BENEFICIATION OF MAGAMI FERRUGINOUS MANGANESE ORE, ZAMFARA STATE, NIGERIA

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ABSTRACT

This work was carried out to beneficiate Magami ferruginous manganese ore via sample collection, sample preparation, chemical and particle size analyses, and concentration tests. The collected materials from the site were prepared in the laboratory to obtain a representative sample by coning and quartering. The elemental composition of manganese in the sample was established as 13.1 % Mn. Sieve analysis revealed that there was no over grinding or under grinding to yield finer or coarser particles respectively; as 87.85 % of the comminuted material passed through the coarsest sieve of 355 µm, 15.99 % highest percentage of particles retained on 63 µm, over 59% was less than 180 µm and just 17.41% was collected at the pan. The separation processes attained enrichment of 38.71 % Mn at a recovery of 29.1 % from 125 µm size using shaking table, while, 24.90 % Mn enrichment at a recovery of 69.44 % was obtained from magnetic separation. Therefore, the concentrates in either of the processes is typically suitable for manganese alloy or manganese pig-iron production by direct smelting.

Keywords: Beneficiation, Chemical analysis, Ferruginous manganese, Representative sample, Size analysis.

1. INTRODUCTION

Manganese is present in various minerals in the form of oxides, carbonates, silicates, sulphides, etc compounds as a predominant or non predominant content (Christie, 2010). According to Read (1980), manganese replaces to a greater or lesser degree two sets of elements; first, the alkaline earth metals (i.e. calcium, barium and magnesium, and secondly, aluminium) and iron. The deposits generally occur as nodules, lumps, pockets, stringers or lenticular masses irregularly scattered through residual clays and weathered rocks (Ali and Amankwah, 2013). In terms of rocks, manganese is found in formations such as granites, schists and sandstones (Kesse, 1985). Manganese minerals have specific gravity ranges from 3.5 to 5, with average from 3.5 to 4, and it is common associates beside clay are limonite ($Fe_2O_3.H_2O$), baryte ($BaSO_4$), ochre (hydrated ferric oxide), bauxite, silica (SiO_2) and limestone ($CaCO_3$) (Abubakar, 2015).

A Manganese deposit containing more than 35% Mn content are considered as manganese ores, however, those having 5–10% Mn are referred to as manganiferous ores, while ferruginous manganese ores fall within the range of 10–35% Mn (Christie, 2010). In addition, manganese ores can be categorised with respect to end users requirements as; (a) Battery ore [exceptionally high MnO_2 content]; (b) ferromanganese stock [containing a minimum of 45% MnO_2 (average 48%)]; (c) spiegeleisen stock [containing from 10 to 45% Mn and higher iron than in ferromanganese stock]; and (d) pig-iron stock [containing from 7 to 10% and upward of Mn] (Ali, 2014; Abubakar, 2015). The

International Manganese Institute (IMnI) (2017) classifies manganese ores into, high (> 44% Mn), medium (30 – 44% Mn) and low (< 30% Mn) marketable grades.

The diverse composition in different manganese ore types indicates that they are associated with various elements.; which include, metallic (e.g. iron, lead, zinc, copper, arsenic, and silver minerals), non-metallic (e.g. sulphur and phosphorous), gangue (e.g. silica, alumina, lime, magnesia and barium) and volatiles (e.g. water, carbon dioxide and organic matters) (Abubakar, 2015). Therefore the dictate of the method of enrichment is also relative to the compositional characteristics of the ore deposit under consideration. Reviews indicated that, both old and modern typical enrichment operations may involve one or a combination of the physical, chemical, pyro, hydro, etc, processes. The physical (mechanical) approach in sequence of, comminution, sizing, and concentration techniques are adopted to enrich manganese oxides, which are of moderately high density, and in some cases of considerable magnetic permeability (Jain, 2008).

