

1-1-2007

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### Recommended Citation

Shen, Ruihua; Zhang, Guangqing; Dell'Amico, Mark; Brown, Peter; and Ostrovski, Oleg: A feasibility study of recycling of manganese furnace dust 2007, 507-519.

<https://ro.uow.edu.au/engpapers/4471>



## A FEASIBILITY STUDY OF RECYCLING OF MANGANESE FURNACE DUST

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### ABSTRACT

*This paper presents results of a feasibility study of recycling manganese furnace dust generated in production of ferromanganese and silicomanganese at Tasmanian Electrometallurgical Company, Australia. Dried manganese furnace dust contains about 20 wt% of carbon, in average 33.4 wt% of manganese and 1.3 wt% of zinc. Manganese in the dust is in the form of MnO, Mn<sub>3</sub>O<sub>4</sub> and MnCO<sub>3</sub>; zinc is mainly in the form of ZnO and ZnSO<sub>4</sub>. Analysis of the zinc balance with dust recycling showed that to keep zinc intake at the acceptable level, it should be partly removed from the dust. In the reduction laboratory experiments, zinc oxide was reduced to zinc vapour by tar of the dust. Reduction of zinc oxide started at 800°C and zinc removal rate increased with increasing temperature; removal of zinc was close to completion at 1100°C. Optimal conditions for removing zinc from the dust include temperature in the range 1000-1150°C, inert gas atmosphere and furnace dust fraction in the furnace dust-manganese ore mixture above 60%. In the sintering of manganese ore with addition of manganese dust in the sintering pot, zinc was reoxidised and deposited in the sinter bed. Removal of zinc in the sintering pot tests was in the range 4-17%. Up to 30% zinc removal was achieved from the bottom layer of the sinter bed. It can be concluded that zinc removal will be low during the processing of manganese furnace dust in the sinter plant. The zinc removal rate will be the highest when pelletised manganese furnace dust is added to the bottom layer of the sintering bed.*

### 1. INTRODUCTION

The Tasmanian Electro Metallurgical Company Pty Ltd (TEMCO) annually produces about 250,000 tonnes of ferromanganese and silicomanganese in four electric ferroalloy furnaces. Three of them are sealed and one is semi-sealed. In the sealed furnaces, dust and volatiles are cleaned from off-gas by two stage venturi scrubbers, forming thick, high-solid aqueous slurries (about 15,500 tonnes per year), which are deposited in settling ponds. In the semi-sealed furnace, the off gas burns at the top of the furnace. The dust in the gas is then collected by fibreglass filtration bags and stockpiled. A sinter plant capable of over 300,000 tonnes per year converts fine manganese ores into sinter to make up part of the feed for the furnaces<sup>[1]</sup>.

Storage of manganese furnace dust presents a long-term environmental concern, which has stimulated a search for technologies to allow its recycling. The furnace dust contains a high concentration of manganese oxide, which is suitable as feed in the production of manganese alloys.

A few examples of manganese furnace dust utilisation have been reported in literature<sup>[2-5]</sup>. An apparently attractive way of recycling of manganese furnace dust is its processing in the sinter plant as an additive to the sinter feed. However, there is little understanding of the behaviour of the zinc, whose content in the furnace dust achieves 1.5 wt%, and other volatile materials, which may cause instability in operation of the smelting furnaces.

Majercak *et al.*<sup>[6]</sup> examined sintering of mixtures containing flue dust from the production of high carbon ferromanganese. They achieved a manganese yield of 67-75% and acceptable mechanical strength of the sinter. Chaichenko *et al.*<sup>[7]</sup> reported that addition of 4-6% dry furnace dust or flue dust improved sinter quality

and sinter plant productivity. Krivenko *et al.*<sup>[8]</sup> sintered the agglomerated mixture of slime, dust and crushed ferromanganese alloy. Removal of zinc was studied by Hjortland and Olsen<sup>[9]</sup>. The manganese furnace dust was first micropelletised with addition of calcium dichloride, and then mixed with coke and sintered. They reported more than 20% zinc removal. However, no detail and systematic study of behaviour of tar and zinc in the sintering process has been reported in literature.

This paper presents results of a feasibility study of recycling manganese furnace dust generated in the production of ferromanganese and silicomanganese at TEMCO, Australia. It includes characterisation of the dust, analysis of the zinc balance in current smelting operations, reduction of zinc oxide and zinc behaviour in the sintering process.

## 2. EXPERIMENTAL

### 2.1 Materials

Manganese furnace dust in the settling ponds has been accumulated for many years from ferromanganese and silicomanganese production at TEMCO. Samples from different locations and depths of a pond were taken for characterisation. The sample used for sintering and zinc reduction examinations was taken from the middle of the pond, 30-60 cm in depth. Samples of raw materials, dusts and products of sinter plant and manganese alloy production were taken from the process itself.

### 2.2 Reduction of Zinc Oxide in Manganese Dust Pellets

The furnace dust was dried in an oven at 105°C for several hours, milled to break lumpy particles and pressed to form pellets of 15 mm in diameter. The typical press load was 20 kN. For examination of the effect of addition of fine manganese ore to furnace dust on zinc removal, the ore was dried, crushed and sieved. Pellets were formed from manganese ore, with size in the range of +45-180 micron, and mixed with dried and milled manganese furnace dust in different proportions. Zinc oxide reduction was examined by sintering of manganese furnace dust in a vertical tube furnace, a muffle furnace and a thermogravimetric furnace (TGA) under different conditions.

### 2.3 Sintering Pot Testing

The as received slurry of manganese furnace dust was too wet for effective granulation. It was homogenised and dried to a water content of between 5% and 34%, and then mixed and granulated with fine manganese ore and coke (from TEMCO) into a mixture representative of the sinter strand mixture. Sinter mixture contained 9-10% moisture. Fine, Laboratory Reagent (LR) grade ZnO was added into the mixture in some experiments to examine behaviour of zinc in the sintering tests. The same amount of fine manganese ore was replaced by added ZnO.

