is composed mainly of Fe. Significant variation in chemical composition exists between various spots of sufficient magnitude to consider it as the result of mineralogical heterogeneity of the surface region. The effects of such variation of the surface region will be examined later.

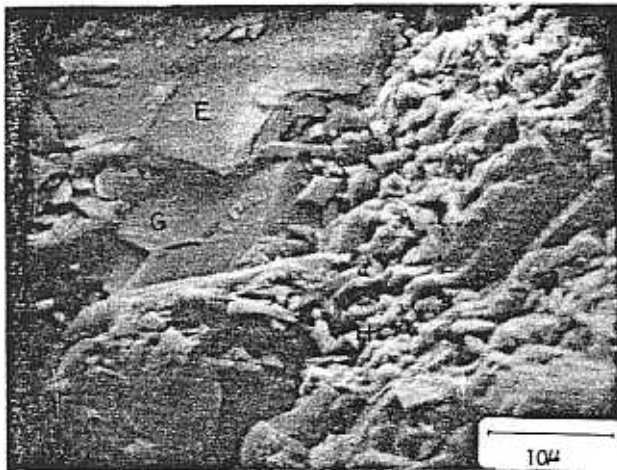
The distribution of Fe and Si on the surface of a washed hematite sample, shown in Fig. 4, suggests hematite and silica or clay to be intimately associated with each other. Liberation of the minerals in such samples for subsequent separation would obviously require finer grinding than is usually employed in their processing.

Slimes produced during mineral processing operations often respond poorly to most separation treatments, and yet they are the source of a huge loss of mineral values. Differences between surface regions of deslimed hematite samples and those of the slime derived therefrom were therefore studied. In addition to the presence of particles of various sizes and shapes, the surface and sub-surface of slimes were found to analyze higher in Mg, Al and Na than those of the deslimed sample (Table 2). This is possibly due to the presence of a large amount of clays in the slime fraction. Auger analysis of the surface of these samples also showed the presence of large amounts of Al and Mg (see Table 3).

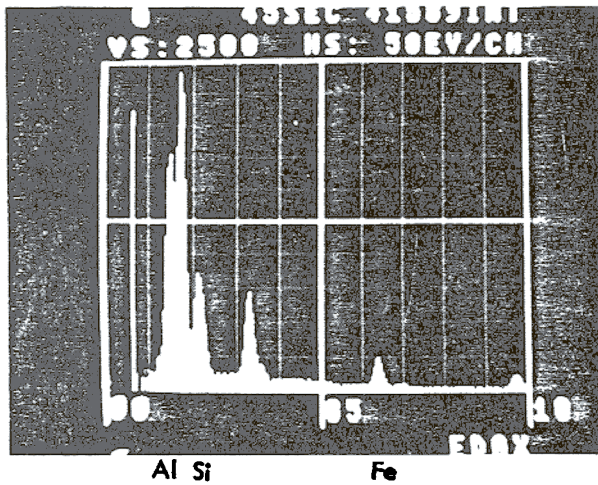
The effect of ultrasonic treatment on the hematite samples was to make the surface more uniform in appearance and pitted, and to cause a significant reduction in Si, Na and Mg, possibly due to removal of clay (see Fig. 5 and Tables 2 and 3). Whereas simple washing

\*While *isoelectric point* describes that condition of the system at which the potential at the plane of shear, *i.e.* the zeta potential as obtained from electrokinetic measurements, is zero, the *point of zero charge* refers to that at which the net surface charge is zero, and can be different from the isoelectric point [8].

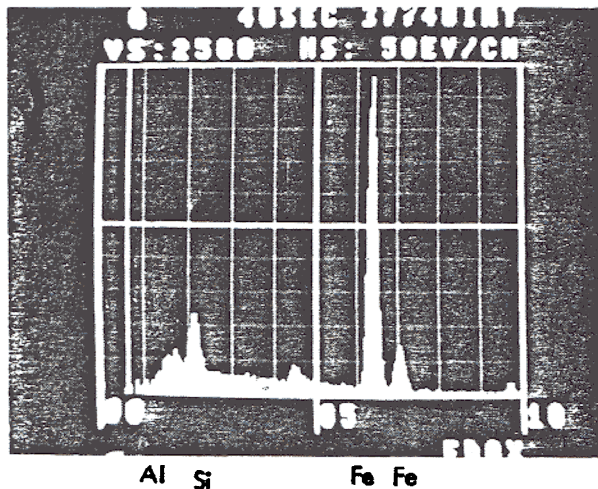
\*\*Oxygen and carbon are excluded for the calculation of the atomic percentages.



