

THE THERMAL DIFFUSIVITY OF RAW MATERIALS FOR FERROMANGANESE PRODUCTION

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ABSTRACT

The thermal diffusivity of five manganese ores and two quartz was tested by applying the laser-flash method. The measurements show that the thermal diffusivity of manganese ore is strongly influenced by three factors: temperature, mineralogy and porosity. The diffusivity in all ores decrease with temperature. In case of MnO₂ rich ores the thermal conductivity is relatively constant from room temperature up to 600°C. Above this temperature the diffusivity decreases rapidly. The diffusivity of Mn₂O₃ rich ores decrease gradually with temperature.

Simulation of temperature distribution inside the particles and clusters were performed. Simulations are based on obtained diffusivity values for the manganese ores. By changing radius of particles/clusters it is possible to find optimal size of the particle/cluster to prevent too big temperature gradients inside the material. Temperature distribution inside the particles/clusters is strongly dependent on its thermal diffusivity, particle radius and temperature gradient between center of sample and environment (gasses).

KEYWORDS: thermal diffusivity, flash method, porosity, manganese ore.

1. INTRODUCTION

Manganese ferroalloys manufacturing involves a combination of quality raw materials and energy source to produce high-quality products with low energy consumption. The thermal diffusivity α of manganese raw materials like ores, sinters, and briquettes are one of many factors that determine the amount of energy needed for processing. With increasing thermal diffusivity, the CO reactivity increases and hence, the energy consumption per ton of metal produced will decrease.

The thermal properties of manganese ores, including the thermal diffusivity, are not widely described in the literature and not sufficient amount of research is done in this field. Furthermore, the knowledge of thermal diffusivity values allows calculating the thermal conductivity of ores, while the specific heat and bulk density of material is identified. The motivation for this research work is the possibility to explore and supply new information about the thermal properties of manganese ores and how that can affect the process where continuous heat exchange between hot gases and/among solids materials occurs.

The thermal diffusivity of ore agglomerates was the subject of a study for the iron industry [1 - 4]. As stepwise reduction of iron ores, which takes place inside the blast furnace, is comparable to manganese oxides behaviour during the smelting process. Diffusivity of iron oxides tends to decrease with temperature. The porosity and phase changes inside the ore are parameters which mostly affect the iron ore diffusivity. Furthermore factors like: average pore size and pore size distribution will influence on the heat transfer inside the material [5]. Akiyama [6] showed that also increased combined water in the pellets decreases its diffusivity values.

2. EXPERIMENTAL

2.1. Thermal diffusivity and porosity studies

In 1961 Parker [7] published the paper introducing the flash method as a technique used for measurement of thermo-physical properties of solid materials. Due to the accuracy and the reliability of the results and the fast measurement time, this method became the most popular, worldwide. Since the introduction of the method by Parker many developments and significant improvements have been done to the non-contact, non-destructive testing technique. The LFA 457 MicroFlash made by NETZSCH is one of the latest systems made for measurement of the thermal diffusivity of materials [8]. Schematic design of the LFA 457 MicroFlash is presented in figure 1. The main idea of the technique is relatively simple. The front face of a small, usually disc shape sample is heated by a short energy pulse, sent from the laser or a flash lamp. An infrared detector (ID) measures the temperature rise on the opposite (rear) surface of the sample versus time.

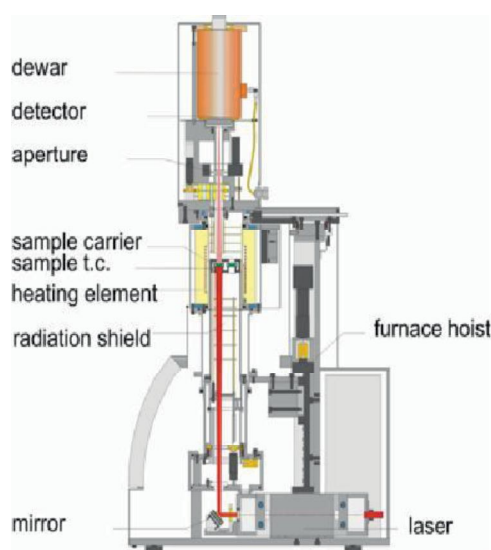


Figure 1: LFA 457 MicroFlash schema [8]

