AN HYDROMETALLURGICAL PROCESS FOR RECOVERING MANGANESE
FROM A WAD TYPE ORE
Carlo Abbruzzese

INTRODUCTION
Before 1950 nearly all manganese ore processing plants consisted solely of crushing and screening facilities. However, since the high-grade deposits have been worked out it has become necessary to concentrate lean ores by more complex flow-sheet which may include flotation, heavy-media separation and magnetic separation. But many manganese ores are difficult to treat by conventional methods and roasting under reducing conditions requires large amounts of energy. Hydrometallurgical processes permit manganese dioxide ores to be treated without any preliminary preparation, apart from crushing and grinding, while producing a relatively concentrated solution of manganese sulphate which can be purified without difficulty.
The research reported here was designed to make a systematic study of manganese recovery from a low-grade ore by means of a hydrometallurgical process. The ore in question cannot be concentrated by conventional methods, so it was treated by leaching with sulphuric acid in the presence of some reducing agents (FeSO₄, Na₂SO₃). The most appropriate technique of purification to obtain an electrolyte suitable for the production of metallic manganese has also received attention.

CHARACTERIZATION OF THE ORE
The manganese deposits of northern Latium occur mainly as unevenly spaced beds or lenses of MnO₂ in pumice and tuff gangue. Two types of orebodies with different manganese grades are found. In one type (low-grade ore) the oxides of manganese (5-10% Mn) are associated wholly with pyroclastic materials. In the other type (high-grade ore) the minerals of manganese (20-40% Mn) are disposed in a sequence of clay
and diatomaceous earth layers.
The studies have been concerned with the low-grade ore
which has the appearance of a blackish earthy material (wad)
with fragments of whitish pumice. X-ray diffraction
analysis has revealed the presence of albite and anorthite
with various aluminium silicates, probably originating from
weathered basic plagioclase, associated with quartz (1).
A small amount of manganese is present in crystalline form
(birnessite).
The foregoing findings were confirmed by thermogravimetric
analysis which revealed a constant weight loss in the 100-
-1000°C range due to the gradual elimination of the water
of hydration (2).
To summarize, the results of the mineralogical and
physico-chemical investigation indicate that the manganese
is present in the raw-material as mixed hydrated oxides in
form of colloidal or sub-colloidal gel.
This accounts for the unsatisfactory results of previous
tests achieved to upgrade the ore by conventional mineral
processing methods (flotation, magnetic separation).
The chemical analysis and the particle-size distribution
of the manganese ore, ground to minus 3 mm, are shown in
Table 1.

ACID LEACHING OF THE MANGANESE
The ore (250 g) was leached in mechanically-stirred glass
reaction vessels immersed in a thermostatically-controlled
water bath.
The variables studied to assess recovery were temperature,
time and acid concentration. The quantity of reducing
agent (FeSO₄·Na₂SO₃) was calculated on the basis of the
stoichiometric values (2). To achieve single-stage leach
process, the slurry had to be diluted to ensure a 1:4
solid-liquid ratio.
Progress of the manganese dissolution was followed by the
Table 1 - Chemical and size composition of the manganese ore

<table>
<thead>
<tr>
<th>Element</th>
<th>Weight %</th>
<th>Fraction mm</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>13.80</td>
<td>+1.65</td>
<td>22.9</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12.50</td>
<td>0.71-1.65</td>
<td>29.5</td>
</tr>
<tr>
<td>SiO₂</td>
<td>46.03</td>
<td>0.50-0.71</td>
<td>9.2</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.09</td>
<td>0.30-0.50</td>
<td>9.6</td>
</tr>
<tr>
<td>Na₂O</td>
<td>1.21</td>
<td>0.20-0.30</td>
<td>6.3</td>
</tr>
<tr>
<td>K₂O</td>
<td>5.30</td>
<td>0.15-0.20</td>
<td>4.3</td>
</tr>
<tr>
<td>CaO</td>
<td>0.18</td>
<td>0.075-0.15</td>
<td>6.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.03</td>
<td>-0.075</td>
<td>11.4</td>
</tr>
<tr>
<td>NiO</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>6.34</td>
<td>Feed</td>
<td>100.0</td>
</tr>
</tbody>
</table>

measurement of the redox potential of the leaching system by means of a combined platinum-calomel electrode connected to a pH-meter (2).

