RECYCLING OF WASTE MATERIALS FROM THE PRODUCTION OF FeMn AND SiMn

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ABSTRACT

The Norwegian Ferroalloy Producers Research Association (FFF), SINTEF and NTNU have been investigating methods to recycle waste materials from the production of ferromanganese and silicomanganese. The principal focus has been to determine a suitable method to recycle the sludge produced in the wet scrubbers.

In the current form it is not possible to recycle the sludge directly, due to the water and tar content and the presence of several problematic elements such as Zn, Pb, K, Na and P. Different methods have been investigated to either utilise the sludge directly to produce Mn or to treat the sludge to allow it to be recycled to the SAF where the Mn can be recovered.

The favoured option is to construct a central processing facility where the sludge will be melted to produce a small quantity of alloy, a Zn rich fume and a high Mn slag containing more than 95% of the Mn which will be utilised in the SAF.

1 INTRODUCTION

Sustainable production of manganese ferroalloys requires that waste materials should be minimised, with a goal of recycling all materials back into the process or to produce other commercially viable materials. Other than the production of manganese alloys, an industrial manganese plant also generates slag, sludge and dust [1].

The largest quantity of these materials is the slag, which contains a minimal amount of Mn making it difficult to recover. Slag is tapped with the metal from the furnace, it is suitable as a road base or fill material, and is often sold at a minimal cost. The next most significant waste material is sludge, which is generated when the off gases from the furnace are cleaned with a wet scrubber. It often contains 35 wt% Mn, but due to the concentration of other elements and the physical properties it is difficult to recycle back into the process. On average, more than 20 000 t of sludge (dry basis) from the Mn industry is deposited to landfill in Norway each year [2]. There is very little other waste materials, and often they are special waste products, such as Hg removed from the off gas.

2 SLUDGE PROPERTIES

To recycle sludge has been the subject of various studies [3]-[7], but at present, to the best of our knowledge, there are no manganese producers who are recycling sludge in a sustainable manner. This is due to the presence of elements such as Zn, Pb, K and Na (which are detrimental to the operation of the furnace) as well as the high water and organic content combined with a small particle size. However the cost of landfill in Norway is increasing, mainly due to changes in the environmental regulations, which is creating a situation where the sustainable treatment of manganese sludge is becoming more important.

The major challenges with recycling sludge were identified as:

- High water content, 40 – 70 wt % water
- Alkalis, K and Na
- Zn and Pb
- Minor elements (P, B, etc)
- Organic compounds, including tar, PAH, etc
- Fine powder, average particle size 1-4 μm.
- Heavy metals, including Hg, As, Cd, etc.
- Transport, the sludge is located at several plants and should be treated in a central location

The weighted average properties of the sludge in Norway are summarised in Table 1 below.

Table 1: Sludge properties

Mn	27%	B	1 000 ppm
Fe	1.5%	S	4 000 ppm
Si	4.5%	As	40 ppm
Zn	2.2%	Cd	350 ppm
Pb	0.35%	Hg	20 ppm
K	3.2%	Particle size	d50 1-4 μm
Na	0.68%	Surface area	3-120 m^2/g
P	400 ppm	C	9.6%
Ca+Mg+Al	Balance	Moisture	64%

2.1 High Water Content

The suspended sludge in the water from the wet scrubbers is currently treated with a flocculating agent and then concentrated in a thickener. The underflow from the thickener is then treated with either a vacuum drum filter or a centrifuge (depending on the plant), both of which discharge a liquid sludge. There have recently been some promising results from trials with a filter press, which was able to reduce the water content from 70 wt% to 46 wt%. Due to the small particle size and high surface area, it is difficult to significantly reduce the water content of the sludge.

2.2 Alkalis

The sludge contains significant amounts of alkalis, which are associated with unstable furnace operation and higher carbon consumption[8]. It is possible to remove alkalis either at a high temperature (>1350 °C) or to dissolve them in water. To remove the alkalis by heat treatment would require a liquid process, as the sludge melts at about 1260 °C. Due to the difficulty in mechanically removing water from the sludge, it would be necessary to use a large amount of water to wash the alkalis from the sludge.

