Cleaner Production of Garnet Sand for Environmental Abatement.

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ABSTRACT

An improved process for the removal of surface coatings of garnet sand that create environmental hazard through dust produced during blasting/water-jet cutting applications is discussed in this paper. The process involves attrition scrubbing in the presence of surfactants and desliming by hydrocyclones. Decontamination of the surface was measured in terms of turbidity of the resultant water expressed in Nephelometric Turbidity Units (NTU). The turbidity of the resultant water was brought down to 30-60 NTU from the initial value of above 1,400 NTU by the above process. The qualitative improvement in surface cleanliness was also expressed in terms of change in surface energy of garnet grains as determined by contact angle measurements before and after the process. The conceptual flow sheet of the process along with the methodology for the estimation of surface contamination of garnet was discussed. Among the various detergents tried as scrubbing aids, the extract from pericarp (outer shell) of soapnut from *Sapindus emarginatus* was found to be most effective.

(Keywords: garnet sand, sand blasting, surface cleanliness, attrition scrubbing)

INTRODUCTION

Garnet sand is extensively used in abrasive water-jet cutting operations. Abrasive particles are driven by a jet of compressed air and are propelled at high velocities to the surface to be prepared. These abrasive materials, like garnet, remove old coatings, corrosion products, mill scale, and other debris and contaminants from the surface and prepare it for coating. The Schematic diagram of a typical open-air blast cleaning is shown in Figure 1. The evaluation process of industrial abrasive minerals characteristics as blast cleaning and water-jet cutting grades include three main steps: material characterization, aptitude test series on laboratory scale, and aptitude test series on pilot plant scale. Estimation of surface cleanliness of the product and dust production during operation is one of the important criteria in this series of tests to be met stringently by the suppliers of garnet. Also, the resultant water should be clean and environmental friendly.

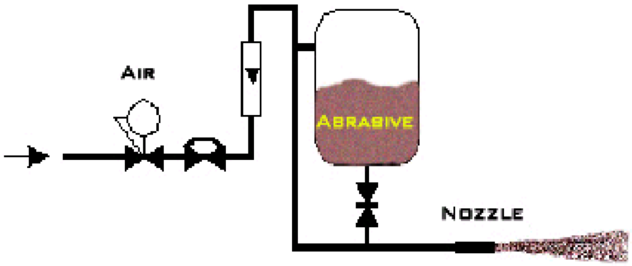

Figure 1: Schematic of a Typical Open-Air Blast Cleaning System.

Of late, there has been growing pressure on the garnet suppliers of the South Tamil Nadu coast of India on this count. In a recent study, it came to light that this problem also haunts the prospective garnet suppliers from the North Andhra Pradesh coast of India. The problem could be attributed to the surface coating of clay, silt, or ferruginous material formed during deposition of the minerals or due to degradation or weathering of silicates like feldspar forming clay which forms as coating on garnet sand grains. Most of the beach sand mining and mineral separation enterprises located in these two coastal areas have been practicing multi-stage washing in screw classifiers/washers, often with the addition of a liquid soap and multi-stage agitation in agitators, sometimes extending to longer duration. All of these efforts met with moderate success, falling way behind the requirements demanded by international buyers and environmental norms apart from consuming lot of water and power. In view of the above, National Metallurgical Laboratory Madras Centre (NML-MC), India had attempted to address the problems associated with garnet sand surface cleaning.

Mineral cleaning was being practiced by different people for various purposes. John Betts [1] gives an interesting account of different techniques practiced by mineral specimen collectors. Farmer et al. [2] studied the effects of ultrasound on surface cleaning of silica particles for the reduction of iron oxide from 0.025% to less than 0.012% Fe_2O_3 to make the material suitable for clear glass container ware that is suitable for table ware. It was pointed out that the cleaner surfaces achieved through the use of ultrasound is beneficial to the electrostatic separation of heavy mineral concentrates into their separate mineral components because of the removal of surface coatings which tend to mask the separation characteristics of the mineral grains. Clarke et al. [3] attempted mechanical (sonication or attrition by quartz) or chemical (pH change or use of complexing agent) methods to remove oxidation products from the surface of several sulfide minerals and studied their influence from flotation process point of view. They also showed that these “cleaning” methods were selective in removing oxidation products in mixed mineral systems.

