METALLOTHERMIC PRODUCTION OF CEMENT EXTENDER FROM MANGANESE WASTE SLAGS

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Introduction

Southern Africa has a rich history in the pyrometallurgical processing of manganese ores. The alloys produced in the manganese ferroalloy industry are silicomanganese, medium and high carbon ferromanganese, and these have monetary value, whilst the slag is discarded as a waste material and has a MnO content of about 25 to 30 wt%. Slag dumps have accumulated over the years and the use of Mn bearing slags in the building industry is hampered by the high environmental toxicity impact posed when MnO is present in high concentrations. In addition, there is contradictory information pertaining to the influence of MnO on the strength of cement. It is reported that high MnO content is responsible for the loss of hydraulic activity, while it is also reported that there is no relationship between the long-term strength loss and the MnO content [1,2].

Ground granulated blast furnace slags (GGBFS), fly ash and silica fumes are currently used as cement extenders and major work has been done in improving these cement extender properties[3-5]. The objective of the pilot plant test work was to develop a process to produce a cement extender from high carbon ferromanganese slags. The slags contained an undesirably high amount of MnO with potential adverse effects on the cement properties. The intention of the test work was therefore to produce cement extender product from ferromanganese slag through metallothermic reductive smelting in a DC arc furnace and simultaneously produce silicomanganese alloy as a saleable by-product.

New Processing Concept

The new concept of producing the cement extender was achieved through the metallothermic reduction of the manganese waste slag. The intention was to produce both a modified slag and a silico-manganese alloy as products, leaving zero waste. Mintek's Pyrosim thermodynamic simulation tool[6] was used to calculate the feed recipes and both experimental test work approaches were conducted using a 40 kW DC "tilting" pot, see Figure 1a.

Results and Discussion

Both the slag and metal samples, see Figure 1, (b)-(d) were analysed by Inductively Coupled Optical Emission Spectrometry (ICP-EOS) methods at Mintek and the bulk chemical analytical results are presented in the sections below. Table 1 presents the initial high carbon ferromanganese (HCFeMn) waste slag composition, the thermodynamically modelled modified slag composition as well as the actual test modified slag composition.

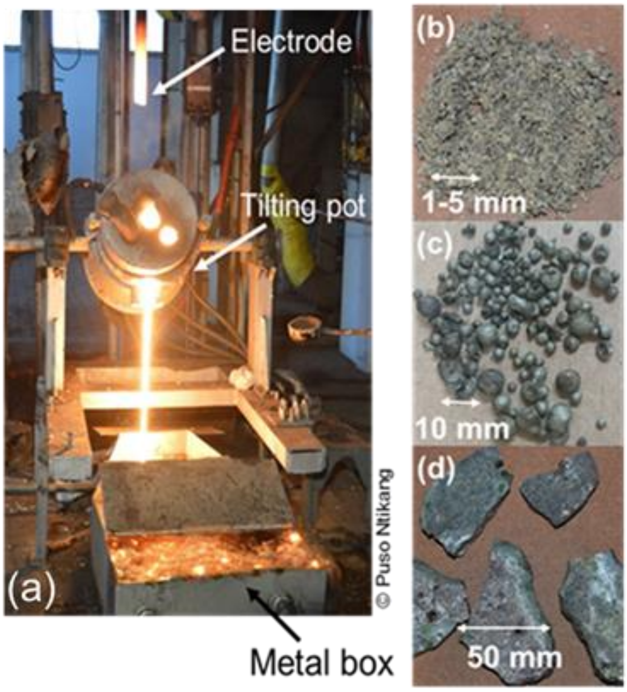

Figure 1: (a) 40 kW DC "tilting" pot facility, (b) Granulated slag product, (c) entrained SiMn product, (d) SiMn alloy product

A thermodynamic modelling program (Pyrosim) was used to calculate the feed recipes needed to meet the modified slag specifications after the metallothermic reduction. This simulation model uses the method of Gibbs free energy minimisation to predict equilibrium conditions. It was found that the feed compositions predicted by Pyrosim led to average composition results from the actual test that were in close agreement to the specifications. The MnO content was also significantly reduced from 31 wt% in the HCFeMn waste slag to 8 wt% in the actual test modified slag.

