

FROTH FLOTATION AND ITS APPLICATION TO CONCENTRATION OF LOW GRADE IRON ORES

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INTRODUCTION

Froth flotation is a process used to separate minerals, suspended in liquids, by attaching them to gas bubbles to provide selective levitation of the solid particles. It is most extensively used process for the separation of chemically similar minerals, and to concentrate ores for economical smelting. Flotation is a selective process and can be used to achieve separation from complex ores such as lead-zinc, copper-zinc etc. Initially developed to treat the sulphides of copper, lead, and zinc, the field of flotation has now expanded to include oxides, such as hematite and cassiterite, oxidised minerals, such as malachite and cerussite, and non-metallic ores, such as fluorite, phosphates, and fine coal.

The flotation method of concentration, used extensively for other metal ores, has only recently been utilized for hematite iron ores. It can be applied as either the sole concentration process or as a final concentration stage to ensure a high-grade product.

In the flotation process, air is bubbled through a suspension of fine iron ore in water to which a small quantity of flotation reagent is added. This reagent modifies the surface of either the iron oxide or the principal gangue component, normally silica, so that these particles attach themselves to the air bubbles and are carried to the surface, where they are removed as a froth.

Flotation of iron ores can be done in two ways, 'direct' or 'reverse'. In the former, iron oxide is floated. Anionic reagents, such as petroleum sulfonates or fatty acids, are most commonly used. Structurally, these reagents have negatively charged ionic 'heads' attached to long-chain organic 'tails'. Adsorption of these substances on surfaces of the iron-bearing mineral particles causes them to float with air bubbles. Conversely, it is possible to float waste rock (mainly silica) with cationic reagents (positively charged heads) if the basicity is kept high (pH 11-12) and other organic depressants, such as starch or synthetic organic polymers, are added to prevent the iron oxide from floating. This is commonly referred to as 'reverse' flotation.

Normally silica is floated using an amine as the flotation reagent. But "reverse" flotation using anionic collectors is also applicable to activated rock minerals (e.g., Ca^{2+} activation of silica) whereby the iron-bearing minerals are depressed.

Much effort has been devoted to developing flotation processes for treating iron ores, particularly of fine-grained hematite varieties, but there are only few plants which are employing flotation on commercial scale for processing of iron ore. The most noted one is the Tilden Mine of Michigan, where amine flotation is used in addition to selective flocculation and desliming. But considering the present scenario the recent developments such as column flotation technology it should be possible to extend the

application of flotation technique to concentration of large reserves of low grade ores and fines.

PRINCIPLES OF FLOTATION

Froth flotation utilises the differences in physico-chemical surface properties of various minerals. After treatment with reagents, such differences in surface properties between the minerals within the flotation pulp become apparent and, for flotation to take place, an air bubble must be able to attach itself to a particle, and lift it to the water surface (Fig. 9.1). The process can be applied to relatively fine particles, as if they are too large the adhesion between the particle and the bubble will be less than the particle weight and the bubble will therefore drop its load.

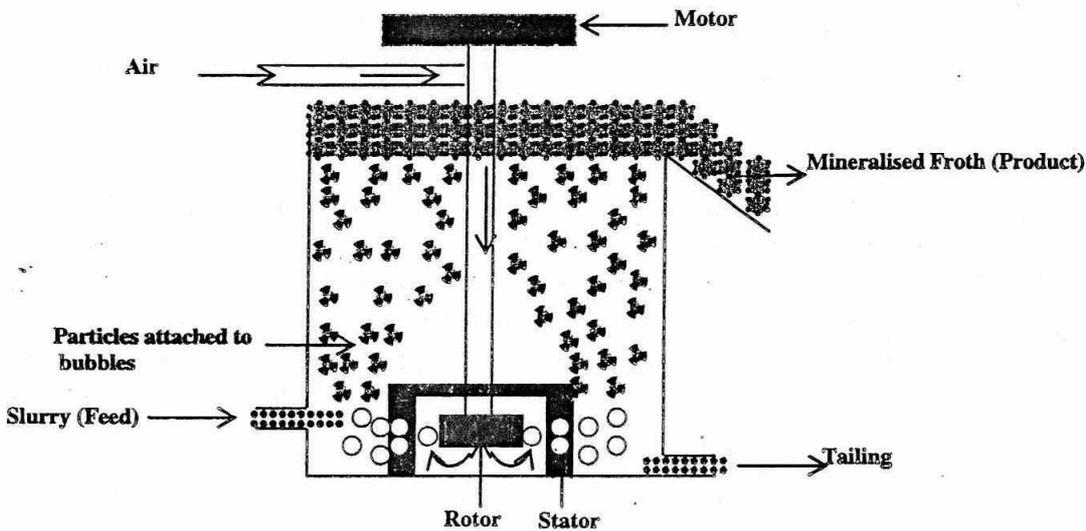


Fig. 9.1: Schematic representation of flotation process.