Most of these cleaning methods were being adopted either on smaller scale as in the case of mineral specimen collectors or for elucidation of certain phenomena that take place prior to flotation process, etc. Hoyer et al. [4] made an important study to improve the quality of ilmenites by reducing the level of alumina-silicate coatings on the ilmenite grains. Their studies on batch and pilot-scale indicated that the Hicom mill can be used as a high-intensity attritioning device to successfully remove a significant proportion of the alumina-silicate coatings from the surface of ilmenite grains, leading to increased product quality and recovery efficiencies.

One of the widely practiced methods of sand cleaning is attrition scrubbing when the clay or silts are more tightly bound to the sand grains. For proper attrition scrubbing, it is important that the solid percentage of slurry is high so that there is good particle-to-particle contact and the viscosity of the slurry is low enough to allow the slurry to move freely in the attrition-scrubbing tank. The actual retention time can vary considerably depending on the amount and type of material that needs to be liberated. Attrition scrubbing circuits may also include more than one attrition scrubbing stage. In order to process the high percent solids slurry on a consistent basis on industrial scale, it is necessary to study the effect of the above parameters and optimize them on laboratory scale attrition scrubber. The generated data would also aid in scale-up and designing of industrial scale scrubbing-desliming circuit of required capacity.

Hitherto, surface cleanliness of garnet sand was being monitored empirically by those involved in quality control section. It was qualitative in nature and involved the visual assessment of the supernatant obtained when a particular quantity of the sand was mixed with a fixed volume of water. It was subjective, error-prone and misrepresentative. NML-MC has developed a new method to quantify the contamination associated with the sand in terms of turbidity units and change in surface energy, the details of which were given later.

MATERIALS AND METHODS

Materials: 200 kgs of the heavy mineral beach sand supplied by one of the leading garnet exporter was used for laboratory scrubbing and desliming studies. The specific gravity of the sample was 3.795. The sample contains 67.4% garnet, 12.6% ilmenite, and 20.0% other minerals. The turbidity of the resultant water under standardized conditions was 1400 NTU. The size distribution of the sand was shown in the Table 1.

Table 1: Size Distribution of Sand.

Size in μm	Weight retained, %
595	0.1
420	1.2
297	2.9
250	7.8
177	41.1
149	27.4
125	8.4
105	7.9
88	1.1
>88	2.1

Liquid soaps, commercially branded detergents, and the extract of pericarp (outer shell) of soapnuts from *Sapindus emarginatus* tree were used to aid the scrubbing. NaOH and H_2SO_4 were used to adjust the pH of aqueous medium.

Attrition Scrubbing: A laboratory scale attrition scrubber in the form of an attachment to Denver D12 laboratory flotation cell was used. A stainless steel attrition tank in rectangular shape, of 1-liter capacity, equipped with a cover to prevent splashing or spillage due to violent agitation of the slurry was used for scrubbing. The suspended stainless steel shaft is driven from a standard T.E.F.C motor (0.18 kW, 4 pole and single phase) with a comparable starter via a variable pitch pulley, permitting a range of operating speeds to be achieved. A tachometer was present to indicate shaft speed. The complete drive shaft assembly was mounted on a spring balanced, movable arm, which can be raised or lowered by a handle and can be locked in any position as required. The twin propellers provide maximum movement and scrubbing of the mineral particles.

