

Ashraf M. AMER\*

## **PROCESSING OF LOW GRADE EGYPTIAN MANGANESE ORE**

Low grade manganese ore from West-Central Sinai consists mainly of pyrolusite and hematite with minor amounts of psilomelane and barite. Manganese dioxide does not dissolve in sulfuric acid under atmospheric pressure, but rapidly dissolves under oxygen pressure in an autoclave in presence of pyrite. Pyrite is oxidized to ferrous sulfate and sulfuric acid which in turn dissolves manganese dioxide to manganese sulfate. This pressure leaching process was systematically studied. Almost complete extraction of manganese was achieved at temperature 220 °C under oxygen pressure of 15 bar after 30 minutes of leaching and at  $\text{MnO}_2/\text{FeS}_2$  molecular weight ratio equal 1.0. The residue is enriched in iron so that it could be used to produce feed stock for iron smelting.

### **INTRODUCTION**

Um Bogma Mn–Fe deposits is located in the lower carboniferous marine intercalations within the clastic Paleozoic section. The ore bodies are irregular in shape which tends to be lenticular. In some parts, the ore body is present as vein filling cutting the surrounding dolomite (Gill and Ford, 1956; Mart and Sars, 1972; El-Gammal, 1984). Many processes have been investigated for the treatment of low grade manganese ores which are not amenable to regular mineral processing techniques. Carbon reduction (Pawlek, 1983) and sulphuric acid leaching lead to removal of Mn as soluble manganese sulfate. Another processes are based on aqueous leaching of manganese ore in the presence of sulfur dioxide (Herring and Ravitz, 1965). Hydrochloric acid leaching of manganese nodules was reported by Kanungo (Kanungo and Jena, 1988). Sulfuric acid leaching with charcoal (Das et al, 1989), under oxygen pressure (Anand et al, 1980) was also applied. Ammonia leaching of manganese nodules was one of the first processes developed (Sanigok and Bayramoglu, 1988). High purity manganese sulfate was prepared from low grade pyrolusite ore using adiabatic reductive leaching with sulfuric acid and hydrogen peroxide as reducing agent (Allen and Corwin, 1989).

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\*Geology Department Faculty of Science, Alexandria University, El-Shatby, Alexandria.

Utilization of sulfur dioxide for the treatment of manganese ore requires certain standards for constructions and safety conditions. Therefore, it can be hardly applied on industrial scale. Moreover, some processes involve and expensive leachants such as ammonia, hydrochloric acid and hydrogen peroxide.

The objective of this work is to investigate a new leaching process of low grade manganese ore from Um Bogma, Sinai, by mixing the ore with pyrite under oxygen pressure at relatively elevated temperature and pressure to produce manganese sulfate suitable for electrolytic production of manganese dioxide. This process is advantageous over the known processes since it does not use a leaching agent, where water is used only in this process.

In addition, the production of manganese sulfate is carried out in one step. Resultant iron sulfate is converted into a basic iron sulfate residue. The influence of temperature partial oxygen pressure, weight ratio of Mn ore to pyrite, grain size of manganese ore and leaching time on the efficiency of manganese extraction were experimentally examined.

## EXPERIMENTAL

### Materials

Samples of low grade manganese ore from Um Bogma, Sinai were used in this study. According to the Magritz et al. (1972) classification the studied samples are of „pyrolusite-hematite” type which consist of approximately equal amounts of Fe and Mn. Quartz and some clay minerals are the main gangues. Complete chemical analysis of studied manganese ore is given in Table 1. Pyrite ore was provided by Institute. of Metallurgy, Technical University, Berlin, (Germany). The analysis of this pyrite is given in Table 2.

### Procedure

Pressure leaching was carried out in 2 liter capacity vertical autoclave (Amer, 1987) with gas inlet/outlet, sampling tube and agitation. Manganese ore mixed with pyrite was placed in the titanium container of the autoclave and then autoclave was thoroughly flushed with oxygen gas. The mixture was heated to the required temperature at agitation of 1200 rpm. Oxygen gas was introduced when the desired temperature was measured. Samples were collected at various time intervals, filtered and analyzed for manganese and iron.

Manganese was determined volumetrically by titration with a standard solution of potassium permanganate (Scott, 1984). While ferrous ion was determined by direct titration with potassium dichromate.