2.3 Zinc and Lead

Zinc and lead are associated with unstable furnace operation, and in some cases explosions. The zinc is associated with bridges forming across the furnace, which results in unstable operation when they collapse [9]. For this reason Eramet have a safety limit on the amount of Zn which can be charge to a furnace [10].

2.4 Minor elements

Minor elements in the sludge include phosphorus and boron, which will end up in any alloy produced. It would be beneficial to remove them from the sludge before it is recycled.

2.5 Organics

There are significant amount of organic components in the sludge, generated from the tar in the electrodes and other carbon materials charged to the furnace [6][11].

2.6 Fine Powder

The sludge is an extremely fine powder, with an average particle size of 1 to 4 μm. This is not suitable to feed directly to the SAF, and may pose some handling problems depending how the sludge is recycled.

2.7 Heavy Metals

Any treatment of the sludge must also control the emission of heavy metals, which will tend to volatilise at relatively low temperatures, requiring suitable gas cleaning equipment.

2.8 Transport

Although the quantity of sludge is significant, the economics of any treatment process will be improved if all of the sludge can be treated at a central location. A simple method with minimal labour requirements to transfer the sludge is therefore critical. All of the manganese plants in Norway are situated on fjords with good port facilities.

3 TREATMENT OPTIONS

Various methods have been investigated and used to recycle or dispose of sludge, ever since it was first produced, including:

3.1 Deposition

The most common method to handle waste sludge is to deposit it in a landfill. This varies from

- shallow open dams, where the sludge may sometimes dry naturally in a dry location
- deeper deposits which are later covered and remediated
- hard rock deposits, such as old mines

Deposition is not sustainable. It requires local approvals, which are becoming more stringent and are beyond the direct control of industry, while also representing a loss of manganese from the operation.

3.2 Wet chemical treatment

It is possible to dissolve the manganese by the addition of acid to the sludge, however only a proportion of the manganese is generally able to be recovered in this manner, and it will also dissolve other elements. The cost of the chemicals is higher than the value of the manganese, and the manganese is not in a suitable form to utilise in a furnace [3].

The sludge can also be washed to remove alkalis, which are generally water soluble. However, large quantities of water are required, as the sludge is extremely fine making it difficult to remove the water mechanically. This only removes the alkalis, but has no effect on the zinc or lead, which are arguably more detrimental to the operation of the furnace [12].

3.3 Biological methods

It is possible to selectively remove elements from the sludge or waste water using biological methods [13], such as:

- precipitation as sulphides through the use of sulphur reducing bacteria (SRB)
- biosorption by either living, or more commonly non-living, biomass.

Although these methods have been shown to be viable under laboratory conditions, there are still very few industrial applications for this type of technology, making it very difficult to determine the economic and technical viability.

3.4 Direct recycling

It is possible to dry and pelletise the sludge, however there would be no removal of problematic elements which would then accumulate within the furnace. Some small open furnaces are operating in this manner, with a cycle of running the burden down to the electrode tips to drive of all of the difficult elements, but it is expected to be difficult with a closed furnace.

3.5 Addition to Sinter

This is a simple method to recycle the sludge, however studies have shown that sinter is produced in a relatively oxidising atmosphere, resulting in the zinc remaining in the sinter as zinc oxide. It is not possible to remove the zinc or alkalis during sintering [3][7].

3.6 Solid state heat treatment – reducing atmosphere

Solid state reduction is possible using equipment such as a rotary hearth furnace (RHF), such as used for other waste materials [14]. Studies have shown that it is possible to remove 99.5% of the zinc and 87% of the lead from sludge by heating to just 1100 °C in a reducing atmosphere [15]. Industrially, this is possible by drying and pelletising the sludge before feeding it into a RHF, however the temperature is not high enough to remove more than 25% of the potassium and 5% of the sodium. The use of a RHF for solid states reduction of manganese sludge would also require significant development.

3.7 Oxyfines burner

In this process wet sludge is pumped into a high temperature flame consisting of oxygen and fuel. Trials have shown that is possible to remove most of the zinc and lead, although most of the alkalis will remain in the slag [4] [16].

3.8 Melting to produce an alloy

If the sludge is dried and calcined, it can be melted in an open bath electric arc furnace. The furnace can be operated to produce an alloy, but due to the impurities in the sludge, there will be a high concentration of minor elements such as P and B. Additionally, sludge is not a consistent product with a wide variation in the composition, so it is expected that it would be difficult to produce a stable alloy composition.