Since the majority of the rich ores being mined are sedimentary and residual deposits, a simple enrichment consisting of a grizzly to remove stumps and other oversized material and a simple crusher to break up coarser particles is often sufficient to produce a high grade concentrate (Aplan, 1985). On the other hand, Aplan (1985) pointed out that manganese ore flotation is not easy as clay slimes prove troublesome and near ultimate removal

of gangue particles to produce high grade concentrates is often a formidable problem. Though manganese is weakly magnetic, many successes were achieved using magnetic susceptibility as a criterion. Khan *et al* (2004) study on the beneficiation by simple techniques of the manganese ores of the Saidgi area, Pakistan, succeeded in upgrading samples from 37.98 wt % and 57.36 wt % to 79.1 wt % and 80.44 wt % of MnO_2 by magnetic separation. Rao *et al.*'s (1998) result of enrichment of manganese content by wet high intensity magnetic separation of Chikla manganese ore, India, yielded a product of 51% Mn at 96% recovery from 44% Mn using particle size less than 100µm. In addition, Lomovtsev *et al* (1995) production-scale application of high-gradient magnetic separator VMS 100/2 to the recovery of manganese from plant tailings obtained 25 to 28% Mn with 65.6% recovery in one stage process and 31.7% Mn with 55.8% recovery in two stage process.

Some chemical, pyro-chemical and pyro-metallurgical processes include; Bradley-Filtch and Dean-Leute processes, using, roasting, leaching with ammonium carbonate and reduction of carbonate succeeded in producing manganese oxide (Abubakar, 2015). Similarly, the Welch process dissolved low grade manganese with sulphuric acid to form $MnSO_4$, and then introduced into electrolytic cell to form MnO_2 of excellent battery grade (Abubakar, 2015). Furthermore, Amankwah *et al* (1999 and 2005) succeeded in producing manganous (MnO) from the low grade Nsuta manganese carbonate via nodulisation and microwave calcinations and sintering processes respectively. The former was attained at $1300^{\circ}C$ and the latter at $1500^{\circ}C$. Also, Yamazaki's (2006) exposition on technological issues associated with commercialising cobalt-rich ferromanganese crust deposit concluded that sea nodules often containing 25 to 30% Mn may well be very important future sources of manganese using hydrometallurgical techniques to separate the metallic constituents. A novel attempt by Srimekanond *et al* (1992) on studies of bacterial degradation of manganese ores, attained best leaching at $50^{\circ}C$ with a mixed culture of 20% molasses added to 20g ground (<0.1 mm) MnO_2 tailings of 17% Mn content.

More than 90% of manganese is consumed by the iron and steel industry, for which no substantial substitute has yet been found, according to Vulcan (2009) and Christie (2010). The remaining consumption is in a variety of industrial, chemical and pharmaceutical applications. Manganese is essential in steel production due to its sulphur fixation (i.e. desulphurisation), oxygen reducing (i.e. deoxidisation) and alloying properties (Corathers, 2008), in order to improve mechanical properties such as toughness,

strength and hardness (Gandhi, 2010). Manganese is added in the form of alloys such as ferromanganese (about 80% Mn: 15–18% Fe), spiegeleisen (12–33% Mn : the remainder Fe) and manganese or Hadfield steel (12-14% Mn); for making rugged alloys used in the manufacturing of armour plates, projectiles, safes, crushers, cutting and grinding machinery, etc (Christie, 2010).   On the other hand, manganese pig-iron is obtained from direct smelting of iron ores containing manganese, in which such manganese would not be paid for except at the same rate as iron (Read, 1980).

Production of alloys in combination with aluminium is the second largest application of manganese in making alloys. In this case, manganese is employed to absorb impurities against galvanic corrosion. For instance, products such as aluminium alloys 3004 and 3104 used for most of the beverage cans have 0.8 to 1.5% Mn content (IMnI, 2017). Other non-ferrous alloys include manganese bronze (Mn, Cu, Sn, and Zn) and manganin (Mn, Cu, and Ni); the former is used for propeller blades on boats and torpedoes due to its resistance to corrosion from seawater) while the latter is used as wires for accurate electrical measurements due to less variation in electrical conductivity with temperature (Christie, 2010).   Bimetallic strips fitted in vehicles for temperature control devices use one of such alloys (72% Mn, 18% Cu and 10% Ni). Another alloy used in the manufacture of small parts for wrist watch manufacturing is a non-magnetic high-strength alloy (60% Cu, 20% Mn and 20% Ni) (IMnI, 2017). "Since 2000, dollar coins, for example the Sacagawea dollar and the Presidential $1 Coins, are made from a brass containing 7% of manganese with a pure copper core" (IMnI, 2017).

