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Tertiary enrichment of a manganese oxide tailings material using heavy medium separation (HMS)

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Abstract

A study was conducted on the enrichment of manganese oxide tailings material generated from sorting spiral concentration at Ghana Manganese Company (GMC) Limited, Nsuta. The investigation explored mineralogical and particle size characterisation and heavy medium separation technique. Analytical methods used include; X-Ray Fluorescence and Atomic Absorption Spectrometry (AAS). The material contained 9.01% Al_2O_3, 27.43 % SiO_2, 23.64% MnO_2 and 9.86% Fe_2O_3, the other oxides range between 0.04 to 1.55 %. By treating the individual size fractions at a bath density of 2.96, the highest ratio of concentration of 3.56 was obtained at 180 µm, while the highest enrichment ratio of 1.84 and manganese grade of 38.25% were obtained at 1180µm respectively. These qualify the enriched material as suitable for Ferro-alloy industry.

Keywords: Manganese oxide; As-received tailing materials; Representative sample; Enrichment ratio; Ratio of concentration; Dense medium

Introduction

Extraction of manganese ore in the Ghana Manganese Company (GMC) Limited mine, Nsuta, began almost a century ago. This occurrence is generally composed of both manganese oxide and carbonate; chiefly pyrolusite (MnO_2) and psilomelane ($BaMn_9O_{16}(OH)_4$), and rhodochrosite ($MnCO_3$) mineral types. Records indicated that between 1916 and 1985 the mine has produced manganese oxides worth more than 27 million tonnes of high grade (52% Mn), low grade (48-50% Mn) and other grades (46% Mn and 42-45% Mn) for the mineral market (Kesse, 1985). These products grades are mostly suitable for use in both chemica and dry-cell battery sectors according to Christie (2010), as the grades fall within the requisition of 44 - 54% Mn.

Due to the depletion of the oxide ore, the current emphasis is on the manganese carbonates which has assay value averaging 34.16% Mn (Kesse, 1985) that is close to metallurgical grade requirement of 38 - 55% Mn (Christie, 2010). The beneficiation of this low grade manganese carbonate will no doubt require extra treatment(s) such as calcination (Amankwah *et al,* 1999; 2005), and/or leaching (Sharma, 1992) to be converted to manganese oxide that is suitable for either battery/chemical grade or metallurgical-grade. Otherwise, O'Shaughnessy *et al* (2004) comparative work on the Nsuta mine carbonate indicated that the carbonates grade is still acceptable for manganese ferroalloy production.

In another development, the manganese oxide primary tailings generated from the initial enrichment via jigging process were reprocessed in the late 1980s with sorting spirals (Anon, 1999). The latter development generated over 40 thousand tonnes of treatable very low grade secondary tailing materials. While considering the fact that the market demand of the battery industry has exceeded 20 billion metric tonnes per year (Anon, 2010) beside that of chemical industry, the secondary tailing materials can be a potential source of manganese oxide. Moreover, the idea of tertiary recovery can be one of the best approaches in order to maintain supply, because, according to Institute of Manganese International (2010), the technological world is still struggling with how to arrive at large scale manganese recycling from steel metals, beverage cans and dry cell batteries.

Hence, the tertiary recovery of manganese oxide using heavy medium separation technique was employed in respect of the significant density variation between the oxide minerals using facilities from Geological Survey of Ghana and University of Mines and Technology, Tarkwa, Ghana.

Materials and methods

Location of nsuta-dagwin manganese deposits

Nsuta town is about 6.5 km south-east of Tarkwa, the capital of Tarkwa-Nsuaem Municipality. The Nsuta manganese

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deposits are located about 60 km north of Takoradi (Fig 1) and about 4 km close to the Sekondi-Kumasi rail line near Tarkwa and Mile 34 Post from Tarkwa on its western end. The mine is precisely 5^{o} 17′ North and 1^{o} 58′ West (Anon, 2011).

