Introducing solar thermal heat into minerals processing: A case study on replacing a diesel burner at a sinter plant

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Abstract

The use of solar thermal energy for process heat has been limited to applications with at temperature range below 400 °C. This paper investigates the barriers to providing process heat with solar thermal at higher temperatures based on the desktop case study of replacing a diesel burner at a sinter plant in the Northern Cape Province of South Africa. The aim of the case study is to assess the feasibility of the concept on technical, environmental and economic terms.

The paper identifies advantages as well as barriers to high temperature solar thermal process heat applications based on the case study and recommends possible solutions for these barriers.

The main concept applied in the paper is development of a mass and energy balance for the case study to inform the design of a solar thermal plant to provide process heat. Sensitivity analysis is used to inform on the sensitivity of the mass and energy balance to important assumptions. Barriers to implementation are briefly discussed.

Keywords: Solar thermal process heat; manganese ore, sinter plant

1. Introduction

The largest use of manganese is as an additive to steel to improve properties such as toughness and wear resistance [1]. Manganese can also act as a deoxidiser in steel. Manganese is added to steel as either ferromanganese or silicomanganese alloys. These alloys are produced in blast furnaces and submerged electric arc furnaces (SAFs) by smelting manganese ores together with reductants (carbon in the form of coke and ferrosilicon) to produce the product alloys. Both blast furnaces and SAFs require the feed material to the furnace to have good burden strength and permeability to ensure that gasses evolving during the smelting process can escape through the burden. This leads to strict size requirements for feed materials. Lumpy manganese ores are sized between 25 mm and 75 mm. Sizing and classification of manganese ores generate fines and these fines are agglomerated in sinter plants. Sinter also has an improved manganese grade due to the thermal decomposition of carbonate minerals and manganese oxides in the ores when heated.

This paper uses the Kalagadi Manganese sinter plant as case study. The Kalagadi Manganese sinter plant plans to sinter all the ore produced at the Kalagadi Manganese mine, which is set to start production in 2018. Until the mine is operational, the sinter plant has been producing sinter for neighbouring mines on a toll treatment basis. The sintering plant was commissioned in 2013 and has since been producing sinter with a typical manganese grade of 48% [2]. The plant is reported as the biggest sinter plant in the world [3] and has a throughput of 2.4 mtpa (million tons per annum). The sinter plant can produce up to 9000 t sinter per day, an average of 375 ton sinter per hour.

The following description of sinter plant operations is written based on a tour of the sinter plant in October 2017 [2]. The ore fines (passing 25 mm screen size) are first crushed to between 0.7 mm and 6 mm with material finer than 0.7 mm sent to slimes dams as waste. The fine ore is then blended with 10 % by weight carbon and 4 - 7 % by weight water and fines re-circulated from the sinter product classification. The wet mixture is rolled in a drum to form nodules. These nodules are important as they ensure that the sinter has good gas permeability. The green sinter (nodules) is transported by conveyors to feed hoppers above the ignition hood of the sinter plant. The ignition hood uses diesel burners to heat the sinter mix above the ignition temperature of the coke. The sinter belt moves at a speed of up to 2.05 m/min and air is drawn from the top of the sinter through the bed by two fans driven by 9 MVA motors. The combustion of coke provides the additional heat required to sinter the material at around 1200°C. The combustion zone moves downwards through the bed until burn through is achieved when all the coke has combusted. The sinter is then air cooled on a separate sinter cooling belt, before crushing and sorting. Hot air recovered from cooling strand is recycled back to the sintering section to preheat the material and reduce diesel consumption. The working of the sinter plant is illustrated in Figure 1.



Fig. 1. Drawing illustrating sinter strand and ignition hood principles.

2. Mass balance and energy balance

2.1 Raw materials

Raw materials going into the sinter plant are manganese ore, carbon and water. Manganese ores have a complex mineralogy and are quire variable in nature. As the Kalagadi Manganese mine is not operational yet, the case study is based on samples from the nearby Mamatwan mine. The mineralogy of the Mamatwan ore is illustrated by scanning electron microscopy (SEM) as shown in Figure 2.