The dry-cell batteries production is the most non-metallurgical application of manganese in the form of manganese dioxide. Crampton (2000) reported that the element acts as a depolarizer by suppressing the formation of hydrogen gas at the carbon (positive) electrode. Also, it was indicated that in the glass industry, manganese compounds are used for (a) the inducing of strong green colour in glass by forming less-coloured iron (III), and (b) slightly pink manganese (II) from manganese (III) reaction with iron (II) compensating the residual colour of the iron (III) (IMnl, 2017). Furthermore, pink coloured glass is produced with larger amounts of manganese while pigments and colouring of ceramics and glasses are also achieved using manganese compounds. The manufacture of oxygen and chlorine gases and drying of black paints used MnO_2 (IMnI, 2017). Manganese sulphate is used as a fertilizer, in dyeing cotton, and in paint and varnish oils (Christie, 2010).

2.   MATERIALS AND METHODS

50 kilograms of field sample was collected from three different pits of 2 m depth and 10 m apart on the manganese deposit in Magami village situated between latitude N11° 37´ 46.6´´ and longitude E 06° 42´ 32.3´´. The location is

about 50 km from Gusau, the capital of Zamfara State, North Western Geopolitical Zone of Nigeria. The field sample was crushed, pulverised and ground using jaw

crusher, pulveriser and ball mill respectively in order to liberate the different grains in the mineralised material.

These particles were used in studying the chemical and sieve analyses, as well as the beneficiation trials of the manganese. In the cases of the analyses and the beneficiation, the comminuted products were exposed to coning and quartering method to generate the head sample. The determination of chemical composition of the representative sample was carried out with X-ray fluorescence (XRF) equipment. ASTM standard screens arranged in descending order of 355µm, 250µm, 180µm, 125µm, 90µm, 63µm based on $\sqrt{2}$ were used in sieve analysis. The feed materials were generated from 15 minutes ball milling and 10 minutes of sieving. Gravity separation test was performed with Denver Equipment Company shaking table, model number S.N. W 79107. Magnetic separation test was carried out with Davies Magnet Works Ltd Dry Disc Magnetic Separator, Model No. 13008/350/4.5V.

The beneficiation of the manganese ore was carried out using gravity and magnetic separation techniques. In case of the former, the head sample was segregated using four size fractions of 600 µm, 425 µm, 250 µm and 125 µm. The products of each fraction were individually subjected to shaking table technique of concentration. At the beginning,

the shaking table was set horizontally (180º) with a plumb and slurry of 25% solid (i.e. 600 g) of each particle fraction was prepared as feed. The machine's reciprocating motion was set at a rate of 1400 rpm, and water flow tangentially through jet nozzles at the rate of 210.10 cm^3 per sec. Three flows of materials in concordance, tangential as well as incline directions with table's motion for the heavy, light and middling minerals were achieved.

Furthermore, magnetic separation was conducted using a feed of hundred grams (100 g) per each size fraction. However, due to limitation of the machine's particles discharging pipe to collectors, fractions coarser than 355µm could not be treated; thereby restricting the process to fractions below 355µm (i.e. -355 to -63 µm).

The machine has two controls using Bercostat power resistor of 350 Ohms and 1.5 Amps to adjust the magnetic intensity and vibratory feeding respectively. The former was set at maximum of 100, while the latter was set at 50. The vibratory feeder directed materials to temporary (electrically) magnetized horizontal rotating disc which picked the paramagnetic materials and discharged them into three collectors while the diamagnetic were discharged into the fourth collector. Each particle fraction was re-routed three times to optimize concentration.

3.   RESULTS AND DISCUSSIONS

Table 1 shows the chemical analysis result of the head sample.

