**Applied Science, Computing and Energy, 2025, 3(3), 624-645**

# Beneficiation of Two Different Low-Grade Nigerian Manganese Ore Deposits to Improve its Quantitative Composition

**Femi Emmanuel Awe, Ganiyu Rafiu Alege, Joe Maduke Nwaedozie and Mukthar Muhammad Namadi**

**19 July 2025/Accepted: 18 October 2025 /Published: 25 October 2025**

*Abstract: The beneficiation potential of two low-grade manganese ores from the Mopa-Muro (Kogi State) and Oban Massif (Cross River State) deposits, Nigeria, was investigated using liberation study, gravity separation, and froth flotation techniques combined with thermal treatment at 950 and 1050°C. Prior to beneficiation, the ores were crushed, milled, and classified into particle sizes of 75, 105, 300, and 425 µm. Mineralogical and structural characterization of the beneficiated ores was carried out using X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. XRD analysis identified pyrolusite ($MnO_2$), manganosite (MnO), spessartine [$Mn_3Al_2(SiO_4)_3$], and quartz ($SiO_2$) as the major mineral phases in both deposits, while goethite [FeO(OH)] was detected only in the Oban Massif ore. Quartz was confirmed as the principal gangue mineral, indicating strong interlocking between manganese-bearing minerals and silicate impurities. The liberation study produced the highest beneficiation efficiency, increasing the pyrolusite content in the Mopa-Muro ore from 10.7% to 75.0%, corresponding to an improvement of 64.3 percentage points, while the Oban Massif ore exhibited a smaller increase from 10.5% to 14.7% (4.2 percentage points). Froth flotation resulted in pyrolusite enrichment from 31.0% to 64.0% (33.0 percentage points) for the Mopa-Muro ore, whereas manganosite increased from 41.0% to 57.0% (16.0 percentage points) in the Oban Massif concentrate. Gravity separation produced moderate upgrading, with manganosite increasing from 15.0% to 40.0% (25.0 percentage points) in the Mopa-Muro ore and spessartine increasing from 23.0% to 49.0% (26.0 percentage points) in the Oban Massif ore. FTIR spectra revealed characteristic Mn–O stretching vibrations within the 775–1029 $cm^{-1}$ region, confirming the presence of pyrolusite, manganosite, and spessartine, while the absence of sharp absorption bands between 3670 and 3550 $cm^{-1}$ indicated effective dehydration and the absence of free hydroxyl functional groups following calcination. The results further demonstrated that increasing calcination temperature from 950 to 1050°C and reducing particle size significantly enhanced mineral liberation and beneficiation efficiency. Although the beneficiated concentrates did not attain the chemical specifications required for metallurgical-grade manganese ores, they exhibited substantial improvement in manganese mineral concentration and are suitable for the production of spiegeleisen (low-grade ferromanganese) and other medium-grade manganese applications.*

***Keywords**: Beneficiation, calcination, froth flotation, low-grade manganese ore, mineralogy, pyrolusite, X-ray diffraction.*

**Femi Emmanuel Awe**
Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria.
**Email:** feawe@nda.edu.ng
**https://orcid.org/0000-0001-8071-8108**

**Ganiyu Rafiu Alege**
Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria.
**Email:** graalege@gmail.com
**https://orcid.org/0009-0006-1202-7157**

**Joe Maduke Nwaedozie**
Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria.
**Email:** jmnwaedozie@nda.edu.ng

**Also available @ http://doi.org/10.5281/zenodo.21313433**

**Mukthar Muhammad Namadi**
Department of Chemistry, Nigerian Defence Academy, Kaduna, Nigeria.
**Email:** mmnamadi@nda.edu.ng

## 1.0 Introduction

Manganese is one of the most important strategic metals used in modern industrial production because of its indispensable role in steelmaking, ferroalloy production, battery manufacture, ceramics, pigments, fertilizers, and several chemical industries (Kamalpour & Rankin, 2004). More than 90% of global manganese consumption is attributed to the iron and steel industry, where manganese functions as a deoxidizer, desulfurizer, and alloying element, significantly improving the hardness, toughness, and wear resistance of steel (Coetsee, 2019). The increasing global demand for high-performance steels and advanced battery materials has intensified the need for sustainable exploitation and beneficiation of manganese resources.

Manganese naturally occurs in a variety of oxide, carbonate, silicate, and hydroxide minerals, with pyrolusite ($MnO_2$), manganosite (MnO), spessartine ($Mn_3Al_2(SiO_4)_3$), rhodochrosite ($MnCO_3$), and braunite being among the most economically important minerals. However, many manganese deposits are associated with significant quantities of silica, iron oxides, alumina, clay minerals, and other gangue materials that reduce ore quality and complicate metallurgical processing (Mehdilo *et al*., 2013). The mineralogical characteristics and degree of mineral liberation largely determine the efficiency of beneficiation techniques and the economic viability of subsequent extraction processes.

Commercial manganese ores are generally classified according to their manganese content. High-grade or metallurgical-grade ores typically contain more than 40–48% Mn and are suitable for direct production of ferromanganese and silicomanganese alloys through carbothermic reduction in submerged electric arc furnaces (Kamalpour & Rankin, 2004). Conversely, low-grade manganese ores containing approximately 20–35% Mn require upgrading before they can be economically utilized for metallurgical applications because excessive gangue minerals increase energy consumption, slag generation, and production costs (Singh *et al*., 2011). Consequently, efficient beneficiation technologies have become increasingly important for transforming low-grade resources into commercially valuable feedstocks.

Beneficiation involves a series of physical, physicochemical, and occasionally hydrometallurgical processes designed to increase the concentration of valuable minerals while removing unwanted impurities (Jain, 2011). The selection of an appropriate beneficiation technique depends largely on the mineralogical composition, particle size distribution, liberation characteristics, and textural relationships between valuable minerals and gangue constituents. Common beneficiation methods for manganese ores include gravity separation, magnetic separation, flotation, roasting followed by magnetic separation, reductive acid leaching, and chemical extraction processes (Mehdilo *et al*., 2013; Xiong *et al*., 2018). Physical beneficiation methods are generally preferred because they require relatively lower operating costs, consume less energy, and generate fewer environmental pollutants than chemical extraction techniques.

Gravity separation remains one of the oldest and most economical beneficiation methods for manganese ores because it exploits differences in specific gravity between manganese-bearing minerals and associated gangue minerals such as quartz and silicates. This technique is particularly effective when sufficient mineral liberation has been achieved through crushing and grinding (Jain, 2011). Froth flotation, on the other hand, separates minerals based on differences in surface

physicochemical properties and has proven highly effective for fine-grained manganese ores where gravity separation alone is inadequate (Shu *et al*., 2019). Recent investigations have also demonstrated that ultrasonic pretreatment can improve collector adsorption and flotation efficiency by enhancing mineral surface cleanliness and dispersion (Shu *et al*., 2019).

Thermal pretreatment through calcination or reduction roasting has emerged as another promising approach for upgrading low-grade manganese ores. During thermal treatment, mineralogical transformations occur that facilitate the separation of manganese-bearing minerals from associated iron oxides and silicate gangue. Reduction roasting followed by magnetic separation has been widely reported to improve the recovery and grade of manganese concentrates by selectively altering the magnetic properties of iron-bearing phases while preserving manganese minerals (Rath *et al*., 2018; Liu *et al*., 2018). The effectiveness of thermal upgrading depends strongly on roasting temperature, residence time, reducing atmosphere, and particle size, all of which influence phase transformation kinetics and mineral liberation (Kuila *et al*., 2016; Belardi *et al*., 2011).

Characterization of manganese ores prior to beneficiation is equally important because mineralogical and chemical analyses provide valuable information on mineral associations, crystal structures, functional groups, and liberation behaviour. X-ray diffraction (XRD) is widely employed to identify crystalline mineral phases, while Fourier Transform Infrared (FTIR) spectroscopy complements XRD by identifying characteristic functional groups and confirming mineral compositions that may not be readily distinguished through diffraction techniques alone (Sandeep *et al*., 2012). Together, these analytical techniques enable accurate evaluation of beneficiation potential and process optimization.

Nigeria possesses considerable manganese ore resources distributed across several geological provinces, including the Mopa-Muro area of Kogi State and the Oban Massif of Cross River State. Despite their abundance, these deposits are predominantly low-grade and remain largely underutilized because their manganese contents are below the metallurgical specification required for direct ferroalloy production. Consequently, significant quantities of these domestic resources remain economically unattractive without appropriate upgrading technologies. Developing effective beneficiation strategies for Nigerian manganese ores could reduce dependence on imported metallurgical-grade manganese, support the local steel industry, and contribute to national mineral resource development.

Although previous studies have investigated beneficiation techniques for low-grade manganese ores from countries such as India, China, Iran, and South Africa (Mehdilo *et al*., 2013; Rath *et al*., 2018; Liu *et al*., 2018), comparatively little information exists regarding the comparative beneficiation behaviour of manganese ores from the Mopa-Muro and Oban Massif deposits in Nigeria. In particular, there is limited understanding of how mineralogical characteristics, particle size, thermal treatment, and different beneficiation techniques collectively influence manganese upgrading in these deposits. Addressing this knowledge gap is essential for selecting suitable processing routes that maximize manganese recovery while minimizing processing costs.