Quantitative X-ray diffraction (XRD) was used to determine how much of each mineral is present in the ore as shown in Table 1. The most common mineral is braunite, followed by calcite.

Mineral	Ideal chemical formulae	Composition
Names		
Hematite	Fe ₂ O ₃	3.7
Hausmanite	Mn ₃ O ₄	7.7
Braunite	Mn ₆ SiO ₁₂	33.8
Ankerite	Ca(Mn,Mg,Fe)(CO ₃) ₂	6.9
Quartz	SiO_2	3.9
Calcite	CaCO ₃	22.1
Kutnahorite	Ca(Mn,Mg,Fe)(CO ₃) ₂	7.8
Crypto- melane	$KMn_6Mn_2O_{16}$	10.0
Todorokite	(Na,Ca,K)2(Mn)6O12.3-4.5(H2O)	4.1
	Total	100.0

 Table 1. Quantitative XRD results for bulk composition of mamatwan ores, mass%



Fig. 2. SEM of Mamatwan ores

For minerals where lattice substitution is common, such as kutnahorite, ankerite and todokorite, the amounts of manganese, magnesium and iron were estimated by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis of the ore. This technique reports the amount of metallic elements present in the sample, but ignores the mineralogy and cannot detect any carbonates or hydrates. The results from the ICP-OES as well as the results from atomic absorption spectroscopy (AAS), used to determine the amounts of sodium and potassium in the ore, are given in Table 2.

K	Na	Al	Ca	Fe	Mg	Mn	Si
0.9	0.2	0.3	9.0	4.7	1.7	34.5	4.1

Table 2. ICP-OES and AAS results, mass%

The lattice occupation of kutnahorite, ankerite and todokorite was investigated by reconciling the elemental analysis with the XRD mineralogy. Although the analysis did not completely reconcile, the exercise converged to the lattice occupations for the Mamatwan sample shown in Table 3.

Mineral name	Chemical formulae
Kutnahorite	$CaMn_{0.1}Mg_{0.6}Fe_{0.3}(CO_3)_2$
Ankerite	$CaMn_0Mg_{0.35}Fe_{0.65}(CO_3)_2$
Todorokite	K ₂ (Mn) ₆ O ₁₂ .3-4.5(H ₂ O)



To use a FactSage 7.2 [4] thermodynamic model to inform the mass and energy balance, the mineralogy was simplified to

compounds available in the FactPS and Fact*oxid* databases. The simplified mineralogy strives to conserve the valency of the different cations, i.e. $KMn_6Mn_2O_{16}$ is modelled as $\frac{1}{2}(K_2O + Mn_2O_3) + 7(MnO_2)$. Where possible, the ratios of substitutional cations were determined to closely match the results of the chemical bulk analysis. The resulting simplified mineralogy is given in Table 4.

Fe ₂ O ₃	Mn ₃ O ₄	MnO	SiO ₂	CaCO ₃	FeCO ₃
3.7	7.7	4.0	7.3	29.4	3.9
Mn ₂ O ₃	MnCO ₃	H ₂ O	K ₂ O	MnO ₂	MgCO ₃
28.5	0.5	0.5	1.21	10.4	3.0

Table 4. Simplified mineralogy, mass%

2.2 Reactions detailing products and energy requirements.

The FactSage thermodynamic equilibrium model allows for an accurate mass and energy balance over the sinter strand that takes into account the complex thermal decomposition and calcination reactions as well as the combustion of coke in air and the phase changes occurring during the sinter process.

The calcination reactions are:

 $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$ [1]

$$MnCO_3(s) \rightarrow MnO(s) + CO_2(g)$$
 [2]

$$FeCO_3(s) \rightarrow FeO(s) + CO_2(g)$$
 [3]

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$
 [4]

The thermal decomposition reactions are:

$$2MnO_2(s) \rightarrow Mn_2O_3(s) + \frac{1}{2}O_2(g)$$
 [5]

$$3Mn_2O_3(s) \rightarrow 2Mn_3O_4(s) + \frac{1}{2}O_2(g)$$
 [6]

These reactions are endothermic and requires energy to be provided to the system.

