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Guar gum as a selective flocculant for the beneficiation of alumina rich iron ore slimes: Density functional theory and experimental studies

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ABSTRACT

Current iron ore processing generates about 25% of very fine material called iron ore slimes. These slimes are being disposed into tailing ponds owing to their high alumina content (10–15%) despite having good iron values (45–60% Fe). Due to the rapid depletion of high grade iron ores, there is an urgent need to develop effective beneficiation processes for utilization of slimes. The very fine size of the slime particles (< 150 μm) makes selective dispersion-flocculation a promising route for their beneficiation. In this paper, we present our first principles density functional theory (DFT) results along with full factorial design of dispersion - flocculation experiments results on the beneficiation of iron ore slimes using guar gum as flocculant. DFT computations have been used to compute the interaction energies and explain adsorption mechanisms of guar gum with hematite, goethite, gibbsite and kaolinite surfaces – the main minerals present in the iron ore slimes. The computed results show that guar gum will be selective towards the hematite surface due to strong $Fe-O_{guar\ gum}$ chemical interactions as compared to only weak hydrogen bonds in the case of the other mineral surfaces. The experiments were designed to study the effect of the three key process parameters namely, pulp density, guar gum dosage and settling time on the beneficiation of iron ore slimes. The experimental data is used to develop models for prediction of yield, iron grade, % alumina and iron recovery in the concentrate. The models thus obtained are utilized to arrive at the optimized process parameters to achieve maximum iron recovery with acceptable iron grades with minimum alumina in the concentrates. These optimized process conditions shall form base line for further scale-up of the process at pilot/plant scale.

1. Introduction

India has rich reserves of iron ores. According to a recent report, India is the 4th largest iron ore producer in the world (Hazara et al., 2013). One of the most immediate technological problems facing the Indian iron ore industry is the processing of high alumina containing iron ore fines and slimes. Indian iron ores are rich in iron content but also contain high amounts of alumina (Al_2O_3) which is deleterious for subsequent processing in blast furnace (BF). The iron ore washing currently practiced in India leads to primarily three products: (a) coarse lumps (−40 + 10 mm) which are fed directly to the BF, (b) fines (−10 + 0.15 mm, 3–5% Al_2O_3) which are fed to the sinter plants and (c) slimes (−0.15 mm, 6–10% Al_2O_3) which, due to their high Al_2O_3 content present mostly in the form of kaolinite and gibbsite, are discarded as waste into tailing ponds (Pradip, 1994).

A high alumina-content in the BF feed significantly affects its productivity by increasing the slag viscosity and volumes. Besides, the higher Al_2O_3 contents in the Indian iron ore fines (3–5% as compared to less than 1% globally) also leads to poor quality of sinter – a standard feed to the BF (Chatterjee et al., 1992, 1993; Murty et al., 1994). Around 10–25% by weight of the total iron ore mined in India is currently being dumped in massive tailing ponds as slimes, posing enormous environmental hazard, apart from loss of millions of tonnes of iron ore values (Ravishankar et al., 1993). According to Weissenborn et al. (1994), the slimes have approximately 40–60% iron content. The recovery of iron values from the slimes will not only increase the overall efficiency of the process plants but also reduce environmental hazards arising out of creation of the tailing ponds.

The slimes contain ultra-fine particles of iron and gangue minerals for which the conventional separation methods such as gravity separation, magnetic separation and flotation, are ineffective (Panda et al., 2013). Selective dispersion-flocculation, although not yet used commercially for iron ore processing in India, is therefore a promising alternative to these conventional processes. Several polymers such as polyacrylamide (PAM), polyacrylic acid (PAA) and poly ethylene oxide (PEO) have been used as flocculants (Somasundaran and

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Ramachandaran, 1989; Moudgil and Behl, 1993; Moudgil et al., 1995; Pradip, 1986; Mathur and Moudgil, 1997). Starch-based materials and guar gum are the most commonly used natural non-ionic polymeric flocculants (Biggs, 2006). Being naturally available, both starch and guar gum are also bio-degradable, non-toxic and relatively cheaper compared to synthetic polymeric flocculants such as PAM, PAA and PEO. Starch consists of both straight-chained (amylose) and branched (amylopectin) components based on the D-glucopyranose units. On the other hand, guar gum consists of β-D-mannopyranose units linked to each other forming a straight chain with a pendant α-D-galactose unit connected to, on an average, every second mannose units. While starch can be obtained from a variety of natural sources like corn, rice and potatoes, guar gum is extracted from the seed of the leguminous shrub Cyamopsis tetragonoloba (Biggs, 2006). Starch has been already shown to be selective towards hematite (Ravishankar et al., 1993; Weissenborn et al., 1994; Gururaj et al., 1983; Rao and Narasimhan, 1985; Mathur et al., 2000; Jain et al., 2013). In this work, we study guar gum, as a selective flocculant for beneficiating alumina-rich iron ore slimes. One of the likely advantages with using guar gum as a selective flocculant, especially in the Indian context, is that India is the largest producer of guar with about 80% of the world production (Guar Industry Outlook, 2015). We aim to achieve a concentrate with less than 3.5% Al_2O_3 which can be utilized for steel making process.