Fig. 1. Map of Ghana showing the location of Nsuta (Source: Nyame *et al,* 1995)

Sampling and sample preparation of the secondary tailings

Random sampling was conducted and 400 Kg manganese oxide tailings materials (referred to as-received tailing materials) were obtained from the company's sorting spirals processing plant tailings dump.

During the preparation of the representative sample, it was noticed that the as-received tailing materials contained considerable moisture. Hence, it was air dried for four days at the rate of eight hours per day. The materials were then mixed thoroughly and processed by continuous coning and quartering until a manageable representative (head) sample was obtained. The head sample was divided into two equal parts using a Riffler (splitting equipment). A part was used for mineralogical/particle characterisations and heavy medium enrichment.

Particle Size Characterization

Size distribution analysis was achieved using a set of ten American Standard (ASTM E11) sieves selected on the basis $\sqrt[4]{2}$ relationship to make possible much closer sizing (Anon., 1977; Wills and Napier-Munn, 2006). The topmost sieve was 2000 μm (10 mesh) and the finest was 180 μm (80 mesh). The set of sieves were fed with 1 kg of the materials and shaken with a Retch model sieve shaker for ten minutes after which the particles remaining on each sieve (sieve fractions) were weighed.

Enrichment Tests Using Heavy Medium

The heavy medium (liquid), 1,1,2,2,-tetrabromoethane ($CHBr_2.CHBr_2$) having a sp. gr. of 2.96 was used in order to facilitate the separation of pyrolusite (manganese oxide sp. gr. 4.75) and the main gangue mineral, quartz (sp. gr. 2.65). The concentration criterion was determined as; (4.75-2.96) ÷ (2.65-2.96) = 5.8. This result (quotient) favours easy separation because according to Anon (2008), it is greater than 2.5.

25 g of each particle fraction was used as feed into a beaker containing 250 ml of the heavy medium, stirred and allowed to settle. Then the sink and the float materials were collected, filtered, rinsed with carbon tetrachloride (CCl_4) and water. The two products of the separation were then dried and weighed.

However, the enrichment test could not accommodate partcles < 180 μm because they remained in suspension for a very long time and separation was not possible. Hence, assaying such particles enrichment was not considered.

Assaying

An X-Ray Fluorescence Spectrophotometer Spectro XLAB 2000 was used in determining the elements in the as-received tailings material head sample. On the other hand Varian AA 240FS Fast Sequential Atomic Absorption Spectrometer was used in the determination of manganese content for each of the discrete size fractions.

In the case of the spectrometry analysis samples from various enriched size fractions were pulverised and sieved to < 90 μm (140 mesh). 0.5 g of each fraction was placed in a test tube and 20 ml of HCl and 3 drops of HNO_3 were added to it and heated at 100^{o}C on a hot plate for 10 minutes to effect digestion. After complete cooling (for 15-20 minutes), individual solutions were mixed with distilled water and shaken for a minute to attain homogenisation. The latter products were then filtered into a collector and topped up to 100 ml with distilled water and exposed to analysis.

Results and discussions

From Table I below, the quantitative analysis result by X-ray Fluorescence (XRF) of the representative sample showed 9.01% Al_2O_3, 27.43 % SiO_2, 23.64% MnO_2 and 9.86% Fe_2O_3, while the other oxides ranged between 0.04 and 1.55 %.