In flotation concentration, the mineral is usually transferred to the froth leaving the gangue in the pulp or tailing. This is direct flotation as opposed to reverse flotation, in which the gangue is separated into the float fraction.

The air-bubbles can only stick to the mineral particles if they can displace water from the mineral surface, which can only happen if the mineral is to some extent water repellent or hydrophobic. Having reached the surface, the air-bubbles can only continue to support the mineral particles if they can form a stable froth, otherwise they will burst and drop the mineral particles. To achieve these conditions it is necessary to use the numerous chemical reagents known as flotation reagents.

The activity of a mineral surface in relation to flotation reagents in water depends on the forces which operate on that surface. The forces tending to separate a particle and a bubble are shown in Fig 9.2. The tensile forces lead to the development of an angle between the mineral surface and the bubble surface. At equilibrium,

$$\gamma_{s/A} = \gamma_{s/w} + \gamma_{w/A} \cos \theta \quad (1)$$

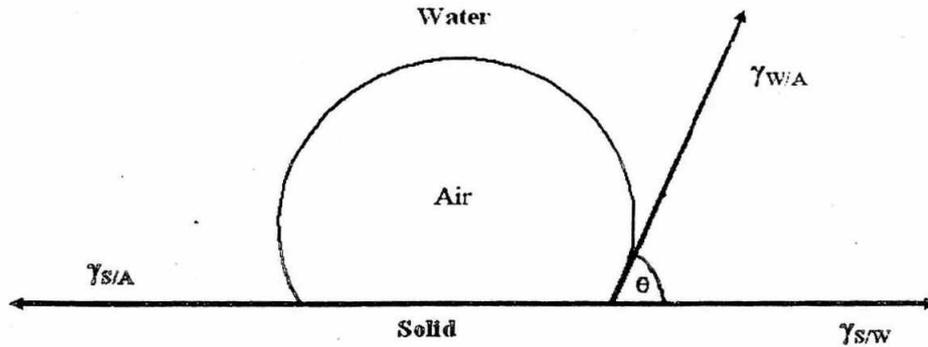


Fig.9.2 : Contact angle between bubble and particle in an aqueous medium.

Where $\gamma_{s/a}$, $\gamma_{s/w}$ and $\gamma_{w/a}$ are the surface energies between solid-air, solid-water and water-air, respectively, and θ is the *contact angle* between the mineral surface and the bubble.

The force required to break the particle-bubble interface is called the *work of adhesion*, $W_{s/a}$, and is equal to the work required to separate the solid-air interface and produce separate air-water and solid-water interfaces, i.e.

$$W_{s/a} = \gamma_{w/a} + \gamma_{s/w} - \gamma_{s/a} \quad (2)$$

Combining with equation (1) gives

$$W_{s/a} = \gamma_{w/a} (1 - \cos \theta) \quad (3)$$

It can be seen that the greater the contact angle the greater is the work of adhesion between particle and bubble and the more resilient the system is to disruptive forces. The floatability of a mineral therefore increases with the contact angle; minerals with a high contact angle are said to be aerophilic, i.e they have a higher affinity for air than for water. Most minerals are not water repellent in their natural state and flotation reagents must be added to the pulp. The most important reagents are the collectors, which adsorb on mineral surfaces, rendering them hydrophobic (or aerophilic) and facilitating bubble attachment. The frothers help maintain a reasonably stable froth. Regulators are used to control the flotation process; these either activate or depress mineral attachment to air-bubbles and are also used to control the pH of the system.

FLOTATION MECHANISM

The essential mechanism of flotation involves the attachment of mineral particles to air bubbles in such manner that the particles are carried to the surface of the ore pulp, where they can be removed. The process encompasses the following steps:

1. Grinding the ore to a size sufficiently fine to liberate the valuable minerals from one another and from the adhering gangue minerals.
2. Making conditions favourable for the adherence of the desired minerals to air bubbles.
3. Creating a rising current of air bubbles in the ore pulp.