Table 1: Result of XRF head sample chemical analysis

Element	Grade (%)
Si	14.40
Al	4.92
P	0.17
S	0.03
K	0.07
Na	0.19
Ca	0.79
Ti	0.19
Mn	13.10
Fe	29.49
Mg	0.56

The chemical analysis revealed that the manganese ore contains 13.1% Mn content; thereby categorising it as ferruginous manganese ore (10 – 35% Mn) according to the classification in Christie (2010). Hence, it is by and large a low marketable grade (IMnI, 2017), typically suitable for either manganese alloy or direct smelting in manganese pig-iron productions (Read, 1980; Gandhi, 2010).

From the result of the sieve analysis in Table 2, 87. 85 % of the comminuted material passed through the coarsest sieve of 355 µm, highest percentage of particles retained of 15.99

% was obtained on 63 µm, over 59% was less than 180 µm and just 17.41% was collected at the pan. These signified that there was no over grinding or under grinding to yield finer or coarser particles respectively.

Table 2: Result of sieve analysis

Sieve size (µm)	Wt. Retained (g)	Wt. Retained (%)	Cum. Wt. Retained (%)	Cum. Wt. Pass. (%)
355	24.25	12.15	12.15	87.85
250	28.90	14.48	26.63	73.37
180	28.67	14.37	41.00	59.00
125	24.38	12.22	53.22	46.78
90	26.69	13.38	66.60	33.40
63	31.90	15.99	82.59	17.41
Pan	34.76	17.41	100.00	0.00
Total	**199.55**	**100.00**	**-**	**-**

Table 3 shows the results of the shaking table concentration.

Table 3: Shaking table assay values

Sieve Size (μm)	Assay (%)			Recovery (%)
	c	m	t	
600	32.44	31.22	9.40	39.8
425	35.00	34.72	10.22	31.1
250	36.21	36.00	10.22	30.6
125	38.71	36.43	10.30	29.1

Notations: c = concentrate assay, m = middling assay & t = tailings assay

These results indicated that by decreasing the particle size, a concentrate with high Mn content is obtained but the recovery also decreased. This agreed substantially with the logic of partial proportion relationship between concentrate grade and recovery (Wills and Napier-Munn, 2006). Therefore, 125 μm size fraction (i.e. -250+125 μm size range) is selected as suitable feed for separation of Magami manganese ore by shaking table which resulted in a concentrate containing 38.71% Mn.

Taking the head sample's grade value uniformly, the result of the magnetic test is presented in Table 4.

Table 4: Result of magnetic separation

Sieve size (μm)	Assay (%)			Recovery (%)
	f	c	t	
355	13.1	-	-	-
250	13.1	8.6	2.41	113.3%
180	13.1	11.41	9.0	148.2%
125	13.1	15.51	6.6	86.4%
90	13.1	24.90	6.31	69.44%
63	13.1	23.60	4.11	83.1%
Pan	13.1	13.0	6.61	100.8%

Notations: f = feed assay, c = concentrate assay& t = tailings assay

The magnetic separation result after chemical analysis confirmed 90 μm particle sizes as the best size where assay value of 24.90% with a recovery of 69.44% was attained.

In both of the enrichment processes, the formula for determining the recovery is thus;

$$Recovery = \frac{Cc}{Ff} \times 100\% \qquad (1)$$

or

$$Recovery = \frac{100c(f-t)}{f(c-t)}\% \qquad (2)$$

4. CONCLUSIONS

The elemental composition of manganese in the sample was established as 13.1 % Mn. The sieve analysis revealed that there was no over grinding or under grinding to yield finer or coarser particles respectively; as 87.85 % of the comminuted material passed through the coarsest sieve of 355 μm, highest percentage of particles retained of 15.99 % was obtained on 63 μm, over 59% was less than 180 μm and just 17.41% was collected at the pan. The separation processes indicated that an enrichment of 38.71 % Mn at a recovery of 29.1% was attained from 125 μm sieve size using shaking table, 24.90 % Mn at a recovery of 69.44 % was obtained from magnetic separation. Therefore, the concentrates in either of the processes is typically suitable for manganese alloy or manganese pig-iron production by direct smelting.

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