Table 2: Treatment options

Treatment	% Zn/Pb returned to SAF	% K/Na returned to SAF	% Waste to be deposited	% Mn Recovered to process	Product	Technological risk
Landfill	0	0	100	0	None	None
Mountain cavern	0	0	100	0	None	None
Hydrometallurgy	0	0	50	50	Mn2SO4	unknown
Briquetting	100	100	0	100	Mn alloy	Poor furnace operation
Direct injection	100	100	0	100	Mn alloy	Poor furnace operation
Sintering	90	90	10	90	Mn alloy	Poor furnace operation
Solid state reduction	<1	90	0-5	95	Mn ore substitute	Operation of RHF may be difficult
Oxyfines burner	<20	65	5-10	90	High Mn slag	O_2 is expensive. Fume not known.
Melting – slag	<1	10	0-10	95	High Mn slag	Drying and calcining
Melting – alloy	0	0	10-15	95	Mn alloy	Alloy spec unknown

3.9 Melting to produce a high Mn slag

Alternatively, if the sludge is melted in an open bath electric arc furnace, the quantity of reductant could be minimised so that the zinc, lead, sodium and potassium are vaporised and a minimal amount of manganese is reduced. In this way the small amount of alloy would collect the minor elements such as phosphorus and boron, while the volatile elements would be evaporated, leaving a clean slag with the majority of the manganese. The slag would then be cast and fed to the existing SAF as a manganese source. This is the most favoured option, as it allows the recovery of the manganese while removing volatile and minor elements into separate streams.

4 PROPOSED TREATMENT OPTION

The proposed method currently being pursued is to melt the sludge to produce a high manganese slag at a central facility. The slag would then be recycled through a closed SiMn furnace. This would require several processes, as illustrated in the process flow sheet below.