The diffusivity α [m^2/s] is usually calculated from the relation:

$$\alpha = \frac{0.1388L^2}{t_{1/2}} \quad (1)$$

Where L is the sample thickness [m] and $t_{1/2}$ [s] (often called “half time”) which is the time needed for the rear surface of sample to reach half of the maximum temperature rise. The heating rate that has been used in all experiments was 20 K/min. First measurement was taken at room temperature. Then the samples were tested every 100°C, starting from 100°C. The final temperature was 1000°C. At relevant temperature, three measurements were taken. The interval between the shots was set up for minimum 3 min. However, next measurements could not be done until the temperature of sample achieve $\pm 1^\circ\text{C}$ of initial temperature. The average time of one test from room temperature to 1000°C took 7 hours.

Bulk thermal diffusivity of two ores was calculated based on the bulk thermal conductivity, bulk density and specific heat of materials [9].

In order to check the influence of porosity on diffusivity values the porosity tests were performed according to ISO 5017. Ores were heated up to 200, 400, 400, 600, 800 and 1000°C in nitrogen atmosphere with heating rate 20 K/min. For all manganese ores the porosity was checked for three samples. Samples were used only once for one individual temperature.

2.2. Materials and sample preparation

Manganese ores investigated in this research are commonly applied for productions of high carbon ferromanganese and silicomanganese alloys. Additionally, thermal diffusivity of two quartz was tested. Hydrothermal quartz (called HP) and pegmatitic quartz (D) are used for metallurgical grade silicon production. Chemical composition of manganese ores are presented in table 1. Chemical analyzes of quartz samples are presented in table 2. Gabonese and Groote Eylandt ores are two MnO₂ rich materials used in this work. Manganese oxides in Assmang, Mamatwan and Wessels ore occurs mostly as Mn₂O₃.

Table 1: Chemical composition of raw materials mass % (XRF analyses)

Material compound	Gabonese	Assmang	Mamatwan	Wessels	Groote Eylandt
Mn tot	49	46.5	41.2	51.6	48.5
Fe tot	2.3	9.8	5.2	9.2	1.5
SiO ₂	5.9	6.8	4.5	6.8	10.8
Al ₂ O ₃	6.4	0.3	0.3	0.3	3.4
CaO	0.14	6.8	11.6	4.4	0.08
MgO	0.01	0.94	2.7	0.39	<0.05
TiO ₂	0.14	0.01	0.01	0.01	0.01
P	0.1	0.03	0.03	0.04	0.07
S	0.01	0.05	<0.01	0.06	<0.01
K ₂ O	1.13	0.02	0.28	0.01	1.7
BaO	0.17	0.16	0.03	0.25	0.84

Table 2: Chemical analyzes of quartz samples [9]

Element	Quartz D	Quartz HP
Al	0,169	0,36
Ca	0,05	0,06
Fe	0,024	<0,01
Ti	0,002	<0,01
Co	0,0001	<0,01
Mn	0,004	<0,01
Cu	0,0002	0,02
K	0,017	0,01
Na	0,002	<0,01

Groote Eylandt ore is mined in Australia. Wessels, Assmang and Mamatwan ore deposits are located in South Africa. Gabonese ore as a name suggests is extracted in Gabon. Assmang ore contains high amount of carbonatic minerals, and has high basicity. Mamatwan ore is rich in dolomite, carbonates and calcite. Braunite is the most common manganese rich mineral in

Mamatwan ore. All investigated ores are inhomogeneous, which is visible with the naked eye in the figures 2. This means that every measurement is an apparent value averaged over the sample. To obtain the desired sample diameter used in this study (12.7 mm) in LFA 457, cylindrical cores were drilled out from the ore lumps. Then the core was cut in 2 mm slices and gently polished in order to achieve a smooth surface.