At the end of each test the solid residue and the leach liquor, separated by filtration, were analysed for Mn by atomic absorption spectrophotometry (3).

A preliminary series of leach tests run at 25°C indicated that after two hours there is little appreciable increase in manganese recovery, as it is evident from Fig.1.

This fact was also confirmed by the trend of the redox potentials, as reported in a previous work (2).

As matter of fact, the potential which starts from a value close to that of the Fe(III)/Fe(II) half-couple, i.e. 0.77 Volt, tends towards the theoretical limit value of about 0.90 Volt when the reaction is practically complete.
Leaching with ferrous salts

Dissolution of MnO₂ in an acid solution containing ferrous ions proceeds according to the following reaction (1):

\[
\text{MnO}_2 + 2\text{Fe}^{2+} + 4\text{H}^+ = 2\text{Mn}^{2+} + 2\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (1)
\]

Two other reactions involving oxidation of ferrous ion and hydrolysis of ferric ion also occur at the same time:

\[
4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ = 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \quad (2)
\]
\[
2\text{Fe}^{3+} + 3\text{H}_2\text{O} = \text{Fe}_2\text{O}_3 + 6\text{H}^+ \quad (3)
\]

It is evident from the experimental results of the leaching tests that reaction (1) is practically complete and that the effect of temperature increase is minimal.

High recoveries, around 90% Mn, are achieved rapidly during the first thirty minutes of reaction, while only a slight increase during the second leach hour occurs.

The influence of temperature and acidity on the manganese ore dissolution with ferrous ions are illustrated in Fig.2. The sulphuric acid concentration in the 50-200 g/L range exerts only a limited effect. Even at room temperature recoveries exceeding 90% Mn are obtained.

However, a higher temperature favours the oxidation and the hydrolysis reaction. The former leads to a decrease in ferrous ion activity, while the latter results in the formation of a gelatinous film of hydrated Fe₂O₃ on the surface of the mineral. This layer can block the active sites of reaction.

In the absence of ferric ion hydrolysis, acidity play only a slight influence on the dissolution rate of manganese.

Nevertheless, the essential role of the sulphuric acid is demonstrated by the fact that at concentrations of less than 50 g/L, lower recoveries occur, while there are marked problems in the filtration of the leach residue represented.
by hydrates and basic salts of iron:

\[
\text{MnO}_2 + 2\text{FeSO}_4 + 2\text{H}_2\text{O} = \text{MnSO}_4 + \text{Fe(OH)}_3 + \text{Fe(OH)SO}_4
\]

Leaching with sulphites
Manganese dioxide dissolves readily in acid sulphite solution (5):

\[
\text{MnO}_2 + \text{HSO}_3^- + \text{H}^+ = \text{Mn}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O}
\] (4)

A value of free energy \(\Delta G_{298}^\circ = -51.5\) Kcal/mole has been calculated for the reaction 1.4.1 at 25°C. This figure is more than twice the value calculated for the reaction between MnO₂ and Fe²⁺ which, however, results in higher manganese recovery (2). The reason is probably to be found in the concurrent dithionate formation reaction, which consumes twice the number of SO₂ moles:

\[
\text{MnO}_2 + \text{SO}_2^{(aq)} = \text{Mn}^{2+} + \text{SO}_4^{2-}
\]

\[
\text{MnO}_2 + 2\text{SO}_2^{(aq)} = \text{Mn}^{2+} + \text{S}_2\text{O}_6^{2-}
\]

In sulphite leaching, an increase in acidity of solution produces an appreciable increase in manganese recovery. Increase in temperature from 25°C to 50°C has a positive influence on Mn dissolution, but at higher temperature a sharp decrease in recovery is noted (Fig.3).

