The recovery of manganese products from ferromanganese slag using a hydrometallurgical route

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Synopsis

The ferromanganese industry is under pressure to deal with the slag arising from the production of ferromanganese, which is discarded in landfills or slag heaps. This material poses an environmental and health risk to surrounding ecosystems and communities, and disposal costs are increasing. Ferromanganese slag contains an appreciable amount of residual manganese metal, which can be exploited. Previous work has shown that the slag can be leached fully, while rejecting the silica to a residue. The methods that were investigated to recover manganese from the leach solution included hydroxide precipitation to upgrade the leach solution followed by manganese carbonate precipitation to produce a pure manganese carbonate product or a manganese carbonate furnace feed material, which would be recycled to increase manganese recoveries in the production of ferromanganese. In addition, electrowinning of electrolytic manganese dioxide from the leach solution was studied. The methods were compared in terms of selectivity, costs, and product quality. Co-recovery of the leach residue, which is a potential cement additive, is discussed.

Among the methods investigated to upgrade the pregnant leach solution, hydroxide precipitation utilizing ammonia to adjust the pH appears to be the most effective in removing major impurities such as iron, aluminium, and silica to less than 1 ppm. The manganese carbonate and impure manganese carbonate furnace feed products met quality specifications. However, although the production of these materials was technically viable, the large amounts of base reagent that were required to raise the pH, and the associated high operating costs, rendered the process uneconomic.

An optimization study was therefore carried out with the primary objective to determine the ideal acid amount to be utilized in the water-starved digestion stage, thereby decreasing acid and base consumption while optimizing the quality of the pregnant leach solution, and producing a leach residue that contained <1% Mn. The outcome was an economically viable process. Additional benefits included an increase in the manganese content of the impure manganese carbonate furnace feed material, and a substantial reduction in the dilution of the pregnant leach solution, thereby maintaining high manganese concentrations that rendered the solution viable for electrowinning of electrolytic manganese dioxide, the production of which yielded a current efficiency of 74%.

Keywords

environment, ferromanganese slag, manganese products, water-starved digestion, precipitation.

Introduction

A high manganese recovery is vital in rendering the ferromanganese production process economically viable. It is particularly crucial in recovering manganese products from secondary sources such as ferromanganese slag. This industrial waste material contains an appreciable amount of residual manganese that can be economically exploited. Ferromanganese slag is a waste product from the production of ferromanganese metal in blast furnaces and submerged arc furnaces. There is an estimated 53 Mt of slag dumped in South Africa (Parker and Loveday, 2006). Discarding the slag not only entails disposal costs, but also poses an environmental and health threat, mainly due to the leaching of mobile manganese in the slag.

The slag can be fed back into the furnace. This option, however, is not favoured due to the build-up of alkali metals and zinc in the smelting process. The slag can also be crushed and ground to produce cement aggregate or slag cement. The disadvantage to this, however, is that there is a danger that manganese can leach out, and only freshly tapped slag can be utilized. A hydrometallurgical route that can be adopted to recycle both the discarded and freshly tapped slag would be advantageous. The slag would be subjected to a water-starved digestion and leached to produce a pregnant leach solution from which manganese could be recovered using various methods, including precipitation and electrowinning, and a residue that can be sold as an additive for Portland cement.

The research focus was therefore aimed at developing economically and technically viable processes to produce a pregnant leach solution with a high manganese content and low impurity concentration. The pregnant leach solution could be utilized to produce saleable products that meet the quality requirements, or products containing manganese in a low oxidation state that could be fed back into the

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ferromanganese production process as a sweetener, thus circumventing the environmental and health impacts of processing ferromanganese slag. In addition, a saleable byproduct such as a cement additive would be produced.

Leaching of ferromanganese slag

Various authors have undertaken prior investigations into the leaching of ferromanganese slag. The leaching processes discussed include ferric chloride in the presence of sucrose, carbamate leaching, and the quick leach (also known as the water starved digestion method) with concentrated sulphuric acid (98–99%).

Naganoor et al. (2000) used the ferric chloride route to leach slag. It was deduced that roasting prior to leaching was essential to ensure that the manganese was converted into a soluble form. A manganese recovery of 82% was achieved in 2 hours at a temperature of 80°C. The oxidation of sucrose, however, increased the rate of leaching, yielding an 86% recovery in 1 hour. The pregnant leach solution can be further treated to produce electrolytic manganese dioxide (EMD) and electrolytic manganese metal (EMM). Mcintosh and Baglin (1992) investigated the feasibility of using ammonium carbamate as a reagent to recover manganese from slag. A recovery of 99% was achieved in 3 hours at a temperature of 65°C. The manganese carbamate can be added as a sweetener in the steelmaking industry or can be further purified.

The slag that was used to produce the pregnant leach solution in previous investigations was first crushed and milled, then premixed with deionized water followed by water starving (digesting) the slurry in concentrated sulphuric acid (98%) (Groot et al., 2013). A solidified cake was produced, which was left to age for 24 hours; this resulted in an increase in manganese recovery. Thereafter, the cake was water-leached in a 1–3 stage water leach, recovering between 75–95% of the manganese into solution. These results, however, were dependent on the number of leaching stages.
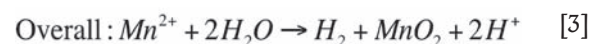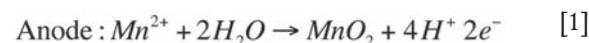
Recovery of manganese as manganese carbonate

Zhang et al. (2010) investigated carbonate precipitation of manganese from a pregnant leach solution at 60°C using sodium carbonate (Na_2CO_3) at different pH values. The experiments were conducted under ambient conditions, but with slow agitation to reduce oxidation by air. It was observed that at pH>7.5 a 90% manganese recovery was obtained with co-precipitation of calcium and magnesium at recoveries of 43% and 13%, respectively. At pH>8.5, 99.5% of the manganese was recovered, with co-precipitation of 97% of the calcium. According to Zhang et al. (2010) the precipitation of manganese carbonate is thermodynamically favoured over magnesium carbonate and (but to a lesser degree) calcium carbonate. This is attributed to the smaller log $K_{(Ca/Mn)}$ value measured in comparison to the theoretical K value. This is an important consideration when attempting to recover manganese carbonate that meets specifications from a solution that contains high magnesium and low calcium concentrations. The results obtained by Zhang et al. suggested that the recovery of manganese via a carbonate precipitation yielded a good quality product. This, however, was dependent on the manganese to magnesium ratio.

