RECYCLING OF FERROCHROME FURNACE BAGFILTER DUST AT SAMANCOR CHROME - A SUCCESS STORY

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ABSTRACT

The recycling of ferrochrome bagfilter dust is examined as an alternative to disposal. A brief overview is given on the history of bagfilter dust handling and force influencing current and future dust handling strategy. A rationale for the selection of the pin agglomerator is given, and after discussing the theoretical aspects of recycling, the practical experience with the pin agglomerator is related. The paper concludes by confirming the successful integral role that bagfilter dust recycling by means of the pin agglomerator has played at two sites.

1. INTRODUCTION

The management of industrial environmental requirements in South Africa, following strong on the heels of its Western European counterparts, is going through a rapid evolutionary change. Not only is this process customer driven, but the current wave of environment legislation is South Africa also requires environmental transparency and responsibility to be demonstrated.

The ferro-alloy industry is not immune to these forces. Remarkably, however, across the industry several environmentally friendly and at the same time, economically sensible developments have taken place.

1.1 Ferro-alloy production technology

The bulk of ferro-alloys (including ferrochrome, ferromanganese, silico-manganese, ferronickel, ferrosilicon and ferrovanadium) is produced in submerged arc furnaces. The process can be described as one in which ores containing the oxide of the metal is carbothermically reduced to the required metal in the presence of a suitable flux. The process consumes large quantities of electrical energy (2400 to 8000 kWh per tonne of metal) and requires cooling for components that may be exposed to temperatures as high as 1000°C. Slag is produced as a by-product, as are off-gases.

Several environmental performance-enhancing technologies have evolved in the past two decades. Of these the most notable are:

- Production of ferro-alloy in closed furnaces (ie. isolated from the atmosphere), thus allowing the carbon monoxide rich off-gas to be used for ladle preheating, or more recently for electricity co-generation[1].
- Metal recovery from slag dumps, by crushing and jigging operations, resulting in a slag by-product that may be used as a multipurpose aggregate for the construction industry[2].
- Pelletising with pre-reduction or pre-oxidation of the pellet feed increasing recovery rates from the ores by 5%-10% and a decrease in overall energy consumption.
- Recycling of furnace off-gas dust to the furnace, either directly as in the case of the cycloned coarse fraction of the dust, or via agglomeration of the fine bagfilter dusts — the topic of this paper.

2. ENVIRONMENTAL CONTROL MEASURES

2.1 Past environmental control measures

The main by-products of the ferro-alloy process are slag, thermal energy and off-gas. Off-gas is treated differently according to whether the process takes place in a semi-closed or closed furnace. Only off-gas treatment in semi-closed furnaces will be reviewed here.

The majority of furnaces of this type in the ferrochrome industry are equipped with fabric bag filtration systems (bagfilters). The bagfilter system at Ferrometals (Samancor) consists of off-gas ductings leading from each furnace to cyclones, which remove the heavier and more abrasive fraction of the furnace dust from the off-gas flow. The off-gas flow from the various furnaces then combines into one stream, passes through the main fans and is cleaned by the bagfilters. The history of disposal of waste bagfilter dust at Samancor, Ferrometals was typical of what occurred in the rest of the industry up to 1998:

2.1.1 *Dry dumping to slag dumps (1970 - 1979).* Dust was transported pneumatically (or at other plants by means of chain or scraper conveyor) to a silo from where it was loaded onto trucks and transported to a slag dump. Water sprays were used to prevent dust nuisance.

2.1.2 *Pelletising and dumping on slag dumps (1979 - 1990).* Dust was conveyed to a silo and fed, together with a suitable binder and water, into a pelletising drum. Pellets were formed and transported to the slag dump. Recycling of pellets to the furnace was not considered at Ferrometals at that time, due to lack of suitable infrastructure to feed pellets back into the furnaces. It is also during this period that recycling of the coarse and dense cyclone underflow from the off-gas system back to the furnaces commenced.

2.1.3 *Transport in water slurry to a tailings dam (1990-1998).* A more robust transport system was sought to deposit dusts directly into a tailing dam, obviating the need for storage, road transport and maintenance of the pelletiser or pneumatic system. Tailings were stored in earthen dams and the water was recycled for use in dust transportation.

2.2 Recent bagfilter dust treatment options explored

Numerous options have been investigated for treating ferrochrome bagfilter. These options have included traditional routes, such as:

- reduction of Cr^{6+} in an aqueous solution using ferrous sulphate, to form a more stable Cr^{3+} complex[3] which does not exhibit toxic characteristics;
- stabilisation of the dust with cements, sodium silicates and magnesium phosphate binders;
- containment in an H:H toxic waste dump site[4].

