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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 ($MnCO_3$) with less cryptomelane, groutite, bixbyite, and todorokite. Goethite, calcite and small amount of quartz present as impurities. Manganese ore samples from Bone are predominantly composed of pyrolusite (MnO_2) with subordinate ramsdellite and hollandite. Barite, quartz, hematite and clay are present as gangue minerals. Chemical compositions determined by using XRF method revealed that Barru samples contain higher in MnO (average is 40.07 wt%) than the Bone samples (average is 34.36 wt%). Similarly, Fe_2O_3 and CaO are also higher in Barru than those of the Bone samples. In contrast, concentrations of SiO_2 and total alkali (K_2O + Na_2O) are lower in the Barru samples. The average P_2O_5 content of samples in both areas is low (<0.2 wt%). Relatively higher grade of Fe_2O_3 in the Barru ore implies that it has potential application for ferromanganese production; whereas the elevated SiO_2 content of the Bone ore is a good indication for silicomanganese manufacture. However, both ores may not favorable to be directly used as raw materials in metallurgical uses. Prior to be used, the ores should be treated by applying physical beneficiation in order to reduce deleterious elements.**

Keywords: rhodochrosite, pyrolusite, barite, XRD.

I. INTODUCTION

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 derives 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 ferro-manganese. 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. P_2O_5, Al_2O_3, SiO_2, 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 Mappesangka 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^o to 70^o with step size of 0.02^o and time/step 2 s. Interpretation of minerals present in samples was performed by using PDX-2 and Impact Match! 2.

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.

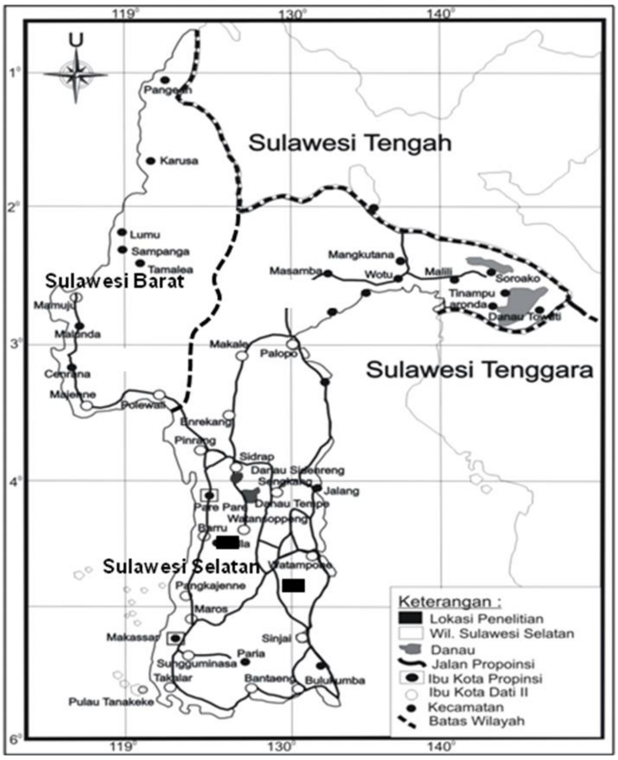

Fig. 1 Sample location map

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_2O). 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-Mn_8O_{16}) and bixbyite $(FeMn)_2O_3$ 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 thickneess 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.

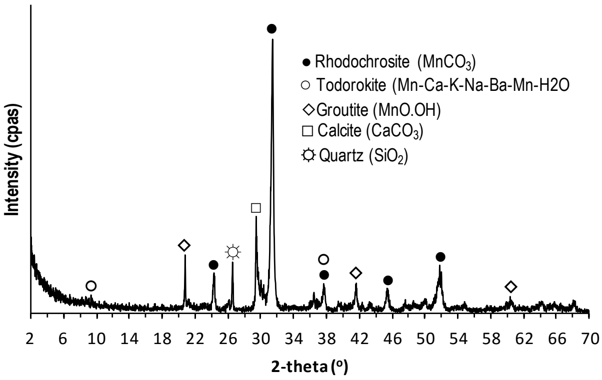

Fig. 2 XRD pattern of a Mn-ore sample from Barru representing the cavity filling type.

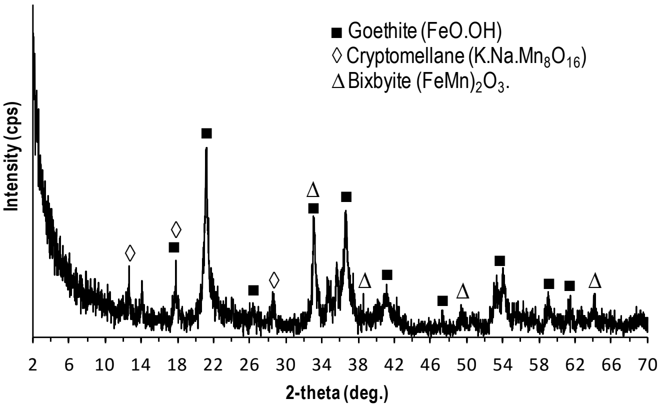

Fig.3 XRD pattern of a manganese sample from Barru representing residual ore type.