An alternative process to produce manganese carbonate ($MnCO_3$) from a manganese solution was developed by INCO for the recovery of metal values from ocean-floor nodules in the presence of 3–8% NH_3 and 1–6% CO_2. The reagent acts both as a lixiviant and as a precipitant for manganese as $MnCO_3$, which is recovered in the residue; nickel, cobalt, and copper are solubilized as stable ammines (Illis and Brandt, 1975; Zhang and Cheng., 2007). Kono et al. (1986) conducted similar studies into the recovery of manganese from nodules using a sulphurous acid leach, with precipitation of manganese as $MnCO_3$ in the presence of $(NH_4)_2CO_3$ while copper, nickel, and cobalt remained in the solution as ammine complexes.

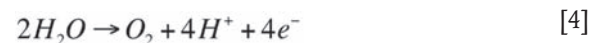## Production of electrolytic manganese dioxide (EMD)

Electrolytic manganese dioxide (EMD) is a vital ingredient in Leclanche-type dry cells. Owing to modern advances in the electronics industry, which have necessitated a greater capacity for manganese dioxide production, natural manganese dioxide (NMD) has been replaced by electrolytic manganese dioxide (EMD) (Rethinaraj and Visvanathan, 1993).

The half-cell reactions are given below:

$$Anode: Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ 2e^- \qquad [1]$$

$$Cathode: 2H^+ + 2e^- \rightarrow H_2 \qquad [2]$$

$$Overall: Mn^{2+} + 2H_2O \rightarrow H_2 + MnO_2 + 2H^+ \qquad [3]$$

The current efficiency at the anode is affected by the following parasitic reactions (Te Riele, 1983):

The evolution of oxygen:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad [4]$$

The oxidation of Mn^{2+} to Mn^{3+}, which diffuses into the electrolyte solution:

$$Mn^{2+} \rightarrow Mn^{3+} + e^- \qquad [5]$$

Mn^{3+} is an unstable ion that disproportionates to produce Mn^{2+} and MnO_2, which forms sludge:

$$2Mn^{3+} + 2H_2O \rightarrow Mn^{2+} + MnO_2 + 4H^+ \qquad [6]$$

An additional parasitic reaction that can occur if there is an appreciable amount of iron in solution, and which is responsible for decreasing current efficiencies and contaminating the final EMD product, is given by:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad [7]$$

Table I shows the effect that different concentrations of iron in solution have on the final product (Te Riele, 1983).

Table I

Effect of iron content of solution on iron contamination in the EMD (Te Riele, 1983)

Fe in electrolyte (ppm)	Fe in final EMD (%)
0–10	0.021
10–50	0.098
45–80	0.149
60–90	0.19

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There are several factors that affect the quality of EMD produced, one of which is the acid concentration of the electrolyte. A high acid concentration (>50 g H_2SO_4 per litre) has a detrimental effect on the amount of battery-active EMD plated. In addition, the morphology is affected, resulting in a less compact deposit, and current efficiency is decreased by the formation of Mn^{3+} which is promoted by the higher acid concentration (Te Riele, 1983). Temperature is another critical factor. A temperature above 90°C results in a desirable current efficiency, which ranges between 90–97%, provided the system is operated at 100 A/m^2 (Te Riele, 1983; Rethinaraj and Visvanathan, 1992). At lower temperatures, however, the current efficiency will be variable depending on the type of materials utilized for the electrodes, and the cell voltage will increase, thereby increasing energy consumption. In addition, lower temperatures result in shorter discharge times on the EMD battery cell (Te Riele, 1983).

Experimental procedure

The flow diagram in Figure 1 summarizes the experimental routes that were investigated to determine the most technically and economically viable methods of producing various manganese products.

Materials and methods

Materials

A South African ferromanganese producer in KwaZulu-Natal supplied the ferromanganese slag utilized in previous investigations. The chemical and phase compositions of the slag were determined using X-ray fluorescence spectrometry (XRF) and X-ray diffraction spectrometry (XRD), which were performed by Scrooby's Laboratory Service and the Department of Geology at the University of Pretoria.

Chemical composition of the ferromanganese slag

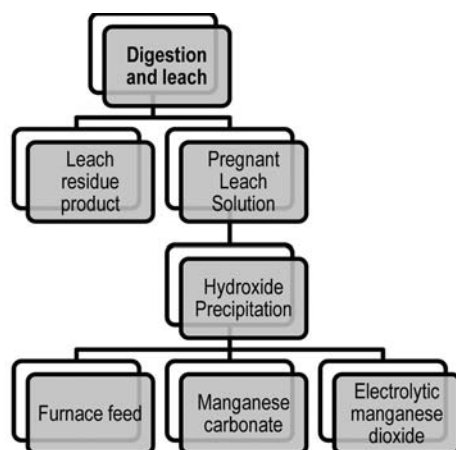The typical composition of the slag, determined by XRF analysis, is given in Table II.