The pot tests were carried out in a sintering rig consisted of a sintering pot, a liquefied petroleum gas (LPG) burner for ignition, an air suction fan and an air flow valve to control the pressure drop over the pot. Thermocouples were installed to monitor ignition temperature and sinter bed exit gas temperature. Suction pressure was monitored by a manometer connected to the pot base. Two sintering pots were used: pot "A" of 150 mm diameter x 300 mm depth, and pot "B" of 100 mm diameter x 500 mm depth. The mixture in the pot was separated into equal sections of 100 mm thickness using Inconel grates.

Sintering experiments started with ignition of the coke in granules at the top of the sinter bed by the LPG burner, which then propagated the combustion front down to the pot bottom. The ignition time was about 90 seconds. Sintering was considered complete when the bottom thermocouple detected a peak temperature, indicating completion of combustion of coke in the sintering bed. Tests were run with durations of 50%, 75% and 100% of the complete sintering time. Sintering was terminated by stopping the suction fan, blowing nitrogen through the pot, and chilling the sinter by spraying cold water onto the pot wall. Sinter from different sections of the bed was collected, weighed, and sampled for analyses.

## 2.4 Sample Analyses

Water content in the slurry of manganese furnace dust was analysed by oven drying at 105-110°C and distillation method (following ASTM standard D95). Carbon content in dried manganese furnace dust was measured by LECO carbon and sulphur analyser. The contents of zinc, manganese and other metals in dried manganese furnace dust, fine manganese ore, other raw materials, sinter, alloys and slags were analysed by X-Ray Fluorescence (XRF). The zinc contents in the sintered laboratory samples were analysed by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). X-Ray Diffraction (XRD) was used for phase identification. A Hitachi S4500II field emission scanning electron microscope (SEM) was used to observe the morphology of ZnO crystals and to determine its main composition by Energy Dispersive Spectroscopy (EDS). Chemical states of zinc in the furnace dust were detected by X-ray Photoelectron Spectroscopy (XPS).

## 3. EXPERIMENTAL RESULTS

### 3.1 Characterisation of Manganese Furnace Dust

#### 3.1.1 Chemical analysis

Chemical compositions of samples of manganese furnace dust taken from different locations in the settling pond are presented in Table 1.

The manganese furnace dust taken in the Northwest part of the settling pond is significantly different from other samples because of addition of lime into this zone. Samples marked as Northwest C are not typical and were excluded from further analysis.

The water content of samples taken from the Middle and South Middle parts of the settling pond is in the range of 55-60%. The oven drying and distillation methods gave very close results, indicating that the content of low boiling point organic compounds in the furnace dust is very low. Drying of the furnace dust at 105-110°C was slow as it took about one hour to remove 50% of water and more than three hours to complete the drying.

Carbon content, measured by LECO analysis, includes carbon of tar and carbonates of different metals. Its concentration in the "Middle" and "South Middle" samples is in the range 17-22% (dry basis), average 20%. The average manganese content is 33.4%, and average zinc content is 1.3% (dry basis).

**Table 1: Chemical composition of manganese furnace dust (wt% dry basis)**

| Sample                | Moisture | Mn   | Zn   | C    |
|-----------------------|----------|------|------|------|
| Middle( 0~30cm)       | 58.2     | 32.9 | 1.43 | 18.6 |
| Middle(30~60cm)       | 59.1     | 32.8 | 1.52 | 19.5 |
| Middle(60~90cm)       | 58.0     | 33.4 | 1.38 | 21.1 |
| South Middle( 0~30cm) | 58.3     | 34.7 | 1.06 | 17.5 |
| South Middle(30~60cm) | 55.6     | 29.9 | 1.50 | 21.8 |
| South Middle(60~90cm) | 55.3     | 32.9 | 0.87 | 19.0 |
| Northwest C( 0~30cm)  | 30.8     | 17.0 | 0.07 | 10.7 |
| Northwest C(30~60cm)  | 37.5     | 21.2 | 0.44 | 16.1 |
| Northwest C(60~90cm)  | 41.9     | 20.7 | 0.34 | 8.5  |

#### 3.1.2 Phase and microanalysis

No zinc containing phases were detected by XRD in the manganese furnace dust samples, due to their low contents. The major phases in the Middle sample were identified as rhodochrosite ( $\text{MnCO}_3$ ), manganosite

(MnO) and hausmannite ( $Mn_3O_4$ ). Phases in samples from the North consist of quartz ( $SiO_2$ ), manganocalcite ( $(Ca,Mn)CO_3$ ) and hausmannite ( $Mn_3O_4$ ).

XPS analysis showed that zinc is present in the furnace dust as  $ZnSO_4$  and  $ZnO$ , with a molar ratio of 1:2 between these compounds.

### 3.2 Zinc Balances

A zinc balance was estimated from operational data and analysis of raw materials and products of sinter plant and ferroalloy furnaces. The results are presented in Figure 1, in the form of schematic flow of zinc. The “raw materials” labelled in the figure exclude sinter and slag if they are charged into a furnace as they are presented as separate streams.

In current operation of the sinter plant, the dust collected from different locations in the exhaust gas ducts, and from the electrostatic precipitator is recycled back to sinter raw materials. In the sinter plant, 90.4% of zinc remains in the sinter; the rest is possibly lost with the dust passing out of the electrostatic precipitator.