The rise in recoveries when \(\text{H}_2\text{SO}_4\) concentration is raised from 50 g/L to 200 g/L, and when temperature is increased to 50°C can be explained by a reduction in the stability of the dithionate ion (6). The sharp fall in manganese recovery at 70°C, instead, is attributable to the big drop in the SO₂ solubility in the solution, with a consequent shift of \(\text{SO}_2^{(g)} \rightleftharpoons \text{SO}_2^{(aq)}\) equilibrium to the left. This produces a decrease in availability of reducing species.
RECOVERY OF MANGANESE

Since the manganese is almost completely dissolved, it is possible to consider successive treatment of the acidic solution for the production of the metal.

The filtered pregnant solution coming from the leaching contains not only MnSO₄ but also impurities. The typical composition of the two leach liquors, obtained respectively from FeSO₄ leaching and from Na₂SO₃ leaching, is shown in Table 2.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>FeSO₄-H₂SO₄ leach system</th>
<th>Na₂SO₃-H₂SO₄ leach system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>27.4 g/L</td>
<td>28.5 g/L</td>
</tr>
<tr>
<td>Al</td>
<td>0.23 g/L</td>
<td>0.27 g/L</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.28 g/L</td>
<td>0.31 g/L</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.037 g/L</td>
<td>0.17 g/L</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.06 g/L</td>
<td>3.84 g/L</td>
</tr>
<tr>
<td>Zn</td>
<td>0.064 g/L</td>
<td>0.076 g/L</td>
</tr>
<tr>
<td>Fe</td>
<td>44.20 g/L</td>
<td>0.66 g/L</td>
</tr>
<tr>
<td>Cu</td>
<td>0.003 g/L</td>
<td>0.002 g/L</td>
</tr>
<tr>
<td>Ni</td>
<td>0.001 g/L</td>
<td>0.001 g/L</td>
</tr>
<tr>
<td>Co</td>
<td>0.0002 g/L</td>
<td>0.0002 g/L</td>
</tr>
</tbody>
</table>

Metals more electropositive than manganese (Zn,Co,Cu,Ni) will decrease the current efficiency and will pollute the cathodic deposit. The maximum levels of metal contaminants tolerated in cell feed solution are reported in Table 3(7). The commercially accepted methods for the purification of MnSO₄ solution are based on the precipitation of impurities either as metals with metallic manganese powder or as insoluble sulphide with ammonium sulphide (8). Iron is currently precipitated as ferric hydroxide.
Table 3. Maximum concentration of metal contaminants in MnSO₄ solution

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>21</td>
</tr>
<tr>
<td>Fe</td>
<td>15</td>
</tr>
<tr>
<td>Zn</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
</tr>
<tr>
<td>Co</td>
<td>0.3</td>
</tr>
</tbody>
</table>

In the actual leach solutions only iron and zinc can give some trouble. The procedure investigated consisted in the development of a full solvent extraction operation to eliminate both metals from the MnSO₄ liquor.

The extraction of iron by means of organo-phosphorous compounds, as an alternative route to the conventional precipitation with a neutralizing agents (CaO, CaCO₃) has been studied since it is well known that Fe(III) can be transferred into organic phase with very high distribution coefficients (9).

However at the high iron concentration present in the leach liquor (40-45 g/L) a gelatinous precipitate has been observed during the extraction tests. As matter of fact, if the aqueous iron concentration exceeds 0.1 M, polymerization of the extracted species may occur because organic phase approaches the saturation (10).

So the large amount of iron present in the leach liquor was eliminated by precipitating the bulky Fe(OH)₃. Before cleaning up the solution, it must be intensely aerated to oxidize the small amount of Fe(II) still present.

The precipitation of Fe(OH)₃, performed by adding CaO up to pH 5, plays also an important role in the purification of the solution, since most of the silica is coprecipitated.

When the solution is cooled down to room temperature, CaSO₄ precipitates too.
The extraction of zinc has been carried out by means of di-(2-ethylhexyl)phosphoric acid (DEHPA), recently proposed to extract zinc, copper and cobalt (11).

