ELECTROLYTIC MANGANESE FROM FERROALLOY PRODUCTION FURNACE FLYING DUST

J.Sancho[1], J.C.Sánchez Recio[2], A.Fuentes[3], J.Ayala[1], J.L.Bernardo[2],C. Rodríguez[3]

[1] Escuela de Minas de Oviedo C/ Independencia, 13 - 33004 Oviedo, Spain; jsancho@uniovi.es, jayala@uniovi.es.
[2] Grupo FerroAtlántica S.A.U.- Madrid, Spain.; jcsrecio@ferroatlantica.es, jlbernardo@ferroatlantica.es.
[3] FerroAtlántica S.A.U.- Boo de Guarnizo. Santander, Spain; afuentes@ferroatlantica.es, crodri@ferroatlantica.es

ABSTRACT

The manganese, an active metal widely used in the steel and aluminium industries [1], [2] is found in the nature combined in diverse minerals, mainly as the oxide pyrolusite and others like the carbonate called rhodochrosite or the hydrated oxides or silicates. A process that allows obtaining of high quality electrolytic manganese using flying fines residua from flue gas furnace ferroalloys production, was developed, that could be used for the integrated management of a residue produced worldwide in important quantities. The above mentioned procedure has been realized by the collaboration, during the last 15 years, between FerroAtlántica Group SAU (Boo Plant-Cantabria) and the laboratory of Metallurgy of the Escuela de Minas de Oviedo, and has given up to several International patents 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.

1 INTRODUCTION

Manganese is an active metal which is found in nature combined in minerals as oxides (pyrolusite, criptomelane), carbonate (rhodochrosite), silicates (braunite) and hydroxides (todorokite) two of the more important minerals are for its abundance, pyrolusite and braunite. Steel 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 deoxidant and desulphurant agent in steel production. Manganese alloys were 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 aluminothermal reduction, but the process is intended for smaller productions. Electrolytic manganese has been produced since 1948 after the process being developed in Boulder City (USA) resolving the problems related to: manganese dissolution from minerals, purification of solutions, development of a diaphragm electrolytic cell, conditioning agents for cathode solution to prevent reoxidation. Mn^{++} ion is very difficult to be reduced in aqueous solution ($Mn^{++}_{(aq)} + 2\ e^- = Mn_{(s)}$ $E^o = -1{,}179$ V) because H_2 gas overpotential on Mn metal can only in special conditions be lower than -1,179 V. It makes very difficult to avoid simultaneous H_2 evolution at cathode, so loosing current for manganese deposition and lowering significantly the Faraday performance [1- 4]. Currently, electrolytic manganese consumption in Spain is approximately 11,000 tons per year, it is imported entirely and used for aluminium alloys. FerroAtlántica Group is the only producer of ferroalloys in Spain, with plants in Europe, Africa, South America and Asia and known very well worldwide.

The process for obtaining electrolytic manganese described in this work has been developed at the laboratory and industrial-pilot scale. It has been developed by the need to make the manufacture of ferroalloys Fe-Mn and Fe-Si, a sustainable process, taking profit of the Mn content of the flying fines and avoiding the waste disposal expenses.

There are other industries producing wastes having fairly high manganese content, like lead anode scale and cube deposits in a huge non-ferrous metal industry, or the ore lodes from the fabrication of MnO_2, used in batteries.

2 EXPERIMENTAL

2.1 Materials

Ferroalloy is an alloy of iron with some other particular element other than carbon. Ferroalloys give distinctive properties to steel and cast iron, performing important functions during iron and steel production cycles. The principal ferroalloys are those of manganese, silicon and chromium. In the manganese case, this metal is essential to counteract the harmful effects of sulphur in the production of virtually all steels and cast irons. It is also a good deoxidant element and gives rise to the singular effect of work-hardening when working with steel pieces or engines, that avoids its wearing in use (tracks, mill's plates, etc). But derived from the manufacture of these ferroalloys, and as a result of the cleaning process of the production furnace exhaust fumes, a waste product is obtained 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 3: Chemical analysis of the residua

	P.C.	Mn	SiO_2	CaO	Al_2O_3	MgO	Na_2O	Fe_2O_3	K_2O	ZnO	C
% Wt	28-32	20-30	20-25	5-8	3-5	2-5	2-3	2-3	1-4	0,5-1	5-8

P.C.: loss on calcination

Mineralogical analysis of residua can be seen in Figure 1 that show the XR diffraction pattern of the fume washed waste. In it one can appreciate the existence of the compounds of manganese: Manganosite (Mn+2, O=) and Hausmannite (Mn+, 2Mn2+, O=.), Ankerite, a carbonate with small amounts of manganese is also found. Calcite and phlogopite (K-mica) are also found, as well as some magnesite and graphite. Other samples give (Mn2+, Mn3+, O=) and manganese silicate.