Table I. Composition of the representative sample

Oxide	% Composition
Na_2O	1.55
MgO	1.24
Al_2O_3	9.01
SiO_2	27.43
P_2O_5	0.17
SO_3	0.04
Cl	0.00
K_2O	0.67
CaO	0.19
TiO_2	0.23
MnO_2	23.64
Fe_2O_3	9.86
L.O.I.	25.97

The MnO_2 value of 23.64% (i.e. 14.93% Mn) is lower than the average value of 83.28% (i.e. 52.61% Mn) of the five manganese oxide ore samples in the original chemical analyses (Kesse, 1985) and 35 to 45% Mn from the secondary tailings (Anon, 1999). At 27.43%, SiO_2 was the major gangue in the as-received tailings material. K_2O was not detected in the original oxide samples analyses, but 0.33% of it was found in the manganese carbonate samples (Kesse, 1985). Additional work conducted by Nyame *et al* (1995) detected that CaO, MgO, Na_2O and K_2O all have values less than 1.00%. The Loss on Ignition (LOI) value of 25.97% significantly acknowledged the presence of volatile matter(s) (particularly clay forming minerals of alumina and silica). These foregoing values signified divergence from the original ore composition due to drastic fall in the % Mn content.

It should be noted that the result in Table I was obtained in elemental form but converted to oxides using Chemical Conversion Factors from Edwards and Harben (1999).

Fig. 2 shows the weight percentage composition by size of the as-received materials in order of magnitude; +850 µm (25.54%), +1400 µm (14.85 %), +650 µm (13.97 %) and +500 µm (10.59 %), while the remaining fractions had less than 10.00%.

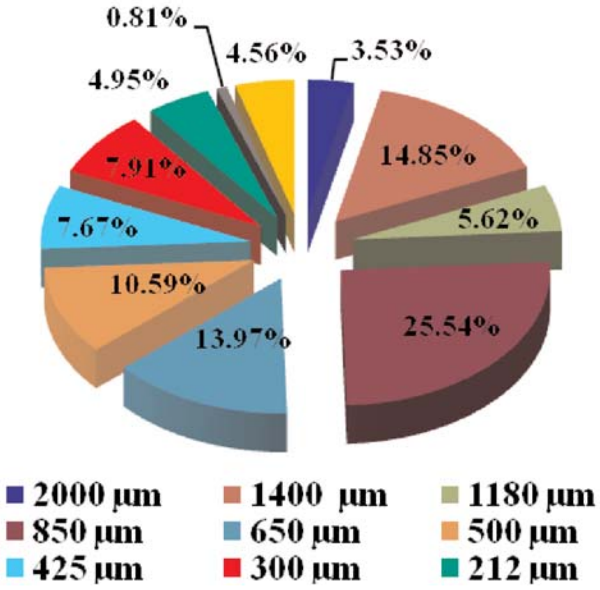

Fig. 2. As-received tailings material characterisation by weight

The results indicated that the composition was mostly of coarse to medium particle size fractions as 74.1% of the bulk material is cumulatively made up of 2000 µm to 500 µm particles. The remaining 25.9% covers the 425 µm to -180 µm fractions.

Fig. 3 depicts the AAS assay values of respective fractions ranging from a maximum of 24.89% Mn at 180 µm fraction to the lowest of 18.39 % Mn at < 180 µm, whereas the fraction with the highest quantity of material (850 µm) has 20.84 % Mn.

The size fractions' maximum and minimum assays were all greater than the XRF head sample value of 14.93% Mn. This could be attributed to the degree of liberation of the particle sizes at discrete fractions. A close review would show that the values from 2000 µm to 650 µm fractions are greater than 20% Mn and a drop to < 20% Mn from 500 µm to 300 µm, then similar rise in values with 212 µm and 180 µm and