More innovative approaches have also been investigated to treat and possibly add value to the dusts, such as:

- formation of in situ sodium silicate to bind ore fines (and other fines) to feed to the furnace (Pat. No. 97/1986);
- use of the bagfilter dust with High Alumina Cement as a binding agent for pelletising or producing bricks from chromite fines (Pat. No. 98/0863);
- production of building products (windowsills, roof tiles) utilising newly developed cements and stabilising agents using existing precast production facilities (current investigation);
- formation of geopolymers (poly-(sialate) or poly-(sialate-siloxo)) with the dust and slag, to produce high strength (+70 MPa) and non-leaching concretes;
- and the topic of this paper : recycling of the dust, after some form of agglomeration, to the submerged-arc furnace[5].

Recycling of Bagfilter dust to the submerged-arc furnace has been implemented at 2 sites (5 furnaces) in Samancor Chrome.

3. WHY RECYCLE?

3.1 Forces influencing the decision to recycle

Several issues over the past decade have forced the industry and Samancor to reconsider the manner in which bagfilter dusts are treated and disposed of. Awareness of the danger that hexavalent chromium may pose to water quality became more prevalent after a number of studies indicated the carcinogenic nature of hexavalent chromium dusts and the susceptibility of aquatic life to Cr^{6+} poisoning [6,7]. Bagfilter dusts contain significant quantities of Cr^{6+} — ranging from 300 to 4500 ppm [4]. Unlike trivalent chromium as found in chromite ores or the metallic ferrochrome product, Cr^{6+} is highly soluble in water.

Secondly, the guideline document: "Minimum Requirements for the Handling and Disposal of Hazardous Waste" [8] was published in 1994. Specifications for construction and monitoring of tailing facilities were detailed in these documents. The ladder approach to waste management, also featured in this document, calls for waste to be preferably managed in the following order:

- Prevent: by waste avoidance and minimisation during production.
- Recycle: waste recycling, recovery, and utilisation.
- Treat: waste treatment in order to reduce toxicity and to minimise the quantities of waste.
- Dispose: waste disposal, probably by incineration, destruction or landfill.

This encourages a movement away from treatment to recycling.

Finally, focus was placed on the rendering of waste products into an economically useful form. Metal recovery from slag dumps, and subsequent secondary uses for graded slag, precludes continued disposal of bagfilter dust onto slag dumps.

Investigation into the agglomeration of bagfilter dust for recycling to the furnace started in 1992, pre-empting environmental pressures and putting Samancor in a position to implement solutions, starting in 1996 [9].

3.2 Agglomerator selection

In order to recycle dust successfully to the furnace, excessive entrainment of dust (back to the bagfilters) must be avoided. A need for dust agglomeration is imperative. Various agglomeration techniques were studied, the analysis of which may be summarised (Table 1).

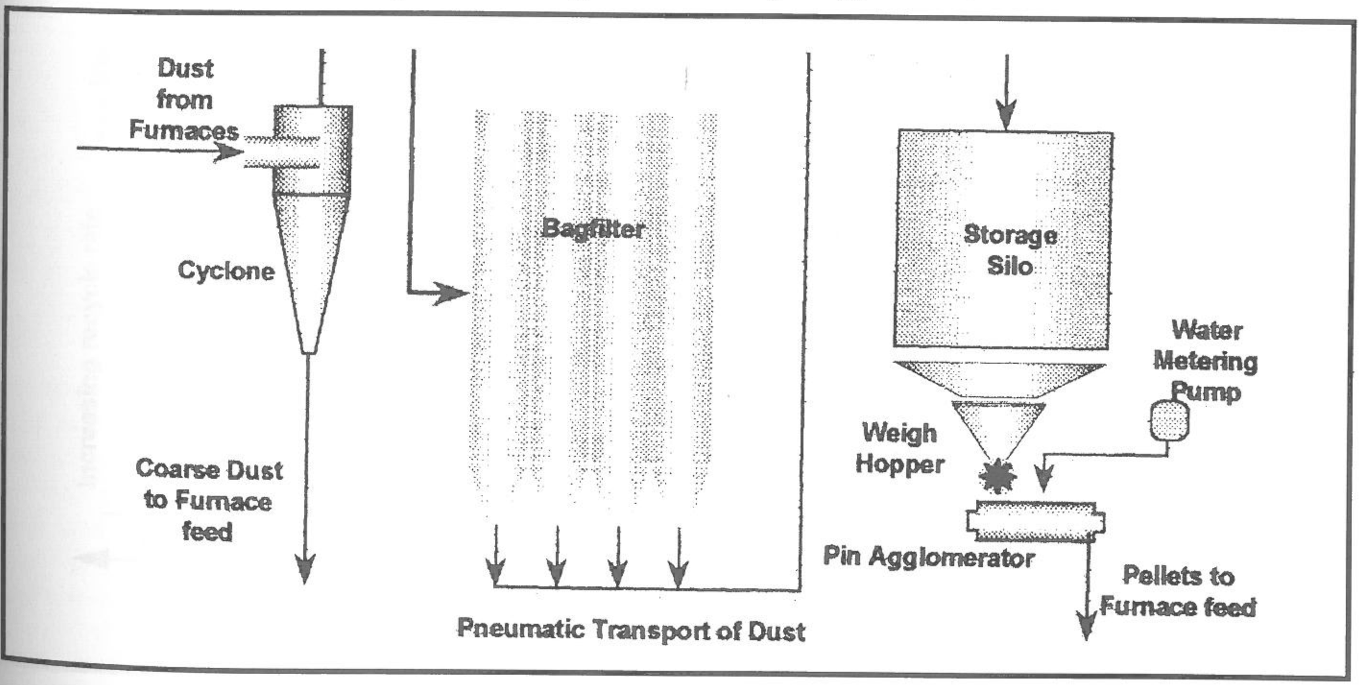
Table 1: Assessment matrix of principal decision making variables for agglomeration technology