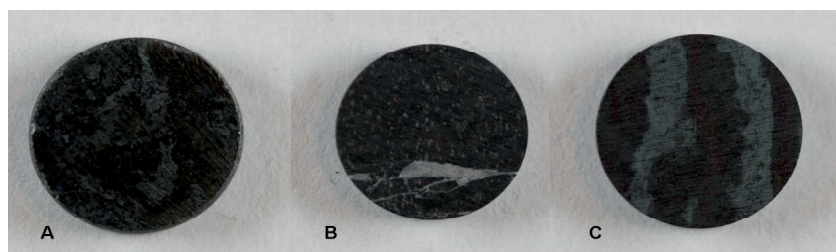


Figure 2: 12.7 mm samples of Groote Eylandt ore (A), Mamatwan ore (B) and Wessels ore (C)

3. RESULTS AND DISCUSSION

Figure 3 presents the comparison of thermal diffusivity of materials used in this research work. In addition the literature data are plotted. Due to technical problems Wessels ore was tested only up to 300°C.

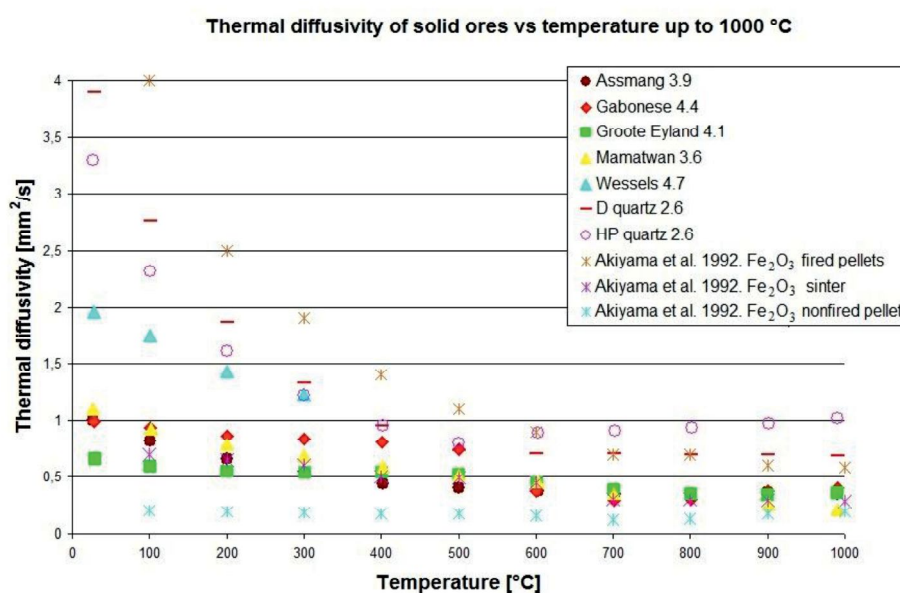


Figure 3: Comparison of thermal diffusivity of ores. Characters located in the legend, placed next to the name of sample, indicate sample density in g/cm³

Quartzes have the highest diffusivity in all temperature range among tested materials. The thermal diffusivity in both decreases up to temperature where phase change from quartz α to β takes place at 573°C [10]. From this point quartz tends to keep constant diffusivity value 0.75 [mm²/s], while HP quartz shows a slowly increases diffusivity. Among manganese ores, Wessels can be characterized by the highest thermal diffusivity at lower temperatures. Unfortunately problems with the samples breakages did not allow completing the measurement in all temperatures. Groote Eylandt ore has the lowest thermal diffusivity at lower temperatures, while the Mamatwan reaches

the lowest values in the high temperatures, between 900 and 1000°C. What is worth to underline is the fact that the all manganese ores reach the same thermal diffusivity above 600°C.

Generally the diffusivity of manganese ores is reduced with increased porosity. Figure 3 indicate that the materials with the low porosity (quartzes and Wessels ore) represent the highest diffusivity. Similar proposal was suggest by Akiyama [6]. During his study on iron sinter, fired and nonfired pellets and Hot Isostatic Pressing (HIP) powder compacts it was found that the porosity of samples was the main impact on diffusivity.