Table 1. Chemical analysis of studied manganese ore

| Oxide                          | Wt., % |
|--------------------------------|--------|
| MnO <sub>2</sub>               | 44.01  |
| Fe <sub>2</sub> O <sub>3</sub> | 38.09  |
| FeO                            | 1.51   |
| SiO <sub>2</sub>               | 7.87   |
| Al <sub>2</sub> O <sub>3</sub> | 4.46   |
| CaO                            | 1.36   |
| MgO                            | 0.11   |
| K <sub>2</sub> O               | 0.39   |
| H <sub>2</sub> O               | 2.95   |

Table 2. Chemical analysis of pyrite sample

| Oxide                          | Wt., % |
|--------------------------------|--------|
| SO <sub>3</sub>                | 37.8   |
| FeO                            | 44.6   |
| Fe <sub>2</sub> O <sub>3</sub> | 13.2   |
| CuO                            | 1.4    |
| PbO                            | 0.5    |
| ZnO                            | 0.1    |
| H <sub>2</sub> O               | 2.0    |

## RESULTS AND DISCUSSION

### Mineralogical investigation

The microscopic study of both polished and thin sections of the studied manganese ore samples revealed that, the opaque minerals consist mainly of pyrolusite and psilomelane. The iron minerals associated with manganese minerals are hematite and goethite. The essential associated gangue minerals are quartz, barite and some clay minerals. Pyrolusite is seen to be a dominant manganese mineral. It exhibits well developed colloform texture. In few polished section pyrolusite generally forms fibrous aggregates. Hematite is the dominant iron mineral and is usually associated with goethite to form well developed betryoidal and colloform texture. Quartz is present in some samples, usually associated with iron minerals. The coarse crystals are highly fractured and sometimes exhibits brecciated form.

## Leaching

Preliminary experiments were carried out to determine the working range of each of the studied leaching variables. The effect of the following parameters was studied in the increasing ranges:

- Temperature: 180, 250 °C,
- Oxygen partial pressure: 520 bar,
- $\text{MnO}_2/\text{FeS}_2$  weight ratio: 0.5–2.0,
- Grain size: 0.43–0.064 mm.

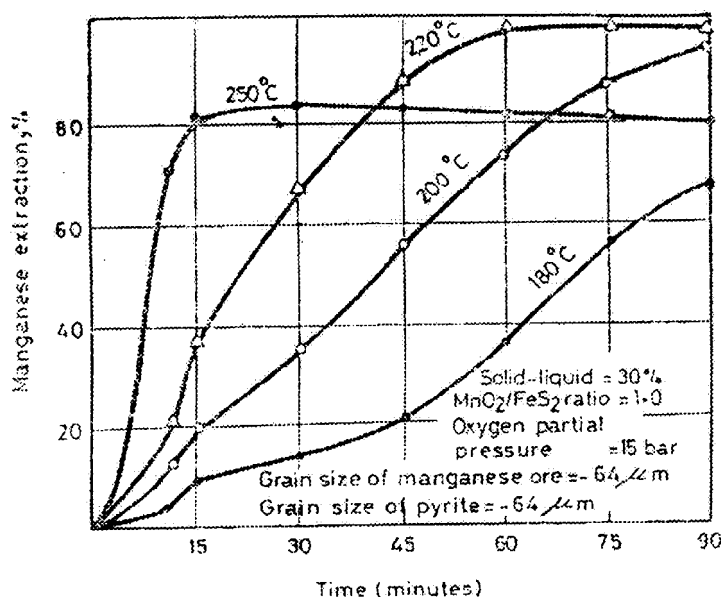


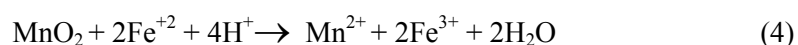
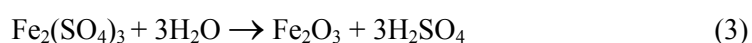
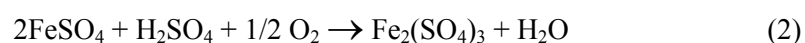
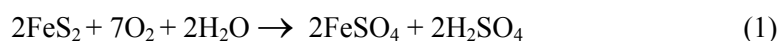
Fig. 1. Effect of temperature on manganese extraction

## Effect of temperature

The effect of temperature on manganese extraction is shown in Fig. 1. The increase in temperature raises the rate of leaching of manganese. Complete dissolution of manganese was achieved at 220 °C and 1 hours of leaching. The extraction decreased at 250 °C, since all pyritic sulphur had been converted to the sulfate which means complete oxidation of pyrite. Therefore no ferrous ions were produced so that, no further dissolution of manganese occurs. At lower temperatures, the rate of formation of ferrous ion from pyrite is low which leads to incomplete dissolution of manganese.