Method of Agglomeration	Capital Expenditure Required	Operating Costs	Suitability of product furnace use	Ease of control	Secondary pollution caused
Briquetting	High	High	Excellent	Easy	Medium
Mixer Pelletiser	Medium	Medium	Medium	Difficult	High
Drum or Pan Pelletiser	Low	Low	Good	Difficult	High
Pin Agglomerator	Medium	Medium	Medium - Good	Medium	Low

From this analysis the pin agglomerator was selected for further development. The method currently used to agglomerate the dust resulted from initial work done by Chrome Alloys Research and Development at Tubatse Ferrochrome on the Turbulator (a high-intensity Pin Agglomerator) [9]. The original Turbulator was designed to produce micro-pellets (<0.5 mm) that would normally be fed to a pelletising operation as nuclei for pellet formation. The current pin agglomerator, developed by Samancor, has improved the capability of the agglomerator to produce pellets of up to 5 mm, using water only as the binder medium. Furthermore, successful engineering modifications have improved the availability of the pin agglomerator from 40% to above 98% [5].

The strength and sizing of the agglomerate is of particular importance, to withstand initial temperatures and up draught on top of the furnace burden. The pellets are required to reach sufficiently far down in the burden without any significant degradation.

Figure 1: Configuration of the pin agglomerator



4. THEORETICAL CONSIDERATIONS IN RECYCLING BAGFILTER DUST

Improvements in the availability of the pin agglomerator have promoted the recycling of the dust to the furnaces to such an extent that over the period December 1998 to June 1999, recycle rates of 98% have been achieved for extended periods.

The effect recycling has on both furnace performance and safety is not yet well understood. In recycling dust, the release (bleeding-off) of volatile species from the furnace is reduced to a great extent, and the level of volatiles re-entering the furnace via the recycled dust is also consistently rising[5]. Hence, these elements (mainly Zn, Na and K) tend to accumulate in certain parts of the furnace, namely in the burden and the dust, where conditions are favourable for volatile vapours to condense.

The most practical indicator, that is currently used, to measure the accumulation of Zn in the system is the Zn content in the dust. Measurements have been ongoing since recycling commenced at MFC in 1995 and since 1997 at FM [5].

4.1 Primary reactions to consider

Three possible reactions may occur in the burden of the furnace to promote the deposition of Zn species, namely:

$$Zn(v) + CO_2 = ZnO(s) + CO \qquad (1)$$

$$Zn(v) = Zn\ (s,l) \qquad (2)$$

Equation 1 indicates the most probable standard reaction that may occur thermodynamically at temperatures of up to 1320°C. The extent of the deposition of ZnO is dependent on the temperature, p_{CO} / p_{CO_2} and vapour pressure of Zn (p_{Zn}) in the emerging gas. Equilibrium Zn vapour pressures (p_{Zn}^{e}) can be calculated from the equation below:

