METHOD OF OBTAINING ELECTROLYTIC MANGANESE FROM FERROALLOY PRODUCTION WASTE

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Abstract

The manganese, active metal very much used in the steel and aluminum industries, is found in the nature combined in diverse minerals, the most important of which are: the oxide pyrolusite and the carbonate called rhodochrosite. This work presents a process that allows the obtaining of high quality electrolytic manganese, using sludge from flue gas furnace ferroalloys production, getting by this way, the integrated management of a residue produced worldwide in important quantities. The above mentioned work has been realized by the collaboration, during the last 10 years, between Ferroatlántica SA (Boo-Cantabria) and the laboratory of Metallurgy of the Escuela de Minas de Oviedo, and has given up to an International patent protecting the production of pure solutions of manganese, suitable to be electrolyzed, from electrical furnaces gas cleaning mud, obtained in the Fe-Mn and Si-Mn production.

Keywords:
Electrolytic manganese, Ferroalloys, Metallurgical waste, Metals recovery

INTRODUCTION

Manganese is an active metal which is not found in nature as a native form, but rather combined in minerals as an oxide (pyrolusite) or carbonate (rhodochrosite), two of the more important minerals. Production processes traditionally requiring the addition of manganese, have been carried out using these minerals in iron metallurgy reduction furnaces for the purpose of using the manganese as an alloy element or as a deoxidant and desulphurant agent in steel production. Afterwards manganese was obtained by thermal reduction in the blast or electric furnaces, in which Fe-Mn and Si-Mn are obtained. Pure manganese can be produced by aluminothermic reduction, but the process is for small productions. Electrolytic manganese has been produced since 1948 after being developed the process in Boulder City(USA) resolving the problems related with: manganese dissolution from minerals, purification of solutions, development of a diaphragm electrolytic cell, conditioning agents for cathode solution to prevent reoxidation. Mn³⁺ ion is very difficult to be reduced in aqueous solution (Mn³⁺(aq) + 2 e⁻ = Mn(s)  E° = -1.179 V) because H₂ gas overpotential on Mn metal only can be in especial conditions lower than -1,179 V. It makes very difficult to avoid simultaneous H₂ evolution at cathode, so loosing current for Mn deposition and lowering significatively the Faraday performance. [1-4]. Currently, electrolytic manganese consumption in Spain is approximately 10,000 tons per year and is imported in its entirely, and used for aluminum alloys. Ferroatlántica Group is the only producer of ferroalloys in Spain, leader in Europe and very well known worldwide.

The process for obtaining electrolytic manganese has been developed at laboratory and pilot scale. It has been developed by the need to resolve the great environmental derived from the manufacture of ferroalloys Fe-Mn and Fe-Si, mailly produced for the disposal of the exaust fume fines washing, producing a fairly high amount of lodes that mast be managed and deposited in save form. There are other industries producing wastes having fairly high manganese content, like lead anode and cube deposits in some metal industry, or the ore lodes from the fabrication of MnO₂ used in batteries.

EXPERIMENTAL

Materials

Ferroalloy is an alloy of iron with some element other than carbon. Ferroalloys give distinctive qualities to steel and cast iron and serve important
functions during iron and steel production cycles and uses. The principal ferroalloys are of manganese, silicon and chromium. In the manganese case, this metal is essential to counteract the harmful effects of sulfur in the production of virtually all steels and cast iron, is also a good deoxidant element and gives rise to the singular effect of work-handering when using steel, that avoids its wearing in use (tracks, mills, etc). But derived from the manufacture of this ferroalloys, and as a result of the processing of the production furnace exhaust fumes, it is obtained a waste product having a high manganese content which is difficult to use as a recyclable material for the furnace due to its physical nature: very fine, polluted and wet. The starting material used in the developed process for obtaining electrolytic manganese is this waste, which composition is given in Table 1:

<table>
<thead>
<tr>
<th>P.C.</th>
<th>Mn</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>K₂O</th>
<th>ZnO</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Wt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>28-32</td>
<td>20-30</td>
<td>20-25</td>
<td>5-8</td>
<td>3-5</td>
<td>2-3</td>
<td>2-3</td>
<td>1-4</td>
</tr>
</tbody>
</table>

Mineralogical analysis of the residua can be seen in Figure 1 that show the diffractogram of the fume waste. In it one can appreciate the existence of the compounds of manganese: Manganosita (Mn+2O), Hausmannita (Mn+2Mn2+3O4.), appearing also Ankerita, a carbonate with small amounts of manganese. Also appear calcite and phlogopita (K-mica), as well as some of magnesite and graphite.

Method

The process which has been conceived starts with a sulphation phase, followed by an hydrometallurgical treatment consisting of four steps: primary lixiviation, purification, secondary purification and conditioning and finally, the electrolysis phase for obtaining electrolytic manganese [5].

In sulphation phase, the quality of the mixed of manganese oxides, H₂SO₄ and water depends primarily on two factors: the amount of H₂SO₄ per kg of initial dry material and the moisture and Mn percentage of the residue. In this work, and to study the effectiveness of the process, 1 kg of material with a humidity of 40% and a Mn content of 15% was used. The material was mixed with 390 g of sulfuric acid and 390 ml of water in a ceramic recipient and the mixture was then poured on a tray which was introduced in a furnace maintained at 300°C for 30 minutes.