Data presented by Akiyama shows that the prior heat treatment (sinter and fired pellets) has a strong effect on diffusivity due changing structure during heating. They reach similar α as solid manganese ores. Iron sinters tested by Akiyama have high diffusivity probably due to better contact between particles, which was partly melted. Change of oxygen content in the sample should be considered, however this factor was not discussed by the authors.

Figure 4 shows that the porous Gabonese ore (20 % at room temperature) has a higher diffusivity than two less porous ores Assmang (3 % at room temperature) and Groote Eylandt ore (5 % at room temperature). It occurs from room temperature up to 600°C, where Gabonese ore levels values to the range of Assmang ore. While diffusivity values of all ores reach similar level 0.4 [mm²/s] at 600°C, porosity of samples as presented in figure 4, still vary significantly. This example shows that Akiyama suggestion can be valid for material with exact the same chemical and mineral composition.

However in case of manganese ores, which may have comparable chemical composition but differ in mineralogy, porosity do not affect strongly the thermal diffusivity. For different kinds of ore; MnO₂ rich (Gabonese and Groote Eylandt) and Mn₂O₃ rich (Assmang, Mamatwan, Wessels) two following dependency can be suggested:

1) Thermal diffusivity of MnO₂ ores up to phase transition temperature (500-600°C) seems to be constant, despite of temperature and porosity changes. Above transition temperature where MnO₂→Mn₂O₃ (2) diffusivity values change significantly.

2) The thermal diffusivity of Mn₂O₃ rich ores seems to be changing (decreasing) especially at lower temperatures where constant porosity was found. The main parameters which determine the decreasing α values in Mn₂O₃ rich ores is the temperature.

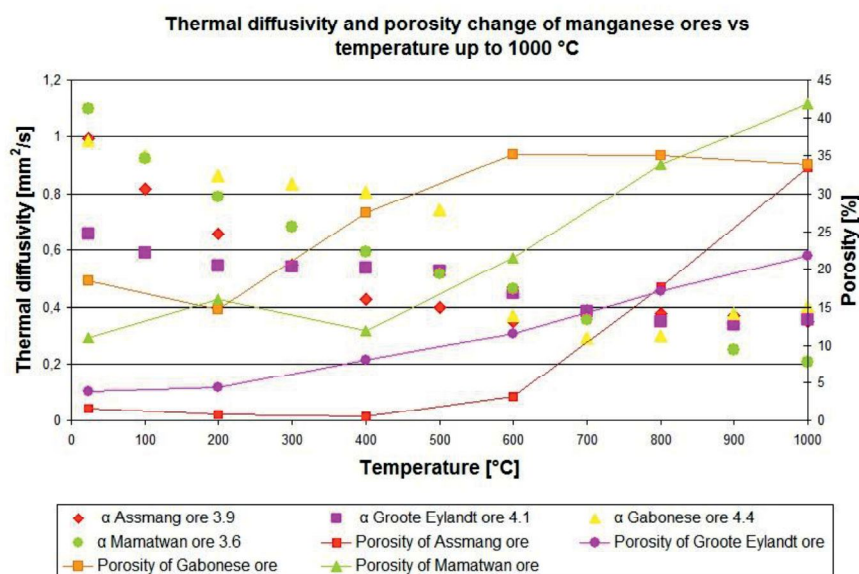


Figure 4: Relation between thermal diffusivity and porosity vs temperature

Figure 5 shows the bulk thermal diffusivity of two manganese ores vs the temperature. Diffusivity of Gabonese ore with fraction less than 1mm decreases values, while diffusivity of Gabonese ore with particle size 4-8 mm tends to increase together with temperature rise. Similar behavior is shown for Assmang ore (4-8 mm fraction) which increase the diffusivity together with temperature. Based on the mass of used samples and its density, the void fraction for each experiment was calculated. Assmang ore 4-8 mm, Gabonese ore 4-8 mm and Gabonese less than 1mm have void fraction equal to 41%, 62% and 68% respectively. Data presented in the figure 5 correlate to the change of void fraction. The lowest bulk thermal diffusivity value represents the test with the highest void fraction. Bulk thermal diffusivity is affected by particle to particle contact, which determines the heat transfer through the bulk. In test where fine particles were used number of particles is higher than in test with the coarser grains. Hence, the thermal diffusivity will be hindered by the higher particle to particle contact.