4. Forming a mineral-laden froth on the surface of the ore pulp.
5. Removing the mineral-laden froth.

Although grinding of the ore is not, strictly speaking, a part of flotation, it does have an important bearing on the process. For optimum flotation results, the valuable minerals should be separated completely from the waste rock (gangue) and from one another in grinding step. In practice, however, this is not often economically feasible, and even when complete separation is attained, other complicating factors may arise. Thus, with the ordinarily used ball mill or rod mill grinding, considerable gangue slimes may be formed which will complicate subsequent flotation steps.

The creation of a rising current of air bubbles is accomplished by a flotation machine which are produced by the mechanical agitation of the ore pulp, the direct introduction of air under pressure, or both. These operations may be considered as the mechanical adjuncts of the flotation process.

FLOTATION REAGENTS

For effective flotation, generally three types of flotation reagents are used. They are collectors, frothers, and modifiers. Table 1 lists flotation reagents commonly used in iron ore processing. In addition to surfactants, a number of inorganic compounds are included. These are either used as pH regulators (lime, soda ash, sulphuric acid, caustic soda, etc.), activators (metal ions), or depressants (soluble silicates and sulfides and organic polymeric compounds).

Collectors

The collector is the most important reagent used in the iron ore flotation process. The function of the collector reagent is to promote affinity between mineral particles and air bubbles by formation of a water-repellent coating on the surface of the mineral particle. Most collectors in current use are heteropolar; i.e., they contain both a polar (charged) and a non-polar (uncharged) group. When attached to the mineral particle, these molecules are so oriented that the non-polar or hydrocarbon group is extended outward. Such orientation results in the formation of a hydrophobic hydrocarbon film on the mineral surface. Fatty acids, resin acids, soaps, and alkyl sulfates or sulfonates are the most commonly used collectors for iron-bearing minerals. Amines are mostly derived from fatty acids and resin acids; their acetate salts and condensates of fatty acids with alkylamines have been used in the past chiefly for flotation of silica and silicate minerals. Nevertheless, ether amines or diamines derived from alcohols and acrylonitrile are most suitable for iron ore treatment.

Frothers

Frothers, as defined by flotation operators, are compounds used specifically for creating a flotation froth. However, most collectors used in iron ore processing produce adequate froths. The general types of these frothing collectors include long-chain carboxylates, sulfonates or sulfates, and amines as listed in Table 9.1.

In practice the most widely used frothers in iron ore flotation are pine oil, aliphatic alcohols, polypropylene glycol, alkyl ethers of polypropylene glycol, and cresylic acids. The preferred alcohols are composed of five to eight carbon atoms such as

mixed amyl alcohols, methyl isobutyl carbinol (MIBC), and certain heptanols and octanols.

Modifying Agents

Modifying agents include all reagents other than collectors and frothers. Although the collector may be considered the heart of the flotation separation, it is the various modifying agents or modifiers that make it possible to adopt the relatively few collectors to a wide variety of mineral systems. The large number of different combinations used and their dependence on the mineral systems treated makes generalization of little value. Discussion of modifier practice is, therefore, restricted to the description of certain specific applications.

Depending on the main aspect of their action, the modifying agents are classified into different groups. Thus, the modifying agents are those additives, inorganic or organic in nature, which may be pH or to inhibit the flotation of either gangue minerals or the valuables depending on whether the concentrate is a froth product or not. Very often, a single product may fall into more than one grouping.

Considerable progress has been made during the past decade in increasing the selectivity of iron ore flotation. This has been brought about, in general, by the judicious application of old and new modifying agents.

Although the proper selection of a collector in a given flotation circuit is quite critical, it is also very important to make sure that modifying agents and frothers are chosen that will give maximum ease and control of operation, recovery of values, and selectivity of the mineral to be floated.

