Manganese Ores from South Sulawesi: Their Potential Uses as Raw Materials for Metallurgical Industry

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Abstract— Characterization of manganese ores from Barru and Bone regencies of South Sulawesi has been conducted with the aim at clarification of their mineralogical and chemical composition for their potential uses as the raw materials for metallurgical industry. Mineralogical properties of the ores analyzed by means of optical microscopy and X-ray diffractometry (XRD) show that samples from Barru consist mainly of rhodochrosite (MnCO₃) with less cryptomelane, gourite, bixbyite, and todorokite. Goethite, calcite and small amount of quartz present as impurities. Manganese ore samples from Bone are predominantly composed of pyrolusite (MnO₂) with subordinate ramsdellite and hollandite. Barite, quartz, hematite and clay are present as gangue minerals. Hematite and clay are present as gangue minerals.

Manganese ores are the main source of Mn metal that is primarily used as raw materials in industry in addition to iron, aluminum, and copper. Approximately 95% of the ore produced is utilized by metallurgical industry mainly for the production of iron and steel and in alloys of steel. The remainder is used for non metallurgical sectors such as battery, chemical and pharmaceutical application [1].

Total reserves of Mn ore globally reach amounts of 4,517 million tons with the largest derivatives from Kalahari, South Africa. Large amounts of Mn have also been found in Groote Eylandt, Australia; Nikopol, Ukraine; and Ucurum, Brazil [2]. In 2013, total of world mine production reached 17,000 tons with the largest producer is South Africa and followed by Australia and China [3]. Although manganese deposits from Indonesia have not been studied in detail to date, manganese deposits are reported to be present all over the country including in Sulawesi. The purpose of this study is to describe mineralogy and chemical compositions of some manganese ore samples collected from the Barru and Bone areas of South Sulawesi with the implication for their potential usage as raw materials particularly in ferroalloys industry.

II. REVIEW OF MANGANESE UTILIZATION

Normal classification of manganese ore can be based on its grade. The ores containing more than 35% Mn are regarded as manganese ore which suitable for manufacture of ferromanganese. Ferruginous manganese ore grading 10-35% is suitable for manufacture of spiegeleisen. The ore containing 5-10% Mn is referred to as manganiferous iron ore and it is suitable for manufacture of pig iron [4,5,6].

The end-uses classification of manganese ores is divided into metallurgical, chemical, and battery grades. Metallurgical grade ore for iron and steel industry ideally contains 35 – 55% Mn, P₂O₅, Al₂O₃, SiO₂, CaO and S are also important. The Mn/Fe ratio is very critical. It needs about 7 kg of Mn to produce one tons of steel. Manganese serves as a desulphurizing, deoxidizing and conditioning agent during the smelting of iron ore. As an alloying element, manganese increases toughness, strength, and hardness of steel [5,6].

Nonferrous manganese alloys include manganese bronze (Mn, Cu, Sn, and Zn) and manganin (Mn, Cu, and Ni). Manganese bronze is corrosion resistance as in the case of seawater reaction. It is therefore suitable to be used for propeller blades on boat or torpedoes. Manganin is used in the form of wire for accurate electrical measurement [5].

III. MATERIAL AND METHODS

Manganese ore samples used in this study were collected from two localities (Fig.1), namely Palluda village, Pujananting sub district of Barru Regency (four samples) and Mapesangka village, Ponre sub district of Bone Regency (eight samples).

Samples of manganese ore were subjected to XRD, SEM-EDS and XRF analyses at the Faculty of International Resource Science, Akita University, Japan. XRD analysis was conducted using a Rigaku Multiflex X-ray diffractometer (Cu-Kα radiation, λ=1.541Å, voltage, V=30 kV, and current I=16 mA). Measurement was done in 2-theta from 2° to 70° with step size of 0.02° and time/step 2 s. Interpretation of minerals
present in samples was performed by using PDX-2 and Impact Match II.

SEM-EDS analysis was utilized to observe the morphology and semi-quantitative chemical composition of minerals containing in samples under polished-thin section. This analysis was carried out by using a JEOL JSM-IT300 scanning electron microscope equipped with energy dispersive spectrometer (Oxford instrument). Chemical composition of manganese ore samples analyzed under pressed powder was determined by using a Rigaku Primus II X-ray fluorescence spectrometer.