### Effect of oxygen partial pressure

Results of varying oxygen partial pressure on manganese extraction are shown in Fig. 2. The tests were conducted at 220 °C, with a  $\text{MnO}_2/\text{FeS}_2$  weight ratio of 1.0. It appears that, the increase in oxygen partial pressure elevates the rate of manganese leaching due to the increased rate of formation of ferrous ion (Cornelius and Woodcock, 1958). At oxygen pressure equal to 15 bar, the rate of manganese extraction is generally higher than is observed at 5 bar. Dissolution of manganese oxide in the presence of pyrite under oxygen pressure follows the following reactions:



According to the reaction (1) the oxidation of pyrite leads to formation of iron sulfate which is converted to ferric sulfate by oxidation as shown in reaction (2). Hydrolysis of ferric sulfate produce the iron oxide and free sulphuric acid according to reaction (3). Eventually, manganese sulfate is obtained according to reaction (4).

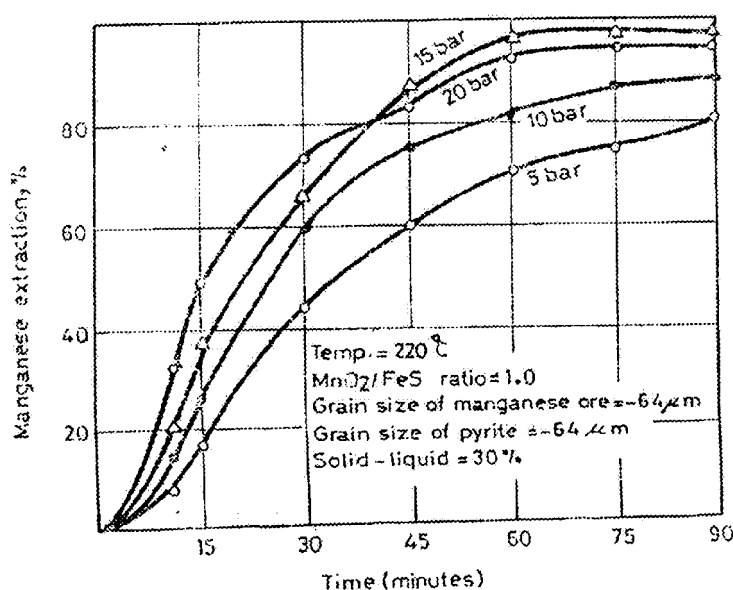


Fig. 2. Effect of oxygen partial pressure on manganese extraction

### Effect of $\text{MnO}_2/\text{FeS}_2$ weight ratio

The results of manganese extraction at varying  $\text{MnO}_2/\text{FeS}_2$  weight ratios are plotted in Fig. 3. The curves show that complete extraction of manganese was achieved at  $\text{MnO}_2/\text{FeS}_2$  weight less than 1.0. At ratios exceeding 1.0 the proportion of dissolved manganese decreases and reaches about 75% at  $\text{MnO}_2/\text{FeS}_2$  weight ratio equal to 2 and after 90 min. At higher ratios, insufficient amounts of ferrous ions are formed to secure complete dissolution of manganese.

