Method to quantify the effect of temperature and rotational speed on the decrepitation of South African manganese ores in a rotary kiln

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Abstract

The lack of knowledge regarding the mineralogical and metallurgical properties of ores is a common problem in the production of ferromanganese alloys. Decrepitation, which is the breakage of solid particles upon heating, is an important quality parameter of manganese ores which has not been adequately studied. This work will study the effect of different parameters on the decrepitation index when the ores are preheated in a rotary kiln. These parameters are the rotational speed, heating rate, temperature, and mineralogical composition. Three South African ores, two from the same mine, will be used for this study. The purpose of the paper is to report on method development.

Keywords: decrepitation, manganese ores, rotary kiln

1. Introduction

Manganese ores are mostly used as raw material to produce manganese ferroalloys. There are several grades of ferromanganese alloys among them are low carbon (LCFeMn), medium carbon (MCFeMn), and high carbon ferromanganese (HCFeMn) [1]. These alloys typically contain 85-90% Mn and 0.75% C, 80-85% Mn and 1.5% C, and 78% Mn and 7.5% C respectively [1]. Of the global consumption of manganese, 92% is directly related to the steel industry, seeing that manganese improves the malleability, toughness and hardness of the steel [2]. The non-ferrous applications of manganese include the production of dry-cell batteries and animal feed. There is a total global reserve of approximately 690 000 tonnes, of which 63% is found in South Africa, Ukraine, Australia, Brazil, and India [3]. A common problem in the production of ferromanganese alloys is the lack of knowledge of the mineralogical and metallurgical properties of manganese ores [4]. Commercially, HCFeMn is produced by carbothermic reduction of manganese ores, primarily in electric submerged arc furnaces (SAFs) [5]. Carbothermic reactions involves the reduction of metal oxides using carbon as a reducing agent. SAFs are generally circular and have three electrodes, each connected to a separate electrical phase [5]. The electrodes are submerged into a mineral bed and the electric current runs through the area below the electrode tips where electrical energy is converted to heat [5].

PREMA is a Horizon 2020 project, funded by the European Union, and aims at demonstrating an innovative suite of technologies, involving utilization of industrial off-gases and solar thermal energy [6]. This is done to reduce energy consumption and CO_2 emissions from manganese production [6]. A pilot-scale campaign, will be conducted at Mintek in 2021 to study the effect of preheating the ore to 600°C in a rotary kiln on submerged arc furnace (SAF) operation, forms part of the test program.

In terms of the rotary kiln operation, one of the unknown parameters is the potential for decrepitation of the manganese ore. Decrepitation is the breakage or disintegration of particles upon heating, resulting in the production of fine particles that cause efficiency losses and reduces the gas permeability of the particle bed in the SAF [2]. Consequently, the process gas will trapped beneath the burden of raw material which may cause an eruption or an explosion [7]. Furthermore, insufficient reduction can occur due to the process gas containing CO being channeled unevenly across the burden.

Currently, a master’s research project looks into the potential for decrepitation of manganese ore during preheating in a rotary kiln. The purpose of the study is to determine if the specific manganese ores considered for the campaign will decrepitate during the pre-heating process. The effects that the particle size, heating rate, kiln rotation speed, temperature, and mineralogy will have on the decrepitation index (DI) of the ore will be investigated. The purpose of the paper is to report on the method development process.

2. Method

The method development consisted of two parts: (1) a review of literature and (2) preliminary test work conducted at a commercial laboratory that quantifies the decrepitation of iron ore.

2.1. Review of literature

2.1.1 Decrepitation of manganese ore

Faria *et al* (2012) studied the effect of mineralogy, moisture content, and porosity of ore on the decrepitation behavior within the context of SAF production of HCFeMn. It was found that all three play a role in the decrepitation of ore.

In their investigation, they studied four different types of ores of which one was from South Africa. 500 g of sample was heated in a muffle furnace at 700°C for 30 minutes. To determine the DI, the sample was screened using a sieve size of 6.3 mm after heating. After screening, the particles that passed the screen was weighed. The equation they used to calculate the DI is presented in
Equation 1.

Equation 1

$$DI = \left({}^{M1}/_{M2}\right) * 100$$

M1 = Mass of particles below 6.3 mm in g
M2 = Total mass of the sample in g

The mineralogy and chemical analysis of the ores in the study is summarized in Table 1 and Table 2.

Table 1: Mineralogy of four types of ores utilized in the study by Faria *et al*.