IV. RESULTS AND DISCUSSION

A. Mineralogy

The manganese ore in the Barru area occurs in two types, i.e., cavity filling and residual materials. The first type is found to be hosted in bedded limestone. The ores are massive and show black with local pink color. The thickness of orebody ranges between 2 cm and 25 cm. The second type occurs as residual massive subangular to rounded black-colored materials with diameter up to one meter and hosted in soil.

Results of XRD examination (Fig. 2) indicate that samples of cavity filling type are predominantly composed of ferroan rhodochrosite (FeMnCO$_3$) with subordinate groutite (MnO.OH) and todorokite (Mn-Ca-K-Na-Ba-Mn-H$_2$O). These phases are associated with gangue minerals that mainly consist of calcite (CaCO$_3$) with minor quartz (SiO$_2$). On the other hand, results of XRD analyses of residual ore type exhibit that cryptomelane (K-Na$_2$Mn$_5$O$_{16}$) and bixbyite (Mn$_2$O$_3$) are the main Mn phases and goethite (FeO.OH) is detected as the principal gangue mineral (Fig. 3).

Optical microscopy and SEM examination of the Barru samples show the typical colloform texture (Fig. 4A). The bands have various thicknesses ranging from 10 to more than 500 microns with circular or wavy form. SEM-images show alternating dark and light bands, indicating the difference metal compositions. The light bands may indicate more various of metal concentrations where the proportion of light metals is less than those of heavy ones (Fig. 4C and 4D). EDS analysis of selected spots indicates the presence of sphalerite (ZnS) as shown in Figure 4B. This mineral occurs as inclusion in rhodochrosite and is characterized by anhedral texture with diameter ranges from 100 to 500 microns. Calcite and silica are also identified within this sample.
Fig. 4 Photomicrograph showing colloform texture (A). SEM images of representative samples from Barru displaying the presence of sphalerite (B) and alternating dark-light colloform texture (C, D).

Manganese ores in the Bone area occur in the form of lensoid and brecciated, associated with chert, carbonaceous shale and volcanic rocks. Results of XRD analysis showed that pyrolusite (MnO₂) is the main manganese phase present with subordinate ramsdellite. Quartz (SiO₂) and barite (BaSO₄) were identified as gangue minerals (Fig. 5).

![XRD pattern](image)

Fig. 5 XRD pattern of a manganese sample from Bone displaying pyrolusite and ramsdellite as the manganese phases with quartz and barite occurring as gangue minerals.

![SEM images](image)

Fig. 6 SEM images of selected samples from Bone showing a good cleavage of a large pyrolusite crystal associated with quartz (A). Medium and fine grained pyrolusite set in quartz (B and C) and elongated prismatic barite crystals associated with silica (D).

Textural features of the Bone samples analyzed by SEM are shown in Figure 6. Mostly pyrolusite occurs in association with quartz. A large pyrolusite crystal (~ up to 5 mm in diameter) shows subhedral and well-developed cleavages in quartz (Fig. 6A). Medium grains of pyrolusite (20–250 micron) within the gangue show subhedral to anhedral and locally display cirlcular shape (Fig. 6B). Pyrolusite also occurs as fine anhedral grains in quartz (Fig. 6C). Barite shows elongated prismatic euhedral crystals with the size up to 700 micron occurring as irregular veins and is associated with silica and iron oxides (Fig. 6D).

B. Chemical composition

Chemical composition of the samples analyzed by means of XRF method from the Barru and Bone areas are presented in Table 1. Major element compositions exhibit that the Barru samples contain low SiO₂ (1.62 – 12.27 wt%; av. 6.18 wt%) as compared to the Bone samples (16.36 – 64.35 wt%; av. 35.17 wt%). Similarly, concentration of Al₂O₃ in the Barru samples (0.17 – 1.20 wt%; av. 0.80%) is lower than those of the Bone samples (0.18 – 13.71 wt%; av. 5.41 wt%). In contrast, Fe₂O₃ and MnO concentrations of the Barru samples (16.17 – 33.26 wt%; av. 25.40 wt% and 35.34 – 44.22 wt%; av. 40.07 wt% respectively) are higher than those of the Bone samples (0.02 – 11.84 wt%; av. 16.31 wt% and 1.56 – 61.54 wt%; av. 34.36% respectively). Similarly, concentration of CaO in the Barru samples ranges between 0.21 and 13.64 wt% (av. 6.77 wt%). This value is higher than those of the Bone samples which contain CaO between 0.10 and 4.29 wt% (av. 2.06 wt%). Concentrations of total alkali (K₂O + Na₂O) in the Barru samples ranges from 0.38 to 0.88 wt% with an average of 0.57 wt% which is lower than those of the Bone samples (0.16 – 3.88 wt%; av. 1.49 wt%). The average content of P₂O₅ in both areas is generally below 0.2 wt%. Value of loss on ignition (LOI) is higher in the Barru samples (average is 18.81 wt%) than those of the Bone samples (average is 8.91 wt%). The average of Mn/Fe ratio in the Barru ores is lower (1.75) than that of the Bone samples (6.02), whereas CaO/MgO ratio of the Barru sample has value of 8.85, far more higher than that of the Bone samples (average is 0.49).