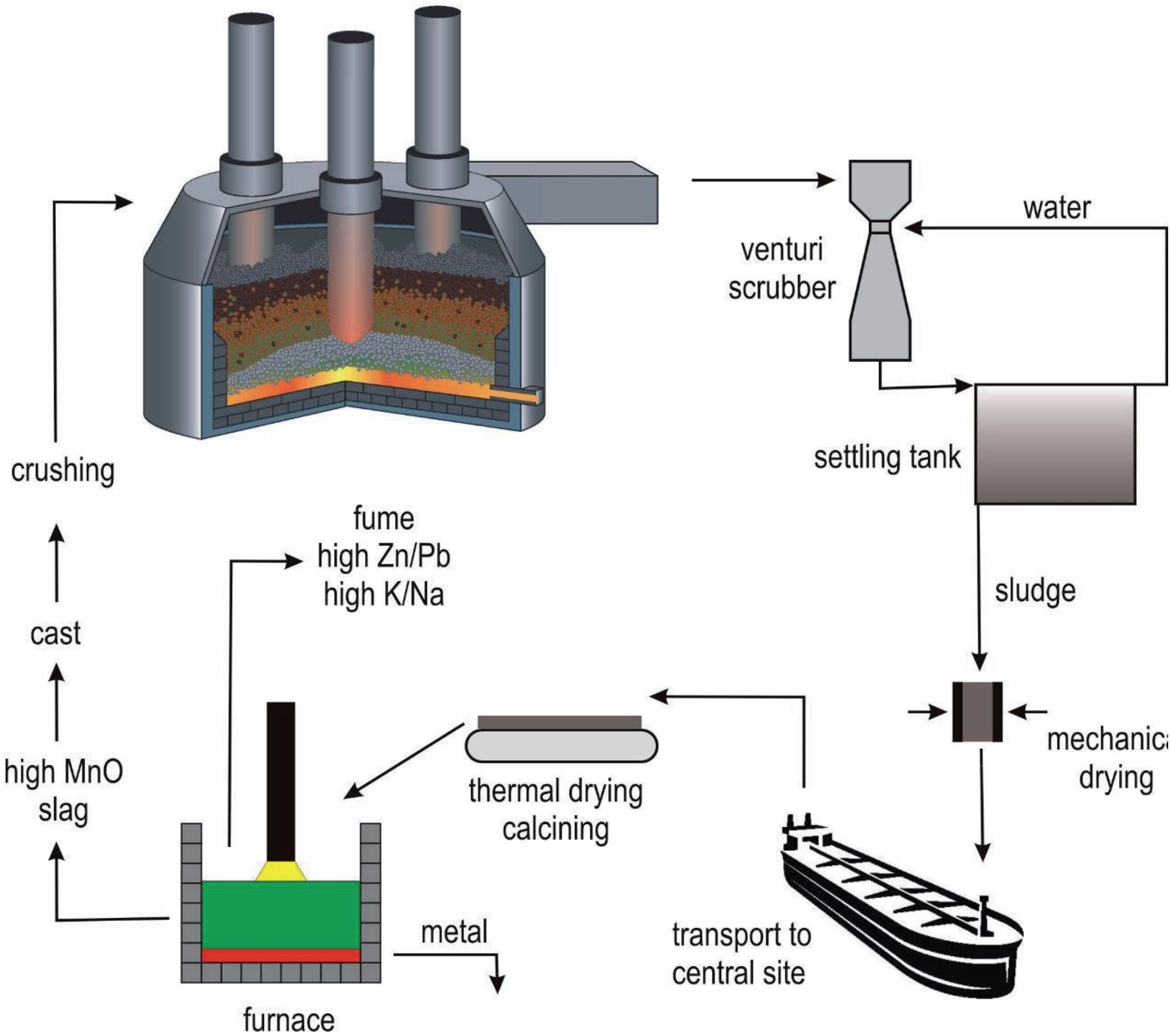

Figure 1: Process flow sheet for proposed treatment option

4.1 Transport

The sludge needs to be transported to a central facility. It is currently possible to pump the sludge onto a ship, which is a relatively automated process. If the sludge is dried to some extent at each plant then it may be necessary to load the sludge onto the ship in a different manner, but any method should be automated as much as possible.

4.2 Drying and Calcining

The sludge will probably benefit from mechanical drying. This is possible either with a press filter or a centrifuge with a solid discharge. At present the best results are from the filter press which has been tested on site. Then the sludge should be dried and calcined to minimise the amount of gases evolved during melting, which will minimise carryover. Trials have been performed with Hosokawa in The Netherlands, which were very positive. It was possible to feed sludge with 70 wt% water directly into the Micron Drymeister [17] with a product containing less than 2 wt% water. Alternatively the discharge from a press filter could be dried on a belt dryer, with a counter current hot gas stream, producing a relatively course product compared to the flash dryer. Both methods are currently being considered, with the final decision depending on the economics of the processes.

The sludge should be heated to a sufficiently high temperature to remove the majority of the gases present, to minimise carryover within the furnace. About 10 wt% of the sludge will be evolved as gas if the material from the flash dryer will evolve approximately 10 wt% gas when melted, while if the sludge is heated to 600 -700 °C then there would only be about 2 wt% gas released during melting. It is currently expected that the sludge will be calcined to at least 600 °C. The mercury and other heavy metal will mainly be removed from the sludge curing the calcining process, so it will be important to ensure that the off gases are treated correctly.

4.3 Melting

The sludge could be melted in either a DC or AC open bath arc furnace, as both options are currently being considered. Pilot scale trials are being planned for 2010.

- Slag - within the furnace the sludge will be melted to produce a slag which will contain the majority of the manganese, with the other elements distributed between the fume and alloy.
- Metal - a small quantity of metal will be produced to capture minor elements such as phosphorus and boron. This alloy will be a very small quantity, so it may be possible to find a suitable customer.
- Fume - the fume from the furnace will contain >99% of the zinc and >90% of the alkalis, with some of the manganese and phosphorus. If the zinc in the fume is a high enough concentration it will be sold to a zinc producer and there will be no waste product. Alternatively some further treatment may be required to further concentrate the zinc.

4.4 Casting, Crushing and Recycling

After the slag is produced it will be cast into pits and then handled in the same manner as HC FeMn slag.

4.5 Current Status

At present further work to determine the exact elemental distribution between the metal, slag and fume is required, although initial tests are promising. A pilot scale trial is planned in 2010, which will be about one tenth of the full industrial scale. A decision will then be taken by the respective industrial partners to determine if the plant will be constructed.