(a)

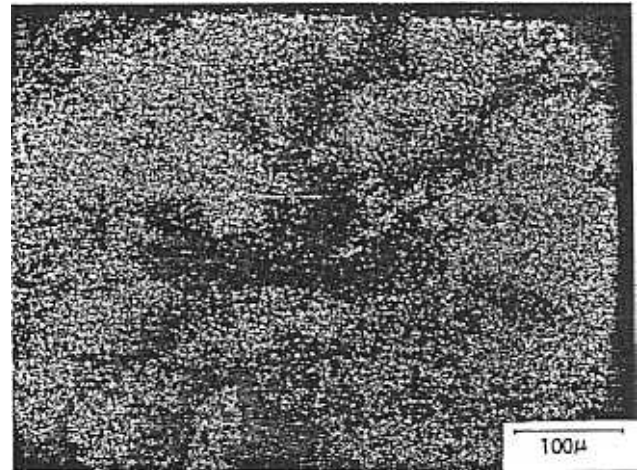


(b)

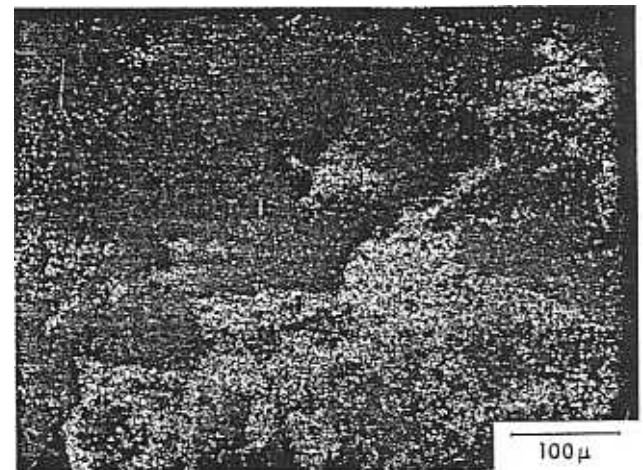


(c)

Fig. 3. (a) Scanning electron micrograph of a hematite sample on which spot analysis was conducted. (b) EDAX analysis of spot G shown in Fig. 3(a). Analysis of spot E was similar to that obtained for spot G. (c) EDAX analysis of spot H shown in Fig. 3(a).



(a)



(b)

Fig. 4. (a) Fe distribution, (b) Si distribution in a typical washed natural hematite sample (No. 2).

removed hematite slime only, ultrasonic treatment apparently removed clays also, changing the Fe content of the surface to approximately that of the unwashed samples. These results clearly suggest that even simple physical treatments such as washing or ultrasonic vibration can cause marked alterations in the surface chemical composition, which in turn can be expected to influence such surface properties as zeta potential.

The most important among the above effects is that of the surface chemical or mineralogical heterogeneity on the interfacial properties. The isoelectric point as determined by streaming potential and electrophoretic measurements of the natural hematite used in the present study was at about pH 3.0. The titration experiments, however, yielded a point of zero charge of 7.1. Also, a maximum

TABLE 3

Auger analysis of various hematite samples

Element	Sample 2 Washed, at. %		Sample 3 Washed and oleic acid treated, at. %		Sample 4 Deslimed, at. %		Sample 5 Slime, at. %		Sample 6 Ultrasonically treated, at. %	
	Excluding O and C	Including O and C	Excluding O and C	Including O and C	Excluding O and C	Including O and C	Excluding O and C	Including O and C	Excluding O and C	Including O and C
	Fe	73.2	22.0	34.6	11.1	50.8	24.5	40.8	16.9	76.9
Si	18.0	5.4	57.3	18.4	24.3	11.7	23.3	9.7	11.9	4.2
Al	6.8	2.1	5.6	1.8	13.9	6.7	26.6	11.1	9.2	3.2
Mg	1.5	0.5	1.7	0.6	3.0	1.4	7.1	2.9	0.85	0.3
Ca	0.5	0.2	0.8	0.3	6.8	3.3	2.2	0.9	0.3	0.1
Ti	—	—	—	—	1.2	0.6	—	—	0.85	0.3
O	—	37.2	—	19.5	—	50.6	—	54.8	—	43.4
C	—	32.3	—	48.3	—	—	—	1.7	—	20.8