Therefore, this study investigates the beneficiation potential of low-grade manganese ores obtained from the Mopa-Muro and Oban Massif deposits using gravity separation, liberation concentration, and froth flotation techniques following thermal treatment. Mineralogical characterization was performed using X-ray diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy to determine the mineral phases

and functional groups present in the ores. Furthermore, the influence of particle size and calcination temperature on manganese upgrading was evaluated to establish the most effective beneficiation route for improving the quantitative composition of these Nigerian manganese deposits and assessing their suitability for metallurgical applications.

## 2.0 Materials and Methods

### *2.1 Materials*

Low-grade manganese ore samples were collected from two major Nigerian manganese deposits: Mopa-Muro, Kogi State, and Oban Massif, Cross River State. These deposits were selected because they represent significant but underutilized manganese resources with relatively low manganese grades requiring beneficiation prior to metallurgical utilization. All chemicals used during the study were of analytical grade. Iodomethane, concentrated acetone (99.5% purity), sodium hydroxide (NaOH), Clerici solution, and double-sided adhesive tape were procured from AG Chemicals Limited, Kaduna, Nigeria. Distilled water was used throughout the beneficiation experiments.

### *2.2 Sample Preparation*

The collected manganese ore samples were initially crushed using a laboratory jaw crusher and subsequently pulverized in a laboratory ball mill to obtain a uniform particle size distribution. The pulverized ores were sieved using standard laboratory sieves to obtain four particle size fractions of 75, 105, 300, and 425 μm. These particle size fractions were used to evaluate the influence of particle size on beneficiation efficiency.

Representative samples from each size fraction were preserved for mineralogical characterization before beneficiation.

### *2.3 Mineralogical Characterization*

The mineralogical composition of the untreated manganese ores was determined using X-ray Diffraction (XRD), while the functional groups and mineral bonding characteristics were identified using Fourier Transform Infrared (FTIR) spectroscopy.

The XRD results revealed distinct mineralogical compositions for the two deposits. The Mopa-Muro ore was predominantly composed of pyrolusite ($MnO_2$), whereas the Oban Massif ore was characterized by a higher abundance of spessartine ($Mn_3Al_2(SiO_4)_3$). Quartz and other silicate minerals were also identified in both deposits, indicating significant gangue mineral intergrowths that necessitate beneficiation before metallurgical utilization.

### *2.4 Beneficiation of Manganese Ores*

Three beneficiation techniques were employed to upgrade the manganese ores, including, (i) Liberation study, (ii) Gravity separation, and (iii) Froth flotation.

The beneficiation experiments were conducted on all four particle size fractions to evaluate the influence of particle size on manganese recovery and concentrate grade.

#### *2.4.1 Liberation Study*

The liberation characteristics of the manganese ores were evaluated by examining the degree of separation between manganese-bearing minerals and associated gangue minerals after grinding. The results were used to determine the optimum particle size for subsequent beneficiation processes.

#### *2.4.2 Gravity Separation*

Gravity concentration was carried out using a laboratory shaking table. The operating conditions were maintained at five table strokes and a water flow rate of 11 L $min^{-1}$ throughout the experiments.

For each particle size fraction, the ore was mixed with water in a solid-to-liquid ratio of 1:2 to produce a homogeneous slurry. The slurry was gradually introduced into the shaking table through the feed hopper, allowing separation according to differences in specific gravity.

Two products were obtained after separation including, (i) Concentrate, representing the manganese-rich fraction, and (ii) Tailings, consisting mainly of gangue minerals.

Both products were collected separately, dried, weighed, and preserved for subsequent analyses.

### *2.4.3 Froth Flotation*

Froth flotation was performed on the ground manganese ore samples to further separate manganese-bearing minerals from silicate gangue based on differences in their surface physicochemical properties. Appropriate flotation reagents were employed to selectively float the valuable manganese minerals while depressing unwanted gangue minerals. The flotation concentrates and tailings were collected separately, dried, and stored for further characterization.

### *2.5 Thermal Treatment of Beneficiated Ores*

To investigate the influence of heat treatment on mineralogical transformation and upgrading efficiency, 30 g of each beneficiated concentrate obtained from the liberation study, gravity separation, and froth flotation processes was weighed into separate dried platinum crucibles.

The samples were heated in an automated Carbolite muffle furnace at two calcination temperatures (950°C, and 1050°C).

Each sample was maintained at the desired temperature for 3 h. Upon completion of the heating cycle, the furnace was allowed to cool naturally for approximately 30 min before the crucibles were removed using long-handled tongs. The samples were then transferred to a desiccator and allowed to cool to room temperature prior to characterization.

The same procedure was repeated independently for both calcination temperatures.

### *2.6 Characterization of Beneficiated Ores*

The thermally treated manganese concentrates obtained from the liberation study, gravity separation, and froth flotation processes were characterized to evaluate the mineralogical and structural changes resulting from beneficiation and calcination.

Mineral phase identification was performed using X-ray Diffraction (XRD), while Fourier Transform Infrared (FTIR) spectroscopy was employed to identify the functional groups and chemical bonding associated with the manganese-bearing minerals and gangue constituents.

The combined XRD and FTIR analyses were used to assess the effectiveness of the beneficiation processes and determine the influence of particle size and calcination temperature on the upgrading of manganese ores from the Mopa-Muro and Oban Massif deposits.

## 3.0 Results And Discussions

### *3.1 Mineralogical Characterization of Beneficiated Manganese Ores*

The mineralogical characteristics of the heat-treated beneficiated manganese ores obtained from the Mopa-Muro (Kogi State) and Oban Massif (Cross River State) deposits were investigated using X-ray diffraction (XRD) to determine the effects of beneficiation technique, calcination temperature, and particle size on the distribution of manganese-bearing minerals. The quantitative and qualitative mineralogical compositions obtained after the liberation study, gravity separation, and froth flotation processes are presented in Tables 1-3, respectively. These results provide valuable information on the enrichment of manganese minerals and the removal of gangue constituents during beneficiation.

The XRD analysis revealed that the manganese ores from the two deposits possess similar primary manganese-bearing minerals but differ in their relative abundances. Four major crystalline phases, namely pyrolusite ($MnO_2$), manganosite (MnO), spessartine [$Mn_3Al_2(SiO_4)_3$], and quartz ($SiO_2$), were identified in both deposits, whereas goethite [FeO(OH)] was detected only in the Oban

Massif ore. The occurrence of quartz indicates that silica is the dominant gangue mineral associated with both manganese deposits, while the presence of goethite in the Oban Massif ore suggests a greater degree of iron mineralization than in the Mopa-Muro deposit. Similar mineral assemblages have been reported for low-grade manganese ores from India, Iran, and China, where manganese oxides coexist with silicate and iron-bearing gangue minerals that adversely affect beneficiation efficiency (Mehdilo *et al*., 2013; Rath *et al*., 2018).

The mineralogical compositions further demonstrate that manganosite and pyrolusite constitute the principal manganese-bearing phases in both deposits, indicating that the ores possess significant potential for metallurgical upgrading. Pyrolusite is the most economically valuable manganese oxide because of its high manganese content and ease of reduction during ferromanganese production. Manganosite, although containing manganese in a lower oxidation state, also contributes substantially to the total recoverable manganese after thermal reduction. Spessartine represents a manganese-bearing silicate mineral that can contribute to manganese recovery but is generally more refractory during beneficiation due to its strong association with silicate gangue (Coetsee, 2019).

A comparison of the beneficiation products shows that the relative proportions of these mineral phases varied considerably with beneficiation method, calcination temperature, and particle size. These variations indicate that beneficiation altered not only the concentration of manganese-bearing minerals but also their mineralogical associations. Thermal treatment at 950°C and 1050°C promoted mineral transformations consistent with carbothermal reduction reactions, resulting in changes in the proportions of pyrolusite and manganosite. Such mineralogical transformations have been widely reported during reduction roasting of manganese ores, where higher temperatures facilitate the progressive reduction of higher manganese oxides into lower oxidation-state phases that are more amenable to concentration (Rath *et al*., 2018; Liu *et al*., 2018).

The observed differences between the two deposits also reflect their distinct geological origins. The Mopa-Muro ore is characterized by a relatively higher abundance of manganese oxide minerals, whereas the Oban Massif deposit contains appreciable quantities of silicate and iron-bearing minerals, particularly spessartine and goethite. The higher quartz and goethite contents in the Oban Massif samples suggest stronger mineral intergrowth and a greater degree of gangue contamination, factors that can reduce the efficiency of physical beneficiation techniques such as gravity separation. Similar observations have been reported by Mehdilo *et al*. (2013), who demonstrated that the liberation characteristics and gangue mineral associations largely determine the upgrading potential of low-grade manganese ores.