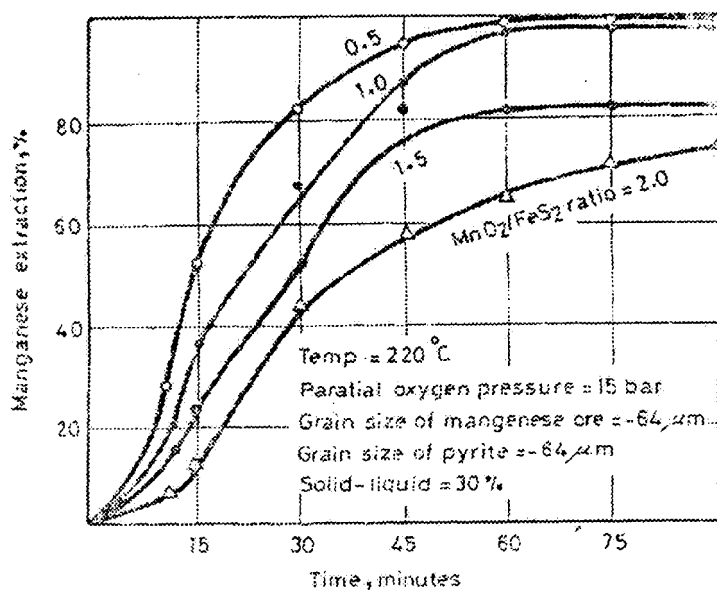


Fig. 3. Effect of  $\text{MnO}_2$  to  $\text{FeS}_2$  ratio on manganese extraction

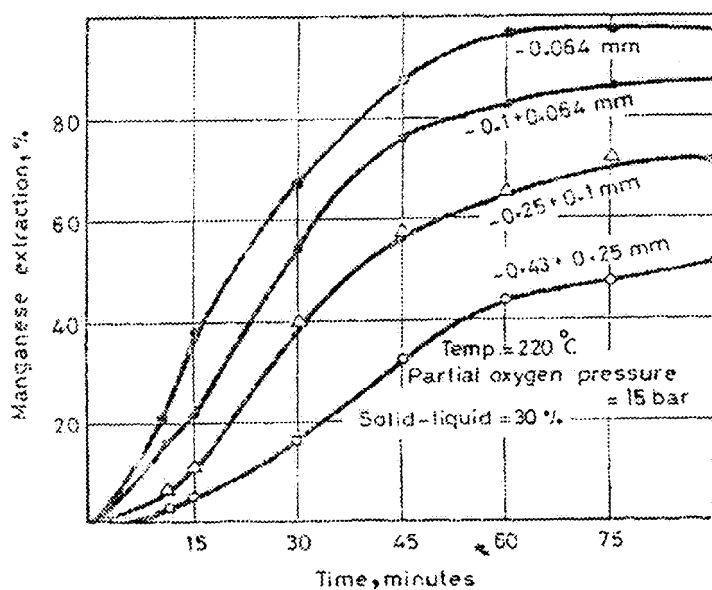


Fig. 4. Effect of grain size on manganese extraction

### Effect of grain size

Figure 4 shows that the rate of manganese dissolution is sharply increased with decreasing grain size of manganese. Maximum extraction of manganese (95%) was achieved at grain size of  $-64 \mu\text{m}$ . An increase in leaching time from 45 to 90 min. has a little effect on manganese extraction at various grain sizes.

### CONCLUSION

The pressure leaching of low grade manganese ore from West Central Sinai mixed with pyrite in presence of oxygen leads to high manganese recovery (95%) at the following conditions: Temperature –  $220^\circ\text{C}$ , pressure – 15 bar,  $\text{MnO}_2/\text{FeS}_2$  – 1.0, grain size of manganese ore =  $-64 \mu\text{m}$ , and leaching time – 60 min.

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**Amer A.M.**, Przeróbka ubogiej egipskiej rudy manganowej. *Fizykochemiczne Problemy Mineralurgii*, 32, 195–202 (w jęz. angielskim)

Uboga ruda manganowa z centralno-zachodniej części Synaju w Egipcie zawiera głównie piroluzyt i hematyt z małą domieszką psydomelanu i barytu. Wiadomo, że ditlenek manganu nie rozpuszcza się w kwasie siarkowym pod ciśnieniem atmosferycznym, ale szybko rozpuszcza się przy podwyższonym ciśnieniu tlenu w autoklawie w obecności pirytu. Z kolei piryt utlenia się do siarczanu żelaza(II) i kwasu siarkowego, który rozpuszcza ditlenek manganu z utworzeniem siarczanu manganu. W pracy systematycznie przebadano proces ciśnieniowego ługowania rudy manganu. Uzyskano niemal całkowitą ekstrakcję manganu w temperaturze 220 stopni Celsjusza pod ciśnieniem tlenu wynoszącym 15 barów po 30 minutach ługowania przy stosunku  $MnO_2$  do  $FeS_2$  jak 1:1. Pozostałość po ługowaniu była wzbogacona w żelazo, tak że materiał ten może być użyty do produkcji żelaza.