A total of 350 cc of water was taken into the attrition tank and agitated over a period of 5 minutes. 1 kg of the sample was slowly fed into the tank. The required quantity of scrubbing aid (like NaOH, H_2SO_4, different brands of detergents, naturally occurring soapnut in the form of its extract etc.) was added. Scrubbing was performed at 1500 rpm for 5 minutes, which was found to be sufficient. At the end of scrubbing, the supernatant was decanted. Afterwards, the scrubbed sand sample was subjected to washing in the conventional flotation cell at lower percent solids with the same agitation mechanism for 5 minutes to clean the surfaces of sand as well as for further liberating the adhering clay and the resultant supernatant was decanted again. This cycle of scrubbing-washing was repeated again under similar conditions, but generally at reduced dosage of scrubbing aid. At the end of 2-stage scrubbing and washing, turbidity of scrubbed sand was measured to ascertain the necessity of further scrubbing. Turbidity of the dried sample was measured as per the procedure described later.

Desliming/Dewatering: All the dewatering tests were conducted in Mozley C700 Cyclone test rig. The C700 Hydrocyclone test rig is a mobile, self-contained unit for laboratory applications for Mozley small diameter hydrocyclones. A trolley mounted MONO Merlin pump is driven via 'V' belts by a 1.5 kW single or 3 phase electric motor. A polypropyline sump is fitted from which the pump delivers slurry under test to the hydrocyclone. A by-pass valve and pressure gauge enable accurate control of hydrocyclone operating pressure.

Feed slurry enters the hydrocyclone tangentially under pressure. As a result of the high centrifugal forces, particles coarser than the 'cut point' migrate into a primary vortex adjacent to the wall and move downwards to discharge with a small volume of water via a spigot/stub. Particles finer than the cut point migrate into a secondary upward moving vortex, along the axis of the hydrocyclone, and discharge with the majority of the water via the vortex finder.

The optimum conditions for desliming are governed by factors like hydrocyclone internal diameter, hydrocyclone length, cone angle, vortex finder diameter, feed pulp density and inlet pressure. The necessary optimum conditions were evaluated on a 2-inch hydrocyclone using different sized vortex finders, stubs / spigots. The operating pressure, in this case, was adjusted in such a way that minimum or no loss of feed solids takes place into the overflow.

2 kgs of sand was scrubbed in batches of 1 kg each in the attrition scrubber using suitable scrubbing aid at 74% solids and 1500 rpm for 5 minutes. The scrubbed sand was diluted to lower percent solids and fed to the cyclone test rig with various configurations of vortex finder and stub / spigot in order to evaluate the best combination for desliming. After the system attains equilibrium under the pre-set operating conditions, samples of overflow and underflow were collected simultaneously into weighed containers. The containers were re-weighed with their contents to obtain pulp weights. The samples were evaporated to dryness. From these, flowrates of solids, slurries and pulp densities of the samples were calculated.

Estimation of Surface Cleanliness: A fixed amount of dried sample (50g) was taken into a beaker and a fixed volume (100cc) of distilled water was added to it. The contents were stirred vigorously with a glass rod or the beaker can be inverted several times by closing its open-end with the palm. The resultant supernatant was checked for turbidity using a digital turbidity meter. A numerical display indicates the turbidity value. Higher values of turbidity (expressed as NTU, Nephelometric Turbidity Units) indicate higher contamination of the sample and lower values indicate cleanliness of the sample.

Sorption measurements were used for determining the surface energy of a powder/grains form solid using Kruss K100 tensiometer. The grains to be measured are filled into a glass tube with a filter base and this is suspended from the balance. After the vessel has contacted the liquid the speed at which the liquid rises through the bulk powder is measured by recording the increase in weight as a function of time.

RESULTS AND DISCUSSION

Attrition Scrubbing: Preliminary tests carried out to optimize the duration of scrubbing indicated that minimum of 5 minutes is required in a single stage to remove the clay/silt coating from garnet grains to a considerable extent. It was also observed that it requires multiple stages of scrubbing and desliming to get rid of the surface coating to achieve the required quality, as there was significant clay content in the form of surface coating. It was prudent to opt for two to three shorter scrubbing times with desliming in between, as it was found to be more effective than one long scrubbing time. This was because once the clay was liberated, the clay acts as a lubricant between the sand grains and therefore reduces the effectiveness of the scrubbing.