In the presence of carbon monoxide gas, thermal decomposition of manganese oxides takes place according to reactions 7 and 8. These reactions are exothermic and release energy to the system.

$$2MnO_2(s) + CO(g) \rightarrow Mn_2O_3(s) + CO_2(g)$$
[7]

$$3Mn_2O_3(s) + CO(g) \rightarrow 2Mn_3O_4(s) + CO_2(g)$$
 [8]

Phase change reactions are the evaporation of water and the partial melting of the sinter mixture.

$$H_2O(1) \rightarrow H_2O(g)$$
 [9]

The Boudouard reaction, reaction 10, is also of importance as it governs the ratio of carbon monoxide to carbon dioxide in the presence of excess carbon. The equilibrium described by the Boudouard reaction favours the formation of carbon monoxide at high temperatures.

$$C(s)+CO_2(g) \rightarrow CO(g)$$
[10]

In addition to the reactions mentioned, due to the complex mineralogy of the ore, other reactions may occur such as the bonding or disassociation of various mineral phases.

Different reductants may be used as carbon source in pyrometallurgical processes. Coke is formed when coal is heated in the absence of oxygen to release volatiles. A description of the different carbon reductants can be found in [5]. The ignition temperature of coke is stated by some sources to be between 450 °C to 600 °C [6] and by others as high as 700 °C [7]. For this paper the ignition temperature of the coke is assumed to be 600 °C. Diesel burners are used to heat the surface of the green sinter to the ignition temperature.

The energy requirement to heat the green sinter from ambient temperature was obtained from FactSage equilibrium modelling and is shown in Figure 3. The equilibrium model uses the principles of minimization of Gibbs free energy to determine the most likely reactions in complex systems. From published data [8], the amount of diesel used to heat Mamatwan ores in the ignition hood is 2.56 kg per ton of product sinter. Assuming a similar value for the Kalagadi Sinter Plant and using a calorific value of 11.83 kW/kg diesel [9] and the determined energy requirement of 0.348 MWh/t green sinter this is sufficient to heat

8% of green sinter to ignition temperature in the ignition hood. This includes the further assumption that the calorific content of the diesel is transferred with 100% efficiency to the green sinter.



Fig. 3. Calculated energy requirement to heat green mamatwan sinter

Reaction 11 describes the combustion of diesel with oxygen when using $C_{12}H_{24}$ as an approximation of the chemical formula for diesel. In reality diesel is a complex mixture of hydrocarbons and modelling all constituents of diesel was seen as outside the scope of this paper.

2.3 Mass and energy balance for diesel burner case study

The material flows and streams used for the mass and energy balances are illustrated in Figure 4.



Fig. 4. Material flows for the Kalagadi Manganese sinter plant mass and energy balance

At the time of writing the exact size of the recycle streams, including the dust recycle and the fines recycle, were unknown and these streams have been neglected in the mass and energy balances.

Energy balances were done for both the ignition hood and the sinter strand and are summarized in Tables 3 and 4. The energy balance for the ignition hood assumes that the calorific content of the diesel combustion pre-heat the top layer of feed to the coke ignition temperature of 600 $^{\circ}$ C.

The mass balance for the ignition hood is based on 10 % excess oxygen on the stoichiometric requirements to combust the diesel completely to carbon dioxide and steam and an air composition consisting of only oxygen and nitrogen.

The ignition hood off-gas consists of the diesel combustion products (12 t/h) combined with the gasses released by the heated green sinter (9 t/h).

The mass balance for the sinter strand assumes 300 % excess oxygen above the stoichiometric requirement to combust all the carbon contained in the green sinter as well as the pre-heated sinter.

