AGGLOMERATION OF CHARGE IN FERROMANGANESE SUBMERGED ARC FURNACES

[1]D. Slizovskiy, [2]M. Tangstad

[1] Norwegian University of Science and Technology/Department of Materials Science and Engineering, Norway; e-mail: slizovsk@nt.ntnu.no
[2] Norwegian University of Science and Technology/Department of Materials Science and Engineering, Norway; e-mail: merete.tangstad@material.ntnu.no

ABSTRACT

The gas/solid reactions in ferromanganese submerged arc furnaces (SAF) are important to the production process. The region where these reactions occur is known as pre-reduction zone. The gas permeability of the charge in the pre-reduction zone is the key factor affecting stable operation of the furnace. In order to evaporate water and achieve a high degree of pre-reduction, the gas permeability of the burden has to be high.

Agglomeration of charge particles in the pre-reduction zone is one of the reasons for decreasing of gas permeability. Different mechanisms of agglomerate formation can take a place in the furnace. These mechanisms, their effect and relevance to agglomeration of the charge were thoroughly studied based on the charge samples taken from industrial SiMn and FeMn furnaces.

KEYWORDS: *Manganese alloys, agglomeration, submerged arc furnaces, industrial samples, zinc deposition, potassium deposition.*

1. INTRODUCTION

The coalescence of charge particles in the pre-reduction zone is usually named agglomeration or sintering. In order to avoid misunderstanding, the term "agglomeration" will be further used with the definition as, the process of coalescence of usually disparate charge particles.

Agglomeration of the charge has a number of negative effects for the furnace operation, such as bridge formation and thereby preventing steady heating and reduction of the charge, uneven flow of charge materials to the coke bed zone and uneven gas distribution. Unreduced and agglomerated charge can thus get to the coke bed zone and react with the slag. The contact and reaction of unreduced and agglomerated charge with the high temperature liquid slag releases a high amount and high velocity of gases. The hazardous effect of this interaction to the furnace operation can hardly be underestimated.

Agglomeration of burden in the pre-reduction zone can be divided into three groups:

1. **Natural agglomeration** or agglomeration of charge particles which is mainly characterised by the combination of high water content, high temperature and a high amount of fines.

2. **Slag agglomeration** is agglomeration formed due to eruption of liquid materials from the coke bed zone into upper parts of the furnace, driven by gas flow and/or due to the melting of charge particles.

3. **Condensate agglomeration** is agglomeration of charge materials due to deposition of compounds, which are acting as a binder.

In industrial furnaces several mechanisms and groups of agglomeration can take place at the same time and interact with each other, enhancing the agglomeration. Therefore, for a better

understanding of agglomeration mechanisms, agglomerated samples from industrial SiMn and FeMn furnaces have been studied.

2. CHARGE SAMPLES AND ANALYSING TECHNIQUES

Six charge samples from SiMn furnaces and four from FeMn furnaces were excavated during scheduled maintenances stops in a period from April 2008 to April 2011. The samples were supplied by two Norwegian ferroalloy producers from six different furnaces. In Norway all furnaces are closed furnaces. Most of the samples were collected from the top of the charge mixture. Only three samples, from a SiMn furnace, were taken 14 cm, 31 cm and 68 cm below the surface of charge mixture.

In industrial furnaces the descending of charge materials and the off-gases velocity rate is higher close to the electrodes. Therefore, it is important to notice that the area around the electrodes (within 1.5 m) or between the electrodes will be further called "the active zone" of the furnace. The samples taken from the areas more than 1.5 m from the electrodes will be recognized as the samples taken from "the inactive zone" of the furnace.

Charge compositions of the samples were classified. To study bulk composition, parts of the samples were crushed and analysed by X-ray fluorescence spectrometer. X-ray diffraction was employed for phase identification. The Electron probe micro analyser was used for analysing phase structure and phase compositions. In addition, the strength of agglomerated samples was tested in a hydraulic tensile machine.