The experimental work was carried out on a MnSO₄ solution varying the pH with ammonia at the same aqueous-organic phase ratio A/O=1. The organic phase contained 20% vol. DEHPA and 5% vol. TBP, as modifier, dissolved in kerosene.

High recoveries of zinc are obtained, while a small amount of manganese is coextracted into organic phase (about 10% for pH = 3.0 (Fig.4).

In the system under investigation zinc is preferentially extracted over manganese in a wide pH range. High recovery of zinc is obtained when pH is greater than 4.0.

Further study is then necessary to set out an appropriate scrubbing of the loaded organic phase to remove manganese. Zinc may be stripped by contacting the extract with a dilute acid solution (5% H₂SO₄), obtaining a purified MnSO₄ solution amenable to electrowinning.

The electrowinning of MnSO₄ solutions is a well known process and represents the final step in the production of the metal. The flow-sheets and the details of the electrolysis conditions are reported by Kuhn (12).

The proposed flow-sheet of the hydrometallurgical process for the manganese recovery from a wad type ore is shown in Fig.5.

CONCLUSIONS

The leaching tests performed have shown that manganese can be extracted with high recoveries (over 90%) from an ore that cannot be concentrated by conventional methods owing to its textural characteristics and the intimate relationship between the manganese mineral and the host rock.

Moreover, differences in lithological species, that may be encountered in the same area, do not pose any feed problems where a hydrometallurgical plant is concerned.

Operating conditions are not demanding or costly, since a temperature of 25-50°C and an average treatment time of
one hour are all that are needed. Steelworks pickling solutions (1-10% H₂SO₄, 15-20% FeSO₄) could possibly be used for leaching manganese ore. This would ensure a low-cost reagent, while reducing the risk of environmental pollution that might be caused by disposal of the pickling solutions.

The results obtained at laboratory scale in the purification of MnSO₄ solutions have shown that solvent extraction is a feasible operation for zinc, whereas iron has to be precipitated as hydroxide. Organo-phosphorous compounds are suitable also for copper, cobalt and nickel eventually present in the leach liquor. Though complete dependence on imports of this strategic metal essential for steelmaking cannot be eliminated in the short term, it is felt that there is bound interest in exploiting domestic sources of manganese. Research work will therefore continue with the optimization of zinc solvent extraction and with a choice of suitable scrubbing agents for manganese ablation from the extract.

ACKNOWLEDGEMENTS
The author wishes to express his gratitude to Professor G. Rinelli for having encouraged this research. Thanks are also expressed to Mr. P. Pornari for his assistance in the experimental work.

REFERENCES
1) P. MASSACCI, P. PIGA, M. SCOTTI. Mining and beneficiation problems related to the manganese deposit in northern Latium. IX World Mining Congress, Istanbul 1979.
4) D.F. KOCH. Kinetics of the reaction between manganese

5) A.P. HERRING, S.F. RAVITZ. Rate of dissolution of MnO₂ in

6) P. PASCAL. Nouveau Traité de Chimie Minerale, Masson,

7) F.E. BACON in C.A. HAMPEL (Ed.), The Encyclopedia of Elec­

8) J.J. HENN, R.C. KIRBY, L.D. NORMAN. Review of major proposed
process for recovering manganese from United States


11) G.M. RITCEY, B.H. LUCAS. Purification of manganese solu­
tions containing copper and zinc by liquid-liquid ex­

12) A.T. KUHN. Industrial Electrochemical Processes. Elsevier
Amsterdam 1971.
Fig. 1 - Kinetics of manganese ore dissolution when leaching at 25°C with acid FeSO₄ solution (H₂SO₄: 50 g/L).

Fig. 2 - Effect of temperature and acidity during FeSO₄ leaching of manganese ore.
Fig. 3 - Effect of temperature and acidity during Na₂SO₃ leaching of manganese ore.

Fig. 4 - Effect of pH on the extraction of Zn and Mn from MnSO₄ solution using DEHPA as extractant.
Fig. 5 - Flowsheet of the proposed process for manganese recovering.