Stream	Tempera -ture	Flow rate	Composition	
	° C	t/h	mass %	
Green sinter	25	523	23.1 % CaCO ₃ , 22.2 % MnCO ₃ , 21.8 % Mn ₂ SiO ₄ , 9.9 % MnO; 6.9 % C, 5.3 % Fe ₃ O ₄ , 4.7 % H ₂ O, 6.3 % Other	
Diesel	25	1	Assumed 100 % C ₁₂ H ₂₄	
Air	25	11	76.8 % N ₂ , 23.2 % O ₂	
Off-gas	200	21	45.8 % CO ₂ , 42.5 % N ₂ , 9.0 % H ₂ O, 2.6 % Other	
Pre-heated sinter	600	33	49.7 % MnO, 26.8 % CaMnSiO ₄ , 11.8 % CaCO ₃ , 6.3 % C, 5.5 % Other	
Green sinter	25	481	See above	
Power requirement			10.75 MW	
Power provided by diesel combustion		11.65 MW		

Table 3. Mass and energy balance for ignition hood diesel case study

Stream	Tempera- ture	Flow rate	Composition	
	° C	t/h	mass %	
Green sinter	25	481	See Table 3.	
Pre-heated sinter	600	33	See Table 3.	
Air	25	1235	76.8 % N ₂ , 23.2 % O ₂	
Sinter strand off- gas	200	1405	67.5 % N ₂ , 13.6 % O ₂ , 10.6 % CO ₂ , 7.8 % CO, 0.5 % Other	
Sinter	Sinter 1200 353		57.7 % MnO, 10.9 % Ca ₇ Mg(SiO ₄) ₄ , 14.6 % CaO, 6.7 % FeO, 6.4 % SiO ₂ , 2.9 % Other	
Power requirement			213 MW	
Power provided by coke breeze combustion in 300% excess air		263 MW		

 Table 4. Mass and energy balance over the sinter strand

2.4 Mass and energy balance for hot air from Solar Thermal Plant case study



Fig. 5. Proposed arrangement for including pre-heated sinter feed into the ignition hood.

In this paper we review the possibility of replacing diesel burners with hot air to heat green sinter to the ignition temperature of coke breeze. It has been determined that heating 8% of the green sinter fed to the ignition hood will be sufficient to replace the diesel burners. A modified mass and energy balance can now be done to determine the effect of using hot air instead of diesel burners in the sinter plant.

Stream	Tempera -ture	Flow rate	Composition
	° C	t/h	Mass %
Green sinter	25	523	See Table 3
Hot air	800	64	76.8 % N ₂ , 23.2 % O ₂
Off-gas	200	73	67.1 % N ₂ , 20.3 % O ₂ , 8.7 % CO ₂ , 2.4 % CO, 1.4 % H ₂ O, 0.2 % Other
Pre-heated sinter	600	33	49.7 % MnO, 26.8 % CaMnSiO ₄ , 11.8 % CaCO ₃ , 6.3 % C, 5.5 % Other
Green sinter	25	481	As in Table 3.
Energy requirement from equilibrium model		10.75 MW	
Energy provided by hot air		11.65 WM	

Table 5. Mass and energy balance for ignition hood -

solar thermal plant case study

The results of the mass and energy balance over the ignition hood with hot air replacing the diesel burners are given in Table 5. The ignition hood off-gas consists of the hot air used for preheating (64 t/h) combined with the gasses released by the heated green sinter (9 t/h). The mass and energy balance over the sinter strand remains unchanged given the assumptions detailed.

A sketch of the revised ignition hood set-up can be seen in Figure 5, with the diesel burner still available to serve as back-up if needed. The design of the heat exchanger between the hot air and the green sinter is considered outside the scope of this paper, but the following assumptions are made for this heat transfer unit:

- Heat transfer efficiency of 100% from air to ore. As the same assumption was made for the diesel burners, the comparison holds true as long a heat losses of both the diesel burners and heat exchanger are similar in magnitude.
- The hot air provided by the solar thermal plant enters the heat exchanger at 800 °C and leaves the heat

exchanger together with gasses formed during the preheating of the green sinter at 200 °C to be treated by the stack to recover dust.

• The size of the heat exchanger is such that it can be incorporated into the current sinter plant without major modifications.