FLOTATION OF IRON ORES AND INDUSTRIAL PRACTICES

Flotation has been used for concentration of low grade ores containing siliceous gangue, which appears to be the most abundant type in the world and the reserves of which, when based on a minimum tenor of 30 to 35 % iron, amounts to a respectable quantity of milliards of tons. Following four reagent schemes have been used for separation of iron bearing and siliceous gangue minerals:

Table 9.1: Most commonly used reagents for iron ore floatation

Reagent	Classification and composition	Usual form of additions	Typical applications and some properties
Collectors	Fatty acids 1. Tall oil (mainly oleic acid) 2. Refined oleic acid 3. Na soap of fatty acids	Liquid emulsion Liquid emulsion 5-20% solution	Collectors for iron ore, readily precipitated by "hard" waters (Ca^{2+} and Mg^{2+})
	Alkyl sulfates and sulfonates C_{12} - C_{16} (dodecyl to cetyl)	5-20% solution	Collectors for iron ores
	Cationic reagents 1. Primary and secondary amines 2. Amine acetates 3. Quaternary ammonium salts 4. Ether amines and diamines	In kerosene 5-10% solution 5-10% solution Undiluted	Used to float SiO_2 Used to float quartz, silicates Used to float quartz, silicates Used to float quartz, silicates
Frothers	Pine oil (alpha-terpineol)	Undiluted	Provides most viscous stable froth
	Cresylic 'acid' (cresols)	Undiluted	Less viscous but stable froth; some collector action
	Polypropylene glycols DF (Dow Froth) 200	Solution in H_2O	Fine, Fragile froth; inert to rubber Slightly more stable froth than with D-200
	DF 250	Solution in H_2O	Slightly more stable froth than with D-250
	DF 450	Solution in H_2O	Controls froth properties
	Fuel oil	Undiluted	Fine- textured froth; frequently used with ores containing slimes
Conditioning agents	Aliphatic alcohols, e.g., MIBC	Undiluted	
	Lime (CaO) or slaked lime $\text{Ca}(\text{OH})_2$	Slurry	pH regulator
	Soda ash, NaOH	Dry	pH regulator; disperses gangue slimes
	Caustic soda, NaOH	5-10% solution	pH regulator; disperses gangue slimes
	Sulphuric acid, H_2SO_4	10% solution	pH regulator
	Ca^{2+} (CaCl_2)	5% solution	Activates silica with fatty acid collectors
	Na_2SiO_3	5-10% solution	Disperses siliceous gangue slimes; embrittles froth
Starch, dextrin	5% solution	Disperses hematite	
Quebracho, tannic acid	5% solution	Depresses CaCO_3 , $(\text{CaMg})\text{CO}_3$	

Flotation with Petroleum Sulfonate

In this case flotation is carried out at acid conditions ($\text{pH} = 3$) in the presence of fuel oil and sulfonate. Desliming is indispensable to obtain good results. The conditioning is done in a thick pulp (65 to 70 % solids).

Hanna Mining Company used the technique for beneficiation of iron ore from Groveland (Michigan) deposit. It was found that a small addition of fatty acid improved the metallurgical performance. The selected ore upgraded by gravimetry (3 stages of spirals). The gravimetric tailings constituted the feed for the flotation. The evolution of that plant (15,000 t/d) is typical for the imposed conditions.

Flotation with Fatty Acids

Flotation with sulphonates had to make way for flotation with fatty acids. The washing plant of Humboldt constructed for the sulphonate process by using fatty acids. The tests done are attractive to justify the change. The essential parameters of this flotation process are:

- (a) Desliming in the vicinity of 15 micrometres. This is carried by separation in cyclones in two stages.
- (b) Conditioning in thick pulp, if high recoveries are to be obtained with a minimum addition of collector.
- (c) The most selective fatty acid is oleic acid but the froth formed is difficult to operate. It is more attractive to use a tall oil composed of a mixture of oleic acid and linoleic acid. Moreover, the froth is controlled by the addition of a frother (MIBC).

The most characteristic example of this technique is given by the plant of the 'Republic Mine' which treats approximately 2,000 t/d of a specular hematite ore.

Flotation of Silica by an Anionic Reagent

The anionic flotation of silicates through the activation of silica by calcium ions was tested by several laboratories, in particular those of Hanna Mining and the U.S. Bureau of Mines, in the form of discontinuous tests as well as pilot circuits (at 900 kg/h).

This type of flotation implies a depression of the iron bearing minerals which are collected at the bottom of the cell. The reagents which are used most commonly are gums, various starches in the form of gels or causticized, and dextrans. The silica is floated in a basic environment by a fatty acid after activation by a calcium salt, usually calcium chloride.

