Effect of mechanical activation on manganese extraction from manganese carbonate ore in acidic media

Volkan Murat Yilmaz & Fatih Apaydin*
Metallurgy and Materials Engineering, Bartin University, Bartin, Turkey

Received 23 February 2013 ; accepted 13 December 2013

A manganese carbonate ore has been mechanically activated at different milling times and the effect of mechanical activation on the ore structure is analyzed by X-ray diffraction, scanning electron microscopy and particle size analysis. The activation procedure leads to amorphisation and structural disordering of the ore structure. Sulfuric acid leaching of the non-activated and activated manganese carbonate ore has been studied at different temperatures, durations, and acid concentrations. The results show that dissolution of manganese increases from 69% to 100% in acidic leaching with 1 M H$_2$SO$_4$ at 70°C after 30 min of mechanical activation, due to amorphisation in structure and creating more surface area.

Keywords: Acidic leaching, Manganese carbonate ore, Manganese extraction, Mechanical activation

Manganese is a strategic element used in several industrial activities such as steel production, preparation of dietary additives, fertilizers, alkaline dry cells and fine chemicals$^{1,2}$. World production of manganese ore in 2010 increased by 26% on a gross-weight basis and by 31% on a contained-weight basis, compared with that in 2009. Manganese is essential to iron and steel production by virtue of its sulfur-fixing, deoxidizing, and alloying properties$^3$. With the rapid development of steel industry, high quality manganese ore resources are becoming scarce. It is therefore essential to make good use of the large quantity of low grade manganese ores (Mn<25%) presently available$^4$. These low grade ores are conventionally processed by pyro/hydro-metallurgical or direct reductive leaching methods. Pyro-metallurgical methods include coal-based reduction roasting$^{5,6}$, pyrite reduction roasting$^7$, and sulphation roasting$^8,9$.

The process of reduction roasting followed by acid leaching plays an important role in the treatment of low-grade manganese ores$^{10}$. Lot of efforts have been made recently to develop a commercial hydrometallurgical process to recover manganese from manganese ores. These direct reductive acid leaching methods include sulphuric acid combined with hydrogen peroxide$^{11}$, oxalic acid$^{12}$, iron(II) sulphate$^{13}$, aqueous sulphur dioxide$^{14,15}$, bioleaching with different microorganisms$^{16}$, ferrous iron$^{17}$ and organic reducing agents$^{18,19}$.

The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering that thermal activation may be bypassed entirely. Within this process, there is a complex influence of surface and bulk properties. Mineral activation leads to a positive influence on the reaction kinetics, an increase in surface area and other phenomena$^{20}$. Mechanical activation is an innovative procedure where an improvement in hydrometallurgical processes can be attained via a combination of new surface area and formation of crystalline disorder in minerals. The lowering of reaction temperatures, the increase of rate and amount of solubility, preparation of water-soluble compounds, the necessity for simpler and less expensive reactors and shorter reaction times are some of the advantages of mechanical activation$^{21}$.

In this study, manganese carbonate ore from the Tavas-Denizli region of Turkey was mechanically activated in a planetary mill. The structural changes in the ore were investigated by x-ray diffraction, scanning electron microscopy (SEM) and particle size analysis. Non-activated and activated ore was leached by sulphuric acid and the effects of mechanical activation on manganese dissolution were investigated under different leaching conditions.
Experimental Procedure

The mechanical activation of manganese carbonate ore from Denizli-Tavas was performed in a Planetary Mono Mill Pulverisette 6 under the milling conditions given in Table 1. X-ray diffraction analysis was performed using a Rigaku Ultima X-ray diffractometer and Cu Kα radiation. A JEOL 6060 LV SEM was used for morphological analysis of non-activated and activated samples. Particle size distribution analysis was carried out with a Mikrotrac S3500 particle size analyzer. Chemical elemental analysis of the ore, performed with XRF (Spectro X-Lab) shows 42.45% Mn, 5.87% Si, 4.35% Ca, 2.56% Fe, 0.96% Mg and 0.83% Al.

The degree of amorphisation (A) of the mechanically activated ore was calculated using the following equation:

$$A = \left(1 - \frac{B_0}{B_x}\right) \times 100$$  \hspace{1cm} \text{(1)}

where $I_0$ is the integral intensity of the diffraction peak for non-activated ore; $B_0$, the background of the diffraction peak for non-activated ore; and $I_x$ and $B_x$, the equivalent values for the activated ore.

Leaching tests were carried out using 10 g of ore and 100 mL of leaching solution in closed glass flasks placed in a thermostated heater with mechanical stirring. The non-activated and activated (30 min) ore was leached by sulphuric acid using the leaching variables concentration (0.5, 1, 1.5 and 2 M), leaching time (15, 30, 45, 60, 90 and 120 min) and temperature (20, 40 and 70°C). After leaching and solid/liquid separation, the manganese content in the liquids was analyzed by atomic absorption spectroscopy. Dissolution of manganese is per cent of dissolved manganese from the ore into acidic solution.

