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Physical, Chemical and Mineralogical Characterization of Fluorspar Flotation Tailings☆

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Abstract

The beneficiation potential of fluorspar tailings to produce high grade haematite pellets was investigated. Detailed characterisation of the tailings was carried out, where physical, chemical, and mineralogical and liberation properties of the sample were determined, with the aim of selecting a suitable beneficiation technique. The XRF results showed that the major oxide component in the sample is Fe2O3 (71.2 wt. %) with main gangue being silica (16.8 wt. %), calcium oxide (3.8 wt. %) and remaining oxides at <1 wt. %. The Fe present in the fluorspar tails as per XRF results was 49.89%. The XRD results showed that the sample is predominantly hematite with moderate quartz and minor amounts of goethite, magnetite and fluorite. The QEMSCAN BMA results showed a subordinate presence of goethite (9.76%), magnetite (5.91%), fluorite (6.21%) and hematite (60.83%). The sample had a grind size of 80% passing 155 µm with Fe concentration increasing in the finer size range, with majority of the Fe-oxide occurring between 10-70 µm. The Fe-oxide mineral liberation characteristics results indicated that 81.11% of the grains are full liberated, while 16.17% are the middlings and 2.72% locked in gangue. Based on the results and a requirement to make high iron grade pellets, reverse flotation method was selected for concentrating Fe in the fluorspar tails.

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Keywords: fluorspar tailing; haematite; characterisation; reverse flotation

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1. Introduction

Fluorite/fluorspar is a widely occurring mineral that occurs globally with significant deposits in many areas where it may occur as a vein deposit, especially with valuable metallic minerals. These valuable minerals usually end up in tailings during the concentration process. Recovery of valuable minerals from tailing ponds is a potentially profitable avenue in mining industries to reduce environmental impacts, reduce tailings disposal costs and increase company revenue [1]. The challenges of processing tailings are that they are generally of low grade, relatively fine particle size and hence cannot be used directly in a blast furnace [2]. According to Ghosh et al. [3] a low grade iron ore is characterized by low iron content and high content of alumina, silica, calcium, etc. Generally, iron ores with Fe content above 65% are desirable to achieve good productivity in the blast furnace. Impurities such as silica and alumina should be within permissible limit for better productivity and fluidity of slag in furnaces. The alumina/silica ratio in the furnace feed must be <1 and alumina content <2wt. %.

To avoid loss of valuable minerals to slimes, it has become increasingly attractive to upgrade the ore tails using the appropriate concentration method (gravity separation, magnetic separation and flotation) as pre-determined by the characterisation results [6]. Generally, gravity and magnetic separation methods are restricted to coarse grain size particles [12]. Research has been done on a number of processes to upgrade ore slimes or tails with the aim to recover the valuables economically. Srivasta et al [2] investigated feasibility of beneficiating iron ore slimes from the washing plants and tailing ponds of Kiribu mines, and found that the gravity concentration technique gave high recoveries of Fe for ores containing a substantial amount of goethite and iron content concentrated in the coarser particles. Umadevi et al [15] investigated the use of hydrocyclone, wet high intensity magnetic separator (WHIMS) and reverse flotation to concentrate iron ore slimes (d_{80}= <45µm) from a thickener assaying 46.7%Fe, 10.82%SiO_2 and 4.58% Al_2O_3. The findings revealed that gravity separation was unable to provide the required high grade concentrate. WHIMS method was able to provide the high grade concentrate at reduced recovery and reverse flotation achieved a concentrate of lower iron assay at high recovery [15]. Rao et al [10] recommend use of magnetic separation for ore that is not too fine and composed of magnetite/hematite. Flotation was recommended for ores that contain quartz of too fine grains [10]. Generally magnetic separation is of lower capacity when compared to flotation and the capital costs are generally higher, especially when the flotation circuit excludes the crushing and milling. There has been extensive advance in reverse floatation reagents with introduction of various effective reagents such as cationic, anionic, mixed collectors, activators and depressants which allows for flotation to be the best method for beneficiation of low grade iron ores [4-9, 13]

This study investigated characterization of fluorspar tails with the aim of identifying the possibility of concentrating the available valuable mineral, hematite, using the appropriate beneficiation technique as determined by the characterisation results.

2. Experimental

2.1 Materials and methods

A Fluorspar tailing sample obtained from a fluorspar mine in Pretoria, South Africa, was used in this investigation. The particle size distribution of the as-received sample was determined using Microtrac Partcicle Size Analyser (PSA) which makes use of the three precisely placed laser diodes to characterise particles from 0.02-2800µm. The chemical composition and mineralogy were determined using a Rigaku ZSX Primus II X-Ray fluorescence (XRF) and a Rigaku Ultima IV X-ray diffractometer (XRD) respectively.