Overall, the XRD results confirm that both Nigerian manganese deposits are composed predominantly of manganese oxide minerals suitable for beneficiation. However, the substantial presence of quartz and other gangue minerals indicates that beneficiation is essential before the ores can satisfy the chemical specifications required for metallurgical applications. The subsequent sections examine how liberation concentration, gravity separation, and froth flotation influenced the quantitative mineralogical composition of the ores under different particle sizes and calcination temperatures.

### *3.1.1 Mineralogical Composition of Heat-Treated Beneficiated Ores Obtained by Liberation Study*

The mineralogical compositions of the heat-treated manganese ore concentrates produced

through the liberation study are presented in Table 1.

**Table 1: Mineralogical Constituents of heat treated beneficiated ores sample through liberation study test @ 950$^0$C(300µm) and 1050$^0$C(300µm)**

| | | MOPA MURO (BMM) | | | | OBAN MASSIF (BOM) | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Qualitative composition** | | 950$^0$C (300µm) | | 1050$^0$C 425µm) | | 950$^0$C (300µm) | | 1050$^0$C 425µm) | |
| Minerals | Chemical Formula | QC | Oc | QC | Oc | QC | Oc | QC | Oc |
| Pyrolusite, | $MnO_2$ | 10.7 | 13 | 75 | 5 | 10.5 | 10 | 14.7 | 12 |
| Quartz | $SiO_2$ | 3 | 5 | 6.7 | 16 | 4.8 | 3 | 10.2 | 16 |
| Spessartine | $(Mn^{2+})_3Al_2(SiO_4)_3$ | 23 | 7 | 14 | 3 | 35 | 4 | 48 | 3 |
| Manganosite, | MnO, | 63 | 7 | 4 | 5 | 44 | 3 | 22 | 2 |
| Geothite, | FeO(OH) | - | - | - | - | 5.7 | 4 | 4.6 | 3 |

**Note: QC: Quantitative composition; Oc: Occurrence**

**Table 2: Mineralogical Constituents of heat treated beneficiated ores sample through gravity separation test @ 950$^0$C(300µm) and 1050$^0$C(105µm)**

| | | Mopa Moro (BMM) | | | | OBAN MASSIF (BOM) | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Qualitative composition** | | 950 $^0$C (300µm) | | 1050$^0$C (105µm) | | 950$^0$C (300µm) | | 1050$^0$C (105µm) | |
| Minerals | Chemical Formula | QC | Oc | QC | Oc | QC | Oc | QC | Oc |
| Pyrolusite | $MnO_2$ | 34 | 11 | 21 | 10 | 4.2 | 11 | 7.5 | 10 |
| Quartz | $SiO_2$ | 28 | 22 | 10 | 5 | 14 | 3 | 4 | 5 |
| Spessartine | $(Mn^{2+})_3Al_2(SiO_4)_3$ | 23 | 7 | 30 | 34 | 23 | 7 | 49 | 6 |
| Manganosite | MnO | 15 | 6 | 40 | 19 | 50 | 5 | 38 | 5 |
| Geothite | FeO(OH) | - | - | - | - | 8.9 | 9 | 2 | 3 |

**Note: QC: Quantitative composition; Oc: Occurrence**

**Table 3: Mineralogical Constituents of heat-treated beneficiated ore samples through froth flotation Test (Aerofloat 64)@ 9500 °C (75µm) and 10500 °C (75µm)**

| | | MOPA MURO (BMM) | | | | OBAN MASSIF (BOM) | | | |
|---|---|---|---|---|---|---|---|---|---|
| **Qualitative composition** | | 950$^0$C (75µm) | | 1050$^0$C (75µm) | | 950$^0$C (75µm) | | 1050$^0$C (75µm) | |
| Minerals | Chemical Formula | QC | Oc | QC | Oc | QC | Oc | QC | Oc |
| Pyrolusite | $MnO_2$ | 31 | 5 | 64 | 2 | 9 | 3 | 5.1 | 5 |
| Quartz | $SiO_2$ | 7.7 | 8 | 9.7 | 6 | 5.6 | 5 | 2.3 | 2 |
| Spessartine | $(Mn^{2+})_3Al_2(SiO_4)_3$ | 14 | 6 | 18.3 | 10 | 37 | 5 | 29 | 7 |
| Manganosite | MnO | 48 | 5 | 7.5 | 4 | 41 | 4 | 57 | 6 |
| Geothite | FeO(OH) | - | - | - | - | 7.2 | 6 | 7.2 | 7 |

**Note: QC: Quantitative composition; Oc: Occurrence**

The table summarizes the quantitative composition (QC) and occurrence (Oc) of the major mineral phases identified in the Mopa-Muro and Oban Massif ores after calcination at 950°C and 1050°C using particle sizes of 300 µm and 425 µm, respectively. The XRD results demonstrate that the liberation process significantly influenced the distribution and concentration of manganese-bearing minerals in both deposits. Four principal mineral phases, namely pyrolusite ($MnO_2$), manganosite (MnO), spessartine [$Mn_3Al_2(SiO_4)_3$], and quartz ($SiO_2$), were identified in the Mopa-Muro ore, whereas the Oban Massif ore contained an additional iron-bearing mineral, goethite [FeO(OH)]. The presence of quartz as the dominant gangue mineral confirms that silica remains the principal impurity requiring removal during beneficiation, while the occurrence of goethite in the Oban Massif deposit reflects greater iron mineralization that may complicate downstream metallurgical processing.

For the Mopa-Muro ore treated at 950°C and a particle size of 300 µm, manganosite constituted the dominant mineral phase with a quantitative composition of 63.0%, followed by spessartine (23.0%), pyrolusite (10.7%), and quartz (3.0%). This distribution indicates that thermal treatment at 950°C promoted the reduction of higher manganese oxides into manganosite, which became the predominant manganese-bearing phase. The relatively low quartz content further suggests effective liberation of the manganese minerals from the silicate gangue, thereby improving the concentrate quality. Similar phase transformations during reduction roasting have been reported by Rath *et al*. (2018), who observed progressive conversion of manganese oxides with increasing reduction intensity.

Following calcination at 1050 °C and 425 µm, the mineralogical composition of the Mopa-Muro concentrate changed markedly. Pyrolusite became the predominant phase with a quantitative composition of 75.0%, while quartz, spessartine, and manganosite decreased to 6.7%, 14.0%, and 4.0%, respectively. This substantial enrichment of pyrolusite indicates that the combined effect of higher calcination temperature and increased particle size favoured the concentration of manganese oxide minerals while suppressing the relative abundance of other associated phases. The increase from 10.7% to 75.0% represents an enrichment of approximately 64.3 percentage points, confirming that liberation coupled with thermal treatment effectively upgraded the manganese concentrate. The observed improvement is consistent with previous studies demonstrating that appropriate thermal treatment enhances mineral liberation and promotes concentration of valuable manganese phases (Mehdilo *et al*., 2013; Liu *et al*., 2018).

In contrast, the Oban Massif ore exhibited a different mineralogical response to thermal treatment. At 950°C and 300 µm, manganosite remained the dominant phase with a quantitative composition of 44.0%, followed by spessartine (35.0%), pyrolusite (10.5%), goethite (5.7%), and quartz (4.8%). The relatively high abundance of spessartine and the presence of goethite indicate a more complex mineralogical assemblage than that observed in the Mopa-Muro deposit. These minerals are closely associated with silicate and iron-bearing gangue phases, making complete liberation more difficult and consequently reducing beneficiation efficiency.

At 1050°C and 425 µm, pyrolusite increased moderately from 10.5% to 14.7%, whereas spessartine increased from 35.0% to 48.0%. Quartz also increased to 10.2%, while manganosite decreased to 22.0%, and goethite decreased slightly to 4.6%. Unlike the Mopa-Muro ore, where pyrolusite became the dominant mineral after heat treatment, the Oban Massif concentrate remained dominated by spessartine. The increase in pyrolusite of

only 4.2 percentage points indicates a considerably lower beneficiation efficiency than that achieved for the Mopa-Muro ore. This relatively limited improvement can be attributed to the stronger interlocking between manganese minerals and silicate gangue, which restricts complete mineral liberation during grinding and calcination.

The occurrence (Oc) values presented in Table 1 further support the mineralogical observations. In the Mopa-Muro concentrate, pyrolusite exhibited the highest occurrence value (13) at 1050°C, whereas spessartine and manganosite showed relatively low occurrence values (3–7), suggesting that pyrolusite became the most abundant crystalline phase after beneficiation. Conversely, quartz displayed the highest occurrence value (16) despite its comparatively low quantitative composition, reflecting the widespread distribution of fine-grained silica throughout the ore matrix. Similar behaviour was observed in the Oban Massif samples, where quartz also exhibited a relatively high occurrence despite its modest abundance, indicating persistent dissemination of silicate gangue within the ore.

Comparison of the two deposits demonstrates that the Mopa-Muro ore responded more favourably to liberation beneficiation than the Oban Massif ore. The substantial enrichment of pyrolusite and corresponding reduction of gangue minerals indicate superior liberation characteristics and a higher potential for producing metallurgical-grade concentrates. Conversely, the persistent dominance of spessartine and the presence of goethite in the Oban Massif samples suggest that additional beneficiation stages, such as magnetic separation or selective flotation, may be required to further improve concentrate quality.