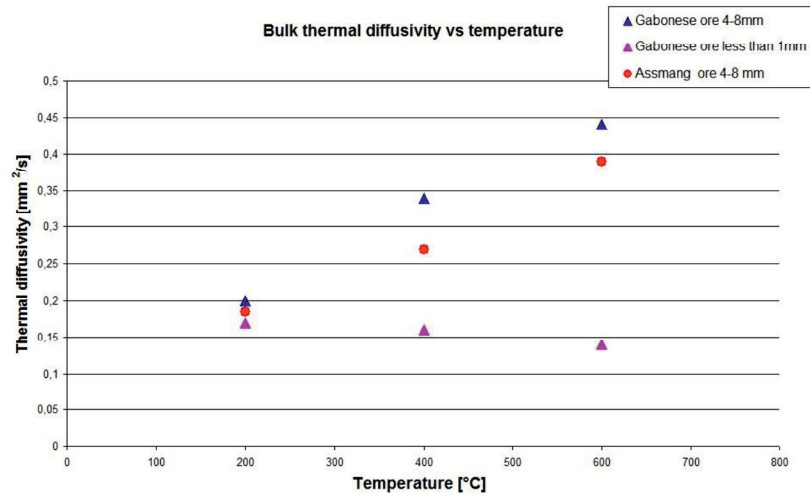


Figure 5: Bulk thermal diffusivity

4. TEMPERATURE DISTRIBUTION CALCULATIONS

Inside the submerge arc furnace (SAF) there are two opposite motions. The first one is downward movement of the burden, and the opposite one is gas flow from the bottom to the top. When the raw materials descend through the pre-reduction zone they become preheated by the ascending CO gas from the coke bed zone. Based on the measured thermal diffusivity for manganese ores and quartzes, simulation of the temperature distribution inside a sphere shaped particle was performed. Calculations are done for single particles and also for *bulk* material based on previous measurements [10]. The term *bulk* describes large numbers of particles involved in the measurement. In order to simulate evolution of temperature profile inside the ore particle three dimensional unsteady state heat conduction equation has to be solved. Since we assume that the ores are spherical particles, it is convenient to formulate this equation in the spherical coordinates. Due to the spherical symmetry we get:

$$\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial T}{\partial r} \right) = \frac{1}{\alpha} \frac{\partial T}{\partial t} \quad (2)$$

where α is thermal diffusivity [m²/s], r radius of particle [m] and T is the temperature [°C]. This equation was solved by explicit finite differences method. For time integration, 4th order Runge

Kutta method was applied. The same method was used for simulation of the temperature distribution in single particle of ore as well as in case of cluster.

4.1. Temperature distribution in single particle

Temperature distributions as a function of time are presented for particle with radius 4 cm, which corresponds to size of raw materials industrially used for ferromanganese production [12]. Calculation made for temperature between 24 to 300°C simulates conditions at upper part of the SAF. While material are inserted into the furnace on the top of the burden the heat exchange is taking place between relatively cold particles and hot (250-300°C) gases. Figure 6 shows temperature profile and temperature in the center of a 4 cm particle. Due to high diffusivity, quartzes and Wessels ore have almost reached the temperature of the environment (300°C), while the center of Groote Eylandt ore particle is 100°C colder. Figure 7 shows similar simulation but for smaller particle. For particle with radius 2 cm, all samples reach 300°C within 500 sec. However it takes twice the time for Groote Eylandt ore to reach this temperature in comparison to Wessels ore.