3. Sensitivity Analysis

The assumption of 600 °C as the ignition temperature of the coke breeze used in the sinter is crucial to determining the mass and energy balance. Keeping all other assumptions the same, the energy balance was recalculated for different coke breeze ignition temperatures. The results are reported in Figure 6 and illustrate that if a coke breeze ignition temperature would change to 700 °C, the energy requirement to the ignition hood would increase by roughly 40 %. This increase in the energy requirement will in turn lead to an increase in the amount of diesel or hot air needed to heat the green sinter to ignition temperature, affecting the mass balance over the ignition hood as shown in Figure 7, where the total ignition hood off gas flow rates are shown for both case studies, as well as flow rates of the gasses released from the heated sinter only.



Fig. 6. Change in energy requirement for different coke breeze ignition temperatures.

4. Barriers to implementation

The use of solar thermal energy for high temperature process heat applications was previously considered technically difficult due to construction material constraints in the solar receiver. Recent advances in particle receivers [10] have demonstrated that particles can be heated up to 1000 °C in a rotating central receiver. These particles can be used both as heat transfer medium and as thermal storage medium. Producing hot air for high temperature process heat applications such as preheating manganese sinter to ignition temperatures can now be investigated. This concept addresses technical barriers to solar thermal process heat by providing a thermal storage ability to counteract the solar resource variability as well as a source of thermal energy at the required temperature. Other barriers to the implementation of the concept include the high capital cost of a solar thermal plant, the lack of pilot scale demonstration of the concept and the entrenchment of the current technology. The siting of the solar thermal plant is not deemed a significant barrier as the location of the sinter plant is sparsely populated and sufficient areas are available in close proximity to the sinter plant.



Fig. 7. Ignition hood off-gas flow rates for different coke breeze ignition temperatures.

5. Discussion and recommendations

The differences between the mass balances for the diesel burner case study compared to the solar thermal plant providing hot air is in the size and composition of the ignition hood off-gas stream, shown in Table 6.

Using hot air to pre-heat the green sinter increases the off-gas volume from 21 t/h to 73 t/h. The increase in gas volume may lead to higher parasitic energy costs if fans are required to move the air. This should be considered during the design of the modifications required for the integration of hot air into the ignition hood. Using hot air rather than diesel burners reduces the carbon dioxide emissions from the ignition hood by a third. The hot air case study still produces 6 t/h carbon dioxide due to calcination reactions that occur when preheating the green sinter.

Ignition hood off-gas	Diesel burners	Hot air
Total, t/h	21	73
O ₂ , t/h	<1	15
N ₂ , t/h	8	49
CO ₂ , t/h	9	6
Other (CO, H ₂ O), t/h	<4	<4

Table 6. Off-gas flow rate and composition comparison

The size of the modifications needed to incorporate hot air for pre-heating will be dependent on the rate of heat transfer into the green sinter. Although some work has been done on the thermal properties of manganese ores [11], it is unclear how the properties of green sinter differ from those of the manganese ores.

6. Conclusion

Detailed mass and energy balances were constructed for the conventional option of using diesel burners to partially pre-heat green sinter to ignition temperature as well as for the alternative case study of using hot air to achieve the same pre-heating. The mass and energy balance was based on sinter production of 353 t/h, which is 94% of the maximum sinter production rate at the Kalagadi Manganese sinter plant [2]. The mass and energy balance shows that the hot air flow required is within the range of gas volumes already handled at the plant.

Carbon dioxide emissions from the ignition hood can be reduced by one third if hot air is used for pre-heating rather than diesel burners.

A techno-economic study of the proposed solar thermal plant is recommended to address such barriers as perceived high capital costs and entrenchment of the current solution. Demonstration of the production of hot air at 800 °C by a solar thermal plant and heating of green sinter by hot air to ignition temperature will be advantageous in promoting the use of a solar thermal plant as a reliable alternative to diesel burners.

Acknowledgements

This paper is published by permission of Mintek. SEM images and mineral identification were conducted by the Mineralogy Division at Mintek. The authors would like to thank Transalloys Pty. Ltd. for donation of the manganese ore sample used for the illustrative case study.

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