Fig. 5. Typical scanning electron micrograph of an ultrasonically treated hematite sample (No. 6).

in the floatability of hematite using oleate, which in many earlier studies has been found to occur at its point of zero charge [9], was obtained here at pH 8 [7]. The above discrepancy between isoelectric point and point of zero charge can be explained on the basis of the mineralogical heterogeneity identified for the surface regions. The presence of silica on the particle surface in significant proportions has evidently caused a shift in the isoelectric point of the sample from that of pure hematite towards that of silica. However, values obtained for the point of zero charge from results of adsorption and flotation are expected to be much closer to that of pure hematite, since the magnitude of these processes is controlled mainly by the surface area and surface charge density of minerals, and since effective surface charge density of

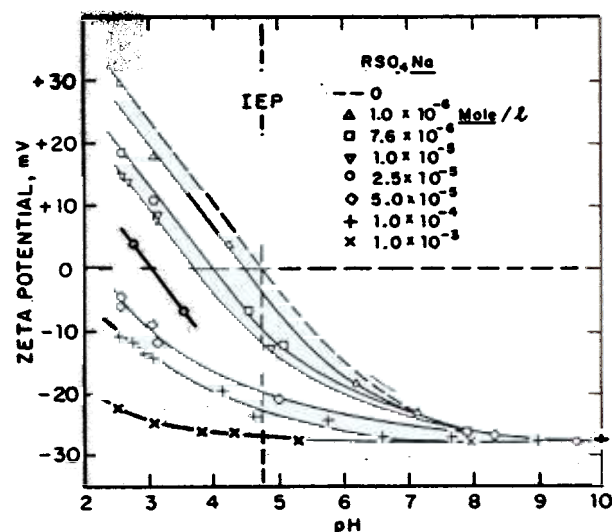


Fig. 6. Zeta potential of natural hematite in sodium dodecylsulfate solutions (data of Shergold and Mellgren [11, 12]).

hematite can be higher than that of the same amount of silica [10]. The difference in appearance between silica regions, E and G, and hematite region, H, in Fig. 3 might also be noted in this regard. Nature of adsorption of a surfactant such as oleate that adsorbs on hematite but not on quartz will be the same for natural hematite containing quartz and for pure hematite. It follows that the electrokinetic processes and adsorption processes can respond differently to the existence of mineralogical heterogeneity on the surface of a particle. Such differences in response reported in the literature, which have often been the source of misleading conclusions with regard to the mechanisms involved, can now be explained on the basis of the observa-

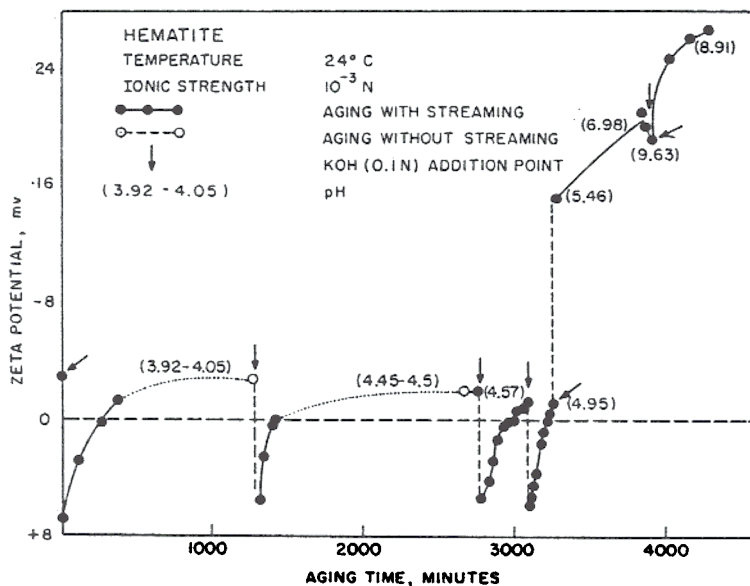


Fig. 7. Zeta potential of natural hematite as a function of aging time with intermittent addition of 0.1 M KOH solution.