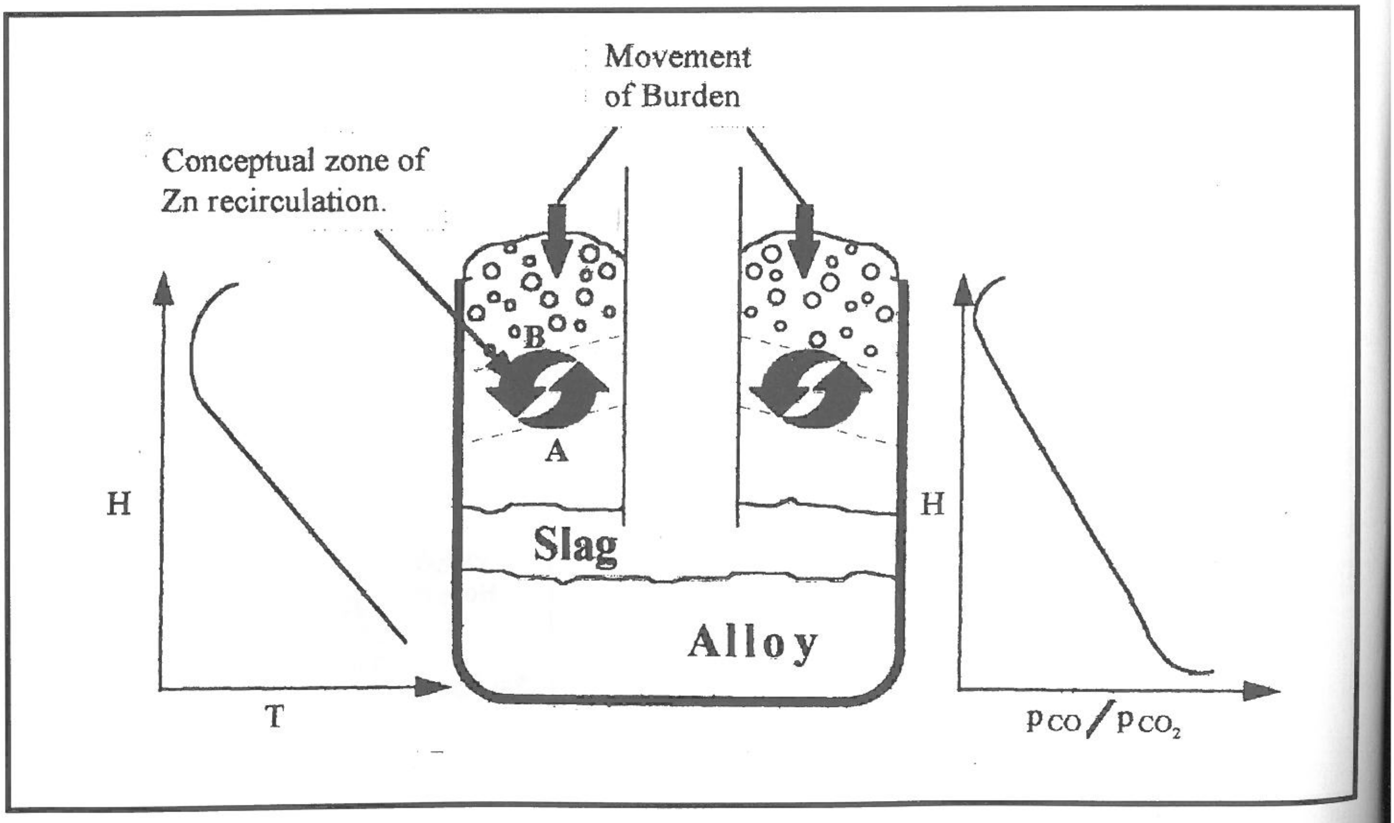
$$\text{From:}\quad K = \frac{a_{ZnO}}{p_{Zn}^{e}} \cdot \left(\frac{p_{CO}}{p_{CO_2}}\right)$$

It has been shown that as p_{Zn} increases, conditions for ZnO deposition extend to more reducing conditions (higher p_{CO} / p_{CO_2}. increasing p_{Zn} permits ZnO depositions at progressively higher temperatures [5].

4.2 Proposed furnace Zn recirculation cycle

Based these thermodynamic considerations, it has been proposed that a Zn recirculation exists within zone (the width of which is demarcated by temperature, p_{CO} / p_{CO_2} and p_{Zn}) in the furnace [5].

Figure 2: Schematic mechanism of Zn recirculation within furnace burden - normal condition



The proposed mechanism involves:

1. recycling of Zn-rich oxidic dust on top of the charge burden;
2. descent of this material to hotter and more reducing regions of the furnace;
3. reduction of ZnO to $Zn_{(v)}$ (reverse of reaction 1, at point A in Fig. 2);
4. upward transport of the $Zn_{(v)}$ with the furnace off-gas, counter-current to the descending charge burden;
5. in cooler, more oxidising regions in the upper charge burden, either;
    - condensation of $Zn_{(v)}$ to $Zn_{(l)}$ (reaction 2, feasible only at temperatures lower than 907°C), or even to Zn(s) (feasible only at temperatures less than 420°C),
    - or, more probably, heterogeneous condensation and reoxidation to $ZnO_{(s)}$ (at point B in Fig. 2 - forward reaction 1);
6. the cycle then repeats itself from steps 2 to 5.