2.2 Mineral distribution in different particle size ranges

The sample was classified into different size fractions, viz; +150µm, -150+106µm, -106+75µm, -75+53µm, -53+45µm, -45+38µm and -38µm. A Micromeritics AccuPyc III 1340 gas pycnometer utilizing N_2 gas was used to measure the density in these selected size ranges to determine valuable mineral distribution.

2.3 Loss on ignition tests

The moisture, organic and carbonates content was determined from the head sample using the loss on ignition

(LOI) method published by National Lacustrine Core Facility [17]. This procedure includes the burning of the head sample in an oven at 100^{o}C, then in the furnace at 550^{o}C and 1000^{o}C to obtain moisture, organic and carbonates content respectively. The loss on ignition was calculated as follows:

$$LOI, \% = \frac{Initial\ mass - Final\ mass}{Initial\ mass} x100 \quad (1)$$

Hematite is a crystalline mineral form of Iron III oxide, which is one of the several iron oxide. Water of crystallization may occur inside the crystal during crystal formation. The chemical state of this water will vary depending on formation stage. Presence of such hydration in the crystal structure will alter the surface properties of the crystal as it forms a film, thus impacting on the choice of mineral beneficiation technique. Presence of such water is characterised by high LOI values and high presence of oxyhydroxides such as goethite.

2.4 QEMSCAN Bulk Modal Analysis (BMA)

QEMSCAN Bulk Modal Analysis (BMA) was conducted on polished sections from the sample to quantify the mineral composition. In addition QEMSCAN Particle Map Analysis (PMA) was conducted on the polished section with an aim of characterising Fe-oxides in terms of the Fe-oxide grain size dimension, Fe-oxide liberation, Fe-oxide exposure and mineral association. QEMSCAN was used in combination with x-ray powder diffraction (XRD) and geochemical analyses to identify and quantify mineralogical characteristics of the tailings.

3. Results and discussion

3.1 Chemical assay and density distribution results

The fluorspar flotation tailings were analysed and the densities at different sizes fractions measured; and the results are shown in Table 1. Hematite (Fe_2O_3) content in the head sample was 71.2 wt. % and assayed as 49.8 wt. %Fe. The sample showed high content of silica 16.8 wt. % of SiO_2, subordinate concentration of calcium oxide levels at 3.8 wt. % CaO and 0.91 wt. % Al2O3. Remaining elements all occurred in concentrations <1 wt. %.

Hematite is found at a specific gravity of 5.3g/cm^3 and that of quartz is 2.66g/cm^3. The head sample had a specific gravity of 4.10g/cm^3, which showed there is appreciable amount of hematite in the sample.

Table 1**:** Density distribution and chemical analysis results

Description	Chemical assay (mass %)					Density (g/cm^3)
	Fe	CaO	Al_2O_3	SiO_2	F	
Head sample	49.80	3.80	0.91	16.8	1.55	4.09
150µm	35.85	10.58	1.46	30.26	3.63	3.51
-150+106µm	46.39	6.34	1.15	20.99	2.37	3.84
-106+75µm	52.70	4.10	0.93	15.38	1.40	4.10
-75+53µm	54.03	3.40	1.05	15.4	0.55	4.23
-53+45µm	55.86	2.60	0.83	14.04	0.35	4.25
-45+38µm	56.49	2.22	0.75	13.7	0.23	4.31
-38µm	57.90	2.55	1.15	9.96	0.66	4.42

The density at different size fractions, shown in Table 1, indicates that the density increases as particles becomes more finer, where 3.51g/cm^3 was obtained at +150µm size fraction and 4.42g/cm^3 obtained in the -38µm size fraction. From these results it was anticipated that the hematite will be more concentrated in the finer sizes. The density results were collaborated by the XRF results where 35.95wt%Fe was found in the +150µm and 57.90wt%Fe in the -38µm. The hematite (Fe_2O_3) content in the head sample was measured as 71.2% and assayed as 49.8%Fe. The sample showed high content of silica 16.8%, subordinate concentration of calcium oxide levels at 3.8wt%CaO and 0.91wt% Al_2O_3. Remaining elements all occurred in concentrations <1wt%.