We have performed first principles density functional theory (DFT) calculations to investigate the mechanism of guar gum adsorption on the surfaces of four main minerals present in the iron ores: hematite, goethite, gibbsite, and kaolinite and predict its performance as a selective flocculant. We followed these DFT computations with a laboratory scale design of experiments study to arrive at the optimized process parameters to achieve optimum Fe-recovery and grades with lower alumina content in the concentrate. We have considered the pulp density, flocculant dosage and settling time as basic variables and recorded their effect on Fe grade, yield and % Al_2O_3 in the final concentrate. The optimized process conditions shall form the basis for the further scale-up a pilot/plant scale.

2. Materials and methods

2.1. Computational methodology

DFT calculations were performed using the PWScf code as implemented within the Quantum Espresso (Giannozzi et al., 2009) package. The main objective was to compute the interaction energies of guar gum with the surfaces of iron and aluminum containing minerals namely, hematite, goethite, gibbsite and kaolinite, respectively, using the following expression:

$$E_{int} = E_{complex} - (E_{slab} + E_{molecule})$$

where $E_{complex}$, E_{slab} and $E_{molecule}$ are the PWScf calculated total energies of the optimized mineral-guar gum complex, mineral slab surface and the guar gum molecule, respectively. The more negative the value of E_{int}, the stronger will be the interactions with the corresponding mineral surface.

We have used the Perdew et al. (1996) generalized gradient approximation [GGA] for the exchange-correlation functional and Vanderbilt ultrasoft pseudo-potentials (Vanderbilt, 1990) for describing the ionic cores. The Kohn-Sham wave functions were expanded using a plane-wave basis-set with kinetic and charge-density cutoffs of 25 Ry (340 eV) and 180 Ry (2449 eV), respectively. The bulk crystal structures of hematite, goethite, gibbsite and kaolinite minerals were fully optimized 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. A force convergence cut off of 0.01 eV/bohr per atom was set for all structural relaxation calculations. The (0 0 0 1), (1 0 0) [Pnma system], and (0 0 1) cleavage surfaces were modeled for hematite, goethite and gibbsite/kaolinite, respectively. A vacuum of 10 Å in z direction was used for all the mineral surfaces. The details of mineral crystal structure and surface computations for hematite, gibbsite and kaolinite are described elaborately in our earlier publication (Jain et al., 2013). All computations for guar gum-mineral surface interactions, owing to the large system sizes with multiple supercells for each mineral, were performed on the gamma point. All the initial structures were created using the graphical visualizer of the Materials Studio 4.1 package (Accelrys, 2006) and optimized structures were plotted using XCrySDen (Kokalj, 2003).

2.2. Experimental details

2.2.1. Materials

The natural iron ore slime sample was obtained from one of the mines of M/S Tata Steel, India. The particle size distribution shows that more than 90% particles are below 10 μm (Fig. S1 in Supplementary Information). The sample was analyzed by wet chemical methods (Raghavan, 2012) and the composition was found to be 58.6% Fe, 6.9% alumina, 5.3% loss on ignition (LOI) and 4.1% silica. X-ray diffraction (XRD) pattern of the slime sample was recorded with Shimadzu XRD 6000 using Cu Kα (wavelength 1.5406 Å) as radiation source (Fig. S2 in Supplementary Information). The diffraction pattern confirms the presence of hematite (Fe_2O_3), goethite (FeO(OH)), gibbsite ($Al(OH)_3$) and kaolinite ($Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$) minerals. A slime slurry was prepared at a given pulp density (wt% solids) and its pH was adjusted using sodium hydroxide solution. Guar gum (procured from Ases chemical works, Jodhpur, India) was used as flocculant without any modification. The molecular weight range for guar gum is 50,000–8,000,000 Da. All experiments were carried out in distilled water prepared using Borosil distillation unit.

2.2.2. Methods

2.2.2.1. Selective dispersion-flocculation. The as received dry slime sample was added in 800 ml of distilled water for the preparation of a slurry at the desired pulp density. The slurry was stirred at 159 RPM for 15 min using DBK flocculator and its pH was adjusted to 10.5. This pH was found to be the optimum pH for flocculation with guar gum in our earlier studies (Tammishetti et al., 2014). The slurry was subjected to ultra-sonication for 5 min at 30% amplitude using Branson sonifier probe (Model: 102C). The pH of the slurry was further re-adjusted to 10.5 and stirring was continued for 15 min at 100 RPM. A measured volume of guar gum (flocculant) solution was added to the slurry while stirring at 40 RPM for 3 min. The flocs thus formed were allowed to settle for a designated time. Finally, the supernatant was decanted, and the concentrate (flocculated) and decanted portions (supernatant) were dried and analyzed by wet chemical methods.

2.2.3. Design of experiments (DOE)

Three parameters and three level full factorial DOE experiments were performed over process parameter namely, pulp density, flocculant dosage and settling time (Table 1).

A regression model (Ericksson et al., 2008) for the response considering three factors and two levels can be written as:

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{12} AB + \beta_{23} BC + \beta_{13} AC + \beta_{123} ABC$$

Table 1
Details of factors and levels for design of experiments.

Factors	Label	Levels		
		0	1	2
Pulp density (%)	A	1	10	15
Flocculant dosage (g/t)	B	300	600	1500
Settling time (min)	C	5	15	30

Total number of experiments for full factorial design = $(\text{levels})^{\text{factors}} = 3^3 = 27$.