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Investigation of the decrepitation phenomenon of polymorphic materials: A theoretical and experimental study

A. Biswas *, Pradipta Kr. Das, Verrender Singh

Research and Development Division, Tata Steel Ltd., Jamshedpur 831001, India

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ABSTRACT

Fine generation during thermal processing (basically roasting) of oxide materials is an unattained issue due to lack of knowledge on the mechanism of particle breakage. An important quality parameter to quantify fine generation for lumpy oxide materials is decrepitation. In this research article, primary reasons for decrepitation of polyformic materials like manganese oxides are addressed by characterization and experiments followed by a theoretical model for particle breakage. Herein, the physical, chemical and mineralogical characterizations of low grade manganese ore lumps from Indian mines are presented. Particle breakage has been correlated with the heat profile in the porous bed for three different packing geometries by variation of parameters: heating rate, time, and temperature. Optimization analysis was performed using response surface methodology to estimate the effect of interaction parameters on fine generation and to estimate the optimum parameter setting with a maximum of 5% fine generation. Secondly, a mathematical model was developed to simulate the heat transfer behavior in a single particle of 6 mm diameter with the objective of moisture evaporation and to estimate the heat distribution in porous bed geometries. Finally, a thermo-mechanical stress model has been developed to support the mechanism of particle breakage. Heat transfer analysis shows that cylindrical bed geometry has better heat distribution due to less bed permeability and larger contact area between the particles. The optimized condition for roasting of low grade manganese ores to achieve transformation of manganese dioxide & up to 5% decrepitation is as follows: temperature:700 °C, heating rate: 10 °C/min, and roasting time: 70 min.

1. Introduction

Decrepitation of lumpy ore particles has been a major challenge for processing engineers and plant operators in view of operating any pyrometallurgical processes. Many materials experience decrepitation during the thermal treatment process and metallurgical ore lumps are no exception, which leads to production of fines inside the furnace [1]. Secondly, due to this in-situ fine generation overall productivity gets affected and hence the process economics. During the thermal treatment of these ores especially during roasting, in-situ generated fines form low melting slag by combining with coal ash and subsequently form accretion over furnace walls. Accretion acts as extra resistance for heat flow and even reduces effective furnace volume. Overall decrepitation leads to lower productivity of these furnaces [2]. For some cases, in-situ fine generation is an advantage like during sintering, which leads to form better slag bonds between the particles. This property adds to better sinter quality and higher productivity. Fine generation mainly depends on the property of the material especially its inherent crystal geometry and it also depends on process conditions like temperature, pressure, gas profile as well as furnace geometry (like cylindrical shape for ferro alloy manufacturing or box type compartment for straight grate sintering furnace). Details about the process parameters and its effect on the decrepitation index are provided in Table 1. Decrepitation depends mostly on process parameters and there have been no previous studies which focused on its importance for polymorphic materials like manganese oxides. Thus, in-situ fine generation becomes a major challenge for the metallurgical and mineral processing industry. So, there is a need to understand how the process parameters affect the heat distribution during the thermal treatment of these polymorphic ores.

Apart from process characteristics, not much fundamental information on the mechanism of decrepitation is available to the research community. Baudrimont [4] has provided an insight into the thermal behavior of many inorganic minerals as well as salts and broadly classified them according to their fine generation behavior as hydrated and un-hydrated minerals. McCauley and Johnson [5] studied the decrepitation behavior of dolomite using thermal treatment. Results concluded that decrepitation behavior is mostly affected by particle size and this fact is supported by characterization and thermal treatments. In their study they have shown that due to the decomposition of carbonates, carbon dioxide is released which causes fine generation. Similar work has been carried out by Galai et al. [6] on providing the growth mechanism of MgO and $CaCO_3$ during dolomite thermal

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* Corresponding author.
E-mail address: arijit.biswas@tatasteel.com (A. Biswas).

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Table 1
Process conditions and its effect on decrepitation index for different processes.

Process	Mode of operation	Operating conditions	Furnace type	Effect on DI	Ref
Ferro alloy making	SAF, DC Arc	$T = 25–1700$ °C[a], $P = 1$ atm	Cylindrical	In-situ generated fines hampers bed permeability due to crust formation	[1]
Sintering	Belt sintering, tunnel kiln	$T = 25–1200$ °C[a] $P = 1$ atm	Rectangular	Fines generated have higher surface area which leads to formation of lower melting slag and bridges two bigger particles.	[1]
Partial reduction for hydrometallurgical applications	Shaft furnace, rotary kiln	$T = 25–800$ °C	Cylindrical	Generated fines lead to larger surface area; thus result in better reducibility and energy saving on grinding before leaching.	[3]

[a] DI occurs between 25 and 800 °C.