Ore			**Mineral type**				**DI ($I_{-6.3}$)**
Name	**Country**	**Size [mm]**	**Cryptomalene**	**Bixbyite**	**Pyrolusite**	**Todorokite**	
			$KMnO_8O_{16}$	$(Mn,Fe)_2O_3$	MnO_2	$(Na,Ca,K)_2Mn_6O_{12} \cdot 3a4.5(H_2O)$	
Urucum	Brazil	-19+6.3	>50%	-	<20%	-	6%
Morro da Mina	Brazil	-19+6.3	-	-	-	-	1%
Azul	Brazil	-19+6.3	>50%	-	-	<20%	6%
Wessel	South Africa	-19+6.3	-	<20%	-	-	12%

Table 2: chemical analysis of four ore types utilized in the study by Faria *et al*.

Sample	**Mn %**	**Fe %**	**Al_2O_3 %**	**CaO %**	**MgO %**	**SiO_2 %**	**P %**	**Total**
Azul	46.96	4.12	6.11	0.09	0.12	3.99	0.097	61.59
Morro da mina	24.48	2.89	5.42	2.87	2.23	23.02	0.076	60.99
Urucum	32.58	6.92	0.78	0.07	0.05	2.11	0.109	42.62
Wessels	40.16	8.08	0.4	7.45	2.05	5.51	0.019	63.67

The study claims that manganese oxides decrepitates mainly due to the decomposition of the cryptomelane and pyrolusite minerals during heating [2]. Manganese oxides (MnO_2) experience phase transformation at 700°C causing volumetric change [2]. The transformation of MnO_2 to Mn_2O_3, began at close to 700°C for Azul and Urucum samples. This led to a volumetric expansion that contributed to the decrepitation of Azul and Urucum ore.

This volume change yields anisotropy that induces stress in specific regions of the particle, which leads to the formation of cracks [2]. Urucum ore has a higher concentration of pyrolusite, which undergoes a considerable reduction in volume when it transforms into bixbyite, and this could cause intense decrepitation [2]. Bixbyite and pyrolusite have a crystal structure of isometric and tetragonal respectively.

Another factor affecting decrepitation, was the removal of structural water from the hydrated phases during the pretreatment [2]. Heating the ore gradually eliminated the physical shock caused by the sudden release of moisture and in turn reduces the decrepitation intensity. When water is heated, its vapor pressure will gradually rise until it reaches the pressure in the surrounding atmosphere, then it can start to boil and evaporate eventually. The vapor pressure from the water molecules trapped in ore pores could be enough to rupture particles [2]. The study by Faria *et al* revealed that decrepitation intensity was considerably increased by moisture for Azul, Urucum and Wessels ores.

The ore with a bigger diameter and volume of micro pores have smaller DIs compared to the ore with a smaller diameter and volume [2]. Bigger volume pores can promote a vapor pressure relief inside the pores of the ore particles, this reduces stress on the lump ore and in turn decreases decrepitation intensity [2]. The pressure build- up causes more stress in closed pores than in open pores, therefore ores with closed pores are more susceptible to decrepitation compared to the ores with open pores [5].

2.1.2. Decrepitation of iron ore

Decrepitation of iron ore in blast furnaces is such an extensive field of study that a standardized methods exists to characterize the ore. One such an example is the ISO standard 8173. The steps followed can be summarized as follows:

- The sample with a size range of -25 +20 mm is dried in an oven at 105°C over night.
- 500g of the sample is weighed.
- The muffle furnace is switched on to heat up gradually until a desired temperature of 700°C is reached.
- The 500g sample is then fed into the rest portion holder.
- Once the furnace reached the desired temperature, the test portion holder is then placed into the muffle furnace.
- The test portion is left the furnace for duration of 30 minutes, and thereafter the sample is removed and allowed to cool down.
- After cooling the sample is screened with a sieve size of 6.3 mm.
- And the DI is determined using Equation 1.

2.2. Preliminary Investigation

For the project presented here, a preliminary investigation was done at Anglo American Research and Development laboratories on two types of South African manganese ore, Ore #A and Ore #B. The purpose of the preliminary investigation was to determine if there was potential for a research project. The Anglo American Research and Development laboratories were chosen because they conduct extensive decrepitation test work on iron ores, and are well familiar with the procedure. Ore #A and Ore #B were chosen because they were readily available at Mintek from previous test work. The chemical composition of the ores are presented in Table 3. Both ores decrepitated to some extent during heating and there was also a difference in the extent to which they decrepitated, as indicated by their respective DIs.