For all four furnaces, the zinc content in alloys and slag is low, as most of the zinc is brought out of the furnace with off-gas and subsequently goes into manganese furnace dust: 76.1 wt% of zinc input to Furnaces 1 and 2 transfers to manganese furnace dust via the off-gas. For Furnaces 3 and 5, 58.2% and 78.9% of zinc enters manganese furnace dust, respectively.

Ferromanganese Furnaces 1 and 2 operate under identical conditions with slightly different throughputs. The overall zinc level in the raw materials of these furnaces is 0.019% (coke, coal and slag forming materials were not included). For silicomanganese Furnaces 3 and 5, the overall zinc level in raw materials is 0.014% and 0.021%, respectively. There is no No. 4 furnace in operation.

The zinc balance with recycling of manganese furnace dust through the sinter plant is also estimated. The corresponding zinc flow data are presented in brackets in Fig. 1. It is assumed that 90.4% of zinc input into the sinter plant enters the sinter as in the case when the furnace dust is not recycled. It is also assumed that zinc partitioning among manganese alloy, slag and furnace dust is not affected by the furnace dust recycling.

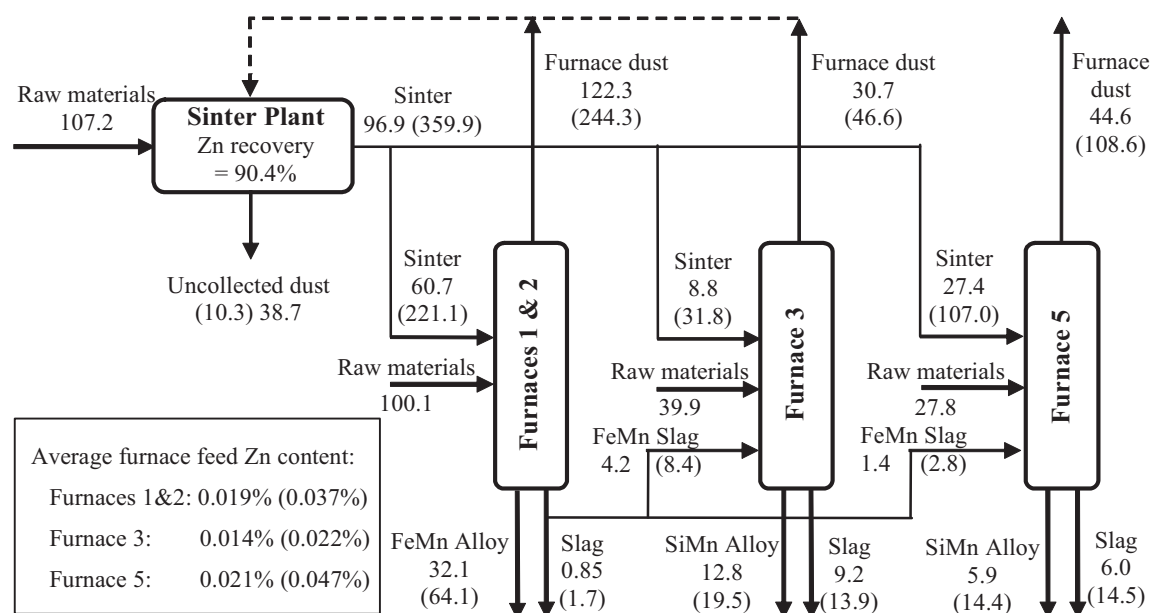


Figure 1: Schematic zinc flow (kg/day) for current smelting operation. Data in brackets are zinc flow data with recycling of the manganese furnace dust from Furnaces 1, 2 and 3

Change in the amount of sinter due to recycling of furnace dust is expected to be small compared to the total amount of sinter and is neglected. The fraction of sinter in the charge is 61.5% for Furnaces 1 and 2, 8.8% for Furnace 3, and 29.7% for Furnace 5. Manganese furnace dust from the semi-sealed Furnace 5 is not recycled.

Recycling of all manganese furnace dust formed in Furnaces 1-3 increases the zinc content in sinter by 270%. This causes a dramatic increase in the zinc level in the raw materials for ferroalloy furnaces, ie 100% increase for Furnaces 1 and 2, 51% for Furnace 3, and 143% for Furnace 5. The increase in the zinc level caused by the furnace dust recycling strongly depends on the use of sinter.

In total, 275 kg/day zinc enters the sintering-smelting processes with the raw materials of sinter plant and smelting furnaces. A total of 98 kg/day goes into ferromanganese and silicomanganese or 36% of total zinc input. The amount of zinc removed with slag will be 30.1 kg/day, or 11%. Up to 108.6 kg/day (40%) of zinc will go into the furnace dust of the semi-sealed Furnace 5, which is a major route for removal of zinc from the process. The zinc removed with uncollected dust from the sinter plant will be only 14% of the total zinc input. The zinc content in manganese alloys may also increase: from 0.007% to 0.014% for Furnaces 1 and 2, from 0.007% to 0.011% for Furnace 3, and from 0.004% to 0.010% for Furnace 5.

Currently, the dust from Furnace 5 is collected in the bag house and stockpiled. However, the zinc content in the bag house dust is low, 0.033 wt% (a significant fraction of zinc escapes the bag house with exhaust gas), and its recycling would not give a significant increase to the zinc input into the ferroalloy furnaces. It is not expected that this pattern will change with manganese dust recycling.

The zinc balance shows that recycling of the manganese furnace dust into ferroalloy furnaces will not put the zinc level in charge materials above the limit, which is estimated to be 0.05 wt%. However, changing composition of supplied raw materials, sinter and other operational factors may put the zinc content above this level. Therefore, to make manganese furnace dust recycling sustainable, part of the zinc should be removed before the furnace dust is recycled to the ferroalloy furnaces.