The major elements were manganese, silicon, and calcium. The iron content was low, which was ideal as iron results in difficulties in the downstream purification stages. The major phases present in the material included glaucochroite, manganosite, and gehlenite as shown in Table III.

The manganese content of the slag (approx. 30%) was sufficient for the investigation to proceed further.

All reagents were of analytical grade, and supplied by Merck Millipore, and distilled water was used throughout. All glass and metal ware was decontaminated with detergent and rinsed thoroughly with distilled water.

Sample preparation

The work was performed on 100 g ferromanganese slag samples that had been pre-crushed to 45 mm. The material was further reduced in size using a gyratory crusher, then milled to a cut size of 600 μm utilizing ball milling, and dry-screened.

Purification of the manganese pregnant leach solution

The objective of the purification stage was to obtain a pregnant leach solution (PLS) that contained high manganese and low impurities concentrations, from which manganese products that meet the quality specifications could be produced.

Figure 1—Flow diagram illustrating the basic process routes investigated for the recovery of manganese products

Table II

Typical composition of the ferromanganese slag

Element	Mass %
C	1
Mn	28
P	0.01
Si	21
Cr	<0.005
Ni	<0.005
Cu	0.006
Al	<0.005
V	<0.005
Ti	0.14
Co	<0.005
Ca	19
Mg	3
Fe	1

Table III

Phase analysis of the ferromanganese slag (Groot et al., 2013)

Phase	Chemical formula	Mass %
Glaucochroite	$CaMnSiO_4$	55.00 – 65.10
Manganosite	MnO	2.28 – 4.50
Gehlenite	$Ca_2Al[AlSiO_7]$	4.00 - 8.49
Monticellite	$CaMgSiO_4$	0.00 – 2.00
Quartz	SiO_2	0.00 – 5.10
Amorphous	-	21.00 – 30.0

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The reagents used to increase the pH for impurity removal included sodium hydroxide (NaOH) or ammonia (NH_3), which were employed in separate purification investigations. The oxidant was hydrogen peroxide (34% H_2O_2), to oxidize Fe^{2+} to Fe^{3+} so that iron was precipitated within a pH window of 3–5.5.

A PLS sample size of 100 ml was used throughout experimental runs. Before base reagent was added, 34% H_2O_2 was added dropwise until the solution turned from pink to a mustard colour. For purification using NaOH, 24 g of NaOH pellets were weighed, and dissolved in 200 ml distilled water to obtain a solution of 120 g/l of NaOH, which was added dropwise to the solution to increase the pH from less than 0 to approximately 5.6. The solution was kept at room temperature and continuously stirred.

A similar procedure was followed for the experiments that involved the upgrading of the PLS using 25% ammonia solution, which was added dropwise to increase the pH to approximately 5.6.

The upgraded PLS was analysed for major elements by inductively coupled plasma – optical emission spectrometry (ICP-OES).

Production of manganese products

Precipitation of manganese carbonate

A 100 ml sample of PLS was used for the investigations utilizing Na_2CO_3 or $(NH_4)_2CO_3$ as base reagents. The Na_2CO_3, at 150 g/l, was added dropwise to the PLS; the $(NH_4)_2CO_3$ was added to the PLS in its solid form. Approximately 15 g of $(NH_4)_2CO_3$ was added to adjust the pH from approximately 5.5 to 8.5, the pH range in which >99% of the manganese was recovered. The system was open to the atmosphere, and the procedure was conducted at room temperature (approx. 25°C) while the solution was agitated. Once precipitation was complete, the product was filtered, washed with distilled water, and dried at 30°C.

The manganese and impurities contents of the barren solution obtained after precipitation were determined by ICP-OES. The precipitate was analysed using XRF and XRD.

Production of a furnace feed material (impure MnCO₃)

The apparatus and reagents used to produce the furnace feed material were the same as for the purification of the PLS and the pure $MnCO_3$ product, except no filtration step was included. The product was dried in an oven at 30°C.

Electrowinning of electrolytic manganese dioxide (EMD)

The electrodes were graphite rods with a diameter of 7.5 mm. A current density of 100 A/m² was adopted, with a plating time of 72 hours to allow a deposit thickness of approximately 2.4 mm, which would produce a mass of EMD >3 g, and a temperature of 90°C. The electrolyte volume was 1.1 litres.

The set-up of the electrowinning experiment for the production of EMD is shown in Figure 2.

The EMD was analysed for gamma and alpha manganese dioxide (MnO_2) by XRD, and an elemental analysis was carried out by XRF. The manganese content of the solution after electrowinning was analysed using ICP-OES.

Results and discussion

Pregnant leach solution and residue

To produce the pregnant leach solution and residue the milled slag material was subjected to a water starved digestion and thereafter water-leached for two hours. Table IV shows a mass balance giving the general recoveries of manganese and impurity elements to the PLS and residue respectively. The mass balance was based on a 200 g slag sample.

The discrepancies in the percentage recovery of elements were probably due to the inhomogeneity of the ferromanganese slag sample. It was assumed that the chemical composition of the slag was as given in Table IV.

Purification of the pregnant leach solution (PLS)

Hydroxide purification

It was essential to obtain a purified PLS in order to produce $MnCO_3$ and EMD that adhered to the chemical specifications. The PLS had to contain >25 g/l Mn for the production of $MnCO_3$, and 27–66 g/l Mn for the production of EMD (Te Riele, 1983). In addition, the PLS should adhere to the specifications in Table V.