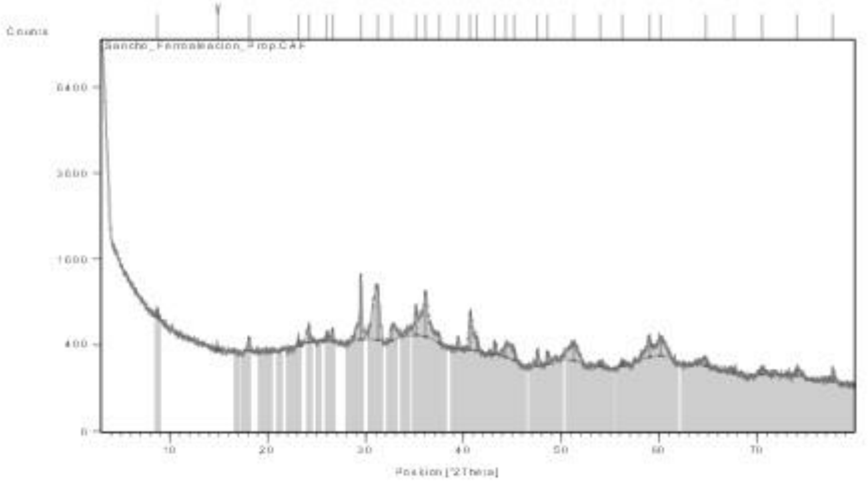

Figure 1. XR pattern of a sample of smoke mud from Fe-Mn making furnace. Signal detected show different manganese oxides, calcite, ankerite, magnesite and graphite from coke

2.2 Method

Thermal sulphating is the base of the first treatment of the waste followed by a hydrometallurgical treatment consisting of four steps: primary lixiviation, purification, secondary purification and conditioning and finally, the electrolysis phase for obtaining electrolytic manganese [5]. Prior to sulphating phase, mixing of manganese oxides lodes, H_2SO_4 and water should be done properly, it depends primarily on two factors: the amount of H_2SO_4 per kg of initial treated material and the moisture and Mn content in it. For this work, and to study the effectiveness of the process, 1 kg of material with a moisture content of 40% and a Mn content of 15% was used. The material was mixed with 390 g of sulphuric acid and 3.9 l of water in a laboratory inox mixer and the mixture was then poured on a tray which was introduced in a furnace hold at 300ºC for 30 minutes. After that, the lixiviation was carried out with prepared synthetic anolyte with a composition of 35 g/l of H_2SO_4. In this process, the residence time for the extraction of Mn was 30 min., during which the pulp was maintained under strong stirring. At the final of the prior stage pH of the solution is around 3.5. For its purification, 70 g of lime were added to the lixiviation reactor and it was left under stirring for half an hour as mentioned, increasing the pH value to 6.5. At this moment, the concentration of Fe and Al in the solution is less than 1 ppm in the liquor.

To separate the solid residual waste contained in the resulting pulp, which has both non-etched material and the precipitated impurities as hydroxides (mainly Fe and Al), the pulp is subjected to pressure 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 solid material was produced is self-compactable, and was qualified as non-toxic by external studies in several environmental agencies.

The minimum Mn concentration must be at this point of 32 g / l in the rich solution. After this, to remove from the filtrated liquor the small amount of organics introduced in solution by our especial method, it passes through an active carbon filter.

Finally, a second purification is necessary for eliminate mainly Zn^{2+}, the heavy metal more abundant in manganese deposits from its genesis, and smaller amounts of (Ni^{2+} and Co^{2+}), because they should be eliminated preferably in the electrolysis process due to their more favourable reduction potential. In this work, the second purification phase involved the addition 11 ml of sulphide solution producing 65 g of zinc sulphide that is separated by settling, with a similar amount of manganese sulphide, 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 both zinc and manganese can be recovered from it. Finally, 1.25 l of liquor was thus obtained. Table 2 shows the composition of the final solution product:

Table 4: Composition of the final cathode feeding solution

Mn (g/l)	**Zn (ppm)**	**Ni (ppm)**	**Co (ppm)**	**Fe (ppm)**	**Mg (g/l)**	**Ca (ppm)**	**SO_4^{2-} (g/l)**
28-32	20-25	5-8	3-5	2-5	2-3	2-3	1-4

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 reducing gas (SO_2), 140g/l buffering ammonium sulphate. Current used is 6A/dm current density. The cathodes are made of stainless steel and the anodes are made of an alloy of 99% lead and 0,5-1% silver. 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. Faraday performance is 63% meaning that only nearly 2/3 on manganese is recovered in metallic form. Even with the strict conditions kept in both anolite and catholite, there is a fairly high amount of hydrogen evolved on the cathode, lowering the current efficiency.

The reactions on the electrodes are expressed as follows:

Cathode: $Mn^{+2} + 2e^- \Rightarrow Mn$ **;** $2H_2O + 2e^- \Rightarrow H_2 + 2OH^-$

Anode: $2H^+ + SO_4^{-2} \Rightarrow H_2SO4$**;** $Mn^{+2} + 2H_2O \Rightarrow MnO_2 + 4H^+ + 2e^-$; $2H_2O \Rightarrow 4H^+ + O_2 + 4e^-$

(In red the products of the cell)

Once the process is finished, 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.

Table 5: Composition of the manganese electrolyte (%)

C	**S**	**P**	**Ti**	**Mg**	**Fe**	**K**
0.015	0.050	0.002	0.001	0.004	0.006	0.004
Si	**Ca**	**Zn**	**Cu**	**Co**	**Ni**	**Mn**
0.002	0.003	0.004	0.001	0.002	0.004	99.9

Figure 2: Picture of Mn covered anode (2m x 1.3m, the biggest used till the moment) and manganese flakes

Figure 3: Overview of industrial pilot plant and cell.

3 CONCLUSIONS

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

Moreover, after the experiments in the laboratory, a 2M€ industrial- 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 3.000 kg produced with industrial cathode size.

Finally, this method has been patented in Spain and an international extension has already been approved in the following countries: USA, South Africa, Australia, Ukraine, Russia, Kazakhstan and Mexico.

4 REFERENCES

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