The conditioning is done in stages in pulp concentrates ranging from 25 to 64% at a total duration of approximately 4 minutes. Lime can replace calcium chloride. It must be remarked that siliceous particles larger than 74 micrometres are difficult to float.

Flotation of Silica by a Cationic Reagent

After depression of the ferriferous minerals by reagents of the starch or dextrine family, the silica is collected by a cationic reagent normally without requiring activation by calcium ions, until at basic pH, the silica and the silicates have a negative surface charge.

The collectors are part of a large group of amines $R-NH_2$. At first used in the form of acetate or chlorhydrate of alkylamine, these reagents were difficult to administer,

specifically at the level of production: difficult dissolution once the alkyl chains were of the stearyl or oleyl type. Only the amines of the lauryl type showed a certain degree of ease of dissolution. The froth remained difficult to manipulate if the desliming was insufficient.

PLANTS USING FLOTATION IN THE CONCENTRATION OF IRON ORE

Flotation is used in a number of major iron ore concentration plants. As mentioned above, anionic flotation employing fatty acids or petroleum sulfonates are used to float the iron oxide minerals away from the waste material. Cationic flotation is used to upgrade fine concentrate by floating the siliceous waste materials away from the iron minerals.

A description of four plants utilizing flotation either as the primary method of concentration or in an auxiliary role in the upgrading of iron oxide ores are given in Table 9.2.

Table 9.2: Comparative data for four plants using flotation in concentration of iron ores

	Republic Mine	Empire Mine	Groveland Mine	Tilden Mine
Location	Republic, Marquette Co., Michigan	Palmer, Marquette Co., Michigan	Dickinson Co., Michigan	National Mine, Marquette Co., Michigan
Type ore	Specular hematite, minor Magnetite, martite chert	Magnetic cherty formation	Magnetite, hematite plus iron silicates and chert	Martite-chert with goethite and hematite
Process	Flotation	Magnetic concentration plus cationic flotation of concs.	Flotation, elutriation, magnetic concentration	Selective flocculation-desliming, flotation
Feed	36.5% Fe	22.5% Magiron	34.5% Fe	35.9% Fe
Concentrate	65.4% Fe, 4.95% SiO ₂	66.5% Fe, 6.48% SiO ₂	64.4% Fe, 6.3% SiO ₂	65.6% Fe
% wt recovery, concentrate	46	32.2	42.2	38.4

ADVANCED FLOTATION TECHNIQUES & SALIENT RESULTS ON PROCESSING OF IRON ORES

Column Flotation

Column flotation which employs a counter current flow of feed slurry and air bubbles has proved to be one of the most promising processes for the recovery of fines. This also has provision for cleaning of froth, leading to an appreciable, enhancement in the grade of the concentrate against the conventional flotation cell. NML has been

Jameson Cell

The development of Jameson cell has provided a new and radical approach to flotation technology. A schematic diagram of Jameson cell is shown in Fig. 9.4. In this cell the central portion of the conventional column cell has been replaced by downcomer. The feed slurry is forced through a nozzle forming a jet of slurry which draws air into the central downcomer. The aerated slurry is discharged into a tank and froth formed is washed by jets of wash water and finally collected in the concentrate launder. The first production cell was installed in 1989 in Mount Isa mines for the flotation of lead slimes and the cell is now being used for the treatment of coal, nickel, copper, zinc, antimony and also for removing organics from electrolyte solutions etc. Due to fast flotation kinetics and high grade of the concentrate, Jameson cell is finding acceptance in the mineral industry. The cell can be used for concentration of iron ore fines and slimes.