During the addition of the base reagent, oxygen was bubbled through the solution at 60°C to oxidize iron from the Fe^{2+} to the Fe^{3+} state, thus allowing iron to precipitate as a

Figure 2—Experimental set-up for the production of EMD

Table IV

Mass balance and recovery of elements to the leach residue and PLS

Element	Slag (feed), g	Residue (g)	Leach solution (g)	% Recovery
Mn	55.4	9.344	31.7	74.1
P	0.02	-	0.115	>100
Si	40.8	13.120	0.034	32.2
Cr	-	-	0.025	>100
Ni	-	-	-	-
Cu	0.012	-	2.927	>100
Al	-	0.346	-	>100
V	-	-	-	-
Ti	0.274	0.057	-	20.8
Co	-	-	-	-
Ca	38.2	21.71	0.367	57.8
Mg	6.34	1.872	6.307	>100
Fe	1.86	0.330	1.205	82.5

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hydroxide below a pH of approximately 5.6. However, this was ineffective due to the slow kinetics of dissolution of oxygen in the leach solution, and was further hindered by the solution pH < 3 (Zhang and Cheng, 2007). The oxygen was replaced with hydrogen peroxide, which was effective in oxidizing iron to the ferric state; therefore, all test work was carried out using hydrogen peroxide as the oxidant at room temperature where applicable.

A window of optimal precipitation of the major impurities, including Fe, Al, and Si, lay in a pH range of 2.5 and 5.6–6. Complete precipitation of impurities occurred between pH 5.5–6. From the results in Table VI, both NaOH and NH_3 were effective reagents in removing impurities from solution. However, NH_3 appeared to be the more effective, resulting in a purified PLS with Fe, Al, and Si contents of less than 1 ppm, in contrast to NaOH where the solution

contained 604 ppm Fe, 8 ppm Si, and 140 ppm Al after precipitation.

Manganese products

Precipitation of manganese carbonate

Manganese precipitated from the purified PLS at pH >6, and manganese recovery reached 99.8% and 98.9% using $(NH_4)_2CO_3$ and Na_2CO_3, respectively, at a pH >8.5. The results of the ICP-OES analyses before and after carbonate precipitation are given in Table VII. The results agreed with those obtained by Zhang *et al.* (2010), who achieved a manganese recovery of >99.5% pH >8.5.

The results in Table VIII indicate that using either $(NH_4)_2CO_3$ or Na_2CO_3 as the precipitating reagent resulted in a $MnCO_3$ product that meets the quality specifications, with the exception of the calcium content, which exceeded the maximum allowable amount. This finding is in agreement with Zhang *et al.* (2010), who argued that carbonate precipitation is more selective for magnesium than calcium, due to the thermodynamics favouring the co-precipitation of calcium, which is attributed to the low log $K_{(Ca/Mn)}$ value determined in comparison to the theoretical K value.

The lower $MnCO_3$ yields from Tests 1, 3, and 5 were due to the co-precipitation of additional phases such as Na_2CO_3 and $(NH_4)_2Mg(SO_4)_2.6H_2O$. These phases, however, are water-soluble; therefore the product was washed with water to yield products that contained >92% $MnCO_3$.

Table V

Standard specifications for a viable manganese PLS

Typical PLS specifications, ppm	
Ni	1
Co	0.3
Fe	15
Si	10
Cu	5
Zn	10

Table VI

Element concentrations in the PLS before and after hydroxide precipitation with NH_3 or NaOH

Species	Units	Reagent			
		NaOH		NH_3	
		PLS pH ~-0.3	PLS pH ~5.6	PLS pH ~-0.3	PLS pH ~5.6
Mn	g/L	36	19	24	15
Cr	ppm	40	<1	20	<1
Fe	ppm	1568	17.8	842	<1
K	ppm	117	4	240	262
Mg	g/L	7	3	4	2
Al	ppm	-	56	2038	<1
Al	g/L	3	-	-	-
Na	ppm	366	-	115	86
Na	g/L	-	56	-	-
Ni	ppm	21	7	11	5
Si	ppm	157	<1	<1	<1
Zn	ppm	11.3	<1	9	<1

Table VII

Chemical composition of the PLS before and after carbonate precipitation

Species	Unit	Reagent			
		Na_2CO_3		$(NH_4)_2CO_3$	
		PLS pH ~5.6	PLS pH ~8.5	PLS pH ~5.6	PLS pH ~8.5
Mn	g/L	18.65	-	14.76	-
Mn	ppm	-	650.3	-	4.8
Ca	ppm	209.1	10.8	181.6	14.1
Fe	ppm	17.8	9.4	<1	<1
Mg	ppm	3437.50	643	2321.69	1608.70

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Chemical composition of the MnCO₃ produced and the standard specifications (www.alibaba, 2013)

Parameter	Standard specification (%)	Test 1 (%)	Test 2 (%)	Test 3 (%)	Test 4 (%)	Test 5 (%)
MnCO₃	>92	56.48	98.7	94.15	98.1	79.54
Mn	>43	44	43.5	42.6	43	44
Iron as Fe	0.08% max.	0.31	<0.01	1.02	0.93	0.02
Nitric acid-insoluble	0.1% max.	-	-	-	-	-
Chloride as Cl	0.1% max.	-	-	-	-	-
Ca	0.1% max.	1.02	1.27	2.34	1.86	1.91
Sulphate as SO₄	1% max.	-	-	-	-	-

A disadvantage of using Na_2CO_3 as a base reagent in this system was that between pH 7.3–7.5 buffering appeared to have occurred, due to the buffering action of the bicarbonate that formed from the dissociation of carbonic acid. To overcome this, a stoichiometric amount of NaOH was added to increase the pH to approximately 8.5.

After the addition of the NaOH the pH was raised to >8.5, resulting in 98.9% Mn recovery, in comparison to 96% Mn recovery at pH 7.5.