The net result can be postulated localised internal build-up and recirculation of Zn species within a zone in the furnace due to repeated reduction of ZnO, volatilisation of $Zn_{(v)}$ and deposition predominantly as ZnO. The location of this zone of Zn recirculation is defined by specific process conditions (furnace temperature, p_{CO} / p_{CO_2} and p_{Zn}).

5. PRACTICAL EXPERIENCE WITH RECYCLING.

5.1 Equipment development

Only pilot scale information was available at the time of purchase of the original pin agglomerator. It was known that a high Cr_2O_3 content in the dust would lead to excessive wear on the pins. Wear-resistant tips were thus fitted to the pins. In an effort to make larger pellets, motor speed was slowed, leading to excessive pin breakage during trial runs. Pin design was then upgraded to be much more robust than originally specified by the manufacturer, and a more wear-resistant cup was fitted to the pin stud. This in turn caused the drive motor to overheat. Initial repairs also needed to be carried out, as manufactured tolerances were inadequate, namely:

- Excessive pin breakage, due to crusting of the dust (reduced by a further upgrade of the pins);
- Modification of the shaft and drive system to remedy frequent bearing failure; and
- Multiple changes were needed to improve the dust feed system to prevent "ratholing" occurring in the weighhopper.

Graph 1: Pin agglomerator equipment development curve

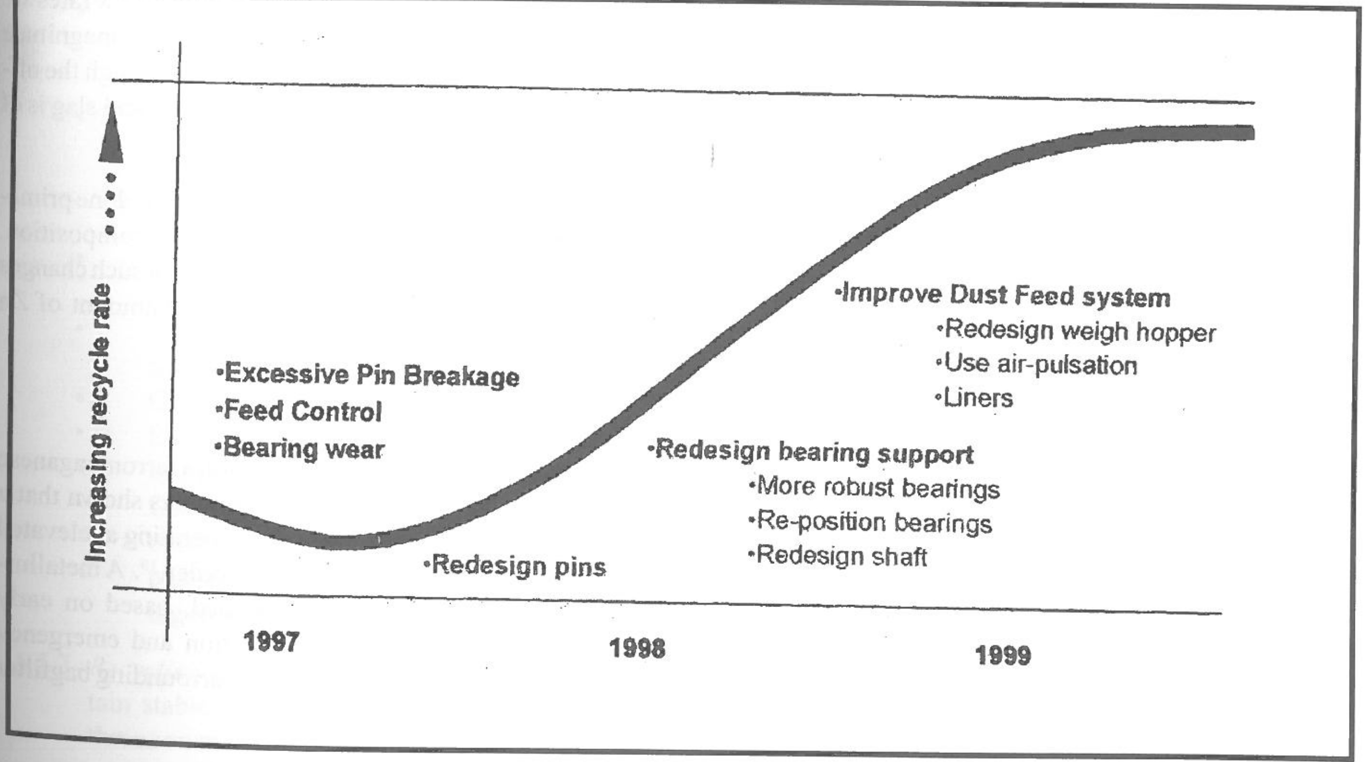
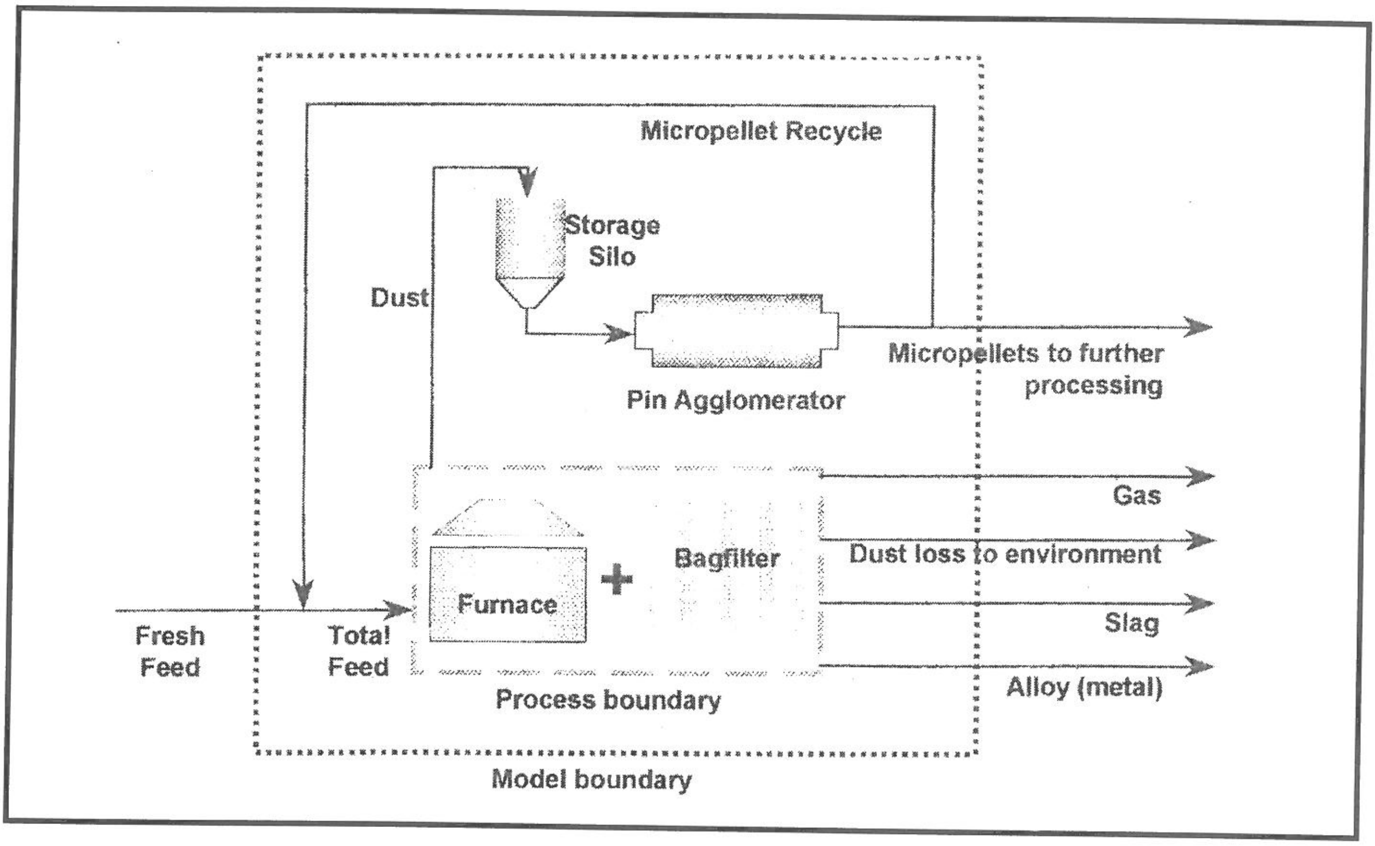


Figure 3: Definition of boundaries and streams used in the predictive model.



Accumulation points in the model are only allowed for within the process boundary and the storage silo (Figure 3).

5.2 Metallurgical experience

A predictive model has been developed by Chrome Alloys and Development of Billiton Process Research (CARD) over the past four years to assist the plants in determining the Zn build-up in the system (dust) as a function of dust recycled. Although the model is far from being able to predict the entire effects of Zn on the system, it offers the opportunity to predict the Zn levels in a system at a given feedrate.