### 3.3 Zinc Removal from Manganese Furnace Dust

Zinc oxide in the manganese furnace dust was reduced by carbon of the tar. No additional reductant was used in the reduction experiments. Pellets of manganese furnace dust were sintered under different conditions to study the effects of temperature, gas atmosphere, pellet size, pressing load, and addition of fine manganese ore to the furnace dust, on the zinc oxide reduction.

#### 3.3.1 Effect of temperature

Effect of temperature on zinc removal from the manganese furnace dust in the vertical furnace is shown in Table 2. About 5 minutes sintering at 1050°C in air resulted in the decrease of the zinc content from 1.5 wt% to 0.072 wt%. Increasing temperature to 1100°C and 1150°C further decreased the zinc content to 0.034 and 0.029 wt%, respectively. Results of the effect of temperature on zinc removal in experiments conducted in the muffle furnace and TGA are shown in Figures 2 and 3, respectively.

**Table 2: Zinc content of manganese furnace dust sintered in vertical furnace**

| <i>Sample</i> | <i>Temperature, °C</i> | <i>Atmosphere</i> | <i>Zn, wt%</i> |
|---------------|------------------------|-------------------|----------------|
| Fume Middle   | Ambient                |                   | 1.50           |
| Pellet        | 1050                   | Air               | 0.072          |
| Pellet        | 1100                   | Air               | 0.034          |
| Pellet        | 1150                   | Air               | 0.029          |
| Pellet        | 1100                   | Argon             | 0.018          |
| Powder        | 1100                   | Air               | 0.528          |

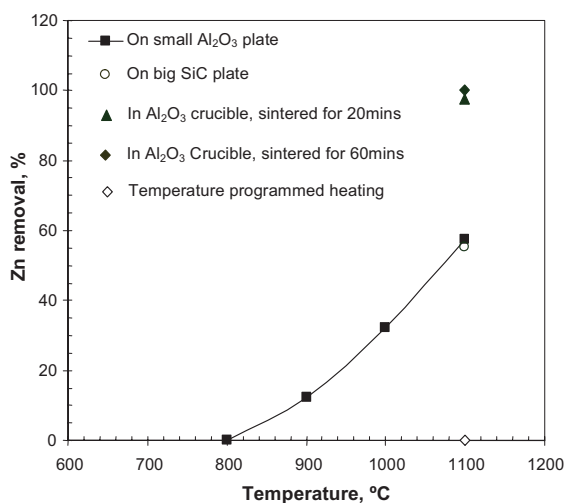


Figure 2: Effect of sintering temperature on zinc removal. The samples were sintered in the muffle furnace for 15-20 minutes

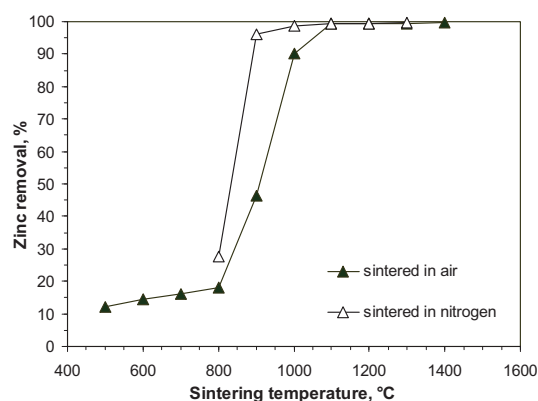


Figure 3: Effect of sintering temperature on zinc removal. Samples were sintered in the TGA furnace with 0.5 L/min air or nitrogen gas flow

In the muffle furnace, the furnace dust pellets were placed on an alumina or silicon carbide plate or in an alumina crucible for 15-20 minutes. When the sample was placed on a plate, the removal of zinc was negligible at 800°C, and became significant at higher temperatures (Fig. 2). Increasing temperature up to 1100°C resulted in about 60% zinc removal from the pellet on the alumina or silicon carbide plate. A remarkable increase in the zinc removal was observed when the sample was contained in a crucible. At 1100°C, the zinc removal achieved 97.5% after 20 minutes of sintering and was close to completion after one hour. A similar trend in zinc removal was observed in the TGA furnace, where samples were sintered at different temperatures in air and nitrogen for 10 minutes. As shown in Fig. 3, at temperatures below 800°C, the zinc removal was below 20%. This increased to 90% at 1000°C and achieved 99% at 1100°C. In the temperature interval 800-1000°C, removal of zinc from furnace dust in nitrogen was faster than in air. At temperatures below 800°C and above 1000°C, effect of furnace gas atmosphere was not significant.

### 3.3.2 Effect of gas flowrate

The effect of gas flowrate on the zinc removal rate was studied in the TGA furnace at 1000°C in air and in nitrogen with a sintering time of 10 minutes. The gas flow rate was varied from 0.5 to 1.6 L/min. For experiments in nitrogen, the zinc content in a pellet decreased with increasing flowrate, from 0.02 wt% to 0.002 wt%, although the zinc removal has been more than 99% at 0.5 L/min of nitrogen. For experiments in air, increasing air flow rate had a detrimental effect on zinc removal as it decreased from 87.4% to 73.1%.

### 3.3.3 Effect of addition of fine manganese ore

The effect of addition of fine manganese ore on the zinc removal rate was examined using the muffle furnace. Pellets with different manganese furnace dust to ore ratios were placed on an alumina plate and sintered at 1100°C for 15-20 minutes. When the furnace dust content in a pellet was lower than 60%, the zinc removal was low. There was a sharp increase in zinc removal-from 8% to 55%-with increasing furnace dust fraction from 60% to 100%. In these experiments, the removal of zinc was relatively low even for 100% of furnace dust in the pellet. These results are consistent with data presented in Fig. 2.