tions made in this study. An interesting example is the observation by Shergold and Mellgren [11] that anionic dodecylsulfate adsorbs above the isoelectric point of their natural hematite sample when its particles are negatively charged. Their plot of zeta potential of hematite as a function of pH in the presence of dodecylsulfate is reproduced in Fig. 6 [11, 12]. The isoelectric point of this hematite is at pH 4.7. The increase in negative charge upon the addition of dodecylsulfate, even above the isoelectric point, suggests adsorption of the surfactant in that pH range also.

Similar adsorption of oleate on negatively charged alumina has been reported by Gupta and Smith [13]. The existence of such an adsorption of negatively charged collectors on negatively charged minerals has often been interpreted to suggest chemisorption, which is not of coulombic origin. In the light of the present discussion on the effects of mineralogical heterogeneity on isoelectric point, it is evident that such an interpretation is unnecessary. Though the isoelectric point of the natural hematite (which usually contains silica in it) used by Shergold and Mellgren [11] was 4.7, the hematite regions on the surface can be considered to be positively charged even in the pH region 4.7 - 8 so as to favour adsorption of sulfonate on it.

The complex electrokinetic behavior exhibited by natural hematite as a function of time can also be explained on the basis of the mineralogical heterogeneity. The change in zeta potential of hematite as a function of time with intermittent addition of alkali is shown in Fig. 7. Initially, a negative zeta potential was obtained for hematite at pH 3.5 - 3.6. Addition of potassium hydroxide solution changed the zeta potential to a positive value. With aging, however, the zeta potential reverted to a negative value. This behavior repeated itself several times until a pH of 5 was reached, above which addition of the alkali produced the usually expected increase in negative zeta potential. Generation of positive potential due to the addition of alkali is unusual, and is possibly due to the dissolution of silica from the surface by the added alkali and/or precipitation of hematite from solution upon the instantaneous increase in pH. Either phenomenon will result in a hematite-rich surface that is positively charged. During subsequent aging, a decrease in pH occurs and this can be expected to cause both reprecipitation of dissolved silica and redissolution of iron hydroxide. Both reactions will again cause the particles to be more siliceous on the surface and hence more negatively charged.

## CONCLUSION

(1) The mineralogical heterogeneity of the surface and sub-surface regions of hematite particles and slime was examined in this study, and the effect of the heterogeneity on their interfacial properties is discussed. Using low-angle X-rays and Auger spectroscopic techniques, hematite particles were found to be richer in silica and clay in the surface region than in the bulk, the proportion of minerals in the surface region being dependent upon the pretreatment that the particles received.

(2) Samples of natural minerals such as hematite exhibit complex interfacial behavior different from that of the pure or synthetic hematite. For example, negatively charged alkylsulfate adsorbs on natural hematite in measurable amounts even above its isoelectric point. Also, the electrokinetic behavior of natural hematite and its response to aging in certain pH ranges upon addition of alkali is unusual. Addition of alkali below pH 5 caused an instantaneous change of zeta potential to a positive value, which upon aging reverted to a negative value.

(3) The complex behavior of natural ore particles can be explained on the basis of the mineralogical heterogeneity of the surface and the concentration of impurities in the surface region. While the electrokinetic properties, such as isoelectric point, will be an average of those for the individual minerals present on the surface, adsorption properties, being the result of processes at a molecular level, can be characteristic of an individual mineral, if other minerals are inert towards the adsorbents. Adsorption, for example, of alkylsulfate on natural hematite can be considered as electrostatic in nature, even above its isoelectric point, if the effect of the concentration of silica or clay on the surface is recognized. Alternative mechanisms, proposed in the past, involving for example chemisorption, are unwarranted.

(4) The study emphasizes the need for monitoring of surface composition while studying interfacial properties of natural minerals, and for the recognition of the effect of the variation in chemical and mineralogical composition on these properties.

## ACKNOWLEDGEMENTS

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