Furnace feed material

The production of the $MnCO_3$ furnace feed material involved the precipitation of impurities followed by the precipitation of manganese as $MnCO_3$, without a filtration step.

As in the production of pure $MnCO_3$, the manganese recovery reached >99% using $(NH_4)_2CO_3$ or Na_2CO_3 as the base reagent at pH >8.5. The XRD and XRF results are given in Tables IX and X.

These results suggest that using NaOH and Na_2CO_3 or NH_3 and $(NH_4)_2CO_3$ resulted in a product that can potentially be fed into a furnace (>35% Mn), as shown in Tests 1 and 3 in Table X. The $MnCO_3$ furnace feed produced by the NaOH and Na_2CO_3 precipitation method contained appreciable amounts of sodium (approx. 13 %), which would be detrimental to furnace operations because of the build-up of alkali metals in the furnace, which may lead to explosions and refractory attack. With the use of NH_3 and $(NH_4)_2CO_3$, approximately 45% of the product contained ammonium phases, which would pose a problem to furnace operations owing to the dissociation of the ammonium phases to NH_3 and the further dissociation of ammonia to H_2 and N_2 at temperatures above 400°C.

The ammonium and sodium phases are water-soluble; to rid the material of these phases a water wash step was employed in order to render the product viable as a furnace feed.

Economic analysis

To determine the net present values (NPVs), it was decided to utilize past and present production and plant history of the supplier of the slag. In addition, the capex and opex values were calculated based on 2013 expenditures. The NPVs for the products investigated were negative, due to the high acid content of the PLS, which required a large base reagent input to neutralize the solution which in turn increased the operating costs.

Optimization study

An optimization study was undertaken with the primary objective of decreasing the base reagent addition required to neutralize the PLS by investigating the ideal acid amount to be used. The benefits of this included a reduced acid and base reagent consumption, which resulted in a reduction in

XRD results for the MnCO₃ furnace feed material produced via NaOH and Na₂CO₃, or NH₃ and (NH₄)₂CO₃ precipitation

Test	Reagent	Phase	Mass %
1	NaOH and Na₂CO₃	MnCO₃	n.d.
		Na₂SO₄	n.d.
		(Ca,Mn)(Ca,Mn,Fe,Mg)(CO₃)₂	n.d.
2	NaOH and Na₂CO₃	MnCO₃	60.26
		Na₂SO₄	39.74
3	NH₃ and (NH₄)₂CO₃	MnCO₃	56.48
		(NH₄)₂Mg(H₂O)₆(SO₄)₂	35.88
		NH₄SO₄	7.64

n.d. A quantitative analysis could not be carried out

Standard specifications (Gous, 2013) and results of tests carried out to produce MnCO₃ furnace feed

		Precipitation method		
		NaOH and Na₂CO₃		NH₃ and (NH₄)₂CO₃
Parameter	Specification (%)	Test 1 (%)	Test 2 (%)	Test 3 (%)
MnCO₃	-	-	60.26	56.48
Mn	>35	44	27.7	36.2
Fe	-	0.31	1.22	0.9
Na	<0.8	#	12.9	*
K	<0.9	*	*	*
Zn	<0.07	Trace amounts	Trace amounts	Trace amounts

Not analysed for   * Element not contained in product

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operating costs, thereby resulting in a positive net profit value and rendering the production processes economically viable. In addition, the technical viability was improved as the amounts of impurities in the leach solution were reduced, as most were precipitated and reported to the residue. This was beneficial for the production of the impure $MnCO_3$ furnace feed material, which had a higher manganese content and lower impurities, thereby yielding a product with a high Mn:Fe mass ratio, which was ideal. In addition, due to the reduction in base reagent consumption, dilution of the PLS was reduced and a high manganese concentration was maintained. This was beneficial for the electrowinning of EMD, since high manganese concentrations (>27 g/l) were required. The results of the study are summarized in Figures 3 and 4.

From the results the ideal acid addition to produce a PLS with high manganese and low impurities content appears to be 40 ml; pH at this amount is approximately 4.3 and an appreciable amount of impurities had precipitated out, as is evident in Figure 4. The concentrations of Al, Fe, and Si obtained were 5 ppm, 684 ppm, and 39 ppm respectively, in contrast to an acid addition of 100 ml, which resulted in Al, Fe, and Si concentrations of 4 g/l, 1.6 g/l, and 157 ppm. This reduced the Al, Fe, and Si contents of the PLS by 99.88%, 42.8% and 75%, respectively, compared with the original water-starved digestion acid amount of 100 ml. The manganese concentrations at 40 ml acid addition were > 29 g/l, which rendered the leach solution amenable to the production of quality manganese products and was suited for the electrowinning of EMD.

The manganese concentration appeared to decrease with acid additions of less than 50 ml. This was attributed to incomplete reaction of the slag, as less than 50 ml is below the stoichiometric amount, and thus the silicate matrices could not be completely destroyed. The slight decrease in manganese concentration between 40–60 ml acid was probably due to material variance; this is further substantiated by the results given in Table XI, which clearly illustrate the difference between the tests conducted with 50 ml acid under identical conditions and with the same slag sample. The manganese concentrations obtained in test 1 and test 2 differed by 6 g/l, and variances existed between the major impurity elements also.

A countercurrent three-stage water wash was employed on the material produced after the slag material was digested using a 40 ml acid addition. It was vital that the manganese content of the residue was brought below 1% for it to be a viable cement additive. Figure 7 illustrates the extent to which manganese was leached from the material using 40 ml of acid.

From the results in Figure 5 it is evident that the three-stage water wash was able to reduce the manganese content of the residue to approximately 2.7 %, which did not meet the specification of < 1% manganese, thus a 40 ml acid addition was not ideal. A further study was therefore carried out to determine the optimum acid addition required to render the residue suitable for a quality cement additive containing < 1% Mn.

