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Can carboxymethyl cellulose be used as a selective flocculant for beneficiating alumina-rich iron ore slimes? A density functional theory and experimental study

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ABSTRACT

India has around 28.52 billion tons of hematite and magnetite ore reserves, over 20% of which is in the form of fines. Also during the mining, crushing and washing of ore, huge quantities of fines are generated, majority of which end up into tailing ponds owing to their high alumina contents (~10–15%). Selective dispersion flocculation is a promising route for beneficiation of such fine ores as opposed to conventional gravity and magnetic separation techniques; however, one requires selective reagents for effective beneficiation. We are engaged in the design and development of selective reagents for beneficiation of iron ores based on a molecular modelling approach. In the present study we have employed density functional theory (DFT) to calculate the interaction energy of hematite (0 0 0 1), goethite (1 0 0), gibbsite (0 0 1) and kaolinite (0 0 1) surfaces with carboxymethyl cellulose (CMC). The magnitudes of the computed interaction energies follow the trend:

Hematite > Goethite ~ Gibbsite ~ Kaolinite Al–OH terminated > Kaolinite Si–O terminated.

Electronic structure analysis revealed that the O-atoms in the hydroxyl and carboxyl groups of CMC form coordinate covalent bonds with surface Fe-atoms of hematite while forming only weak hydrogen bonds with goethite, gibbsite and kaolinite surfaces thus explaining the trends in the interaction energies.

These DFT findings were validated by experimental flocculation results which show that a final concentrate of 64.4% Fe, 4.2% Al_2O_3, and 1.9% Silica with a yield of 56% can be obtained from a feed containing 56.5% Fe, 7.0% Alumina, and 4.9% Silica.

Mineral wise estimation of chemical assay shows that CMC can be selective in flocculating hematite mineral particles over goethite, gibbsite and kaolinite. Our work thus highlights the important role of molecular modeling techniques such as DFT in screening and design of selective reagents for beneficiation of alumina-rich iron ore slimes.

1. Introduction

Huge quantities of slimes are produced during the mining and processing of iron ores, especially in India. Due to their high alumina content (10–15%), these slimes cannot be used for blast furnace operations because of the deleterious effects of high alumina contents on blast furnace operations. In current practice, these slimes are being dumped into massive tailing ponds. Consequently, a significant quantity of iron ore (~10–25%) containing ~40–60% Fe is wasted resulting in huge economic losses and as well as various environmental problems associated with the creation of tailing ponds (Pradip et al., 1993). In order to cope with the increasing global demand of steel, it is a need of the hour to develop efficient technologies for beneficiating these alumina-rich iron ore slimes. These slimes contain particles ranging from −37 μm to 150 μm which are difficult to separate using conventional methods such as magnetic separation, gravity separation and froth flotation. Several researchers have tried these techniques, but have found it difficult to get good grades with reasonable yields (Sarkar, 2011; Pal et al., 2010; Zhang and Chen, 2014; Suresh et al., 2012; Manna et al., 2011; Chaurasiya and Markandeya, 2012). Selective flocculation, owing to the finer size ranges of the slime particles, is a promising technique. However, its success is critically dependent on the appropriate selection of a selective reagent which can efficiently separate the gangue minerals.

In our earlier studies, we have demonstrated that using selective flocculation technique it is possible to beneficiate these fines and slimes

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having particle sizes even less than 37 μm with desired yield and Fe grade. Starch and guar gum have been used as selective flocculants for hematite and goethite (Gururaj et al., 1983; Hanumantha Rao and Narasimhan, 1985; Kumar and Mandre, 2015; Weissenborn et al., 1994; Mathur et al., 2000; Jain et al., 2017; Jain et al., 2013; Orumwense, 1994; Tammishetti et al., 2016; Tammishetti et al., 2014). Various other polymers such as polyacrylamide (PAM), polyacrylic acid (PAA), and Poly (ethylene oxide) (PEO) have also been used as flocculants (Somasundaran et al., 1988; Moudgil and Behl, 1993; Moudgil et al., 1995; Pradip, 1986). In a recent review, Shrimali and Miller (2016) have discussed in detail about application of polysaccharides as depressants for iron ores and their interactions with the minerals present in iron ores. There are a few experimental studies reported in the literature regarding carboxymethyl cellulose (CMC) as a flocculant and depressant for iron bearing minerals (Kumar et al., 2001; Praes et al., 2013). However, the underlying interaction mechanisms with the mineral surface at the molecular level have not been investigated. This is crucial for efficient design and development of tailor made reagents for selective flocculation. With the advent of high performance computers and development of sophisticated codes, molecular modeling techniques such as density functional theory (DFT) and classical molecular dynamics (MD) have made such studies very much possible today.

In the present study, we have investigated, using DFT, the interactions of CMC with the surfaces of the key minerals present in alumina-rich iron ore slimes, viz., hematite (Fe_2O_3), goethite, gibbsite and kaolinite. The interaction energies of CMC with the corresponding mineral surfaces were calculated and validate with experimental selective flocculation results obtained using iron ore slimes containing all the minerals studied theoretically.