decomposition. Kinetic analysis of the thermal decomposition of dolomite has been established by performing thermal decomposition experiments using TGA–DTA. The analysis shows that the rate controlling step for the growth of MgO and hence fine generation is due to the diffusion of magnesium through the MgO phase. Decrepitation of carbonate minerals has been carried out extensively by various researchers and analysis concluded that particle size holds the major role in controlling fine generation [7–9]. Other than carbonates, silicate based minerals also have a tendency of generating fines during the thermal release of water [10]. Quartz when heated tends to release adsorbed water at the temperature range of 150–200 °C followed by a sudden release of water at the temperature of 550 °C and above. This released water is detected using mass spectral analysis,quantifying the mechanism of water inclusion in quartz minerals. Similar work in this area has been carried out for granite rocks as well [11]. Oxide minerals of transition metals show a multiple oxidation state that leads to phase transformation and hence fine generation. Structural deterioration of iron ore particles during thermal treatment has been analyzed for two minerals of iron: goethite and hematite. The authors tried to measure the heat flow behavior inside the particles and subsequently measured the rate of change in the particle diameter using dilatometry experiments. Expansion data were related to evolve gas analysis to conclude that due to water evolution with heating, particle breakage happens and predominately observed with goethite due to the presence of structural water [12]. Aotsuka et al. [13] have established test repeatability analysis for decrepitation of iron ore samples by following ISO 8371 and suggested changes in the standard DI procedure. Their work concentrated on the effect of holder geometry, heating profile and heating temperature on fine generation behavior of iron ores. Faria et al. [14] have studied the fine generation behavior of high grade manganese ores (Mn > 45%) collected from Brazilian mines and they studied the effect of mineralogy as well as drying behavior on the decrepitation index.

Though a lot of work has been carried out by various researchers in order to establish the conditions and reasons behind fine generation, there still remains some ambiguity on the exact mechanism. Analyses establish that decrepitation occurs due to evaporation and release of moisture from the crystal matrix, leading to generation of cracks and eventually particle breakage. However, it has also been shown that in dried manganese ores decrepitation does happen, which puts ambiguity on the partial theory of fine generation [4,14]. Decrepitation in materialsalso happens due to volumetric phase transformation and it depends on how heat transport happens in particles. Due to these structural changes an uneven volumetric stress is experienced and thus leads to expansion of the crystal matrix [10]. Such internal stresses eventually produce fractures and in turn fragmentation of the crystal matrix. Decrepitation is a very complicated phenomenon as it involves many physics like coupled heat and mass transport followed by structural mechanics, and also depends on the mineralogy of the material. Polyformic materials like quartz and manganese oxides have a different heat transfer behavior than carbonates which inherently depends on phases present. An in-depth analysis of decrepitation is incomplete, and secondly there lies a need to utilize this information in designing equipment for these kinds of materials.

Thus, the objective of this work is two-fold: a) to find optimized parameters for roasting of low grade manganese ores like bed geometry, heating profile, and size distribution of ores or compacts [3,15,16], and b) to find a theoretical heat and mass transfer model to investigate particle cracking. In order to understand the decrepitation behavior of metallurgical ores, a low grade manganese oxide bearing ore from Indian mines has been selected as the material of the study. Finally, the data obtained are linked to find the actual reason for fine generation in manganese oxides.

2. Experimental & model equations

Phase transformation in all variants of polymorphic oxides like manganese oxide ores (as shown in Fig. 1) depends on heat transport inside the particle. Heat transfers affect the interfacial energy for phase transformation and hence affect the overall kinetics. The experiments are designed according to ISO 8371 with additional parameters: heating rate and geometry of the holder. Experiments have been performed for three different bed shapes by varying the holder geometry which results in different bed permeabilities. To validate the test results and establish the repeatability of experimental data, relative standard deviation (hereinafter referred to as "RSD") was used [13]. RSD indicates the standard deviation of measurements divided by their average value expressed as a percent. In other words, RSD represents relative variation in measurement.

$$\mathrm{RSD}\,(\%) = \frac{\mathrm{SD}}{\overline{\mathrm{X}}} * 100 \tag{1}$$

2.1. Materials & sample characterization

A manganese ore with a Mn:Fe ratio of approximately 1 has been chosen as the test material and this material is classified as a low

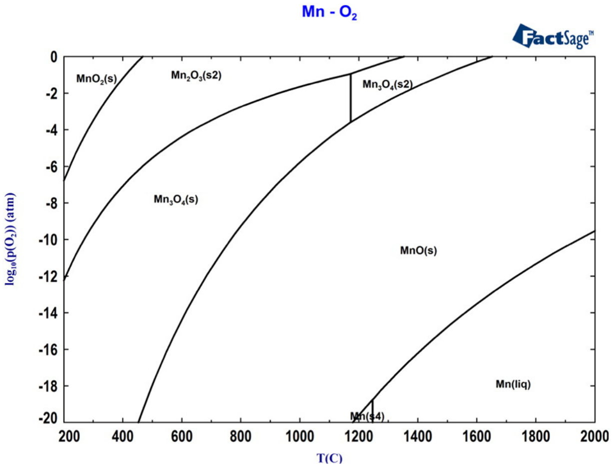

Fig. 1. Predominance area diagram of Mn–O system.