Overall, the liberation study confirms that calcination temperature, particle size, and intrinsic mineralogical characteristics collectively control the beneficiation efficiency of Nigerian manganese ores. The superior performance of the Mopa-Muro ore demonstrates that mineral liberation is strongly influenced by the original textural relationships between manganese minerals and gangue constituents. These findings agree with previous investigations, which reported that successful upgrading of low-grade manganese ores depends largely on the degree of mineral liberation achieved before physical separation (Jain, 2011; Mehdilo *et al*., 2013; Rath *et al*., 2018). The results further indicate that liberation concentration produced the highest manganese enrichment among the beneficiation techniques evaluated in this study, highlighting its suitability as a primary upgrading method for the Mopa-Muro deposit.

### *3.1.2 Mineralogical Composition of Heat-Treated Beneficiated Ores Obtained by Gravity Separation*

The mineralogical composition of the heat-treated manganese ore concentrates obtained through the gravity separation process is presented in Table 2. The table summarizes the quantitative composition (QC) and occurrence (Oc) of the principal mineral phases identified in the Mopa-Muro and Oban Massif manganese ores after calcination at 950°C (300 μm) and 1050°C (105 μm). These results were used to evaluate the influence of gravity concentration, particle size reduction, and thermal treatment on the upgrading efficiency of the two Nigerian manganese deposits.

The XRD analysis showed that the gravity separation process retained the same major mineral assemblage observed during the liberation study, namely pyrolusite ($MnO_2$), manganosite (MnO), spessartine [$Mn_3Al_2(SiO_4)_3$], and quartz ($SiO_2$) in both deposits, while goethite [FeO(OH)] remained exclusive to the Oban Massif ore. However, the relative proportions of these mineral phases differed considerably from those observed after liberation concentration, indicating that gravity separation produced a different upgrading response due to the influence of

density differences between manganese minerals and associated gangue constituents.

For the Mopa-Muro ore calcined at 950°C and 300 µm, pyrolusite was the dominant mineral phase with a quantitative composition of 34.0%, followed by quartz (28.0%), spessartine (23.0%), and manganosite (15.0%). The relatively high quartz content indicates that although gravity concentration successfully separated a significant proportion of the heavy manganese minerals from the lighter gangue, a substantial amount of silica remained associated with the concentrate. Quartz possesses a relatively low specific gravity compared with manganese oxides, but incomplete mineral liberation and interlocking between quartz and manganese minerals often reduce the effectiveness of gravity separation, particularly in low-grade ores (Jain, 2011).

Following calcination at 1050°C and a reduced particle size of 105 µm, the mineralogical composition of the Mopa-Muro concentrate changed considerably. Manganosite increased from 15.0% to 40.0%, while spessartine increased from 23.0% to 30.0%. In contrast, pyrolusite decreased from 34.0% to 21.0%, and quartz decreased substantially from 28.0% to 10.0%. The reduction in quartz content demonstrates that finer grinding enhanced the liberation of silicate gangue from manganese-bearing minerals, thereby improving concentrate purity. The increase in manganosite also suggests that thermal reduction promoted the conversion of higher manganese oxides into lower oxidation-state manganese phases under the prevailing calcination conditions. Similar observations have been reported for reduction-roasted manganese ores, where elevated temperatures and improved liberation increase the concentration of reduced manganese oxides (Rath *et al*., 2018).

The reduction in quartz by approximately 18 percentage points represents a significant improvement in concentrate quality because silica is the principal impurity affecting ferromanganese production. Excessive silica increases slag volume, energy consumption, and flux requirements during smelting, thereby reducing process efficiency (Coetsee, 2019). Consequently, the observed reduction in quartz demonstrates that gravity separation was effective in removing a considerable fraction of the silicate gangue from the Mopa-Muro ore.

The Oban Massif ore exhibited a markedly different beneficiation behaviour. At 950°C and 300 µm, manganosite constituted the dominant mineral phase with a quantitative composition of 50.0%, followed by spessartine (23.0%), quartz (14.0%), goethite (8.9%), and pyrolusite (4.2%). The relatively high manganosite content indicates that thermal reduction effectively transformed manganese oxides within the ore. However, the persistent presence of quartz and goethite suggests that the concentrate remained contaminated with silicate and iron-bearing gangue minerals.

After calcination at 1050°C and 105 µm, the mineralogical composition changed appreciably. Spessartine increased significantly from 23.0% to 49.0%, becoming the dominant mineral phase, whereas manganosite decreased from 50.0% to 38.0%. Pyrolusite increased slightly from 4.2% to 7.5%, while quartz decreased markedly from 14.0% to 4.0%, and goethite declined from 8.9% to 2.0%. These results indicate that finer particle size substantially improved the removal of both silica and iron-bearing impurities, although the increase in spessartine suggests that manganese remained partly associated with silicate minerals.

The reduction of quartz from 14.0% to 4.0% and goethite from 8.9% to 2.0% demonstrates that gravity separation was particularly effective in eliminating low-density gangue minerals from the Oban Massif ore. Nevertheless, the comparatively modest increase in pyrolusite indicates that the upgrading efficiency remained lower than that observed for the Mopa-Muro deposit. This

difference is attributed to the stronger mineral intergrowth and more complex textural relationships characteristic of the Oban Massif ore, which hinder complete liberation of manganese minerals from silicate and iron-rich gangue (Mehdilo *et al*., 2013).

The occurrence values presented in Table 2 further support these observations. In the Mopa-Muro samples, quartz exhibited the highest occurrence value (22) at 950°C despite its moderate quantitative composition, confirming its widespread dissemination within the ore. Following calcination at 1050°C, spessartine displayed the highest occurrence (34), indicating that the mineral became more uniformly distributed throughout the concentrate. Similarly, in the Oban Massif ore, pyrolusite exhibited relatively high occurrence values (10–11), while goethite displayed lower occurrence values (3–9), reflecting its partial removal during beneficiation.

Comparison between the two deposits indicates that particle size exerted a greater influence on beneficiation efficiency than temperature alone. Reducing the particle size from 300 µm to 105 µm enhanced mineral liberation, allowing more effective separation of manganese-bearing minerals from quartz and goethite. This finding agrees with previous studies, which demonstrated that finer particle sizes improve the efficiency of gravity concentration by increasing the degree of liberation of valuable minerals from gangue constituents (Jain, 2011; Singh *et al*., 2011).

When compared with the liberation study discussed in the preceding section, gravity separation produced lower pyrolusite enrichment but achieved a more pronounced reduction in quartz content, particularly in the Oban Massif ore. This observation suggests that gravity concentration is more effective for removing gangue minerals than for selectively enriching pyrolusite. Consequently, gravity separation may be more suitable as a pre-concentration step prior to flotation or magnetic separation rather than as a standalone beneficiation process.

Overall, the results presented in Table 2 demonstrate that gravity separation significantly improved the mineralogical quality of both Nigerian manganese ores through the removal of silica and iron-bearing gangue. However, the extent of upgrading depended strongly on ore mineralogy, particle size, and calcination temperature. The Mopa-Muro ore exhibited superior beneficiation characteristics because of its simpler mineralogical composition and better liberation behaviour, whereas the Oban Massif ore may require additional beneficiation stages to achieve metallurgical-grade manganese concentrates.

### *3.1.3 Mineralogical Composition of Heat-Treated Beneficiated Ores Obtained by Froth Flotation*

The mineralogical compositions of the heat-treated manganese ore concentrates obtained through froth flotation are presented in Table 3. The concentrates were produced using the Aerofloat 64 collector after calcination at 950°C and 1050°C with a particle size of 75 µm. The results provide insight into the effectiveness of froth flotation in selectively enriching manganese-bearing minerals while rejecting silicate gangue from the Mopa-Muro and Oban Massif manganese deposits.

Froth flotation produced four major manganese-bearing mineral phases in the Mopa-Muro ore, namely pyrolusite ($MnO_2$), manganosite (MnO), spessartine [$Mn_3Al_2(SiO_4)_3$], and quartz ($SiO_2$), while the Oban Massif concentrate additionally contained goethite [FeO(OH)]. The flotation process exploits differences in the surface physicochemical properties of minerals rather than their densities, making it particularly suitable for finely disseminated ores where gravity separation becomes less effective (Shu *et al*., 2019). Consequently, the use of a fine particle size of 75 µm enhanced mineral liberation and increased the probability of

selective attachment of manganese-bearing minerals to flotation bubbles.

For the Mopa-Muro ore, calcination at 950°C produced a concentrate containing 48.0% manganosite, 31.0% pyrolusite, 14.0% spessartine, and only 7.7% quartz. The relatively low quartz content indicates that froth flotation effectively rejected the silicate gangue during beneficiation. The predominance of manganosite suggests that thermal treatment promoted partial reduction of higher manganese oxides, while flotation selectively concentrated the liberated manganese minerals.