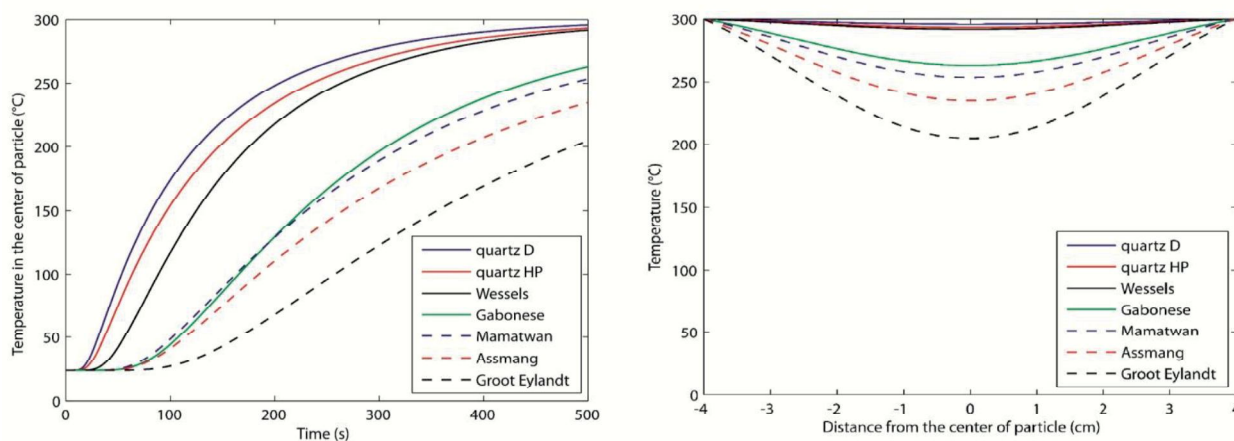


Figure 6: Temperature in the center (left) and temperature profile (right) of the particle after 500 sec. with radius 4 cm. Temperature 24-300°C

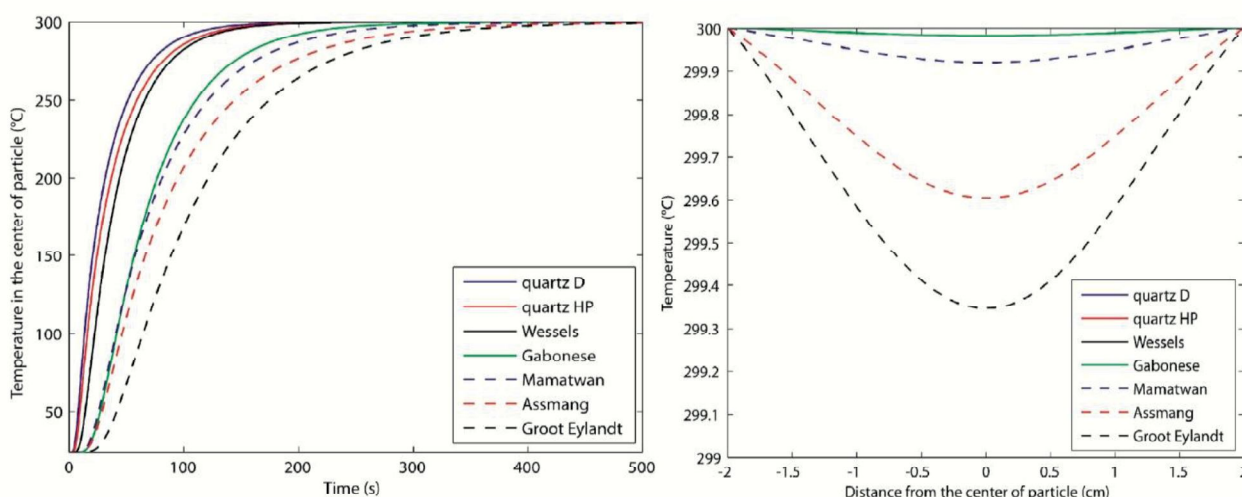


Figure 7: Temperature in the center (left) and temperature profile (right) of the particle after 500 sec. with radius 2 cm. Temperature 24-300°C

In order to present variation in temperature distribution inside the particle as function of its radius terms $t_{5\%}$ and $t_{95\%}$ were applied. $t_{5\%}$ and $t_{95\%}$ stand for time needed for center of sample to reach 5 % and 95 % of max temperature. Figure 8 shows comparison of temperature distribution inside the slowest and the fastest sample in temperature between 24-300°C. Terms slow and fast materials are used to describe materials which need long time and short time to reach 5 % and 95 % of total temperature increase.