5 CONCLUSIONS

An exhaustive study has been made on the different methods to recycle sludge from the production of ferromanganese and silicomanganese. It was found that the most suitable option for the manganese producers in Norway was to melt the sludge to produce a high manganese slag, a small amount of alloy and a fume. The alloy and fume will contain the majority of the unwanted elements, while the slag will contain most of the manganese.

Further work is being performed to determine the exact elemental distribution, but current results are promising.

A pilot scale trial of the process is expected to be performed in 2010.

6 ACKNOWLEDGEMENTS

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7 REFERENCES

[1] Olsen, S.E, Tangstad, M., Lindstad, T., “Production of manganese ferroalloys”, Tapir Academic Press, 2007, ISBN 8251921910, pp. 220-221.
[2] Hunsbedt, L., Cowx, P.M., Flatabø, R., Johansen, K.E., Bustnes, J.A., ”Environmental challenges for the Norwegian Mn - industry”, International Congress on Ferroalloys (INFACON XI), New Delhi, February, 2007, pp.446-456.
[3] Tangstad, M., “Return of Mn from Effluent”, Elkem Ferroalloys, Report No. FA 15/90
[4] Schéele, J. von, OXYFINESTM TECHNOLOGY FOR THE RE-MELTING OF FINES, DUST AND SLUDGE, International Congress on Ferroalloys (INFACON X), Cape Town, South Africa, 1-4 February 2004, pp.678-686.
[5] Shen R., Zhang G., Dell'Amico M., Brown P., and Ostrovski., “Characterisation of Manganese Furnace Dust and Zinc Balance in Production of Manganese Alloys” ISIJ International Vol. 45 (2005) , No. 9 pp.1248-1254.
[6] Shen R., Zhang G., Dell'Amico M., Brown P., and Ostrovski., Reduction of Zinc Oxide in Manganese Furnace Dust with Tar”, ISIJ International, Vol. 46 (2006) , No. 1 pp.8-13.
[7] Shen R., Zhang G., Dell'Amico M., Brown P., and Ostrovski., “Sintering Pot Test of Manganese Ore with Addition of Manganese Furnace Dust”, Vol. 47 (2007) , ISIJ International, No. 2 pp.234-239.
[8] Jakub Kaczorowski, Tor Lindstad and Martin Syvertsen, “The Influence of Potassium on the Boudouard Reaction in Manganese Production”, ISIJ International, Vol. 47 (2007) , No. 11 pp.1599-1604.
[9] Lee, Y.E. and Kozal, D.S., “The role of zinc in the eruption of high carbon FeMn smelting furnace”, Electric Furnace Conference Proceedings, Washington, 8-10th November, 1993, 145-150.
[10] Pochart, G., Joncourt, L., Touchard, N., and Perdon, C., “Metallurgical benefit of reactive high grade ore in manganese alloys manufacturing”, International Congress on Ferroalloys (INFACON XI), New Delhi, February, 2007, pp.217-230
[11] Hamano, T., Zhang, G., Brown, P., and Ostrovski, O., “Manganese Furnace Dust: Drying and Reduction of Zinc Oxide by Tar”, ”, ISIJ International, Vol. 48 (2008) , No. 7 pp.906-911
[12] Lobo, S., Gaal, S., “Washing of sludge from the production of manganese ferroalloys”, SINTEF Report F4615
[13] Netzer, R., “Biorecovery of heavy metals from industrial wastewater – A literature review”, SINTEF Report No. F11469
[14] Hansmann, T., Fontana, P., Chiappero, A., Both, I., and Roth, J.-L., “Paul Wurth technologies for the optimum recycling of steelmaking residues”, METEC InSteelCon, Düsseldorf, Germany, 11 - 15 June 2007 pp.1044-1051
[15] Gaal, S., “Roasting sludge from the production of manganese ferroalloys”, SINTEF Report No. F4054
[16] Røynestad, O.J., Gjenvinning av slam fra Silikomanganproduksjon ved bruk av OXYFINES – teknikken”, Hovedprosjekt for ingeniørutdanning, Avdeling for teknologi, HIST Trondheim.
[17] http://www.hosokawamicron.nl/