Increasing the calcination temperature to 1050°C produced a remarkable change in mineralogical composition. The quantitative composition of pyrolusite increased dramatically from 31.0% to 64.0%, representing an enrichment of approximately 33 percentage points, whereas spessartine increased moderately from 14.0% to 18.3%. Conversely, manganosite decreased substantially from 48.0% to 7.5%, while quartz increased slightly from 7.7% to 9.7%. The considerable enrichment of pyrolusite demonstrates that elevated calcination temperature enhanced the crystallization and concentration of manganese dioxide, making it the dominant mineral phase after flotation. This observation suggests that flotation, when combined with thermal pretreatment, is highly effective for concentrating pyrolusite in the Mopa-Muro ore.

The reduction in manganosite at higher temperature may be attributed to phase transformation reactions occurring during calcination. Manganese oxides undergo complex oxidation–reduction equilibria depending on temperature and oxygen availability, resulting in changes in the relative proportions of $MnO_2$ and MnO (Rath *et al*., 2018). The predominance of pyrolusite in the final concentrate therefore indicates that the calcination conditions favoured the stabilization of manganese dioxide during cooling, thereby increasing its apparent abundance in the XRD analysis.

In contrast, the Oban Massif ore exhibited a different flotation behaviour. At 950°C, the concentrate contained 41.0% manganosite, 37.0% spessartine, 9.0% pyrolusite, 7.2% goethite, and 5.6% quartz. Unlike the Mopa-Muro deposit, manganosite remained the dominant manganese-bearing mineral, while pyrolusite accounted for only a small proportion of the concentrate. The higher abundance of spessartine further indicates that a significant fraction of manganese remained incorporated within silicate minerals that are relatively difficult to separate by flotation.

Following calcination at 1050°C, the mineralogical composition changed appreciably. Manganosite increased further to 57.0%, becoming the overwhelmingly dominant mineral phase, whereas pyrolusite decreased from 9.0% to 5.1%. Spessartine decreased from 37.0% to 29.0%, while quartz was reduced from 5.6% to 2.3%, indicating improved gangue removal. Interestingly, goethite remained constant at 7.2%, suggesting that the flotation process had little influence on the separation of the iron-bearing mineral under the operating conditions employed.

The decrease in quartz from 5.6% to 2.3% demonstrates that froth flotation effectively rejected silicate gangue from the Oban Massif ore. Nevertheless, the simultaneous reduction in pyrolusite indicates that flotation recovery was influenced not only by mineral liberation but also by the surface chemistry of individual manganese minerals. Pyrolusite and manganosite possess different surface charge characteristics and collector adsorption behaviours, which influence their flotation responses (Shu *et al*., 2019). Consequently, flotation selectively concentrated manganosite in the Oban Massif ore while favouring pyrolusite enrichment in the Mopa-Muro deposit.

The occurrence values reported in Table 3 further support these observations. For the

Mopa-Muro concentrate, pyrolusite occurrence decreased from 5 to 2 despite its substantial increase in quantitative composition, suggesting that the mineral became concentrated into fewer but larger crystalline domains following calcination. Conversely, spessartine occurrence increased from 6 to 10, indicating a broader distribution of this mineral within the concentrate. In the Oban Massif ore, occurrence values generally increased with calcination temperature for manganosite and goethite, whereas quartz occurrence decreased, reflecting progressive elimination of silicate gangue during flotation.

A comparison of the two deposits demonstrates that froth flotation produced contrasting beneficiation responses owing to differences in mineralogical composition and ore texture. The Mopa-Muro ore showed exceptional enrichment of pyrolusite, whereas the Oban Massif ore was characterized by substantial concentration of manganosite. These differences highlight the importance of mineralogical characteristics in determining flotation performance. Previous investigations have similarly reported that flotation efficiency depends strongly on mineral surface properties, liberation characteristics, and collector adsorption mechanisms (Mehdilo *et al*., 2013; Shu *et al*., 2019).

When compared with the liberation study and gravity separation discussed in the preceding sections, froth flotation achieved the greatest reduction in quartz content, particularly in the Oban Massif ore where quartz decreased to only 2.3%. This demonstrates that flotation is highly effective for removing finely disseminated silicate gangue. However, the beneficiation response varied between deposits because flotation preferentially enriched different manganese-bearing minerals depending on their surface chemistry and mineral associations.

Overall, the results presented in Table 3 confirm that froth flotation is an effective beneficiation technique for upgrading Nigerian low-grade manganese ores, particularly after fine grinding and thermal pretreatment. The substantial enrichment of pyrolusite in the Mopa-Muro ore and the high manganosite concentration obtained from the Oban Massif deposit demonstrate the capability of flotation to selectively recover valuable manganese minerals. Nevertheless, the contrasting mineralogical responses suggest that flotation reagent selection and operating conditions should be optimized separately for each deposit to maximize manganese recovery and concentrate grade.

### *3.2 Comparative Evaluation of Beneficiation Techniques*

The effectiveness of the three beneficiation techniques investigated in this study, namely liberation study (LST), gravity separation (GST), and froth flotation (FFT), was evaluated by comparing the quantitative composition of the major manganese-bearing minerals identified in the beneficiated concentrates. The comparison was based on the enrichment of the economically valuable manganese minerals, particularly pyrolusite ($MnO_2$) and manganosite (MnO), together with the reduction of the principal gangue mineral, quartz ($SiO_2$). The comparative mineralogical data obtained from Tables 1 to 3 demonstrate that the beneficiation efficiency varied considerably with the processing technique, calcination temperature, particle size, and the inherent mineralogical characteristics of the two deposits.

Among the three beneficiation methods, the liberation study produced the highest degree of manganese enrichment, particularly for the Mopa-Muro deposit. After calcination at 1050°C, the pyrolusite content increased from 10.7% in the untreated concentrate to 75.0%, representing an enrichment of approximately 64.3 percentage points. Similarly, the Oban Massif ore exhibited an increase in pyrolusite from 10.5% to 14.7%, although the improvement was substantially lower than that observed for the Mopa-Muro ore. The superior

performance of the liberation process indicates that adequate comminution successfully separated manganese-bearing minerals from associated gangue, thereby enhancing subsequent concentration during thermal treatment.

The outstanding performance of liberation concentration is primarily attributed to the improved degree of mineral liberation achieved before calcination. During grinding, interlocked mineral particles are progressively broken apart, allowing valuable manganese minerals to exist as discrete particles rather than composite grains with quartz and silicate gangue. Previous studies have demonstrated that mineral liberation is one of the most important factors governing beneficiation efficiency because incomplete liberation limits the effectiveness of all subsequent physical separation techniques (Jain, 2011; Mehdilo *et al*., 2013).

The froth flotation process ranked second in beneficiation performance. For the Mopa-Muro deposit, pyrolusite increased from 31.0% at 950°C to 64.0% at 1050°C, representing an enrichment of approximately 33 percentage points. In contrast, the Oban Massif deposit exhibited an increase in manganosite from 41.0% to 57.0%, while pyrolusite decreased slightly. These results indicate that flotation selectively recovered different manganese-bearing minerals depending on their surface chemistry and mineralogical associations. The higher flotation efficiency observed for the Mopa-Muro ore can be attributed to the predominance of oxide minerals with favourable collector adsorption characteristics, whereas the Oban Massif ore contains larger proportions of silicate-associated manganese minerals such as spessartine that exhibit comparatively poorer flotation behaviour (Shu *et al*., 2019).

An important advantage of froth flotation was its ability to reduce the quartz content to very low levels. The quartz concentration in the Oban Massif ore decreased to 2.3%, representing the lowest silica content obtained among all beneficiation methods. This finding indicates that flotation is particularly effective for removing finely disseminated silicate gangue, which is difficult to separate by gravity concentration once particle sizes become very small. Similar observations have been reported for low-grade manganese ores, where flotation significantly improves concentrate quality by selectively removing silica-rich gangue minerals (Shu *et al*., 2019).

The gravity separation process produced comparatively lower manganese enrichment than the liberation and flotation techniques. Nevertheless, it effectively reduced the amount of gangue minerals through density-based separation. The highest quantitative composition obtained by gravity concentration was 50.0% manganosite in the Oban Massif ore and 40.0% manganosite in the Mopa-Muro ore after calcination at 1050°C. Similarly, spessartine increased to 49.0% in the Oban Massif concentrate, while quartz decreased substantially in both deposits. The relatively lower recovery of pyrolusite during gravity separation may be attributed to incomplete liberation and the close association of manganese oxides with quartz and silicate minerals, which reduced the density contrast between valuable and gangue particles.

The comparative results further reveal significant differences between the two manganese deposits. Throughout the beneficiation experiments, the Mopa-Muro ore consistently exhibited higher pyrolusite enrichment, whereas the Oban Massif ore remained dominated by manganosite and spessartine. This variation reflects differences in the geological formation and mineralogical characteristics of the two deposits. The Mopa-Muro ore appears to contain more freely liberated manganese oxide minerals that respond readily to physical beneficiation, whereas the Oban Massif ore contains more complex mineral intergrowths involving

silicates and iron-bearing phases, thereby reducing beneficiation efficiency. Similar deposit-dependent beneficiation behaviour has been reported for low-grade manganese ores from Iran, India, and China, where mineral texture and gangue association significantly influence upgrading performance (Mehdilo *et al*., 2013; Rath *et al*., 2018).