As it can be seen in figure 8, to reach the 95% of total temperature increase the Groote Eylandt ore needs twice the time than Wessels ore. With increased radius the temperature gradient inside the particle for Groote Eylandt becomes bigger. This can effect that the phase transformations and reduction of manganese oxides, which are temperature dependent.

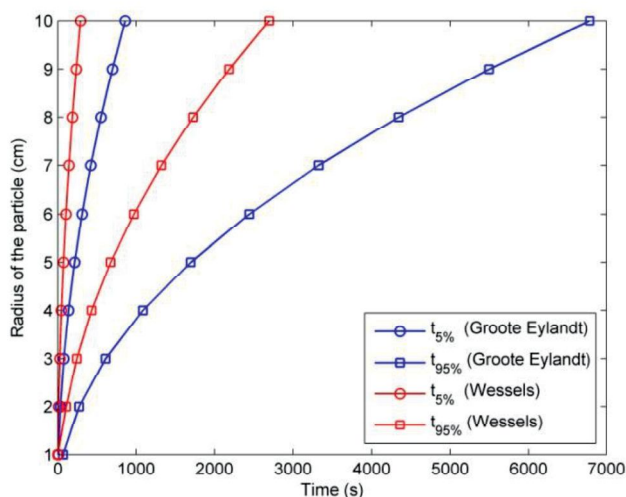


Figure 8: $t_{5\%}$ and $t_{95\%}$ dependency from the radius of particle in temp between 24-300°C

4.2. Temperature distribution in bulk materials

It is very important to have a good gas permeability of the burden during the production process; otherwise the gas will find alternative routes. For example the gas may form channels through the charge and in this way the gas will not be preheating the charge properly. That will give an off gas with high temperature and high content of CO which will cause higher energy consumption. There are also other problems related to the poor burden permeability. It has been observed that the fines are sintered in the pre-reduction zone causing the bridges and clusters. Not many publications have been known focusing on this phenomenon. Mostly the knowledge about it is based on industrial observations.

In the following, the temperature distribution is calculated for such a “manganese ore cluster”. In the calculations, the radius of 20 cm of the cluster was used. Simulation was performed for cluster which consists of Gabonese ore with particle size 4-8 mm, Gabonese ore with less than 1mm and Assmang ore with particle size 4-8 mm. Calculation of thermal diffusivity for cluster were done based on knowledge of bulk thermal conductivity, bulk density and specific heat of material [10]. Additionally following assumptions were made:

- Bulk thermal diffusivity changes linearly.
- The cluster descends continuously downwards 5 m, within the time of 8 hours.
- When cluster starts to descend its initial temperatures correspond to zone 1 (previously described) and the final environment temperature is 1000°C.

Figure 9 presents change of the temperature in center of the cluster as a function of temperature. The black line represents the cluster consist of Gabonese ore with particle size less than 1mm. Assmang and Gabonese 4-8 mm still keep initial temperature (24°C) after 4 hours, and after this time the temperature in the center of cluster slowly increase. Situation looks different in case of finer ore fraction. Cluster made of particles less than 1mm, increase in temperature after 2 hours. This is related to relatively high bulk diffusivity of this material at lower temperatures. However, after the 8 hours, when cluster reach the 1000°C Gabonese less than 1 mm and Assmang 4-8 mm has still a low temperatures inside the clump of particles, which is around 250°C. Central temperature of cluster made of Gabonese 4-8 mm reached 350°C at the same time.