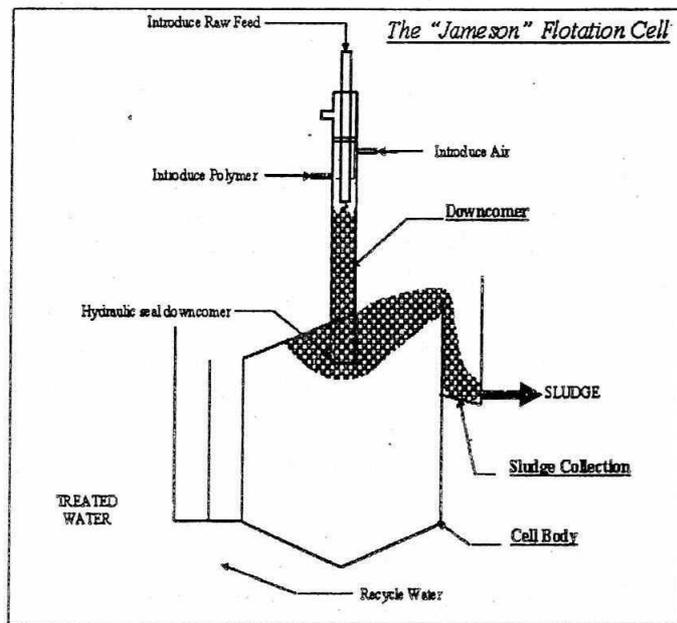


Fig. 9.4: Schematic diagram of Jameson flotation cell

Air Sparged Hydrocyclone (ASH) flotation

Development of the Air-Sparged Hydrocyclone (ASH) flotation has been under development during the past few years. The machine combines the froth flotation principles with the flow characteristics of a hydrocyclone, leading to a fast separation of minerals. The retention time of mineral particles in ASH is extremely short. In ASH flotation the ore slurry is fed tangentially through a conventional cyclone header into porous cylinder. This develops a swirl flow in radial direction; which is discharged through the annular opening located at the bottom of the ASH. Air is sparged through the jacket porous cylinder which allows attachment of bubbles with the particles. With a reduction in the tangential velocity of hydrophobic particles these are transported with the bubbles into a froth phase, supported by a froth pedestal and discharged as an overflow product. The hydrophilic particles are discharged as an underflow product through the annulus between the porous cylinder wall and the froth pedestal. The pilot scale ASH machine has been tested for the flotation of various

minerals such as copper, gold, coal etc. The machine gives comparable efficiency as that of conventional machines with an added advantage of fast flotation rate and high capacity.

PROCESS FOR BENEFICIATION OF FINE GRAINED IRON ORE FROM UKRAINE

Processing of finely disseminated ore poses specific problems in producing high grade concentrate. The beneficiation of such ores involves fine grinding to achieve liberation of valuable minerals from gangues followed by concentration involving multi-stage processing viz. magnetic separation, flotation, selective flocculation etc. The oxidized ferruginous quartzite deposits of Krivoy Rog area of Ukraine belongs to this category. Studies were undertaken at NML for beneficiation of typical iron ore sample from Ukraine.

Beneficiation studies of the iron ore sample (41.1% Fe) involving wet high intensity magnetic separation followed by froth flotation resulted in a high grade concentrate assaying 65.7% Fe with 80% iron recovery

SUPER-CONCENTRATION OF IRON ORE FOR HIGH-TECH APPLICATIONS

Ferrites are the mixed metal oxides containing iron oxide as their main constituent. For the manufacture of ferrites, super concentration of iron ore is required to achieve low level of impurities (alumina and silica) in the concentrate.

NML has undertaken studies on development of process for super-concentration of iron ore fines involving flotation and chemical beneficiation routes. Table 9.3 shows salient results on super-concentration of iron ore samples from different sources. The properties of the Mn-Zn and Ni-Zn synthesised using iron ore super-concentrate was found satisfactory.

CONCLUDING REMARKS

Flotation is a versatile technique for concentration of low grade ores and fines. Recently it has found in application in processing of low grade iron ore with siliceous gangues. Particularly with the development of column flotation technology there exists scope to produce high grade concentrate from low grade iron ore fines and slimes. Studies are to be undertaken on development of novel flotation reagents for effective separation of alumina bearing minerals from iron ores.

Table 9.3: Typical results on super-concentration of iron ore

Source	Feed Assay, %			Product			
	Fe	SiO ₂	Al ₂ O ₃	Wt.%	Assay %		
					Fe	SiO ₂	Al ₂ O ₃
Blue dust, SAIL	68.5	0.44	0.53	82.4	69.6	0.22	0.15
Iron Ore fines, Hospet, MSPL	62.9	4.16	3.50	40.7 (R1)	69.5	0.31	-
				59.0 (R2)	69.7	0.29	-
				45.4 (R3)	69.3	0.40	-
Blue dust, Ghatkuri Mines, Rungta Mines (P) Ltd.	67.7	0.85	0.26	77.9	-	0.50	-
Magnetite, KIOCL	63.5	7.90	0.38	85.7	-	0.80	-
				86.5 (R1)	-	0.27	-
				76-80 (R2)	-	0.05-0.15	-

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