Relatively higher contents of Fe₂O₃ and CaO in Barru samples are ascribed to the presence of ferroan rhodochrosite (Fe-MnCO₃) as the main Mn-phase and calcite (CaCO₃) as impurity in Barru samples; whereas the elevated concentrations of silica in the Bone samples are consistent with the presence of quartz as the main gangue mineral.

Regarding about trace elements, it is shown that the Barru samples have high concentrations of As, Pb, Sr and Zn as compared to the Bone samples. On the contrary, Ba, S and V content have higher in the Bone samples. Significant concentration of Ba and Sr in Bone samples is due to the occurrence of barite (BaSO₄) within the ores. Meanwhile, the high concentrations of Pb, As, and Zn in the Barru samples are not only connected to the presence of sulfide phase such as sphalerite, but also the existence of goethite that has significant concentrations of trace elements. This mineral has high capacity to adsorb such cations from solution during chemical weathering [7].

C. Potential uses as raw materials in metallurgical industry

In term of utilization of manganese ore in metallurgical sector, analytical results indicate that Mn-ore from Barru may have good potential uses as raw material for the manganese ferroalloy production due to the relatively higher content of Fe₂O₃. In modern steelmaking, the existance of rhodochrosite can act as effective desulfurizer. However, the higher moisture content (av. 18.81%) of these ores is problematic because the higher energy is required in reduction the moisture thereby the increase of production cost.

Significant concentration of SiO₂ and Al₂O₃ containing in the Bone samples implies that such ores may be favorable to be used as raw material for the production of silicomanganese.
Silicon and aluminum are deoxidizing agents in steelmaking [8]. Other elements present in the ores have also effect on the production of silicomanganese. Basicity (CaO + MgO)/(Al₂O₃) of the Bone sample is 1.2 which is closed to the optimum value of 1.8 [9].