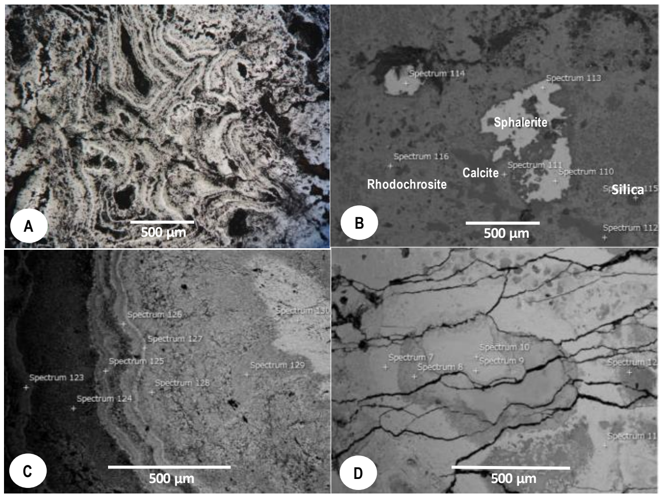

Fig. 4 Photomicrograph showing colloform texture (A). SEM images of representative samples from Barru displaying the presence of sphalerite (B) and alternating dark-light colloform texture (C, D).

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 (MnO_2) is the main manganese phase present with subordinate ramsdellite. Quartz (SiO_2) and barite ($BaSO_4$) were identified as gangue minerals (Fig. 5).

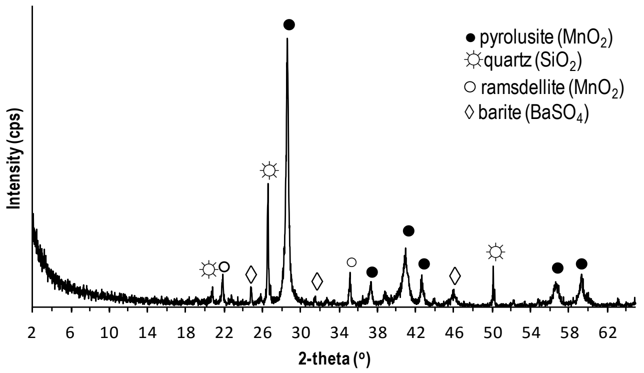

Fig. 5 XRD pattern of a manganese sample from Bone displaying pyrolusite and ramsdellite as the manganese phases with quartz and barite occuring as gangue minerals.

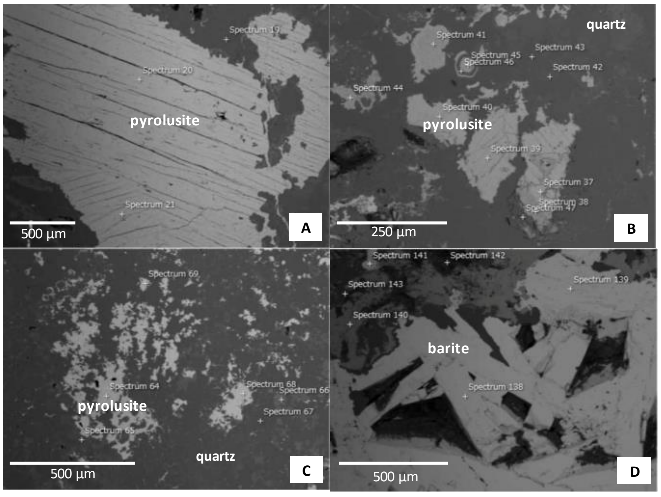

Fig.6 SEM images of selected samples from Bone showing a good cleavage of a large pyrolusite crystal associated with quartz (A). Medium and fine grained pyrolusite set in quartz (B and C) and elongated prismatic barite crystals associated with silica (D).

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 cirlular shape (Fig. 6B). Pyrolusite also occurs as fine unhedral grains in quartz (Fig. 6C). Barite shows elongated prismatic euhedral crystals with the size up to 700 micron occuring 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 SiO_2 (1.62 – 12.27 wt%; av.6.18wt%) as compared to the Bone samples (16.36 – 64.35 wt%; av. 35.17 wt%). Similarly, concentration of Al_2O_3 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, Fe_2O_3 and MnO concentrations of the Barru samples (16.17 – 33.26wt%; 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 (K_2O + Na_2O) 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 P_2O_5 in both areas is generally below 0.2 wt%. Value of loss on igniiton (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 Fe_2O_3 and and CaO in Barru samples are ascribed to the presence of ferroan rhodochrosite (Fe-$MnCO_3$) as the main Mn-phase and calcite ($CaCO_3$) as impurity in Barru samples; whereas the elavated 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 S in Bone samples is due to the occurrence of barite ($BaSO_4$) 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 Fe_2O_3. 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 SiO_2 and Al_2O_3 containing in the Bone samples implies that such ores may be favorable to be used as raw material for the production of silicomanganese.

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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)/(Al_2O_3) of the Bone sample is 1.2 which is closed to the optimum value of 1.8 [9].

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].

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

Oxide	Barru Samples					Bone Samples								
	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.
SiO_2 (%)	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**
TiO_2	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**
Al_2O_3	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**
Fe_2O_3	32.79	17.36	16.17	35.26	**25.40**	5.02	11.84	0.02	10.60	3.08	0.82	10.96	8.14	**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**
Na_2O	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**
K_2O	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**
P_2O_5	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**	31542	336	4652	3221	1089	3723	733	1079	**5797**
Cu	31	32	31	17	**28**	39	5	38	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. Comminution 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 Fe_2O_3, MnO and CaO than that of Bone samples. On the contrary, the concentration of SiO_2 and Al_2O_3 show higher in Bone as compared with Barru.
3. Both studied ores may have potential uses in the manufacturing of ferromanganese and silicomanganese. However, such ores are not favorable to be directly used because they still contain some of deleterious elements. It is therefore highly suggested to reduce those impurities through conventional beneficiation such as size reduction followed by gravity or magnetic separation.

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