Discard of the finer size range will result in high metal loss since the valuable mineral in this case is concentrated in the finer size range. The results depicted by density and chemical assay analysis eliminates the use of gravity separation and magnetic separation techniques since the fluorspar tailings will require uneconomic settling times during gravity separation and is not coarse enough for effective magnetic separation.

3.2. XRD analysis

Results of the mineralogical analysis of the fluorspar tailing sample are shown in Table 2 and Figure 1.

Table 2: Semi-quantitative mineral abundances determined from XRD.

Mineral Name	Approximate chemical formula	Abundance (wt %)
Hematite	$Fe^{3+}{}_2O_3$	>50
Quartz	SiO_2	10-20
Geothite	$Fe^{3+}O(OH)$	3-10
Magnetite	$Fe^{3+}{}_2Fe^{2+}O_4$	3-10
Fluorite	CaF_2	3-10
Siderite	$Fe^{2+}(CO_3)$	≤3
Pyrite	$Fe^{2+}S_2$	≤3
K-feldspar	$KAlSi_3O_8$	≤3
Monazite	$(Ce,La,Nd,Th)PO_4$	≤3

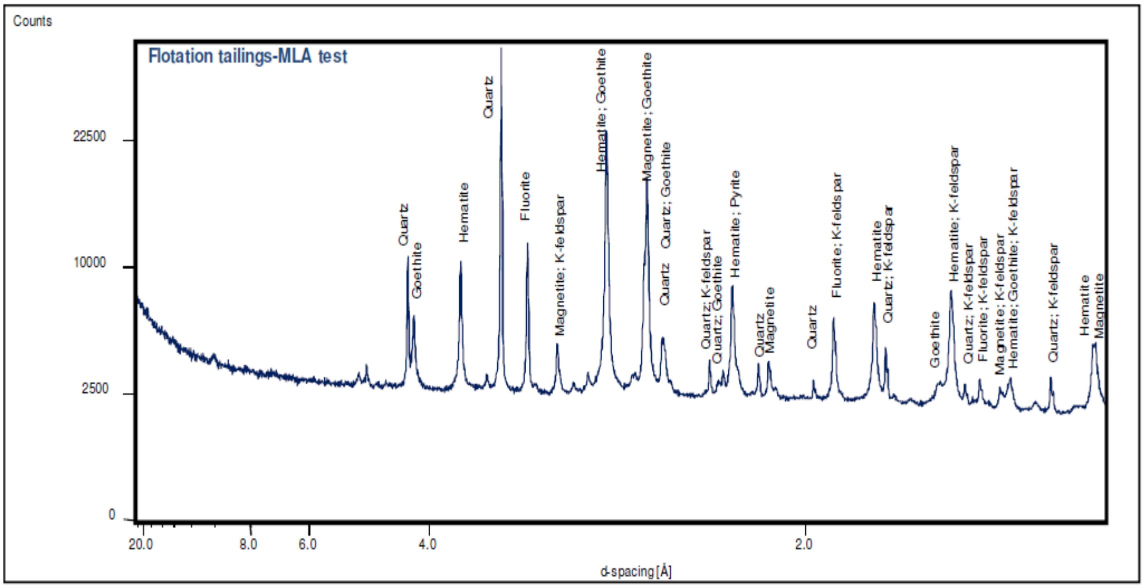

Fig. 1: Fluorspar tails XRD pattern

The results depicted in Table 1 and Figure 2 indicate that the head sample is composed predominantly of hematite at >50%, with quartz being the main gangue at 10-20%. The sample also contains minor amounts of goethite, magnetite and fluorite, at 3-10%. Trace minerals within the sample are made up of pyrite, K-feldspar and monazite.

3.3 Particle size analysis

The size distribution of a fluorspar is shown in Figure 2. It can be seen that the sample is fine with 80% passing 155µm. It was also observed that 10% of the particles are <20µm and 30% of the particles are between 34-80µm. This confirms that the sample is a flotation tailing and has been milled since it is of fine texture.