**Table 1 Bulk chemical composition of manganese ore samples from Barru and Bone Regencies determined by XRF method**

| Oxide | Barru Samples | Bone Samples | Av. |
|-------|---------------|--------------|-----|
|       | PD-01 | PD-03 | PD-04 | PD-05 | Av. | ST-1A | ST-1C | ST-IIA | BN-02 | BN-04 | BN-05A | BN-05B | BN-05C | Av. |
| SiO₂ (%) | 1.62 | 8.74 | 12.27 | 2.07 | **6.18** | 17.21 | 48.14 | 31.18 | 16.36 | 64.35 | 17.38 | 45.81 | 40.89 | **35.17** |
| TiO₂ | 0.04 | 0.03 | 0.05 | 0.01 | **0.03** | 0.02 | 2.92 | 0.02 | 0.03 | 0.01 | 0.44 | 1.80 | 1.58 | **0.85** |
| Al₂O₃ | 0.92 | 0.90 | 1.20 | 0.17 | **0.80** | 1.52 | 13.71 | 0.80 | 0.96 | 0.18 | 3.50 | 11.83 | 10.79 | **5.41** |
| Fe₂O₃ | 32.79 | 17.36 | 16.17 | 35.26 | **25.40** | 5.02 | 11.84 | 0.02 | 10.60 | 3.08 | 0.82 | 10.96 | **6.31** |
| MnO | 44.22 | 39.93 | 35.34 | 40.78 | **40.07** | 61.54 | 1.56 | 51.90 | 56.01 | 26.30 | 55.98 | 6.63 | 14.99 | **34.36** |
| MgO | 0.21 | 1.36 | 1.27 | 0.22 | **0.77** | 0.37 | 8.26 | 0.49 | 0.30 | 0.26 | 4.06 | 9.88 | 10.15 | **4.22** |
| CaO | 0.27 | 13.64 | 12.97 | 0.21 | **6.77** | 0.99 | 4.27 | 0.79 | 0.44 | 0.10 | 1.76 | 4.29 | 3.82 | **2.06** |
| Na₂O | 0.20 | 0.09 | 0.10 | 0.30 | **0.17** | 0.23 | 3.32 | 0.11 | 0.21 | 0.08 | 0.89 | 3.10 | 1.81 | **1.22** |
| K₂O | 0.55 | 0.23 | 0.28 | 0.54 | **0.40** | 0.26 | 0.56 | 0.15 | 0.10 | 0.08 | 0.13 | 0.39 | 0.50 | **0.27** |
| P₂O₅ | 0.11 | 0.04 | 0.06 | 0.21 | **0.11** | 0.12 | 0.37 | 0.07 | 0.15 | 0.04 | 0.22 | 0.27 | 0.18 | **0.18** |
| LOI | 18.58 | 17.49 | 19.80 | 19.35 | **18.81** | 8.54 | 4.31 | 14.06 | 14.16 | 4.63 | 14.10 | 4.57 | 6.94 | **8.91** |
| Total Oxides | 99.51 | 99.81 | 99.51 | 99.12 | 99.49 | 95.82 | 99.26 | 99.58 | 99.33 | 99.09 | 99.29 | 99.52 | 99.79 | **98.96** |
| Ag (ppm) | 21 | 10 | 12 | 13 | **14** | 7 | 4 | 6 | 11 | 4 | 9 | 5 | 3 | **6** |
| As | 191 | 535 | 750 | 299 | **444** | 10 | 2 | 13 | 6 | 15 | 2 | 2 | 2 | **7** |
| Ba | 942 | 28 | 26 | 1511 | **627** | 3154 | 336 | 4652 | 3221 | 1089 | 3723 | 733 | 1079 | **5797** |
| Cu | 31 | 32 | 31 | 17 | **28** | 3 | 3 | 3 | 30 | 31 | 34 | 73 | 43 | 135 | **50** |
| Pb | 1362 | 3114 | 3902 | 1813 | **2548** | 138 | <1 | 125 | 20 | 45 | <1 | <1 | 1 | **41** |
| Rb | 6 | 9 | 12 | 8 | **9** | 5 | 7 | 4 | 3 | 1 | 3 | 8 | 8 | **5** |
| S | 162 | 790 | 938 | 231 | **530** | 5882 | 196 | 566 | 275 | 122 | 105 | 100 | 105 | **919** |
| Sr | 373 | 91 | 90 | 948 | **376** | 1079 | 253 | 267 | 195 | 140 | 258 | 269 | 387 | **356** |
| V | 30 | 35 | 27 | 89 | **45** | 250 | 399 | 55 | 115 | 64 | 204 | 272 | 271 | **204** |
| Zn | 2166 | 726 | 829 | 1376 | **1274** | 265 | 89 | 68 | 43 | 58 | 35 | 59 | 59 | **85** |

Despite manganese ores from both areas can be potentially used as raw materials in ferromanganese and ferrosilicone productions. However, they are not suitable for direct use because the ores still contain some deleterious elements such as S, P, Pb, Zn, Cu and Ba. In order to meet the specification required, it is highly suggested to remove these impurities, hence, both ores should be treated through beneficiation. Communion followed by screening and classification then gravity and magnetic concentrations may be applied.

**V. CONCLUSIONS**

From the results of mineralogical and chemical characterization of manganese ores from South Sulawesi with the implication for the potential uses as raw materials in metallurgical industry, some of the following conclusions can be drawn:

1. Rhodochrosite is predominant manganese phase containing in the Barru samples; whereas pyrolusite is the major constituent of Mn minerals occurring in the Bone samples.
2. Manganese ore from the Barru samples are characterized by higher in Fe₂O₃, MnO and CaO than that of Bone samples.
3. Both CaO and MgO may increase MnO activity in the silicate melt, but CaO has greater effect than MgO. Therefore the higher CaO/MgO ratio may result in higher metallic yield and manganese recovery. The presence of MgO is also favorable for silicon reduction [9].

On the contrary, the concentration of SiO₂ and Al₂O₃ show higher in Bone as compared with Barru.

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