From the results in Figure 6 it appears that an acid addition of 50—55 ml would be ideal, and would yield a manganese content of less than 1% in the residue while still producing a pregnant leach solution of pH 3.5–4 (Figure 3), from which products with a high manganese content can be produced.
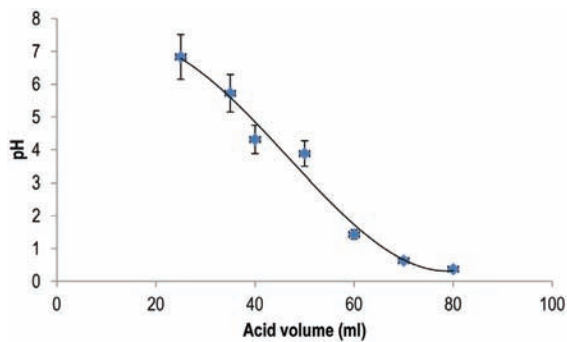

Figure 3—pH of the pregnant leach solution as a function of acid addition

Figure 4—Effect of acid addition on the concentrations of Mn, Mg, Al, Fe, and Si in the PLS

Table XI

Example of elemental variance in the PLS at 50 ml acid volume in the water-starved digestion

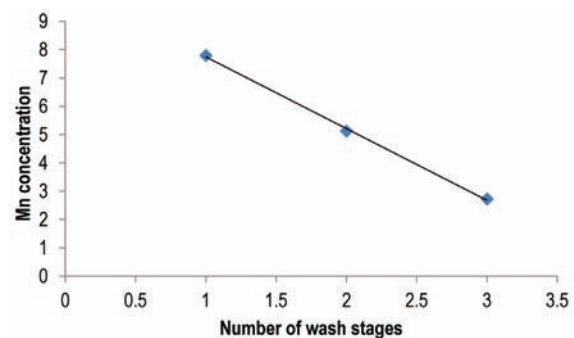| Acid volume 50ml		
Element	Test 1	Test 2
Mn	30 g/L	36 g/L
Al	313 ppm	359 ppm
Fe	917 ppm	883 ppm
Mg	6 g/L	7 g/L

Figure 5—Manganese concentration as a function of the number of water wash stages carried out on the cake produced with 40 ml acid in the water-starved digestion

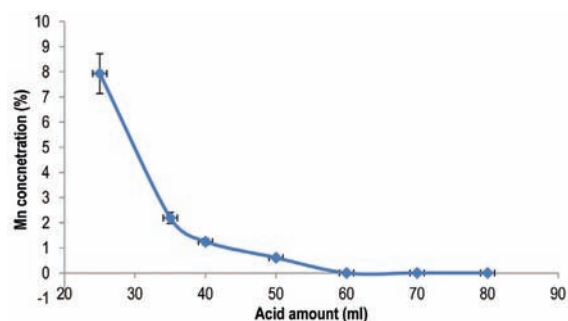# The recovery of manganese products from ferromanganese slag

Figure 6—Manganese content in the leach cake as a function of acid amount employed in the water-starved digestion

Production of a furnace feed material

The pH of the PLS utilized to produce the impure manganese carbonate furnace feed product was approximately 4.3. The manganese and impurities contents are given in Table XII.

Since reducing the acid amount from 100 ml to 40 ml resulted in an increase in pH to 4.3, it was decided to add Na_2CO_3 or $(NH_4)_2CO_3$ to increase the pH to >8 in order to precipitate manganese as $MnCO_3$. However, phases such as $(NH_4)_2Mg(SO_4)_2.6H_2O$ and Na_2SO_4 co-precipitated and contaminated the product, rendering it unsuitable as a furnace feed. The product was therefore subjected to a washing step with distilled water, as these phases are water-soluble, in an attempt to produce a viable furnace feed. A pure manganese carbonate (>92%) resulted; the XRF analysis is given in Table XIII. The resulting manganese carbonate precipitates yielded >95% $MnCO_3$, with >45% Mn content, and contained less than 9% impurities, of which iron constituted 1–1.2%. Manganese and iron co-precipitated at a pH of approximately 7 when iron was not oxidized and carbonate was added to the PLS (Pakarinen, 2011). As shown by Figure 7, the formation of $FeCO_3$ is impossible due to the high redox potential; however, iron will most likely precipitate as ferric oxohydroxide ($FeO(OH)$).

It is evident from the results that the composition of the furnace feed material was improved by increasing the pH. Furthermore, the water-soluble phases were effectively removed by washing with water. It can be concluded that the process conditions resulted in a technically viable product.

The XRF analyses in Table XIII indicate that a product with high manganese content and high Mn:Fe ratio of approximately 48:1 was obtained, which acceptable as an additive in ferromanganese production.

Economic outcome

To render the production of the various manganese products viable, changes were made to the water starved digestion process after an optimization study had been undertaken to determine the ideal acid amount that would be required to decrease the base consumption. It was determined that an acid amount of 50 ml would be ideal to achieve this. The economic outcome of this alteration is that it rendered the NPVs of the various manganese products positive.