The influence of calcination temperature was evident across all beneficiation methods. Increasing the temperature from 950°C to 1050°C generally enhanced manganese mineral enrichment and reduced the proportion of undesirable gangue minerals. Higher temperatures promote reduction roasting reactions, improve mineral recrystallization, and weaken the interlocking between manganese minerals and gangue, thereby facilitating subsequent separation (Liu *et al*., 2018). However, the extent of improvement depended on the beneficiation technique employed and the mineralogical composition of the ore.

Similarly, particle size exerted a pronounced effect on beneficiation performance. Finer particle sizes generally produced higher concentrate grades because of improved mineral liberation. As particle size decreases, composite particles are progressively broken into individual mineral grains, increasing the efficiency of gravity separation and flotation. Nevertheless, excessively fine particles may reduce gravity separation efficiency owing to the diminished settling velocity of fine particles, whereas flotation generally benefits from finer particle sizes because of increased particle–bubble interactions (Jain, 2011).

Considering the overall beneficiation performance, the three methods may be ranked according to their manganese upgrading efficiency as follows:

Liberation study > Froth flotation > Gravity separation.

This ranking is based on the maximum quantitative compositions of the principal manganese-bearing minerals achieved after beneficiation. Liberation concentration produced the highest pyrolusite content (75.0%) in the Mopa-Muro ore, froth flotation achieved the second-highest enrichment (64.0%), whereas gravity separation produced comparatively lower enrichment but demonstrated superior gangue rejection through density separation. Consequently, liberation concentration appears to be the most suitable primary beneficiation technique for the studied Nigerian manganese ores, while froth flotation can serve as an effective secondary upgrading method for finely liberated concentrates.

Although significant improvements in manganese concentration were achieved, the final concentrates still contain appreciable quantities of silicate minerals and therefore do not fully satisfy the chemical specifications required for high-grade metallurgical manganese ores, which typically contain 40–50 wt.% Mn with very low silica and iron impurities (Coetsee, 2019). Additional upgrading processes, such as magnetic separation or hydrometallurgical treatment, may therefore be required to produce concentrates suitable for the manufacture of high-carbon ferromanganese. Nevertheless, the beneficiation routes investigated in this study substantially improved the quality of both Nigerian manganese deposits and demonstrated their potential as alternative raw materials for ferroalloy production.

### *3.3 Fourier Transform Infrared (FTIR) Characterization of the Beneficiated Manganese Ores*

The Fourier Transform Infrared (FTIR) spectra of the heat-treated beneficiated manganese ores obtained from the Mopa-Muro and Oban Massif deposits are presented in Figs. 1 and 2, respectively. FTIR spectroscopy was employed to identify the functional groups, metal–oxygen vibrations, and hydroxyl species associated with the manganese-bearing minerals after beneficiation and thermal treatment. The spectra complement the XRD

results by confirming the chemical bonding environments and the mineralogical transformations that occurred during beneficiation and calcination.

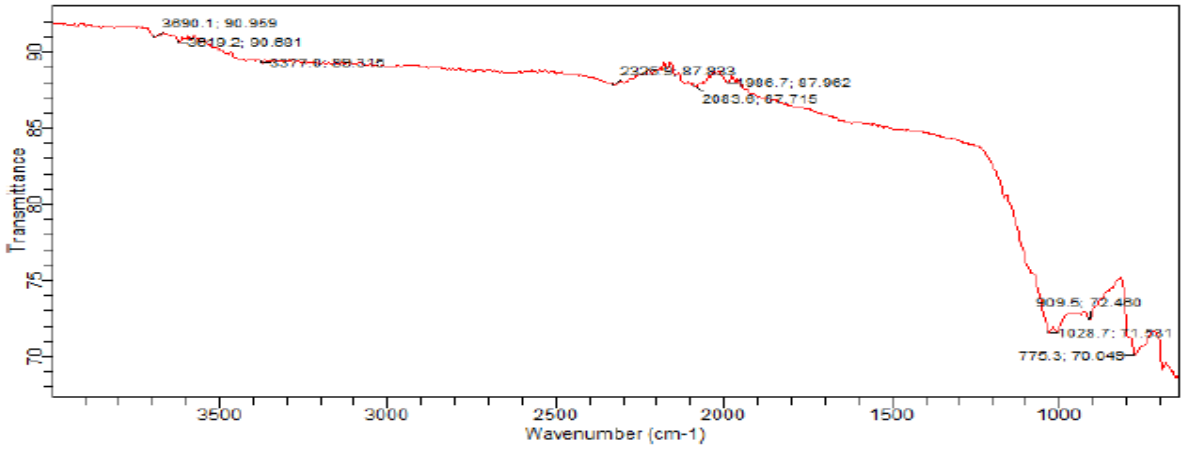


**Fig. : FTIR spectrum of heat treated beneficiated Mopa muro manganese sample**

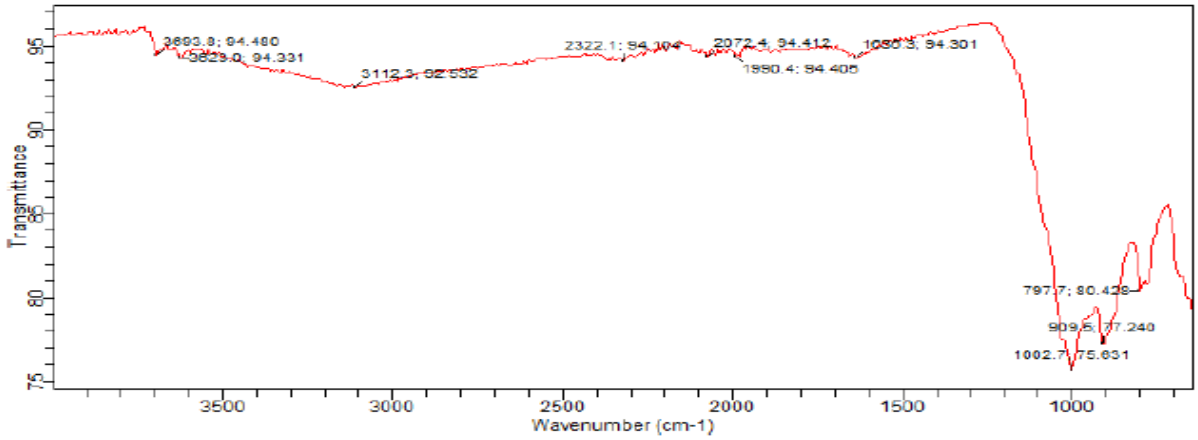


**Fig. 2: FTIR spectrum of heat treated beneficiated Oban Massif manganese sample**

### *3.3.1 FTIR Spectrum of the Mopa-Muro Beneficiated Manganese Ore*

Fig. 1 presents the FTIR spectrum of the heat-treated beneficiated manganese ore from the Mopa-Muro deposit. The spectrum exhibits several absorption bands distributed within the functional group region (3700–3000 $cm^{-1}$) and the fingerprint region (1100–600 $cm^{-1}$), indicating the presence of both hydroxyl-containing minerals and manganese oxide phases.

A broad absorption band centred around 3890–3378 $cm^{-1}$ corresponds to the stretching vibration of hydroxyl (–OH) groups. Although relatively weak after calcination, this band indicates the presence of structurally bound hydroxyl groups and adsorbed moisture associated with manganese oxide minerals and minor hydrous silicates. The reduced intensity of this band compared with untreated manganese ores suggests that dehydration occurred during calcination at elevated temperatures. Similar observations have been reported for thermally treated manganese oxides, where increasing calcination temperature removes physically adsorbed water while retaining only structurally bonded hydroxyl species (Belardi *et al*., 2011).

The weak absorption bands observed at approximately 2326, 2084, and 1987 $cm^{-1}$ are attributed to O–H bending vibrations and weakly bonded hydroxyl species associated with manganese oxide lattices. These bands

may also indicate residual carbonate or atmospheric carbon dioxide adsorbed on the mineral surfaces following cooling after calcination. Their relatively low intensity demonstrates that thermal treatment effectively removed most volatile constituents from the ore.

The most significant absorption features occur within the fingerprint region. Strong absorption peaks located at approximately 1029 $cm^{-1}$, 910 $cm^{-1}$, and 775 $cm^{-1}$ are characteristic of Mn–O stretching vibrations associated with manganese oxide minerals, particularly pyrolusite ($MnO_2$) and manganosite (MnO). These bands confirm the abundance of manganese oxide phases identified by XRD analysis. The intense absorption near 1029 $cm^{-1}$ is attributed to asymmetric Mn–O stretching vibrations, whereas the bands near 910 $cm^{-1}$ and 775 $cm^{-1}$ correspond to lattice vibrations of Mn–O octahedra. Similar FTIR signatures have been reported for pyrolusite-rich manganese ores and thermally treated manganese oxides (Belardi *et al*., 2011).