After that, the lixiviation was carried out with prepared synthetic anolyte with a composition of 35 g/l of H₂SO₄. In this process, the residence time for the extraction of Mn was 1 hour, during which the pulp was maintained under strong stirring.

As the final of the prior stage pH of the solution in these conditions is of 3.7, for its purification, 70 g of lime were added to the lixiviation reactor and it was left under stirring for half an hour, increasing the pH value to 6.5. Thus, the final concentration of Fe and Al is less than 1 ppm in the liquor.

To separate the waste contained in the resulting pulp, which has both non-etched material and the precipitated impurities as hydroxides (mainly Fe and Al), it was subjected to vacuum filtration. The waste separated here was subjected to washing with water to recover part of the manganese that it had entrained and to improve its chemical and physical characteristics prior to its subsequent deposition – the material is self-compactable-. The minimum Mn concentration must be at this point of 32 g / l in the rich solution. After this, to remove from the filtration separated liquor the organics in solution it passes through an active carbon filter.

Finally, a second purification is necessary for eliminate Zn, (Ni y Co), mainly since they harm the process of electrolysis. In this work, the second purification phase involved adding 11.1 ml of...
sulphide producing 0.65 g of zinc sulphide that is separated by settling, so there was less than 1 ppm of the above mentioned metals in the liquor.

The obtained precipitate was separated by means of filtration and finally, 1.25 l of liquor was thus obtained. Table 2 shows the composition of the final product:

Table 2: Composition of the final product:

<table>
<thead>
<tr>
<th>Mn</th>
<th>Zn</th>
<th>Ni</th>
<th>Co</th>
<th>Fe</th>
<th>Mg</th>
<th>Ca</th>
<th>SO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>(g/l)</td>
<td>(ppm)</td>
<td>(ppm)</td>
<td>(ppm)</td>
<td>(g/l)</td>
<td>(ppm)</td>
<td>(g/l)</td>
<td></td>
</tr>
<tr>
<td>30-</td>
<td>0.2-</td>
<td>0.5-</td>
<td>0.3-</td>
<td>0.2-</td>
<td>2.5</td>
<td>300-</td>
<td>100-</td>
</tr>
<tr>
<td>32</td>
<td>0.6</td>
<td>0.8</td>
<td>0.6</td>
<td>0.6</td>
<td>5</td>
<td>800</td>
<td>110</td>
</tr>
</tbody>
</table>

Table 3: Composition of the electrolytic manganese.

<table>
<thead>
<tr>
<th>MnE (kg)</th>
<th>C (%)</th>
<th>S (%)</th>
<th>P (%)</th>
<th>Ti (%)</th>
<th>Mg (%)</th>
<th>Fe (%)</th>
<th>K (%)</th>
<th>Si (%)</th>
<th>Ca (%)</th>
<th>Zn (%)</th>
<th>Cu (%)</th>
<th>Co (%)</th>
<th>Ni (%)</th>
<th>Mn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.216</td>
<td>0.015</td>
<td>0.050</td>
<td>0.002</td>
<td>0.001</td>
<td>0.004</td>
<td>0.006</td>
<td>0.004</td>
<td>0.002</td>
<td>0.003</td>
<td>0.004</td>
<td>0.001</td>
<td>0.002</td>
<td>0.004</td>
<td>99.9</td>
</tr>
</tbody>
</table>

The electrolysis process is carried out in diaphragm cells in which the anolyte and catholyte are separated by a semi-permeable material and both have a similar composition, although anolyte has a lower pH and noticeably manganese-depleted, catholyte is controlled for: temperature 34ºC, 8.2 pH, 0.3g/l reductant (SO2), 140g/l buffering ammonium sulfate, 6A/dm current density. The cathodes are made in stainless steel and the anodes are made of an alloy of 99% lead and 1% silver.

For starting the cell requires a catholyte concentration of 12-14 g / l of Mn, while feed solution should be between 30 - 33 g / l of Mn. Over time, the metal is deposited on the surface of the cathode in the form of flakes. While the electrolytic manganese flakes are deposited on the cathode, manganese dioxide accumulates on the anode. Farady performance is 63%

**Cathode**

\[
\text{Mn}^{2+} + 2e^- \rightarrow \text{Mn} \\
2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^-
\]

**Anode:**

\[
2\text{H}^+ + \text{SO}_4^{2-} \rightarrow \text{H}_2\text{SO}_4 \\
\text{Mn}^{2+} + 2e^+ + \text{O}_2 \rightarrow \text{MnO}_2 \\
2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4e^-
\]

Once the process has concluded, the metal load is separated by mechanical means and this product also requires washing with water. Table 3 shows the composition of the obtained electrolytic manganese.

**CONCLUSIONS**

The investigations of the process for obtaining electrolytic manganese from the treated sludge of the exhaust gases of ferroalloy production furnaces have shown that can be an economic and ecological way for recycling this waste and with the advantage of produces a product with a high market value.

Moreover, after the experiments in the laboratory, a 1M€ pilot plant was constructed, and it demonstrated the effectiveness of the process on an industrial scale, yielding a manganese with 99.9% of purity, after more than 1,000 kg produced with industrial cathode size.

Finally note that this method has been patented in Spain and also there an international extension already approved in countries as important in Metallurgy such as South Africa and Kazakhstan.

**REFERENCES**