In addition, the change to acid amount yielded an impure $MnCO_3$ furnace feed material with a manganese content of > 45%, which was higher than the ideal manganese content

Table XII

Chemical composition of the PLS using 40 ml acid addition in the water-starved digestion

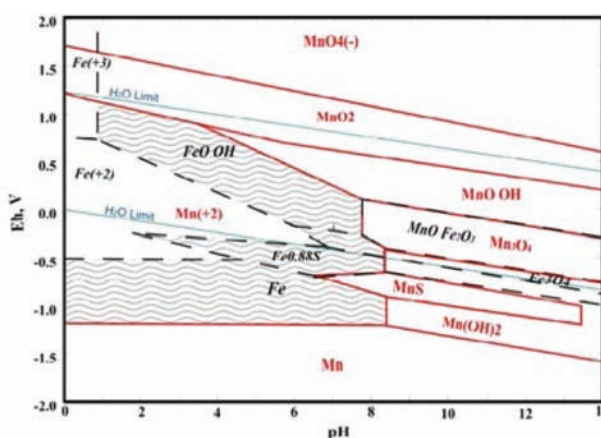| Major element analysis on PLS – 40 ml acid volume		
Element	Unit	Concentration
Mn	g/l	29.85
Al	ppm	6
B	ppm	240
Ca	ppm	637
Cr	ppm	<1
Fe	ppm	663
K	ppm	104
Mg	ppm	5411
Na	ppm	143
Ni	ppm	7
Si	ppm	52
Sr	ppm	9
V	ppm	<1
Zn	ppm	2

Figure 7—Eh-pH diagram for manganese and iron compounds (Pakarinen, 2011)

Table XIII

XRF analyses of impure $MnCO_3$ furnace feed produced using $(NH_4)_2CO_3$ or Na_2CO_3 as base reagents

Element (%)	Base reagent	
	$(NH_4)_2CO_3$	Na_2CO_3
Mn	48.8	47.3
P	<0.005	<0.005
Si	<0.005	<0.005
Cr	0.09	0.09
Ni	<0.005	<0.005
Cu	<0.005	<0.01
Al	<0.01	<0.01
V	<0.005	<0.005
Mo	<0.005	<0.005
Co	<0.005	<0.005
Ca	4.43	4.83
Mg	1.71	3.72
Fe	1.13	1.07

of between 35–40%, which is sought after by the ferroalloy industry. The benefits of the feed material produced via the hydrometallurgical route include a high quality feed material which will result in an increase in the production of ferromanganese metal per day as the recoveries of manganese will be increased, and thereby industry will have the option of purchasing lower grade ore (high Fe ore) at a reduced cost (Steenkamp, 2013).

Electrowinning of EMD

We decided to electrowin electrolytic manganese dioxide (EMD) from the PLS by water-starved digestion of the slag with 40 ml of sulphuric acid. The cake was then water-leached with 350 ml of distilled water to ensure that the manganese concentration in the leach solution was >27 g/l, allowing it to be amenable to electrowinning of the EMD product. This method was employed due to the chemical variance of the slag sample, and to ensure that the recovery of manganese to the leach solution was >27 g/l. The concentrations of the manganese and impurity elements in the leach solution before and after purification with ammonia solution are given in Table XIV.

The mass of EMD produced over a 72 hour period was 8.3 g, thus yielding a current efficiency of approximately 74%. A current density of 100 A/m^2 should result in current efficiencies that typically lie between 90–97%, as was achieved by by Te Riele (1983). The current efficiency in this investigation, however, may have been affected by the increase in acid concentration, which promoted the formation of Mn^{3+}. This can be overcome by increasing the pH by adding a base reagent such as ammonia, in order to increase the pH to 5–6, thereby maintaining an ideal current efficiency.

The results in Table XV indicate that a product that meets specifications can be produced. The iron content was high; however, this result is not in agreement with the ICP-OES analysis of < 1 ppm Fe (Table XIV). According to Te Riele (1983) a pregnant leach solution containing < 1 ppm Fe should yield a product with only 0.021 % Fe. Furthermore, SEM-EDS analysis of the material did not detect iron.

The micrograph in Figure 8 clearly show slight pitting of the surface of the EMD.

Figure 9 is considered to show the typical morphology of EMD. The morphology appears to be similar to that obtained by Liu *et al.* (2007). Thus, good quality EMD can be produced from the leaching of ferromanganese slag.

Conclusions and recommendations

The manganese content of the slag (>30%) rendered the material attractive for further processing. A pregnant leach solution with typical manganese concentration of 25–35 g/l and low impurities content was obtained. Impurities were effectively removed using ammonia or sodium hydroxide. Ammonia was the most effective reagent, removing Fe, Si, and Al to levels of <1 ppm.

Figure 8—SEM micrographs of the surface of the EMD deposit at 500 μm and 250 μm resolution

Table XIV

Chemical composition of the PLS used for electrowinning of EMD before and after purification with NH₃

Species	Unit	Before purification pH ~ 4.5	After purification pH ~5.6
Mn	g/L	30.8	30.8
Cr	ppm	1	< 1
Fe	ppm	674	< 1
K	ppm	162	234
Mg	g/L	5.6	5.1
Al	ppm	81	< 1
Na	ppm	181	237
Ni	ppm	6	6
Si	ppm	79	22
Zn	ppm	2	< 1

Figure 9—SEM micrograph of the surface of the EMD deposit at 2.5 μm resolution

Table XV

Analysis of the EMD product

Parameter	Battery-active EMD specifications	Results
MnO₂	91%	> 95%
Mn	>59%	68%
Fe	<10 ppm	700 ppm
Al	<100 ppm	5 ppm
Cu	<5 ppm	< 1 ppm
Pb	< 5 ppm	Trace

The recovery of manganese products from ferromanganese slag

Water-starved digestion of the slag with 100 ml sulphuric acid and purification of the resulting solution led to a manganese recovery of >99.7% into a manganese carbonate product at a pH >8.5. However, co-precipitation of calcium carbonate resulted in the product exceeding the maximum specified calcium content. Further investigations will be aimed at investigating the kinetics of co-precipitation in order to decrease the amount of calcium carbonate precipitated.