Table 3: Typical composition of two types of manganese-bearing ores sourced for the campaign (mass %)

Raw Material	**Mn**	**Fe**	**Al_2O_3**	**SiO_2**	**CaO**	**MgO**	**H_2O**	**P**	**S**	**Total**
Ore #A	36.5	5.5	0.2	5.1	13.6	4.1	0.8	0.02	0.01	65.83
Ore #B	44.8	10.7	0.3	5.4	7.4	1.5	0.8	0.04	0.18	71.12

The method from ISO standard 8371 DI of iron ores was applied in the preliminary investigation and the results were presented below. The DI was calculated using Equation 1.

Table 4: Preliminary investigation results

Ore type	Test no	M1(g)	M2(g)	DI %	Average DI (%)
Ore #A	1	482.4	61.7	12.8	13.0
	2	480	63.1	13.1	
Ore #B	1	480.7	47.2	9.8	10.8
	2	479	56.1	11.7	

3. Results and discussion

Based on the results of the literature review and the preliminary investigation, it was decided to continue with the project using the manganese ores that will be used during the campaign. The manganese ores were sourced from the Kalahari manganese field (KMF), located in the Northern Cape province of South Africa. Three types of ores were considered: Ore #C and Ore #c were sourced from the same mine and Ore #D from a different mine. The size range studied was 75 mm to 6 mm.

3.1. Research questions

In order to achieve the objective of the study, the research question were tailored as shown below.

- How does the size distribution of particles affect the DI of manganese ore?
- How does the temperature affect the DI of manganese ore?
- How does the heating rate affect the DI of manganese ore?
- How does the rotation speed of the rotatory kiln affect the DI of manganese ore?
- How does the mineralogy of the ore affect the DI of manganese ore?

3.2. Method

In order to obtain answers to these questions, a laboratory-based method was developed at MINTEK. At the heart of the method lies the tumbling and decrepitation tests. However, the method will include material preparation and characterization i.e. Particle size distribution, bulk chemistry, and bulk and specific phase chemistry.

3.2.1. Decrepitation test

The decrepitation test will adopt a method from ISO 8371 (DI of iron ores).

- 1 kg of the sample will be weighed using a balance.
- The sample will then be fed into the rotary kiln.
- The kiln power and rotation speed will then be switched on to control the desired parameters (heat rate and rotational speed) stated in the experimental design matrix for each run.
- Once the desired temperature is reached, the sample will be kept at the temperature for 30 minutes.
- The kiln will then be switched off and the sample will allowed to cool down inside the kiln.
- After cooling the sample will be screened to determine the fraction below the lower limit of a particular size range, 6 mm screen for +6 -20 mm, 20 mm screen for +20 -40 mm and 40 mm screen for +40 -75 mm.
- The rotating tube will be cleaned by blowing it with compressed air after every run to avoid contamination.
- The control panel is equipped with a rotational speed controller and it will be validated by observing the rotation and count the revolution per minute.
- The thermocouples will be calibrated prior to the experiment.

The experimental set-up is illustrated in Figure 1.

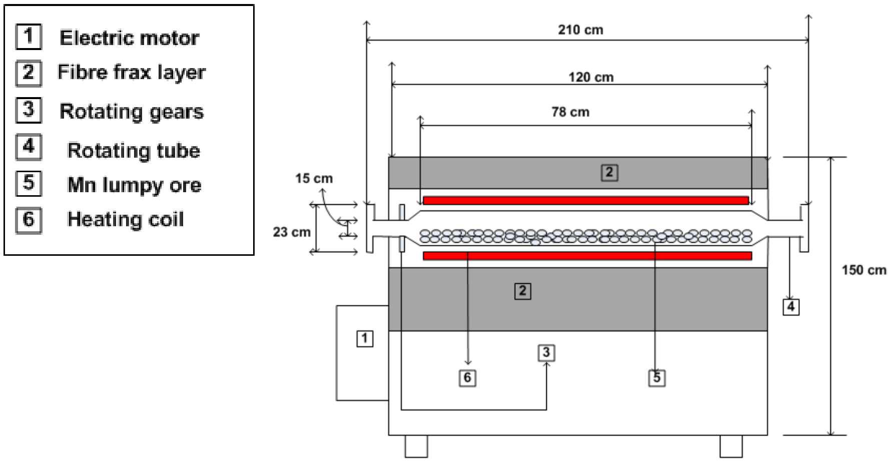

Figure 1: Experimental set-up of a rotatory kiln.