The effect of manganese ore fraction (in the furnace dust-ore mixture) on zinc removal was also investigated in the TGA furnace. These tests were carried out at 1300°C for 10 minutes in air and nitrogen with a gas flow rate of 0.5 L/min. Zinc removal was much higher than in experiments conducted in the muffle furnace. When the content of manganese furnace dust was 60% or higher, the zinc removal was close to completion both in



air and in nitrogen. Decreasing the dust content below 60% resulted in decrease in zinc removal rate, especially when sintered in air. At 20% dust content, the zinc removal rates were 22% and 52% in air and in nitrogen, respectively.

### 3.3.4 Effect of pellet size

The effect of pellet size on removal of zinc was studied in the TGA furnace at 1000°C in air and nitrogen with a sintering time of 10 minutes. Pellet size was varied from 5 to 15 mm. In air the zinc removal rate increased with increasing pellet size-from 62% to 87%. For experiments conducted in nitrogen, the zinc removal was close to 100% for all samples in the range 5-15 mm diameter - regardless of the size.

### 3.3.5 Effect of the press load

The effect of the pellet press load (applied during preparation of furnace dust pellets) on the zinc removal, was examined in the muffle furnace at 1100°C. The press load varied from 5 to 25 kN. However, no effect on the zinc removal was observed. After 20 minutes of sintering, the zinc removal was about 57% regardless of the press load applied originally to the pellet.

## 3.4 Behaviour of Zinc in Sintering Pot Test

The mixture of fine manganese ore, manganese furnace dust, returns and coke, with addition of zinc oxide in some experiments, was charged into a sintering pot. Composition of the sintering mixtures, the sinter yield and zinc removal rates after sintering are summarised in Table 3. Sinter yield is defined here as the ratio of sinter weight to the dry weight of sintering mixture and expressed as a percentage.

For sintering of manganese ore with added manganese furnace dust in sinter pot A (150 x 300mm) in test series 1 and 2, both sinter yield and zinc removal rate consistently decreased with increasing sintering time, and the overall zinc removal rate was low, in the range of 11.5- 23% depending on the sintering time. It increased to 17-32% when 3.6% of zinc oxide was added to the sintering mixture (test series 3). Table 4 presents the change of zinc content in different sections in these tests after sintering for different time. The high level of zinc removal was observed from the bottom section in tests with 50% and 75% sintering time (data in brackets). This situation will be discussed in Section 4.

In test series 6-8, zinc oxide was added into the sinter mixture in different sections of pot A. Table 5 presents the change of zinc content in three sections after complete sintering. When part of the zinc was removed from a section other than bottom section, most of the removed zinc was captured by the section/sections beneath it, resulting in low zinc removal rate. Relatively, the zinc removal rate was higher when zinc oxide was added into the bottom section; up to 30% of the zinc was removed.

Zinc behaviour during sintering was further studied using sintering pot B (100 x 500 mm) in test series 9-12. The sinter yield followed the same trend as in pot A. However, the overall zinc removal rate in pot B increased with increasing sintering time. Table 6 presents the change of zinc content in different sections in progress of sintering. It was observed that most of the zinc removed from the upper section was captured by the lower sections. The least amount of zinc was removed when additional zinc oxide was added into the second from the top section (out of 5), while the maximum zinc removal rate, 26%, was achieved when zinc oxide was added into the bottom section. This trend was similar to results obtained in pot A.

## 4. DISCUSSION

In the reduction of zinc oxide from the manganese dust, the reductant was predominantly carbon in the tar in the manganese furnace dust. To simplify analysis, the activity of the carbon in the tar can be considered to be the same as graphite, i.e. unity. Zinc oxide and sulphate are reduced to zinc vapour by Reactions (1) and (2):

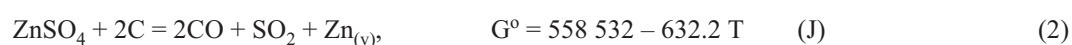
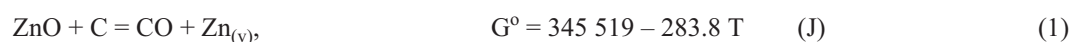




Table 3: A summary of sintering yield and zinc removal in sintering experiments under different conditions

| Series No. | Sintering mixture composition, % <sup>a)</sup> |                |              |                         | Moisture content % | Pot | Zinc content, ppm | Sinter yield, % |                   |                   | Zinc removal, %    |                   |                   |
|------------|--|----------------|--------------|-------------------------|--------------------|-----|-------------------|-----------------|-------------------|-------------------|--------------------|-------------------|-------------------|
|            | Furnace dust                                   | Fine ore       | Return fines | ZnO                     |                    |     |                   | Coke            | 50% <sup>b)</sup> | 75% <sup>b)</sup> | 100% <sup>b)</sup> | 50% <sup>b)</sup> | 75% <sup>b)</sup> |
| 1          | 11.6   | 88.4           | 12.0         | 0                       | 6.6                | A   | 662               | 79.4            | 77.9              | 73.3              | 21.8               | 16.4              | 11.5              |
| 2          | 17.5   | 82.5           | 12.0         | 0                       | 5.5                | A   | 935               | 80.3            | 78.5              | 73.6              | 23.6               | 18.9              | 14.9              |
| 3          | 11.2   | (85.2)         | 12.0         | (3.6) <sup>5</sup>      | 6.6                | A   | (27900)           | 78.3            | 76.9              | 72.1              | 32.2               | 28.5              | 16.8              |
| 4          | 9.2  | 90.8           | 12.1         | 0                       | 6.7                | A   | 670               |                 |                   | 71.8              |                    |                   | 7.2               |
| 5          | 9.2  | 90.8           | 12.1         | 0                       | 6.7                | B   | 670               |                 |                   | 73.1              |                    |                   | 3.9               |
| 6          | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>1</sup> | 6.2                | A   | 670<br>(20500)    |                 |                   | 70.2              |                    |                   | 4.4               |
| 7          | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>2</sup> | 6.2                | A   | 670<br>(20500)    |                 |                   | 72.2              |                    |                   | 1.7               |
| 8          | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>3</sup> | 6.2                | A   | 670<br>(20500)    |                 |                   | 73.0              |                    |                   | 28.4              |
| 9          | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>1</sup> | 6.0                | B   | 670<br>(20500)    | 86.9            | 76.9              | 72.6              | 0.3                | 6.0               | 7.0               |
| 10         | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>2</sup> | 6.0                | B   | 670<br>(20500)    | 86.8            | 80.1              | 74.4              | 0.0                | 0.7               | 1.0               |
| 11         | 9.2  | 90.8<br>(87.8) | 12.1         | 0<br>(3.0) <sup>4</sup> | 6.0                | B   | 670<br>(20500)    | 87.9            | 80.6              | 74.8              | 6.9                | 12.7              | 23.4              |
| 12         | 9.2  | (87.8)         | 12.1         | (3.0) <sup>5</sup>      | 6.0                | B   | (20500)           | 86.8            | 80.1              | 74.4              | 0.0                | 0.7               | 1.0               |