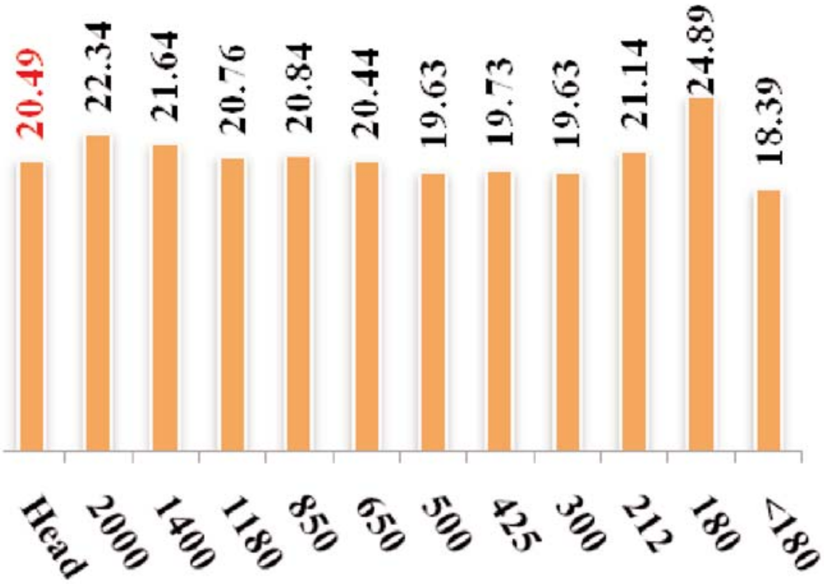

Fig. 3. Assay of sieved fractions of the as-received sample

finally a drop at the -180 µm. The head sample fraction value of 20.49% Mn was generated from calculation to check the XRF value.

Table II on the other hand indicates the % Mn values of each size fraction after the heavy medium enrichment test. The values were exceptionally higher than the head sample values, particularly with coarser size fractions, but low in the cases of 212 and 180 µm size fractions.

Table II. Manganese content in each fraction after enrichment test

Size fraction (µm)	% Mn
2000	34.96
1400	25.32
1180	38.25
850	24.96
650	26.56
500	25.72
425	23.20
300	22.72
212	24.54
180	24.1
<180	-

Enrichment Parameters

(a) Ratio of Concentration

$$\text{Ratio of concentration} = \frac{\text{Weight of feed}}{\text{Weight of concentrate}}$$

According to Wills and Napier-Munn (2006) this ratio measures the efficiency of concentration process and is closely related to the marketable content of the concentrate.

The highest values were in order of 180 µm (3.56), followed by 500 µm (3.53) and 850 µm (3.34) indicating better

Table III. Ratio of concentration

Size fraction (µm)	Quotient
2000	1.71
1400	1.80
1180	2.30
850	3.34
650	3.16
500	3.53
425	2.94
300	2.49
212	2.46
180	3.56
<180	-

upgrading by weight than in the other fractions because, "high ratio of concentration translates to increase in grade of concentrate" (Wills and Napier-Munn, 2006).

(b) Enrichment Ratio

$$\text{Ratio of concentration} = \frac{\text{Weight of feed}}{\text{Weight of concentrate}}$$

This expresses the relationship between the grade (assay) of the concentrates and those of the feeds or it is an impression of how enriched the feed material became.

On examining Table IV, it indicates that the enrichment had a maximum value of 1.84 (1180 µm) and minimum value of 0.97 (180 µm). In the cases of enrichment ratios that are less than 1, it means that the assay value of the feed is higher than that of the concentrate.

Finally, 2000 µm, 1400 µm, 1180 µm, 850 µm, 650 µm, 500 µm, 425 µm and 300 µm fractions were more enriched out of ten fractions.

Table IV. Enrichment ratio

Size fraction (µm)	%
2000	1.56
1400	1.17
1180	1.84
850	1.20
650	1.30
500	1.31
425	1.18
300	1.16
212	1.16
180	0.97
<180	-

Conclusion

The investigation conducted with the aim of enriching the tailings material confirmed the presence of very low grade manganese (14.93%). The major particle constituent is +850 µm having 25.54% of the bulk material. The successful manganese enrichment to medium (38.25% Mn) and low (22.72% Mn) grade range was attributed to the ability to clearly separate the denser minerals from the lighter ones. Taking cost and toxicity into consideration, a dense medium using a pseudo-solution of -212 µm ferro-silicon (15% Si) at density >3.00 may be used at the industrial scale instead of tetrabromoethane.

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