2. Materials and methods

2.1. Computational methodology

The CMC-mineral surface interactions were modelled using DFT as implemented in PWscf code within the Quantum Espresso-5.0.2 package (Giannozzi et al., 2009). We have used the generalized gradient approximation of Perdew, Burke and Ernzerhof for the exchange correlation functional (Perdew et al., 1996). The ionic cores have been described by Rappe Rabe Kaxiras Joannopoulos's ultrasoft pseudo-potentials (Rappe et al., 1990). The Kohn–Sham wave functions were expanded using a plane–wave basis-set up to a kinetic energy cut-off of 25 Ry and charge density with a cut-off of 180 Ry. The bulk structures of hematite, goethite, gibbsite and kaolinite were relaxed until the total force on each atom was less than 0.01 eV/Bohr with Brillouin zone integrations sampled on Monkhorst-pack grids of 3 × 3 × 2, 4 × 4 × 4, 2 × 2 × 2, and, 5 × 3 × 4 k-points, respectively. The (0 0 0 1), (1 0 0) [Pnma system], and (0 0 1) cleavage surfaces were considered for hematite, goethite and gibbsite/kaolinite, respectively for the interaction energy computations as these are the principal cleavage planes for the corresponding minerals. The details of crystal structure and surface computations for all the four minerals studied here, are described in our previous publications (Jain et al., 2017; Jain et al., 2013). Owing to the large supercell sizes, all computations for the CMC-mineral surface interactions were performed on the gamma point. To avoid self-interaction, the surfaces were created by introducing a vacuum of 10 Å along the z- axis in the bulk structure of the minerals. The interaction energy was calculated using the following expression:

$$\Delta E = E_{complex} - (E_{surface} + E_{molecule})$$

where $E_{complex}$ is the total energy of the optimized complex structure (molecule + surface), $E_{surface}$ and $E_{molecule}$ are the total energies of the isolated mineral surface and molecule respectively. All initial structures were created using Biovia Materials Studio 4.1 (Accelrys Inc., 2006) and the optimized structures were plotted using XCrySDen (Kokalj, 2003).

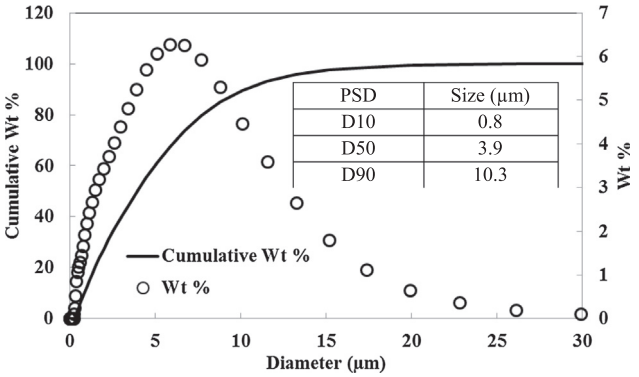

Fig. 1. Particle size distribution of the slime sample.

2.2. Experimental details

2.2.1. Materials

The iron ore sample was obtained from Barsua iron ore mine, Steel Authority of India Limited, Odisha, India. These were high alumina containing iron ore lumps which were crushed and ground to -37 μm size (- 400 mesh) in order to represent Indian iron ore slimes.

The particles size analysis was performed by Horiba LA 950 particle size analyser. It was found that approximately 90% of the particles was below 10.3 μm and the mean particle size was 3.9 μm Fig. 1. The slime sample was analysed by wet chemical methods (Raghavan, 2012) and found to have the chemical composition: Fe 56.56%, Al_2O_3 7.01%, Silica 4.91% and LOI 6.85%. The X Ray Diffraction pattern (Fig. 2), recorded using Shimadzu XRD 6000 and Cu Kα (wavelength 1.5406 Å) as radiation source, shows the presence of hematite (Fe_2O_3), goethite (FeO(OH)), gibbsite ($Al(OH)_3$), kaolinite ($Al_2O_3.2SiO_2{\cdot}2H_2O$) and quartz ($SiO_2$) in the sample. CMC and NaOH were procured from Merck India. All the experiments were carried out at room temperature in distilled water.

2.2.2. Methods

The series of steps involved in batch selective flocculation process is depicted in Fig. 3. The slurry of defined pulp density was prepared in distilled water and stirred at 159 RPM to suspend all the mineral particles. The pH was adjusted to the desired value and ultra-sonication was performed for 5 min to break the agglomerates present in the slurry, if any. After ultra-sonication, the pH of the slurry was found to decrease due to the formation of new surfaces. Hence, the pH was re-adjusted to the desired value and the slurry was left for pH conditioning for 15 min at 100 RPM. Subsequently, the desired dosage of flocculant was added and conditioning was allowed for 3 min at 40 RPM. The stirring was stopped and the flocs were allowed to settle for a specified time. The supernatant was decanted and both flocculated and supernatant portions were dried and analysed by wet chemical methods.

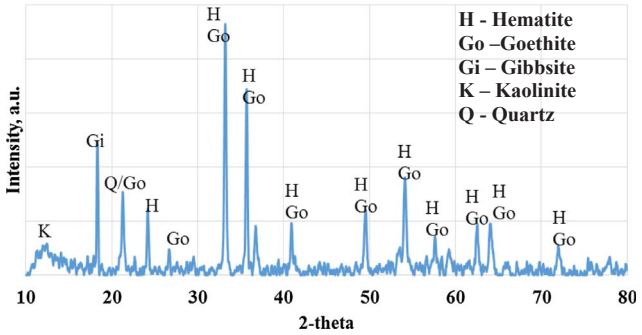

Fig. 2. X-ray diffraction pattern of slime sample.