The relatively sharp and well-defined Mn–O absorption bands indicate improved crystallinity following calcination. Elevated temperatures promote recrystallization of manganese oxide phases, thereby producing more ordered crystal structures and stronger infrared absorption. This observation agrees with the XRD results, which showed significant enrichment of pyrolusite after liberation and thermal treatment.

Notably, no distinct absorption peaks were observed between approximately 3670 and 3550 $cm^{-1}$, indicating the absence of free hydroxyl groups and confirming that dehydration was largely completed during calcination. The disappearance of these bands further demonstrates the effectiveness of thermal treatment in removing physically adsorbed water and unstable hydroxyl species.

Overall, the FTIR spectrum confirms that the Mopa-Muro concentrate is dominated by manganese oxide minerals, with only minor contributions from hydroxyl-bearing phases. These findings are consistent with the XRD results, which identified pyrolusite and manganosite as the principal mineral phases after beneficiation.

### *3.3.2 FTIR Spectrum of the Oban Massif Beneficiated Manganese Ore*

The FTIR spectrum of the beneficiated Oban Massif manganese ore is presented in Fig. 2. Although the spectrum shares many similarities with that of the Mopa-Muro ore, several important differences reflect the more complex mineralogical composition of the Oban Massif deposit.

A broad hydroxyl stretching band extending from approximately 3693 to 3112 $cm^{-1}$ is more pronounced than that observed in the Mopa-Muro sample. This stronger hydroxyl absorption indicates the persistence of hydrous minerals after calcination and agrees with the XRD identification of goethite [FeO(OH)], which contains structural hydroxyl groups. The broader band also suggests stronger hydrogen bonding arising from residual hydrous iron oxides and silicate minerals.

Additional weak absorption bands occur near 2322, 2072, and 1990 $cm^{-1}$, corresponding to hydroxyl bending vibrations and adsorbed molecular species. The persistence of these bands indicates that the Oban Massif ore retained slightly more hydroxyl-containing phases than the Mopa-Muro concentrate, reflecting differences in mineralogical composition between the two deposits.

The fingerprint region exhibits strong absorption bands at approximately 1003 $cm^{-1}$, 910 $cm^{-1}$, and 798 $cm^{-1}$. These bands are assigned to Mn–O stretching vibrations associated with pyrolusite, manganosite, and other manganese oxide minerals. Their presence confirms that manganese oxide phases remained the dominant constituents after beneficiation despite the higher abundance of silicate and iron-bearing minerals in the Oban Massif ore.

Compared with the Mopa-Muro spectrum, the absorption bands in the Oban Massif ore are broader and slightly less intense. This broadening suggests greater structural disorder arising from the coexistence of manganese oxides, silicates, and iron oxyhydroxides within the concentrate. The observation is consistent with the XRD analysis, which showed appreciable quantities of spessartine and goethite alongside manganese oxide minerals.

The spectrum also exhibits weak Si–O stretching contributions around 1000–1030 $cm^{-1}$, confirming the persistence of quartz and manganese silicates after beneficiation. These residual silicate phases correspond well with the quartz and spessartine identified by XRD and explain why complete upgrading of the Oban Massif ore was not achieved using the beneficiation techniques investigated.

Similar to the Mopa-Muro spectrum, the absence of strong absorption peaks between 3670 and 3550 $cm^{-1}$ indicates that free hydroxyl groups were largely eliminated during calcination. The remaining hydroxyl absorption therefore arises mainly from structurally bonded hydroxyl groups within goethite rather than physically adsorbed water.

### *3.3.3 Comparative Interpretation of the FTIR Spectra*

Comparison of Figs. 1 and 2 reveals that both manganese ores possess similar fundamental manganese oxide structures but differ in the abundance of associated hydroxyl and silicate minerals. The Mopa-Muro ore exhibits stronger Mn–O stretching bands and weaker hydroxyl absorption, indicating a higher concentration of manganese oxide minerals and a lower proportion of hydrous gangue minerals. Conversely, the Oban Massif ore displays broader hydroxyl bands and slightly weaker Mn–O vibrations owing to the presence of goethite and silicate minerals.

The FTIR results strongly support the mineralogical observations obtained from XRD analysis. Both techniques consistently identify pyrolusite, manganosite, and spessartine as the dominant manganese-bearing minerals, while quartz is confirmed as the principal gangue mineral and goethite is detected only in the Oban Massif ore. The agreement between FTIR and XRD demonstrates the reliability of the mineralogical characterization performed in this study.

The reduction in hydroxyl absorption after calcination further confirms that thermal treatment promoted dehydration and mineral transformation, processes that facilitate the liberation of manganese minerals during beneficiation. Previous studies have shown that calcination weakens the bonding between manganese oxides and gangue minerals, thereby improving the efficiency of subsequent physical separation processes (Belardi *et al*., 2011; Rath *et al*., 2018).

Overall, the FTIR investigation demonstrates that beneficiation and thermal treatment significantly enhanced the concentration of manganese oxide minerals while reducing hydrous and silicate impurities. These structural modifications are consistent with the improved mineralogical compositions observed by XRD and explain the higher beneficiation efficiencies obtained for the Mopa-Muro deposit relative to the Oban Massif deposit.

### 3.3 Beneficiation Mechanism and Phase Transformation During Reduction Roasting

This section should be about **2–3 pages long**, include properly numbered equations (e.g., Equations 3.1–3.5), discuss the thermodynamics of manganese oxide reduction, explain the XRD phase transformations observed in the study, and integrate the effects of temperature, particle size, and silica interaction. Adding this section would make the manuscript suitable for publication in a mineral processing or extractive metallurgy journal.

wtite the section, 3.3 Beneficiation Mechanism and Phase Transformation During Heat Treatment

### *3.4 Beneficiation Mechanism and Phase Transformation During Heat Treatment*

The beneficiation of the low-grade manganese ores from the Mopa-Muro and Oban Massif deposits was enhanced through the combined effects of particle size reduction, physical separation, and thermal treatment. During calcination at 950–1050 °C, important mineralogical transformations occurred that increased the concentration of manganese-bearing minerals while reducing the abundance of gangue constituents. The beneficiation mechanism is governed by reduction roasting reactions, mineral liberation, and phase transformation of manganese oxides, which collectively improve the quality of the manganese concentrate.

During calcination, carbon present in the furnace atmosphere or produced from the decomposition of carbonaceous materials reacts with carbon dioxide to generate carbon monoxide (CO), which serves as the principal reducing agent for manganese oxides. The reduction reaction is represented by equation 1

$$C + CO_2 \rightarrow 2CO \quad (1)$$

The carbon monoxide produced subsequently reduces the higher oxidation-state manganese oxides in a stepwise manner. Initially, pyrolusite ($MnO_2$), which contains manganese in the +4 oxidation state, is partially reduced to bixbyite ($Mn_2O_3$) according to equation 2

$$2MnO_2 + CO \rightarrow Mn_2O_3 + CO_2 \quad (2)$$

Further reduction of $Mn_2O_3$ produces hausmannite ($Mn_3O_4$), as shown in equation 3:

$$Mn_2O_3 + CO \rightarrow Mn_3O_4 + CO_2 \quad (3)$$

Continued reduction converts $Mn_3O_4$ into manganosite (MnO), the most stable manganese oxide under strongly reducing conditions, according to equation 4,

$$Mn_3O_4 + CO_2 \rightarrow MnO + CO_2 \quad (4)$$

MThe formation of MnO represents an important intermediate stage during manganese beneficiation because manganosite possesses improved metallurgical properties for subsequent reduction during ferromanganese production. The progressive reduction sequence,

$$2MnO_2 \rightarrow Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$$

demonstrates the continuous decrease in manganese oxidation state from +4 to +2 with increasing temperature and reducing atmosphere. Similar reduction pathways have been reported during reduction roasting of low-grade manganese ores (Rath *et al*., 2018; Liu *et al*., 2018).

The liberated manganese oxides may subsequently react with silica ($SiO_2$), the principal gangue mineral identified in both deposits, leading to the formation of manganese silicates. This reaction is represented by equation 5 or 6 in alternative

$$2MnO + SiO_2 \rightarrow Mn_2SiO_4 \quad (5)$$

$$2MnO + SiO_2 \rightarrow MnSiO_3 \quad (6)$$

The formation of manganese silicates explains the persistence of spessartine and other silicate-associated manganese minerals observed in the XRD patterns, particularly for the Oban Massif ore. These silicate phases are relatively stable at elevated temperatures and reduce the efficiency of beneficiation because manganese becomes chemically bonded within the silicate lattice rather than existing as discrete oxide minerals. Consequently, complete separation of manganese from quartz becomes increasingly difficult once manganese silicates are formed (Mehdilo *et al*., 2013).