Results and Discussion

Structural characterizing

Results of the X-ray diffraction analysis of the non-activated and activated ore samples are presented in Fig. 1. The height of the biggest manganese carbonate diffraction peak is seen to decrease with mechanical activation. This is consistent with partial amorphisation and structural disordering in the ore, as reported elsewhere. Tromans & Meech found that mechanical activation results in a large number of dislocations and associated strain fields, which may lead to an overall decrease in long range lattice periodicity. Extended milling causes X-ray diffraction peaks to exhibit line broadening or disappear altogether, which may be interpreted as the formation of a metastable amorphous phase.

The degree of amorphisation of manganese carbonate calculated by Eq. (1) is found 51% after 15 min of activation. This value progressively increases to about 64% after 120 min of activation. For activation time of up to 120 min, the...
formation of new surface stagnates due to aggregation of particles, and hence the 30 min activated sample is considered for all subsequent tests.

SEM micrographs and particle size analysis of the samples are given in Fig. 2. It is clear that the particle size decreases during mechanical activation. SEM imaging is in good agreement with the particle size distribution data (Table 2). As per common practice, the cumulative distributions are reported for 10, 50, 90%, specified as \(d_{10}, d_{50},\) and \(d_{90}\). They are taken directly from the mass-based cumulative particle size distribution. The \(d_{50}\) particle size distribution created by a 30 min mechanical activation is decreased from 43.90 to 5.99. The \(d_{90}\) particle size distribution decreases from 211.5 to 28.45.

Particle size reduction or comminution is an important step in many technological operations. The process itself is defined as the mechanical breakdown of solids. It may be used to create particles of a certain size and shape, to increase the surface area and to induce defects in solids which is needed for subsequent operations such as chemical reactions. Milling not only increases the surface area of solids, but it is likely to increase the proportion of regions of high activity in the surface. During high-energy milling, the size of crystals decreases to some critical values. Further energy supply to these crystals of limiting size causes further deformations of crystals, energy accumulation in the volume or at the surface of crystals, and subsequently amorphisation\(^{20}\). Therefore, coarse particles of the ore are reduced in size and then amorphisation occurs during mechanical activation.

Acidic leaching

The non-activated and activated manganese carbonate ore samples have been leached with a 1 M \(\text{H}_2\text{SO}_4\) solution at 20°C for different leaching times. The results are given in Fig. 3. To investigate the effect of initial acid concentration, leaching experiments are performed at 20°C for 15 min with \(\text{H}_2\text{SO}_4\) solutions of 0.5, 1, 1.5 and 2 M initially. The effect of initial acid concentration on manganese dissolution is given in Fig. 4.

<table>
<thead>
<tr>
<th>Activation time, min</th>
<th>(d_{10}, \mu m)</th>
<th>(d_{50}, \mu m)</th>
<th>(d_{90}, \mu m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (Non-activated)</td>
<td>0.752</td>
<td>43.90</td>
<td>211.5</td>
</tr>
<tr>
<td>30</td>
<td>0.701</td>
<td>5.99</td>
<td>28.42</td>
</tr>
</tbody>
</table>

![Fig. 2 – SEM micrographs of (a) non-activated and (b) activated (30 min) ore](image-url)
As seen from Fig. 3, most of the manganese in the ore is dissolved in the first 15 min (~71% from the activated ore and ~52% from the non-activated ore). In all cases, the dissolution of manganese is higher for the activated ore. This result is attributed to the amorphisation of the ore. Dissolution of manganese does not increase significantly with longer leaching time, especially for the activated ore. Momade\textsuperscript{23} investigated sulphuric acid leaching of the Nsuta (Ghana) manganese carbonate ore and stated that extraction was affected by acid concentration, initial particle fraction and leaching temperature. He also reported that manganese carbonate dissolution in acid was more favoured at elevated temperatures. Figure 4 shows that the increasing acid concentration causes an increase in manganese dissolution, although to a lesser extent than mechanical activation.

Reaction temperature has a considerable influence on manganese dissolution from the ore, as shown in Fig. 5. Manganese extraction from the activated ore increases from ~71% to 100% when the reaction temperature is increased from 20°C to 70°C. The equivalent values for the non-activated ore are 54% and 69% respectively.

**Conclusion**

Non-activated and activated manganese carbonate ore was leached with sulphuric acid solutions and the results indicate that high energy ball milling increases the manganese dissolution from the ore. This is attributed to structural disordering. Furthermore, the increase in surface area allows for more contact surfaces between ore and acidic solution. Overall, manganese extraction from the activated ore is higher than those from non-activated ore at the same leaching conditions. Best conditions are found to be 30 min of high-energy milling and 15 min leaching with 1 M $\text{H}_2\text{SO}_4$ at 70°C.

**References**