By removing the liberated clay slimes, and then adding another stage of scrubbing, the scrubbing circuit would be more effective. Multi-stage scrubbing with water alone did not yield the desired results. Thus it was found essential to add scrubbing aid for improving the efficiency of de-coating. Similarly, tests were conducted at 65%, 70%, 75%, and 80% solids by weight. When the solids percentages were lower at 65-70% solids by weight, there was sufficient water in the slurry to allow the particles to stay apart and prevent the necessary particle-to-particle contact required to scrub the clay from the surfaces. When the solids were 80%, the slurry was found to be too viscous and the impellers would not be able to move the slurry and in that condition the slurry did not adequately move and therefore particle-to-particle contact was not possible. It was found that the solid percentage of slurry within a range of 72-75% by weight was optimum for proper attrition scrubbing so that there was good particle-to-particle contact and the viscosity of the slurry was low enough to allow the slurry to move freely in the attrition-scrubbing tank. Keeping all these factors in view, test work was formulated with different combinations of scrubbing aids and varied number of stages of scrubbing and desliming/dewatering at 74% solids by weight and 5 minutes of scrubbing at each stage to achieve the objective.

A 2-stage scrubbing in aqueous medium/water of pH 5.0 (pH adjusted by adding H_2SO_4) with intermediate desliming reduced the turbidity from 1400 to 23 NTU which was quite satisfactory. There are two main uses while scrubbing with acidified water. It removes traces of shells (calcium carbonate) that are generally present in beach sand and aggressive removal of iron oxide stains/coatings on the surfaces of sand grains. Unfortunately, these advantages are offset by other factors such as difficulty in handling acids, corrosion of metallic components that come in contact with it during the process, and environmental compatibility with regard to discharge of acidified slimes into the surroundings.

Tests conducted under identical conditions at pH 10.0 (pH adjusted by adding sodium hydroxide) indicated that the turbidity could be brought down to 38 NTU. Sodium hydroxide could be a good alternative to concentrated H_2SO_4 in terms of ease of handling and to avoid the detrimental effect of acid on the equipment. Commercially available liquid soaps and branded detergent powders available in India (like Surf®, Tide®, and Ariel®) were also tested for their efficacy as scrubbing aids. Most of them responded well in reducing the turbidity in 2-stage scrubbing with intermediate desliming as shown in Figure 2.

Their action in removing the dirt / dust from the sand appears to be akin to their cleansing action on fabrics. It is to be noted, here, that pH of solutions of all commercial and branded detergents was in the range of 9.0 to 10.0 and the discharge or the sludge from the process would not be biodegradable and environmental friendly. This forced the investigators to search for further alternatives for scrubbing aids from cost, availability and environmental compatibility point of view.

A plant-based surfactant extracted from fruit pericarp (outer shell) of *Sapindus emarginatus* was tried as scrubbing aid. This is widely known as ritha and is the popular natural cleansing agent for Indians. This nut produces a rich and foamy lather when mixed with water that persists longer than sodium lauryl sulfate, the normal chemical surfactant. The fruit of this tree contains saponins which are claimed to be mild and can be utilized as cleanser and detergent. The detergent property in soapnut is due to the presence of triterpene saponins. The saponin content in soapnuts varies from 10 to 18% [5].

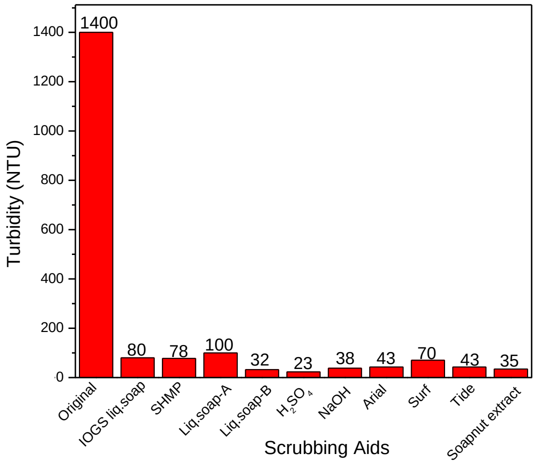

Figure 2: Scrubbing Aids.