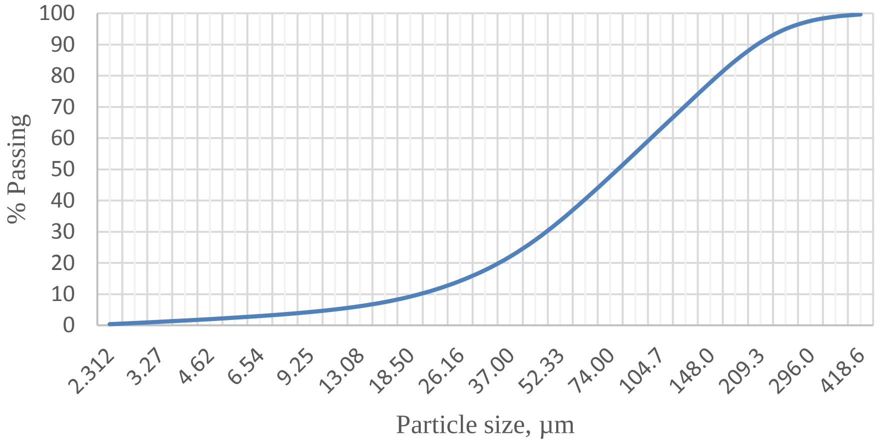

Fig. 2: Particle size distribution of the studied sample

3.4 Loss on ignition results

The total LOI obtained from the head sample was 2.7wt%. From these results it was anticipated that the iron would be present in predominantly oxide form. Leonel and Peres [16] investigated the impact of high LOI in the pelletizing of iron ores. Their research concluded that low grade iron ores with LOI above 3.5wt% present challenges of decreased yield in the beneficiation stage and high loss of productivity in the pelletizing process. The resulting LOI of 2.7wt% would permit usage of flotation as a better Fe concentration method, since negligible alteration to minerals surface properties is anticipated. This alteration could be due to remarkable presence of goethite and carbonates/sulphides.

3.5 QEMSCAN Bulk Modal Analysis

The BMA results were consistent with both chemical assay and XRD data since it revealed that the fluorspar tails sample is dominated by iron oxide, mainly hematite (60.83wt%) followed by minor goethite (9.76wt%) and magnetite (5.91wt%) as well as an iron carbonate in the form of siderite (0.54%). These results are in agreement with LOI predictions whereby data revealed that the fluorspar tails sample will predominantly contains iron oxide. The QEMSCAM BMA results are also in agreement with XRD results displayed in Table 2. BMA results further revealed the sample was composed of quartz with minor fluorite (6.21wt %) which accounts for the other major mineralogical phases. The remaining components all occurred in concentrations <1wt%.

3.6 QEMSCAN PMA results: Grain size dimension

The grain size distribution shown in Figure 3 indicated that the largest portion of iron oxides (12.04wt %) occurred between 40-50µm and that the majority of Fe-oxide in the sample occurred between 10-70µm. These results agree with the XRF results which depicted that majority of Fe-oxide in finer size ranges. The finer grinds which contain low grade iron are difficult to treat with other techniques hence flotation has become a separation technique of choice in processing of low grade ores and tailings [14]. Flotation is the usual concentration method for fine size range ores (<149µm) [6].

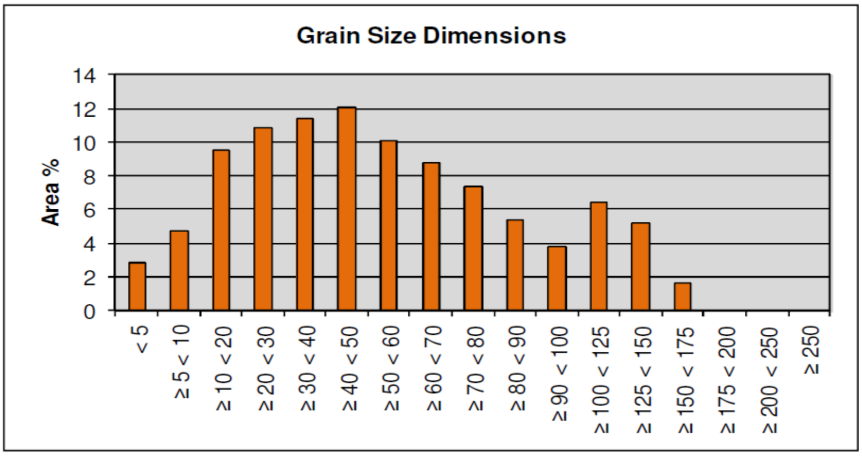

Fig. 3: Grain size dimension

3.7 QEMSCAN PMA results: Mineral liberation analysis (MLA) results

The exposure classes and liberation characteristics are explained in Figure 4 and Figure 5 below.