Temperature in the center of cluster as a function of its radius is presented in the figure 9 (right). Figure indicates what should be the maximum radius of the cluster in order to reach temperature in the center of clump high enough for reaction to occur. Dotted line show the 250°C, where is believed that the water starts to evaporate and also higher manganese oxides start to reacts with CO gas. Small change of radius in the range between 15-20 cm can cause high temperature change in the center of the cluster.

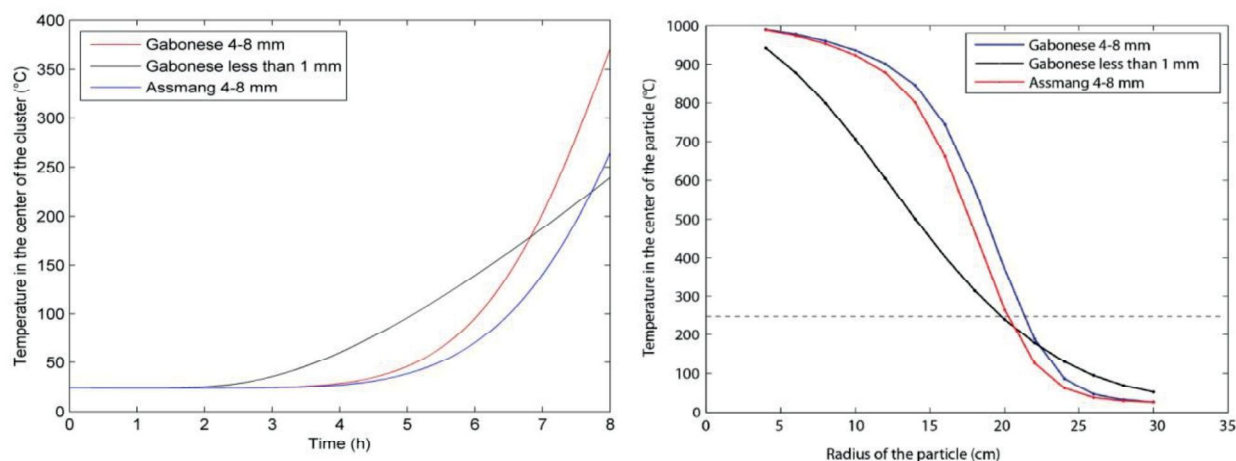


Figure 9: Change of the temperature in the center of the cluster (radius 20 cm) vs time (left). Temperature in the center of cluster as a function of its radius after it sank into the high temperature region (1000°C) (right)

5. CONCLUSIONS

It is shown that the thermal diffusivity in all tested material decrease with temperature. At 600°C thermal diffusivity of all manganese ores reach similar level 0.4 [mm²/s] and keeps decreasing with temperature. Depending on initial mineralogy, α of manganese ores changes in two different manners. The diffusivity of MnO₂ rich ores up to phase transition temperature (500-600°C) is constant despite of temperature and porosity changes. Phase change occurs around 600°C, (2) MnO₂ → Mn₂O₃ corresponds to significant decrease in the thermal diffusivity. In case of Mn₂O₃ rich ores the main parameters which determine the decrease in diffusivity is the temperature.

Quartzes decrease its diffusivity up to 573°C where phase change from quartz α to β occurs. Above this temperature the diffusivity of both quartzes is almost constant.

It was shown that the temperature distribution inside the particle is strongly dependent on its diffusivity and radius of particle.

Calculations presented in figure 9 shows that the cluster with radius 20 cm can enter into the hot temperature zone (1000°C) relatively cold (250°C), with no prereduced materials. That means that the reaction of water evaporation, removal of combined water and reduction of higher

manganese oxides (which should take place in temperature between 100-300°C) can suddenly start at temperature 1000°C or even higher. This situation can lead to increase of carbon consumption and unstable process operation. The effect of the sudden contact between relatively cold materials (250-350°C) and hot environment (hot liquid slag 1300-1400°C) will be an instantaneous dissociation of oxides and water. Potential eruptions can have effects on facilities and even, as it was reported, for human life [12].

6. ACKNOWLEDGEMENTS

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