Note: Data in brackets show additional zinc oxide being added to: 1: section 1 (top section); 2: section 2; 3: section 3 (bottom section for pot A); 4: section 5 (bottom section for pot B); 5: all sections. a) Relative to furnace dust, fine ore and ZnO; b) Relative sintering time.

**Table 4: Change in zinc content (%) in progress of sintering in pot A**

| Relative sintering time                           | 50%     | 75%     | 100%  |
|---|---------|---------|-------|
| <i>Mixture with 11.6% dust</i>                    |         |         |       |
| Section 1   | -18.3   | -18.5   | -20.4 |
| Section 2   | -4.6    | -12.6   | -12.3 |
| Section 3   | (-42.4) | (-25.8) | -9.8  |
| <i>Mixture with 17.5% dust</i>                    |         |         |       |
| Section 1   | -5.3    | -9.1    | -12.5 |
| Section 2   | -3.6    | -7.7    | -10.8 |
| Section 3   | (-65.0) | (-39.2) | -20.0 |
| <i>Mixture with 11.2% dust and 3.6% added ZnO</i> |         |         |       |
| Section 1   | -19.5   | -21.3   | -14.1 |
| Section 2   | -13.8   | -10.0   | -15.5 |
| Section 3   | (-63.7) | (-52.8) | -21.7 |

**Table 5: Change in zinc content in g and % (in brackets) in pot A when ZnO is added into different sections**

| Section with added ZnO | Section 1 <sup>1</sup> | Section 2 <sup>2</sup> | Section 3 <sup>3</sup> | In all Sections <sup>4</sup> |
|------------------------|------------------------|------------------------|------------------------|------------------------------|
| Section 1              | -6.4 (-12.7)           | -0.09 (-5.5)           | -0.09 (-5.1)           | -12.0 (-16.7)                |
| Section 2              | 2.82 (192)             | -4.25 (-9.5)           | -0.05 (-3.4)           | -10.1 (-14.1)                |
| Section 3              | 1.24 (84.3)            | 3.53 (240)             | -13.4 (-30.0)          | -14.0 (-19.5)                |

Initial zinc content: 1: 50.2 g in section 1, 1.47 g/section in other sections; 2: 1.65 g in section 1, 44.6 g in section 2, and 1.47 g in section 3; 3: 1.77 g in section 1, 1.47 g in section 2, and 44.6 g in section 3; 4: 71.7 g/section in all sections.

**Table 6: Change in zinc content in g and % (in brackets) in progress of sintering in pot B**

| Relative sintering time                                | 50%           | 75%           | 100%          |
|--|---------------|---------------|---------------|
| <i>ZnO was added to the first section<sup>1</sup></i>  |               |               |               |
| Section 1  | -2.30 (-10.3) | -3.85 (-17.2) | -3.93 (-17.5) |
| Section 2  | 1.96 (254)    | 1.68 (218.2)  | 1.45 (188.3)  |
| Section 3  | 0.12 (15.6)   | 0.30 (39.0)   | 0.32 (41.6)   |
| Section 4  | 0.08 (10.4)   | 0.25 (32.5)   | 0.22 (28.6)   |
| Section 5  | 0.05 (6.5)    | 0.08 (10.4)   | 0.14 (18.2)   |
| <i>ZnO was added to the second section<sup>2</sup></i> |               |               |               |
| Section 1  | -0.04 (-5.2)  | -0.05 (-6.5)  | -0.06 (-7.8)  |
| Section 2  | -1.62 (-7.0)  | -1.89 (-8.1)  | -2.20 (-9.4)  |
| Section 3  | 1.27 (165)    | 1.32 (171)    | 1.54 (200)    |
| Section 4  | 0.25 (32.5)   | 0.16 (20.8)   | 0.36 (46.8)   |
| Section 5  | 0.12 (15.6)   | 0.27 (35.1)   | 0.08 (10.4)   |
| <i>ZnO was added to the fifth section<sup>3</sup></i>  |               |               |               |
| Section 1  | -0.04 (-5.2)  | -0.06         | -0.06         |
| Section 2  | -0.01 (-1.3)  | -0.01 (-1.3)  | -0.01 (-1.3)  |
| Section 3  | -0.01 (-1.3)  | -0.01 (-1.3)  | -0.01 (-1.3)  |
| Section 4  | -0.01 (-1.3)  | -0.01 (-1.3)  | -0.01 (-1.3)  |
| Section 5  | -1.78 (-7.6)  | -3.27 (-14.0) | -6.11 (-26.1) |
| <i>ZnO was added to all the sections<sup>4</sup></i>   |               |               |               |
| Section 1  | -2.27 (-9.7)  | -3.18 (-13.6) | -4.02 (-17.2) |
| Section 2  | 0.30 (1.3)    | 0.81 (3.5)    | 1.16 (5.0)    |
| Section 3  | 0.14 (0.6)    | 0.12 (0.5)    | -0.30 (-1.3)  |
| Section 4  | 0.15 (0.6)    | -1.92 (-8.2)  | -1.58 (-6.8)  |
| Section 5  | -2.81 (-12.0) | -2.25 (-9.6)  | -2.44 (-10.4) |

Initial zinc content: 1: 22.4 g in the first section, 0.77 g/section in all other sections; 2: 23.3 g in the second section, 0.77 g/section in all other sections; 3: 23.4 g in the fifth section, 0.77 g/section in all other sections; 4: 23.4 g/section in all sections.