Table 1: Chemical compositions of slags, wt%

	MgO	Al_2O_3	SiO_2	CaO	MnO	FeO
HCFeMn slag (average from 4 bags)	7	4	30	26	31	2
Standard deviation	0.64	0.05	0.91	3.64	2.35	0.87
Pyrosim	7	15	37	34	6	0
Actual results (average from 6 taps)	9	14	40	31	8	2
Standard deviation	0.78	0.92	0.76	0.77	1.55	0.02

The abovementioned MnO specification was based on previous leaching test results which indicated that 8 wt% was environmentally acceptable[7]. The other modified granulated slag specifications were based on that of ground granulated blast furnace slag (GGBFS) specifications (EN-197)[8] which is widely used in the cement industry. Table 2 contains the GGBFS target specifications and the corresponding modified slag results. A mineralogical analysis was conducted to determine the presence of entrained metal after physical separation, the phase chemical composition, as well as the quantity of glassy (amorphous) phase formed in the product slag. The specifications for cement extender grade dictates that the slag must consist of >95% glassy phase and as it can be seen from the table, the modified slag met all specifications. In addition, no metal was found to be entrained in the slag after physical separation.

Table 2: Slag parameters

	GGBFS specs	Modified slag
$\sum$ $MgO+CaO+SiO_2$ wt%	> 67	80
B3 = [$(MgO+CaO)/SiO_2$]	≥ 1	0.9 to 1.05
Glass content, wt%	> 95	99
MnO, wt%	N/A	8 ± 2

Similar to the modified slag, the alloy composition predicted by Pyrosim was in close agreement with the alloy composition from the actual test. The alloy met the ASTM grade B specifications[9], where the Si was in the range 16-18.5 wt% and the Mn was within the range 65-68 wt%. The SiMn alloy produced therefore met the grade B ASTM specification for silico-manganese, as can be seen in Table 3.

Table 3: Alloy parameters

	SiMn specs	Modified slag
Si, wt%	Grade C1: 12.5 - 16	18 ± 5
	Grade B1: 16 – 18.5	
	Grade A1: 18.5 – 21	
Mn, wt%	65 - 68	70 ± 5

Strength and Leaching stability tests

The metallothermically-modified slag is expected to pass the cement strength tests, based on strength test results from slags produced by the initial approach which involved dilution only. Synthetic Precipitation Leaching procedure (SPLP), which focuses on environmental conditions, was conducted on the metallothermically-modified slag. In comparison to composite cement in the class CEM V/A (S-V) 32.5N, it was found that the slag was very stable under aggressive acid leaching conditions[10].

A high-level techno-economic evaluation was conducted on six conceptual flowsheets for a plant modifying 355 kt/annum of waste slag. Because of different MnO levels in the starting waste slag, it was found that dumped HCFeMn could be processed profitably by remelting and slag treatment in an EAF, but silico-manganese slag would need to be modified in the molten state using a ladle/ladle furnace, in order for the waste slag processing to become economically viable. In addition, it is more profitable to use silicon and FeSi than aluminium as the reductant and rather modify alumina levels in the slag as required through the addition of bauxite.

Conclusions

The development of the metallothermic process for production of a cleaner slag with low MnO concurrently with SiMn alloy was successful, and a provisional South African patent has been filed[11]. Slag met the specifications for the GGBFS (EN-197) and was very stable under aggressive acid leaching conditions. There were minor deviations between the Pyrosim simulations and the actual averaged results. Overall, it was demonstrated that the slag can be used as a cement extender. A high-level economic assessment indicates that the processing of manganese waste slag according to the new concept would be economically feasible.

References

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