Natural surfactant solutions are also known to enhance the aqueous solubility of hydrophobic organic compounds that may be found as surface coatings over the sand grains. Because of this, they were also being used in soil flushing/remediation [6]. pH of the solution made from soapnut extract was found to be 7.0 which was an indication that the process slimes/sludge that will be discharged would be environmentally more benign. Other attractive features of soapnut include their non-toxicity, availability in abundance and at relatively cheaper price, virtually no problem in handling and it is a renewable resource that can be grown in any type of wasteland. Figure 3 shows flow-chart for 2-stage scrubbing wherein the initial turbidity could be reduced to 35 NTU clearly indicating its efficacy in cleaning sand.

<u>Surface energy measurements:</u> Bulk powder/grains through which a liquid flows can be regarded as being bundle of capillaries. This means that for the calculation of the advancing angle, which corresponds to the contact angle between the solid and the liquid, the Washburn equation which applies to capillaries can be used

$$l^2 / t = (\sigma \, . \, r. \cos \theta) / 2\eta \qquad \textbf{(1)}$$

where,
l = flow front
t = flow time
σ = surface tension of liquid
r = capillary radius
θ = advancing angle and
η = viscosity of liquid

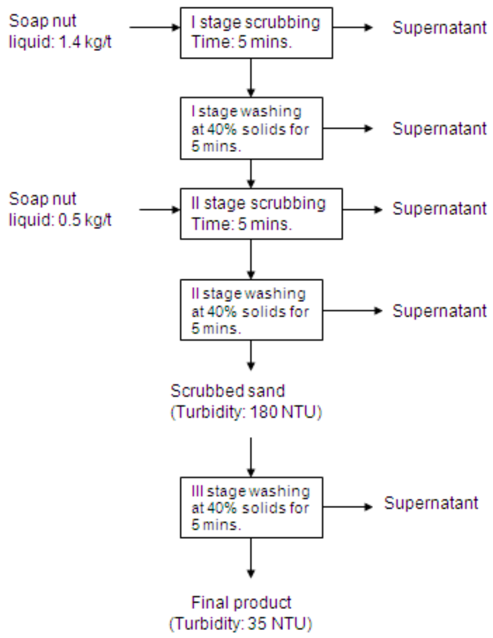

Figure 3: Flowchart for 2-Stage Scrubbing.

The capillary radius 'r' for bulk powder must be replaced by a quantity which describes the orientation of the microcapillaries 'c' and the mean radius. As a result 'r' is replaced by the constant (c.r), this applies to a particular powder.

$$l^2 / t = [(c. r). \sigma \ \cos \theta] / 2\eta \qquad \textbf{(2)}$$

This assumes that the bulk density of the powder is uniform.

As the flow front cannot be determined directly, it must be calculated from the measured increase in weight, the liquid density and the tube diameter. The viscosity and the surface tension of the liquid are known, only two unknown quantities remain: the required advancing angle (contact angle) and the material constant (c.r). A measurement with an optimally wetting liquid (hexane, whose advancing angle is virtually zero) was carried out first which gave a value for $\cos\theta$ of approximately 1. When the term $2\eta\, l^2 / \sigma$ is plotted against 't' a linear section is obtained whose slope is (c.r), (i.e., the required constant).

For measurements with other liquids this constant can be inserted into the Washburn equation, so that the advancing angle θ can be determined for other liquids. From the contact angle data the surface energy of a solid can be estimated by one of various methods like Equation of state, Fowkes, Owens-Wendt-rabel-Kaelble, Wu and Zisman. The contact angle was measured for garnet grains against a polar liquid (water) and a non-polar liquid (diido - methane) before and after scrubbing with soapnuts from *Sapindus emarginatus* and the resultant change in surface energy, which is an indicator of improvement in surface cleanliness, was calculated from the Equation of state approach. Thus the surface energy of garnet grains before scrubbing was found to be 40.4 mN/m. It increased to 50.0 mN/m after garnet was subjected to scrubbing, a clear indication of improvement in the surface cleanliness.