3.2.2. Tumbling test

- A tumbling drum will be used for the test. The drum has a capacity of 5 kg and the rotational speed can be varied between 5 and 30 rpm.
- The different size fractions for each of the three sample types will be split using a rotary splitter to obtain representative samples that will be used for the tumbling tests.
- One kilogram will be fed into the drum which will be switched on, starting with rotational speed of 5 rpm for 30 minutes.
- The step above will be repeated with the rotational speed of 10 rpm and again with the speed of 20 rpm.
- After the tumbling test, the sample will then be screened to obtain the percentage of particles reporting below the lower limit of a particular size fraction that was used for that test and also to determine if there has been changes in the particle size distribution of the sample.

Figure 2: A picture of a tumbling drum that will be used for the test

3.2.3. Overall procedure

The overall procedure is outlined in Figure 3.

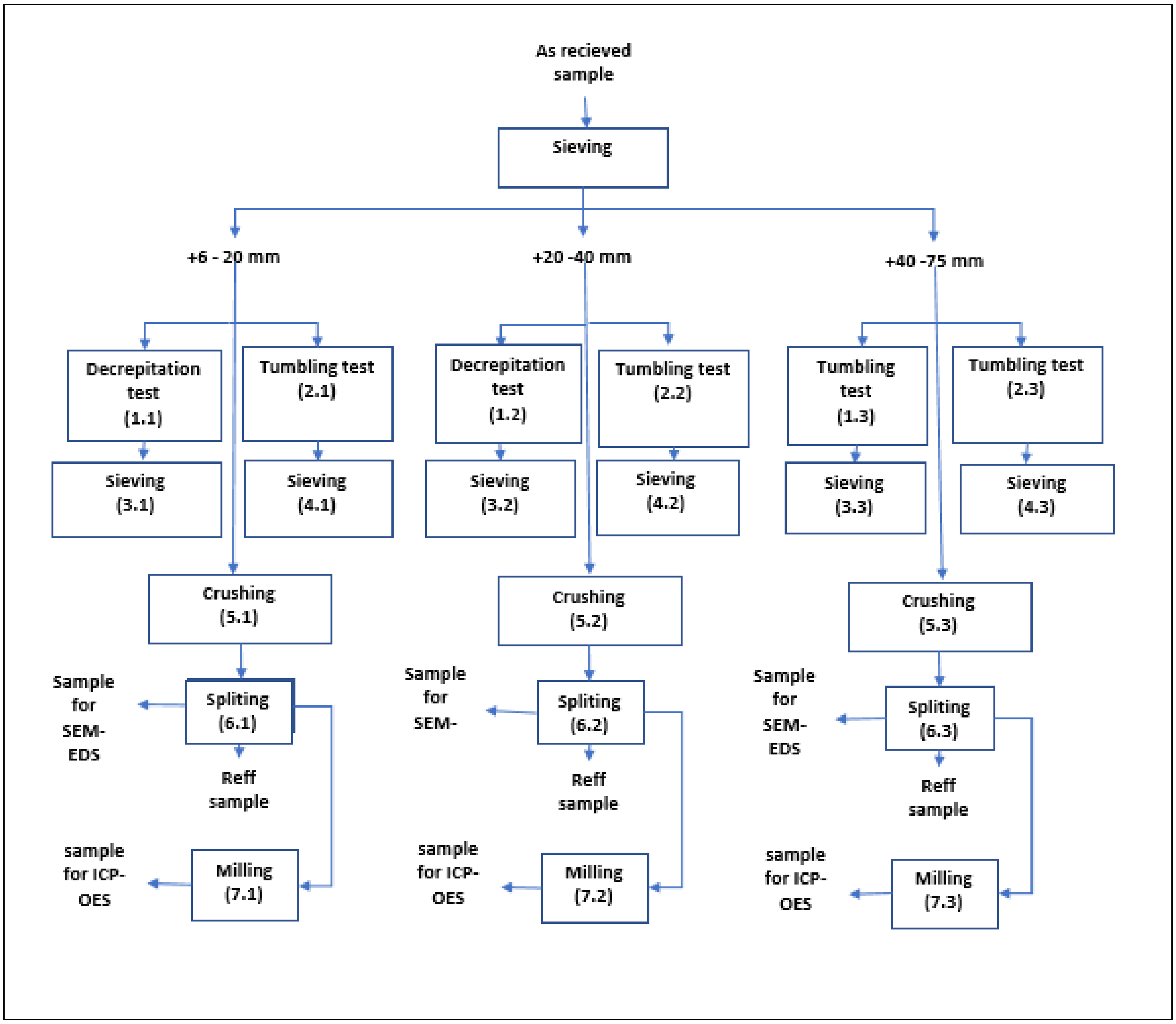

Figure 3: Methodology flowsheet

- 250 kg of each sample is sieved to the size fraction of +6 -20 mm, +20 -40 mm and +40 -75 mm using screens.
- The sample will be split and the representative sample will be obtained using a rotary splitter in order to obtain samples for the decrepitation test, tumbling test and for crushing as shown by 1.1, 2.1, and 5.1 in Figure 3.
- After the decrepitation and tumbling tests the samples will be screened as shown by 3.1 and 4.1 in Figure 3.
- The crushed sample will be split using a rotary splitter (6.1) to obtain a sample to be milled for bulk chemical and phase chemical analyses (7.1), to stores as reference sample, and for a sample to be analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS).
- The milled sample will then be used for bulk analysis inductively coupled plasma optical emission spectrometry (ICP-OES), x-ray fluorescence (XRF), and qualitative x-ray diffraction (QXRD).
- Contamination will be prevented by thorough cleaning of the equipment before it is used for another sample.

3.3. Method comparison

The method used in the preliminary investigation has minor similarities to the decrepitation test method developed at Mintek. The preliminary test method only investigates if manganese ore decrepitates when heated to 700°C for 30 minutes, whereas the method developed at Mintek will also investigate the effect of experiment temperature, heating rate and the rotational speed of the rotary kiln on the DI. From literature it was discovered that another factor affecting DI of manganese ore is the removal of structural water from hydrated phases [2]. Heating the material to temperatures higher than 700°C will remove more structural water from hydrated phases, which will increase the DI of the sample. Using a higher heating rate will cause the removal of moisture to happen at higher rate, which will bring the issue of thermal shock into play. This will be even more intense for the moisture that is trapped in the closed pores of the sample. When the moisture experience a sudden change in temperature the vapor pressure of the moisture will also increase suddenly, sometimes the pressure increase may be enough to rapture the walls of the pore and break the sample into smaller particles sizes. This will increase the DI of the sample.