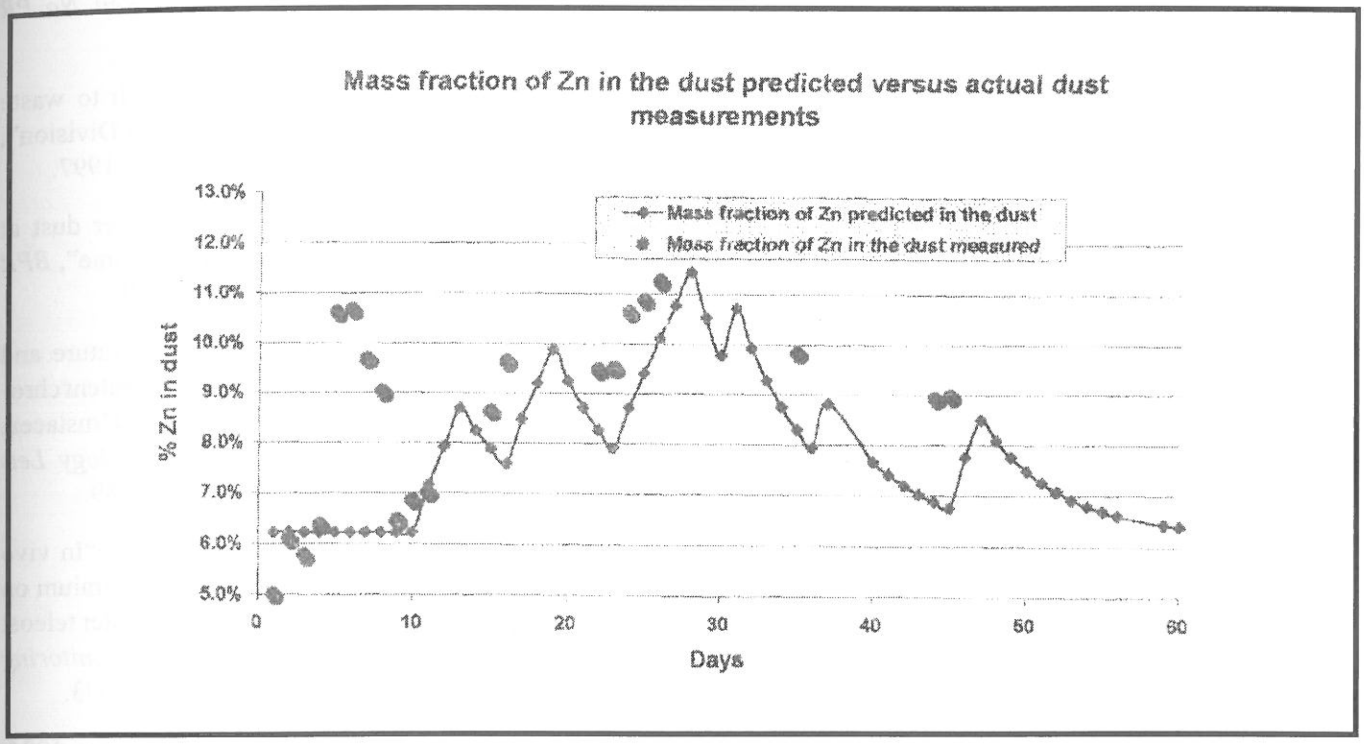
Practical and reliable data obtained to date confirm that under steady-state conditions, equilibrium in the amount of Zn in the system (mainly in the dust and burden) is reached.

- Graph 2 shows the effect of recycling and stockpiling on the predictor model. Although the model follows the general pattern of the data measured, it tends to underestimate these figures by 1% - 2%. Longer data runs could not be obtained due to operational difficulties — however, these were not related to the pin agglomerator.
- In order to be able to accurately complete the Zn mass balance, accurate Zn analysis as well as total mass measurement of the alloy and slag are required. As the slag and alloy mass flow rates are generally more than two orders of magnitude higher than the Zn mass flow rate through the off-gas system, the Zn analysis of alloy and slag is of particular concern
- Metallurgical control of the furnace is done primarily by means of altering the slag composition. Preliminary test work has shown that such changes may have a major impact on the amount of Zn removed by the slag stream.

5.3 Safety considerations

An eruption related to zinc build-up on a ferromanganese furnace at the Marietta site of Elkem has shown that a real explosion hazard exists when operating at elevated zinc concentrations in the furnace burden[10]. A metallurgical management system is needed, based on early detection, operating recommendation and emergency action, to address the safety issues surrounding bagfilter recycling.