Desliming / Dewatering: By definition, desliming is the process that removes the >100 micron material. These slimes are generally clay type minerals that are detrimental. Although there are many different methods of desliming, only two are widely used in the industry: cyclones and hydrosizers. It should be noted that some conventional plants may still contain screw classifiers, but due to their high capital and maintenance costs they are not found in new plants.

Cyclones are low cost and effective in removing a majority of the slimes. The main criterion by which hydrocyclones differ is the diameter, measured across the top of the parallel section, before it meets the cone. The reason for different diameters being used is to provide for different separation forces necessary to achieve specific cut sizes. Considering the relatively coarseness of sand (80.5%, +150μm), a two-inch hydrocyclone was chosen for testing purpose with different vortex finder and stub/spigot attachments to accomplish desliming/dewatering of scrubbed sand. The objective was to see that to what extent slimes from the sand slurry generated during scrubbing could be eliminated with minimum feed solids carry over into the overflow and simultaneously a target underflow percent solids of 75% is achieved. In such a case, the underflow would be an ideal feed in terms of percent solids for subsequent scrubbing or for final discharge. It was found that hydrocyclone with stub attachment was superior to spigot attachment in dewatering the slurry with minimum carryover of feed solids into the overflow. Scrubbed sand that was fed at 24.3% solids and at volumetric flow rate (VFR) of 435.41 liters per hour to the cyclone (2-inch hydrocyclone whose vortex finder is 11.0 mm and stub 6.7 mm) resulted in an underflow of 75.2% solids with negligible amount of feed solids getting carried over into overflow. As much as 89.5% of water containing clay from the feed slurry could be removed in the process. The corresponding results are shown in Figure 4.

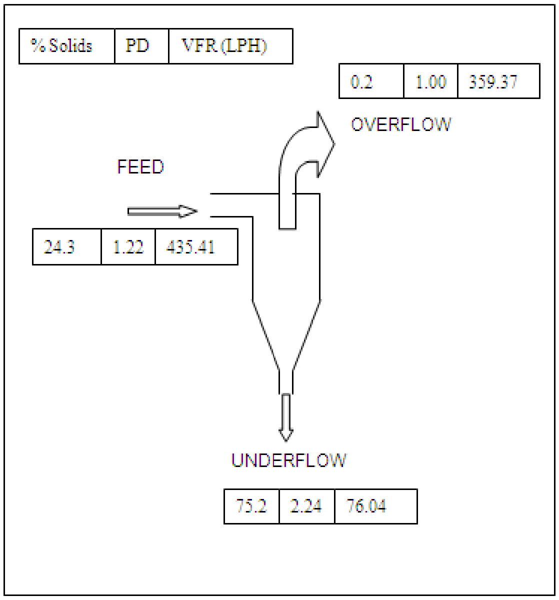

Figure 4: Cyclone Results.

CONCLUSIONS

Adopting a 2-stage attrition scrubbing with intermediate desliming by hydrocyclones can eliminate the surface contamination of the garnet sand. It was found imperative to use a scrubbing aid to enhance the scrubbing action. Among several scrubbing aids tested, the extract from pericarp (outer shell) of soapnut from *Sapindus emarginatus* was found to be the most suitable both in terms of effectiveness and environmental friendliness. The turbidity of supernatant of original sand which was 1400 NTU (an indicator of high contamination of garnet sand) could be reduced to 30-60 NTU(an indicator of very clean garnet sand) which is acceptable by the customers. This was further corroborated by the change in surface energy before and after scrubbing as measured from contact angle measurements.

It is anticipated that the results would improve further when operated consistently on industrial scale as the movement of the slurry passing through the pump and pipeline further loosens the small amounts of fines or clay that adhere to the sand grains. A conceptual flow sheet (Fig. 5) has been developed in order to implement it on industrial scale.

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