Heat decomposition cryptomelane and pyrolusite to Mn_2O_3 ,according to Faria this may contribute to the decrepitation phenomenon [7]. This is because according to Faria cryptomelane and pyrolusite have their volumes respectively 5.4 % and 0.6 % higher than Mn_2O_3 [7]. This means that the decomposition will cause a reduction in volume for these phases, and this induces stress in specific regions of the particles leading to formation of cracks. The formation cracks can lead to particle disintegration especially when the sample is being rotated. Therefore if the ores sourced from the KMF have cryptomelane and pyrolusite as their mineral type, it means that the ore that will be used for our test work have a potential to have elevated DIs.

The rotation makes the sample more susceptible to disintegration which will be regarded as decrepitation in this test work, because the mechanical breakage of particles come into play as result of collision between particles. The collision which is caused by the rotation movement of the kiln. The mechanical breakage particles will depend on the strength of the sample and the rotary speed of the kiln. Increasing the rotation speed of the kiln will results in the particles of the sample colliding more with more force and more frequently this can increase the disintegration index (dI) of the sample, The dI is calculated the same way as the DI. When the particles collide more frequently with more force they more vulnerable to mechanical breakage. For the decrepitation test both the disintegration due to thermal treatment and the rotating of the sample will be the main factors having an impact on the DI unlike during the preliminary investigation where the mechanical breakage was absent. The material that is not strong enough in terms of strength will be more susceptible to disintegration because they will break easily when they collide with each other.

4. Conclusions

After reviewing the literature and conducting preliminary investigation based on a standard test for iron ore, a method has been developed at Mintek to determine the potential for decrepitation of manganese ore in a rotary kiln. Three types of ores will be split into three size fractions each, and the DI determined based on the experimental plan in Table 5.

Table 5: Experimental plan

Particle size range[mm]	Rotational speed (rpm)	Heating rate (°C/min)	Temperature (°C/min)
+6-20	10	2	600
+6-20	10	2	700
+6-20	10	2	800
+6-20	10	1.5	700
+6-20	10	2	700
+6-20	10	2.5	700
+6-20	5	2	700
+6-20	20	2	700
+20-40	10	2	700
+40-75	10	2	700

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