A viable MnCO3 furnace feed material with a high manganese (> 45% Mn) and low iron content (< 2% Fe) was produced from the pregnant leach solution utilizing NH_3 and $(NH_4)_2CO_3$ or NaOH and Na_2CO_3 to increase the pH to >8.5. Water-soluble phases containing ammonia and sodium that formed could be detrimental to furnace operations. To rid the feed material of these phases and to yield a quality product the material was washed with water, which yielded a product containing >95% $MnCO_3$.

Although the processes were shown to be technically feasible, the large amounts of the base reagent required to adjust the pH of the pregnant leach solution from less than 0 to 5.6 when 100 ml of sulphuric acid was utilized in the digestion stage resulted in an increase in operating costs, rendering the production of the manganese products unviable. Therefore, to improve economic viability a study was undertaken to optimize the quality of the PLS, and to produce a leach residue (cement additive) that contained < 1% Mn. It was found that decreasing the sulphuric acid addition to approximately 50 ml resulted in an increase of the pH of the PLS to approximately 3.4–4, and within this pH range most of the major impurity elements precipitated out and reported to the residue. This adjustment resulted in the production of a $MnCO_3$ furnace feed material with a manganese content >45% and a high Mn: Fe ratio.

In addition, to produce pure manganese carbonate, a smaller amount of neutralizing reagent would be required to adjust the pH to 5.6 when utilizing an acid addition of 50 ml. This adjustment rendered the process economically viable. Additional benefits of using 50 ml of acid in the digestion stage include a significant reduction in the dilution of the pregnant leach solution with large amounts of base reagent, thereby maintaining a high manganese concentration in the leach solution, and eliminating potential gelling problems.

The use of a hydrometallurgical process to recover manganese products and produce a leach residue that is saleable as a cement additive is beneficial to the environment and surrounding communities in ferromanganese-producing areas. Both slag dumps and current arisings can be utilized, thereby reducing the environmental and health risks posed by the leaching of mobile manganese contained in the slag. In addition, all potential waste streams produced during the hydrometallurgical process, such as the barren solution, can potentially be recycled to produce additional marketable by-products, including ammonium sulphate or sodium sulphate. However, further investigations would have to be carried out to confirm this.

References

ALIBABA GROUP. 2013. Manganese product specifications and price. http://sjzbcchem.en.alibaba.com/product/517509869-213404979/sell_manganese_carbonate_MnCO3.html [Accessed 15 August 2013].

GROOT, D., KAZADI, D., POLLMANN, H., DE VILLIERS, J., REDTMANN, T., and STEENKAMP, J. 2013. Utilization of ferromanganese slags for manganese extraction and as a cement additive. *Advances in Cement and Concrete Technology in Afric*a, Emperor's Palace, Johannesburg, 28– 30 January 2013. pp. 984–985.

GOUS, J. 2013. Transalloys. Personal Communication.

ILLIS, A. and BRANDT, B.J. 1975. Selective process for the recovery of metal values from sea nodules. CA Patent no. 974371.

KONO, Y., MIZOTA, T., and FUJII, Y. 1986. A precipitation separation method for copper, nickel, and cobalt recovery from sulfurous acid leach liquor of sea manganese nodules. *Nippon Kogyo Kaishi*, vol. 102, no. 1183. pp. 585–590.

LIU, B., THOMAS, P.S., RAY, A.S., DONNE, S.W., and WILLIAMS, R.P. 2007. DSC characterisation of chemically induced electrolytic manganese dioxide. *Journal of Thermal Analysis and Calorimetry*, vol. 88. pp. 177–180.

MCINTOSH, S.N. and BAGLIN, E.C. 1992. Recovery of manganese from steel plant slag by carbamate leaching. *Report of investigations*, US Department of the Interior, Bureau of Mines.

NAGANOOR, P.C., PRASANN, A.S.R., SHIVAPRASAD, K.H., and BHAT, K.L. 2000. Extraction of manganese from ferro-manganese slag. *International Symposium on Processing of Fines*, Jamshedpur, India, 2–3 November 2000. National Metallurgical Laboratory, Jamshedpur. pp. 300–306.

PAKARINEN, J. 2011. Recovery and refining of manganese as by-product from hydrometallurgical processes. Colloqium, Lappeenranta University of Technology, Finland. p. 29.

PARKER, J. and LOVEDAY, G. 2006. Recovery of metal from slag in the ferro-alloy industry. Hidden Wealth. *Southern African Institute of Mining and Metallugy*, Johannesburg. pp. 7-15.

RETHINARAJ, J.P. and VISVANATHAN, S. 1993. Preparation and properties of electrolytic manganese dioxide. *Journal of Power Sources*, vol. 42. pp 335–343.

STEENKAMP, J. 2013. Department of Materials Science and Metallurgical Engineering, University of Pretoria. Personal Communication.

STEENKAMP, R. 2013. Exxaro. Personal Communication

TE RIELE, W.A.M. 1983. Electrowinning of manganese dioxide. SAIMM Vacation School Electrometallurgy, Randburg. *South African Institute of Mining and Metallurgy*, Johannesburg. pp. 238-261.

WELLBELOVED, D.B, CRAVEN, P.M., and WAUDBY, J.W. 2003. Ullmann's Encyclopedia of Industrial Chemistry. Wiley and Sons, New York. Chapter 6.

ZHANG, W. and CHENG, C. 2007. Manganese metallurgy review Part II: Manganese separation and recovery from solution. *Hydrometallurgy*, vol. 89, no. 3-4. pp 160–170.

ZHANG, W., CHENG, C., and PRANOLO, Y. 2010. Investigation of methods for removal and recovery of manganese in hydrometallurgical processes. *Hydrometallurgy*, vol. 101, no. 1–2. pp 58–63. ◆