The boiling point of zinc is 907°C. Under standard conditions, Reaction (1) is at equilibrium at 944°C, and Reaction (2) at 605°C. The zinc vapour diffuses out of the pellets and is removed from the furnace dust.

In experiments in nitrogen, the partial pressure of CO and zinc vapour in the pellet interior at the carbon-oxide reaction interface is below 1 atm, which means that zinc oxide can be reduced at temperatures below 944°C. This was confirmed experimentally and demonstrates that the experimental results are in agreement with this simple thermodynamic assessment.

When experiments were run in an oxidising atmosphere, i.e. in the muffle furnace and in a flowing air atmosphere, zinc vapour from the reduction Reactions (1) and (2) may be reoxidised. For oxidation reaction of zinc vapour in air:

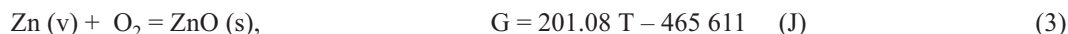


Figure 4 shows the equilibrium partial pressure of zinc vapour in gas phase at different temperatures and oxygen partial pressures.

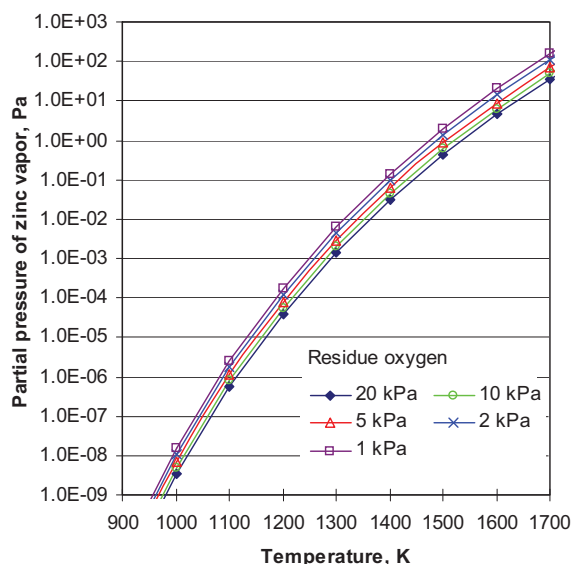


Figure 4: Equilibrium partial pressure of zinc vapour in gas phase at different temperatures



Figure 5: A piece of cold sinter prepared from fine manganese ore and manganese furnace dust

However, this reoxidation of zinc vapour occurred only on the crucible wall or contained materials rather than in the gas phase, due to constrained nucleation of zinc oxide. This observation is in agreement with literature data. In the kinetic studies of zinc vapour oxidation in CO-CO<sub>2</sub> atmosphere, Clarke and Fray<sup>[10]</sup> and Stott and Fray<sup>[11]</sup> concluded that oxidation occurred only on the reactor walls but not in gas phase. Weidenkaff *et al.*<sup>[12]</sup> observed that oxidation of zinc vapour by oxygen is heterogeneous and, in the absence of nucleation sites, zinc vapour and oxygen coexist in a metastable state. Chen *et al.*<sup>[13,14]</sup> claimed parallel processes of oxidation of zinc vapour and zinc particles or droplets in gas phase. In the experiments involving sintering pellets held in a crucible in a muffle furnace, whisker crystals were observed on the crucible walls and were subsequently proved by chemical and EDS analyses to be deposited ZnO. Similar deposition of ZnO whiskers was observed in sintering pot tests on the grates between sections.

Temperature and gas atmosphere are major factors affecting the zinc removal. In experiments in air, particularly when a furnace dust pellet was kept on a plate, zinc vapour was reoxidised to ZnO which precipitated on the pellet exterior, although in the excess of tar, conditions in the pellet interior were reducing.

As shown in Table 2, in a vertical furnace at 1100°C, after sintering in nitrogen a pellet contained 0.018% wt% Zn, while sintering in air under otherwise the same conditions, decreased the zinc content to only 0.029% wt%. Significantly higher zinc removal rate was observed in nitrogen than in air in experiments in the TGA furnace, eg 96% of zinc was removed at 900°C in nitrogen. To achieve the same removal of zinc in air, the temperature had to be 100°C higher.

Removal of zinc from a furnace dust pellet was different from dried furnace dust powder. Sintering of furnace dust powder at 1100°C in air decreased the zinc content to 0.53 wt%, while sintering of the furnace dust pellet under the same conditions resulted in the zinc decrease to 0.034 wt%. Obviously, the major difference in these experiments was sample porosity. Air could ingress into the loosely packed furnace dust powder, increasing oxygen partial pressure of gas in the sample interior and partially reoxidising the zinc vapour.

The results from experiments on manganese dust and the pellets in different experimental arrangements (as well as different temperatures and atmospheres) demonstrate the way in which zinc is easily reduced with carbon in tar, but also how quickly it can be reoxidised by oxygen. These results are highly relevant to the behaviour of zinc during sintering of sinter granules in the sinter pot or bed.