The results obtained in this study clearly demonstrate that temperature plays a critical role in controlling these phase transformations. Increasing the calcination temperature from 950°C to 1050°C accelerated the reduction reactions and promoted recrystallization of manganese oxide phases. This phenomenon was particularly evident in the Mopa-Muro ore, where the pyrolusite concentration increased from 10.7% to 75.0% following liberation and thermal treatment. The higher temperature also weakened the interlocking between manganese minerals and silicate gangue, thereby facilitating more efficient separation during

liberation, gravity concentration, and froth flotation.

Particle size also exerted a significant influence on beneficiation efficiency. Reduction of the ore particle size from 425 μm to 75 μm increased the degree of mineral liberation by exposing fresh mineral surfaces and reducing the proportion of composite particles containing both manganese minerals and quartz. Improved liberation enhanced collector adsorption during froth flotation and increased density contrast during gravity separation, resulting in higher concentrate grades. These observations agree with previous investigations that identified mineral liberation as the principal factor controlling beneficiation efficiency of low-grade manganese ores (Jain, 2011).

The XRD results further demonstrate that the Mopa-Muro deposit responded more favourably to thermal beneficiation than the Oban Massif deposit. The Mopa-Muro ore exhibited a remarkable increase in pyrolusite concentration after calcination, whereas the Oban Massif ore remained dominated by spessartine and manganosite because of stronger mineral intergrowth and greater iron-bearing gangue content. The presence of goethite [FeO(OH)] in the Oban Massif ore further complicated the reduction process because iron oxyhydroxides undergo dehydration and phase transformation simultaneously with manganese oxides, thereby producing a more complex mineral assemblage.

The FTIR spectra support the proposed beneficiation mechanism. The intense Mn–O stretching vibrations observed between 775 and 1029 $cm^{-1}$ confirm the formation and enrichment of manganese oxide minerals following calcination. Similarly, the absence of sharp hydroxyl absorption bands between 3670 and 3550 $cm^{-1}$ indicates that dehydration occurred during thermal treatment, resulting in the removal of free hydroxyl groups and adsorbed moisture. These structural changes improve mineral brittleness, promote grain boundary separation, and enhance liberation during beneficiation.

Overall, the beneficiation mechanism observed in this study involves the synergistic effects of thermal reduction, mineral phase transformation, particle liberation, and selective physical separation. Calcination promotes the progressive reduction of manganese oxides, weakens the bonding between manganese minerals and silicate gangue, and increases the concentration of valuable manganese phases. The subsequent application of liberation, gravity separation, and froth flotation further concentrates these liberated minerals, producing higher-grade manganese concentrates. The superior beneficiation response of the Mopa-Muro ore compared with the Oban Massif ore is attributed to its simpler mineralogical composition, lower gangue content, and greater susceptibility to thermal phase transformation. These findings demonstrate that reduction roasting combined with appropriate physical beneficiation techniques provides an effective approach for upgrading Nigerian low-grade manganese ores for potential ferroalloy applications.

## 4.0 Conclusion

This study demonstrated the beneficiation potential of low-grade manganese ores from Mopa-Muro and Oban Massif using liberation, gravity separation, and froth flotation combined with thermal treatment at 950–1050°C. XRD and FTIR analyses confirmed that the ores are dominated by pyrolusite, manganosite, spessartine, and quartz, while goethite was identified only in the Oban Massif deposit. Quartz was the principal gangue mineral responsible for mineral interlocking.

Among the beneficiation methods, the liberation study achieved the highest upgrading efficiency, increasing pyrolusite from 10.7% to 75.0% in the Mopa-Muro ore, followed by froth flotation, which produced 64.0% pyrolusite, while gravity separation effectively reduced silica and other gangue minerals. The Oban

Massif ore exhibited comparatively lower beneficiation efficiency because of its more complex mineralogical composition and stronger association of manganese minerals with silicate and iron-bearing phases.

Higher calcination temperature and finer particle size improved mineral liberation and manganese enrichment. FTIR results corroborated the XRD findings by confirming Mn–O bonds and the removal of hydroxyl groups after calcination. Although the beneficiated concentrates did not attain metallurgical-grade manganese specifications, they are suitable for the production of spiegeleisen (low-grade ferromanganese). Overall, the Mopa-Muro deposit exhibited greater beneficiation potential than the Oban Massif deposit.

Future studies should optimize the beneficiation process by integrating liberation, froth flotation, and magnetic separation to improve manganese recovery and reduce silica impurities. The effects of flotation reagents, calcination conditions, and particle size should be further investigated to enhance concentrate quality. Additional characterization using XRF, SEM–EDS, and automated mineralogical analysis, together with pilot-scale beneficiation studies, is recommended to evaluate the commercial feasibility of the Mopa-Muro and Oban Massif deposits. Complementary magnetic and hydrometallurgical treatment should also be explored to produce concentrates that meet international metallurgical-grade manganese specifications.

## 5.0 Reference


Belardi, G., Ballirano, P., Ferrini, M., Lavecchia, R., Medici, F., Piga, L., & Scoppettuolo, A. (2011). Thermochemical characterization of manganese-bearing minerals. *Thermochimica Acta, 526*, 169–177.

Coetsee, T. (2019). A review of ore smelting in high-carbon ferromanganese production. *Mineral Processing and Extractive Metallurgy Review*. https://doi.org/10.1080/08827508.2019.1575271

Jain, S. K. (2011). *Mineral processing* (2nd ed.). CBS Publishers and Distributors.

Kamalpour, S., & Rankin, W. J. (2004). The behaviour of coke in submerged arc furnace smelting of ferromanganese. In M. Abdul-Latif et al. (Eds.), *Transformation through Technology: Proceedings of the Tenth International Ferroalloys Congress (INFACON X)* (pp. 381–391). Document Transformation Technologies.

Kuila, S. K., Chatterjee, R., & Ghosh, D. (2016). Kinetics of hydrogen reduction of magnetite ore fines. *International Journal of Hydrogen Energy, 41*, 9256–9266.

Kursunoglu, S., & Kavya, M. (2014). Beneficiation characteristics of manganese ores. *Physicochemical Problems of Mineral Processing, 50*, 39–53.

Linganiso, L. Z., Buthelezi, T., & Motaung, T. E. (2019). A comparative study of sugarcane bagasse and softwood. *Wood Research, 64*(2), 273–280.

Liu, B. B., Zhang, Y. B. J., Wang, Z. J., Su, G. H., Li, G. H., & Jiang, T. (2018). New understanding on separation of Mn and Fe from ferruginous manganese ores by the magnetic reduction roasting process. *Applied Surface Science, 444*, 133–144.

Mehdilo, A., Irannajad, M., & Hojjati-Rad, M. R. (2013). Characterization and beneficiation of Iranian low-grade manganese ore. *Physicochemical Problems of Mineral Processing, 49*(2), 725–741.

Metso Minerals. (2015). *Determining the Bond efficiency of industrial grinding circuits*. Global Mining Standards and Guidelines Group. http://www.globalminingstandards.org

Rath, S. S., Tripathy, S. K., Rao, D. S., & Biswal, S. K. (2018). Characterization and reduction roasting studies of an iron-rich manganese ore. *Transactions of the Indian Institute of Metals, 71*, 861–872.

Sandeep, S., Mehta, D., & Agarwal, R. D. (2012). Characterization and thermal analysis of hydroxyapatite bioceramic powder synthesized by sol-gel technique. *International Journal of Advance Science Research and Technology, 2*(3), 281–282.

Shu, K. Q., Xu, L. H., Wu, H. Q., Fang, S., Wang, Z. J., Xu, Y. B., & Zhang, Z. Y. (2019). Effects of ultrasonic pretreatment on the flotation of ilmenite and collector adsorption. *Minerals Engineering, 137*, 124–132.

Singh, V., Ghosh, T. K., Ramamurthy, Y., & Tathavadkar, V. (2011). Beneficiation studies on low-grade manganese ores. *International Journal of Mineral Processing, 99*, 84–86.

Xiong, S. F., Li, X., Liu, P. L., Hao, S. H., Hao, F., Yin, Z. L., & Liu, J. X. (2018). Recovery of manganese from low-grade pyrolusite ore by reductive acid leaching using lignin as a low-cost reductant. *Minerals Engineering, 125*, 126–132.

## Declarations

### Ethical Approval and Consent to Participate

This study did not involve human participants, animals, or human biological materials. Therefore, ethical approval and informed consent were not required.

### Consent for Publication

Not applicable.

### Funding

The authors received no financial support from any funding agency in the public, commercial, or not-for-profit sectors for the conduct of this research.

### Data Availability Statement

The data supporting the findings of this study are included within the article. Additional information may be made available by the corresponding author upon reasonable request.

### Authors' Contributions

Femi Emmanuel Awe conceived the study, conducted the experiments, analysed the data, interpreted the results, and drafted the manuscript. Ganiyu Rafiu Alege supervised the research, contributed to the study design, and revised the manuscript. Joe Maduke Nwaedozie assisted with mineralogical characterization and data interpretation. Mukthar Muhammad Namadi validated the data, edited the manuscript, and approved the final version with all authors.

### Competing Interests (Conflict of Interest)

The authors declare that they have no competing interests or conflicts of interest regarding the publication of this manuscript.