Fig. 4: Exposure classes

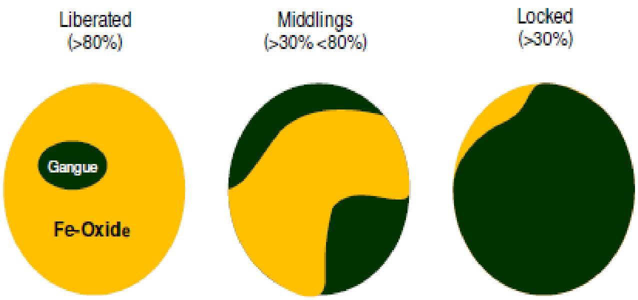

Fig. 5**:** Liberation characteristics

The mineral exposure and liberation characteristics shown in Figures 6 indicates that majority (81%) of Fe-oxide within the sample occur within ≥80% exposure class and that >80% of the Fe-oxide particles are liberated.

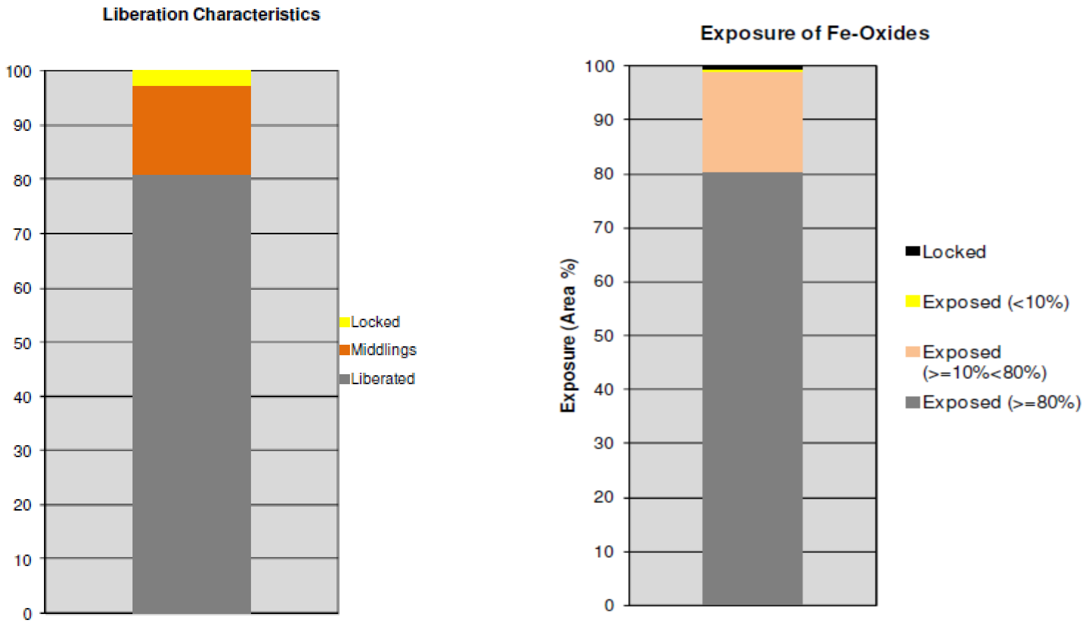

Fig. 6, 6(a): Liberation characteristics of Fe-oxides; 6(b) Exposure characteristics of Fe-oxides

Figure 6a further showed that 16.17% of the Fe-oxide occurred as middlings while <2.72% was found locked in gangue. Figure 6b further showed that~18% of the Fe-oxides occurs within the ≥10 %< 80% classes and only 0.5% of all Fe-oxides occurred as locked particles. Due to iron oxide concentrated in the finer size range and the fact that >80% of Fe-oxide occurs as liberated there is no need for further grinding of the fluorspar tailings.

5. Conclusions

The focus of the above investigation was to characterise Fe-oxide within the fluorspar flotation tailings in terms of physical and chemical properties, mineralogy, grain size dimension, liberation and exposure at a grind size of 80% passing 155µm. The conclusions drawn from this study are as follows:

- Mineralogical analysis by XRD and chemical assay show that the sample is predominantly composed of hematite at 71.2wt% with main gangue being quartz at 16.8wt %. The sample was classed as low grade iron ore due to low Fe grade (49.8wt %) and high silica (16.8wt %) content.
- Other Fe-oxides within the sample include goethite (9.7%) and magnetite (5.91%) which accounts for 11.49wt% and 7.99wt% of the total Fe respectively.
- QEMSCAN PMA shows that the majority of Fe-oxides within the sample occur between 10-70µm. Liberation characteristics of the Fe-oxides showed that~81% of all Fe-oxide were liberated, hence no need for further grinding.
- From the characterisation results it was concluded that reverse flotation is the suitable separation process to concentrate the Fe in the fluorspar tailing to acceptable levels of 65wt%Fe required in blasting furnaces. Reverse cationic flotation is generally recommended for beneficiation of low grade iron ores due to its high flotation rates and high selectivity [11].

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