At temperatures used in this research, reduction of manganese oxides of the ore to MnO and iron oxides to metallic iron are thermodynamically feasible. However, analyses of the carbon contents of sintered samples by LECO showed that carbon loss did not increase along with increase in manganese ore content, perhaps due to relatively low reduction rate and short calcination time. Therefore, reduction of manganese ore was not significant under experimental conditions of this work.

Sintering of manganese ore in the sintering pot tests, with addition of up to 17.5% of manganese furnace dust, produced well sintered product (Figure 5). However, zinc removal from the manganese furnace dust in the sintering pot was relatively small. In these tests, overall zinc removal rate was low as reoxidation always took place in the oxidising atmosphere of the sintering process. The maximum sintering temperature may go up to 1400°C, while the residue oxygen pressure is generally higher than 5 kPa. At this temperature and oxygen partial pressure, the equilibrium zinc vapour pressure for Reaction (3) is 0.04 kPa. However, as shown in Fig. 4, the equilibrium zinc vapour pressure decreases sharply with decreasing temperature. It is in the order of  $10^{-3}$  and  $10^{-7}$  Pa at 1000°C and 800°C, respectively. This means that if equilibrium was achieved, zinc vapour produced under sintering conditions would be totally oxidized to zinc oxide.

It is hypothesised that zinc vapour formed by reduction of zinc oxide in dust diffuses to the surface of the sinter granules in the mixture, flows downward with process gas, is oxidised and then deposited on the surface of granules lower in the bed, resulting in migration of zinc to the lower layers. If oxidation does not progress fast enough, part of zinc vapour may be quenched by the cooler materials in lower layers, resulting in formation of fine zinc dust in the gas phase, which may be captured in the lower layer where the materials still contain unvapourised moisture.

The migration of zinc during sintering was demonstrated by changes in the zinc contents of the sinter sampled from different sections. As previously described, zinc oxide was added to facilitate tracking zinc transfer and to improve the accuracy of chemical analysis. In experiments in pot A (Table 5), out of 50.2 g zinc in the first section, 6.4 g was removed by sintering. However, most of the zinc from the top section was unable to escape from the sintering bed. About 40 % of zinc vapour generated in the top section was deposited in the middle section, and another 40% of the rest in the bottom section. When zinc oxide was added to the middle section, zinc removal was much less than from the top section. About 80% of zinc reduced in the middle section was captured in the bottom section beneath it. Best results on the zinc removal, up to 30%, were achieved when zinc was added to the bottom section.

In experiments in pot A, the zinc removal was higher when sintering was interrupted compared to experiments with 100% sintering time. The data presented in Table 4 show that, when the sintering was not complete (50% and 75% relative sintering time), zinc was mostly removed from the bottom section. Nonetheless, after complete sintering, the difference in zinc removal across the bed became insignificant. Relatively high rate of zinc removal from the bottom section of pot A in experiments with 50% and 75% of the sintering time can

be attributed to drying and disintegration of granules with formation of manganese dust which was blown away by the quenching inert gas.

Compared to the sintering in pot A, zinc removal in pot B was much lower, obviously due to thicker sintering bed which decreased the opportunity of zinc vapour to escape from the bed. Table 6 shows that in the section to which zinc oxide was added, the zinc content decreased by about 10-20%. However, the reduced zinc was captured in the section below. The zinc content in sections further beneath also increased, but to much lower levels. In both pots, the zinc content after sintering in the bottom section was the lowest. However, in experiments in pot B, the zinc removal increased with increasing sintering time. No evidence of granule disintegration was observed in these tests.

## 5. CONCLUSIONS

Manganese furnace dust is formed from fumes of ferroalloy furnaces. It contains 30-60% water, carbonaceous materials or tar, and metal oxides. The carbon content of the dried furnace dust is about 20% and the average manganese and zinc contents are 33.4 and 1.3%, respectively. Manganese in the furnace dust is present in the form of oxides  $MnO$  and  $Mn_3O_4$ , and carbonate  $MnCO_3$ , while zinc is in the form of oxide  $ZnO$  and sulphate  $ZnSO_4$ .

If manganese furnace dust is recycled to ferroalloy furnaces through the sinter plant, the overall zinc input will increase by 51% for silicomanganese Furnace 3, by 100% for ferromanganese Furnaces 1 and 2, and by 143% for the silicomanganese Furnace 5. Sustainable utilisation of manganese furnace dust should therefore include partial zinc removal.

Zinc oxide in manganese furnace dust was reduced to zinc vapour by tar in the furnace dust. Temperature and gas atmosphere are key factors affecting the zinc removal. Reduction of zinc oxide from furnace dust pellets started at 800°C, and the zinc removal rate increased with increasing temperature. In the TGA furnace, removal of zinc was close to completion at 1100°C. Optimal conditions for removal of zinc from the furnace dust include temperature in the range 1000-1150°C, inert gas atmosphere and furnace dust fraction in the furnace dust-manganese ore mixture above 60%.

In the sintering of manganese ore with addition of up to 17.5% manganese furnace dust in sintering pots, zinc removal was low because the zinc vapour formed by reduction of zinc oxide was reoxidised and deposited on the layers beneath. The zinc removal rate was the highest from the bottom section of the pot and lowest from the central sections. It can be concluded that zinc removal will be low during the processing of manganese furnace dust in the sinter plant. The zinc removal rate will be the highest when pelletised manganese furnace dust is added to the bottom layer of the sintering bed.

## 6. ACKNOWLEDGEMENTS

Financial supports from Tasmanian Electro Metallurgical Co Pty Ltd and GK Williams CRC for Extractive Metallurgy are acknowledged. The authors would also like to thank CSIRO Minerals for use of laboratory and support of staff.

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