Graph 2: **Predicted Zn levels from actual plant recycle date, compared to actual Zn levels**



5.3.1 *Possible Signs of Imminent Zn-related Eruptions.* Eruptions have been associated with reduced gas permeability of the furnace burden, as well as high Zn/ZnO concentrations in the furnace burden. Several warning signs serve as indications for these conditions, namely:

- The appearance of vast amounts of white/grey (ZnO) substance covering the charge mix 5.
- 'Hot top' conditions due to a Zn-rich zone that exists in the furnace (location and extent being determined by prevailing temperature conditions, p_{CO} / p_{CO_2} and p_{Zn}).
- Marked increase in off-gas temperatures in an open top furnace operation.
- Unusual hard bank development and reduced burden permeability.
- Green flames on the burden.
- Excessive blowing of taphole (white fumes).
- Increased Zn levels in the alloy and slag.
- Generally poorer and troublesome furnace operation, symptomatic of reduced burden porosity, possibly resulting from Zn/ZnO causing charge bridging.

5.3.2 *Recycling Recommendations.* In order to maintain stable and predictable furnace conditions, three common sense recommendations are made.

- Feeding of the dust to the furnaces must be done in a controlled fashion. The dust must be fed over a 24-hour period on a trickle-feed basis.
- Monitoring of dust analyses and dust quantities must be done more frequently as the zinc concentration increases, to try to anticipate conditions potentially disruptive to furnace performance before they develop.
- Regular visual checks should be made of the furnace burden during periods of dust recycling to check for the signs mentioned above.
- Complete Zn balance to reliably predict build-up of Zn in furnace burden.

5.3.3 *Remedial Action.* If conditions indicate an imminent eruption, or if normal recycling leads to excessive Zn concentrations in the recycle dust, emergency control measures are required.

- Eliminate the charging of turbulator dust into the furnace.
- Burn down the furnace bed [11].

6. CONCLUSION

Although many problems were encountered on the way to achieving 100% recycling of the dust, these have been addressed in a systematic and logical fashion, and resolved. Experience relating to equipment design, metallurgical control and safety precautions can be readily transferred to similar operations.

Recycle rates of 98% of the bagfilter dust produced by furnaces at Ferrometals have consistently been achieved. Zinc levels in the dust have seldom peaked above 17% at Ferrometals. Zinc contents in the alloy have remained unchanged, while that in the slag fluctuates, and it is difficult to determine whether recycling is the cause of these changes.

A predictive model has been developed to assist the chrome plants in predicting the Zn levels in the dust, at a given recycle rate.

Finally, recycling of the bagfilter dust has become accepted as an integral part of the operation at two plants within Samancor Chrome.

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8. REFERENCES

1. Kolbenstein, L, et al. "Energy recovery in the Norwegian Ferroalloy Industry", *7th International Ferroalloys Congress Proceedings*, Trondheim-Norway, June 1995.
2. Gericke, WA, "Environmental solutions to waste products from ferrochrome production", *8th International Ferroalloys Congress Proceedings*, Beijing-China, June 1998.
3. Broadhurst, JL, "Treatment of Tubatse charge chrome silo dust with ferrous sulphate : a comprehensive testwork programme", *BPR Rep. No. PR 95/40*, 8 June 1995.
4. Language, P, "A strategic approach to waste disposal : Samancor Chrome Alloys Division", *BPR CARD Rep. No. CR96/11*, May 1997.
5. Language, P, "Recycling of Bagfilter dust at Ferrometals and Middelburg Ferrochrome", *BPR CARD Rep. No. CR95/19*, Feb. 1999.
6. Pantani, C, et al. "Action of temperature and water hardness on the toxicity of hexavalent chromium in Grammus Italicus Goedm. (Crustacea, Amphipoda), "*Environmental Technology Letters (Lancaster UK)*, Vol 10, No7, 1989.
7. Venugopal, NBRK and Reddy, SLN, "In vivo effects of trivalent and hexavalent chromium on renal and hepatic ATPases of a freshwater teleost Anabas scandens", *Environmental Monitoring and Assessment*, Vol 28, No 2, Nov. 1993.
8. Department of Water Affairs and Forestry, 1994. Waste Management Series. Minimum Requirements for the Handling and Disposal of Hazardous Waste. (First Edition).
9. Language, P, "Engineering modifications made to the 14T11 Ferro-tech Turbulator. Period July 1993 to December 1993", *CARD Report No. CR94/01*, Jan. 1994.
10. Lee, YE, "The role of zinc in the eruption of high carbon FeMn smelting furnace", *Electric Furnace Conference*, 1993.
11. Van Blerk, JB, "Recycling of turbulator dust", *MFC Internal Memo No. JvB/01*, Jan. 1999.