3. RESULTS AND DISCUSSION

The present investigation o industrial samples has shown that the charge mixture may be agglomerated due to slag eruptions, deposition of potassium and zinc compounds or under the influence of both types. Some examples of agglomerated charge samples are shown in figure 1 and figure 2. The samples with natural agglomeration or agglomerated samples with a significantly high amount of water and fines were not observed during excavations.

Figure 1: The typical example of charge agglomeration due to slag eruption

Figure 2: The typical example of charge agglomeration due to alkali deposition

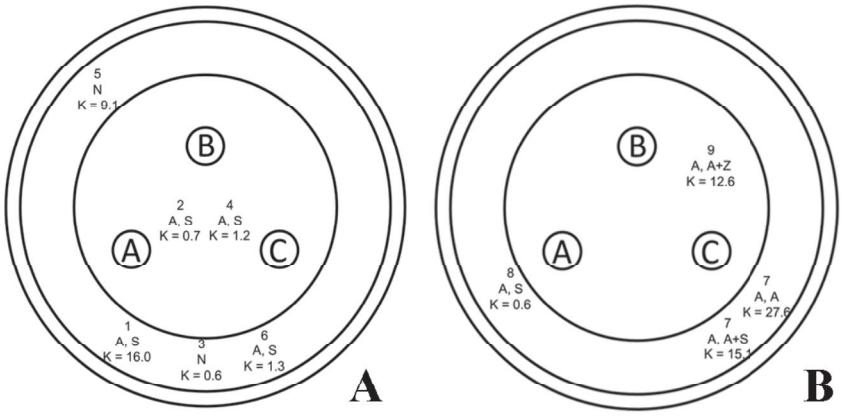
The summary of charge investigation from SiMn and FeMn furnaces are shown in table 1 and table 2, respectively. The binder phases and concentrations of potassium in agglomerated charge samples from SiMn and FeMn furnaces are shown in figure 3.

Table 1: The different parameters of charge samples taken from SiMn furnaces

№	Furnace	Furnace №	Position	Burden	Binder phase	K_2O, wt. %	Na_2O, wt. %	Zn, wt. %	Fines %
1	SiMn	1	Inactive zone	Agglomerated	Slag	19.3	5.7	0.03	–
2	SiMn	1	Active zone	Agglomerated	Slag	0.9	0.1	0.15	–
3	SiMn	1	Active zone	Not agglomerated	–	0.7	0.1	0.07	16.2
4	SiMn	2	Active zone	Agglomerated	Slag	1.4	0.2	59 ppm	–
5	SiMn	2	Inactive zone	Not agglomerated	–	5 – 11	0.2 –0.4	1.1 –2.6	48
6	SiMn	3	Inactive zone	Agglomerated	Slag	1.7	0.08	0.02	–

Table 2: The different parameters of charge samples taken from FeMn furnaces

№	Furnace	Furnace №	Position	Burden	Binder phase	K_2O, wt. %	Na_2O, wt. %	Zn, wt. %	Fines
7-A	FeMn	1	Inactive zone	Agglomerated	Alkali	33.3	2.0	0.6	–
7-B	FeMn	1	Inactive zone	Agglomerated	Alkali, Slag	18.2	0.9	2.0	–
8	FeMn	2	Inactive zone	Agglomerated	Slag	0.7	0.1	76 ppm	–
9	FeMn	3	Active zone	Agglomerated	Zn + Alkali, Slag	13.3 - 15.2	0.5 –1.1	3.3 – 4.6	–



A – SiMn furnaces, B – FeMn furnace. The top line is the number of the sample. The first letter in the middle line: A – agglomerated charge, N – not agglomerated charge. The second letter in the middle line shows the binder phase: S – slag, A – alkali, Zn – zinc. The bottom line represents concentration of potassium in the sample

Figure 3: Schematic illustration of the furnace area and position of charge samples taken from

It can be seen from figures above, that agglomerates taken from the inactive zone more frequently contain a higher amount of potassium in comparison to the active zone. This statement is fair for both types of furnaces.

3.1. Natural agglomeration

Sample no. 5 was taken from the Furnace no. 2 three weeks after Sample no. 4. The operation of the furnace was improved, but the off-gas temperature was still high. The sample attracts a special attention due to the discrepancy of the sample's shape and conditions it experienced. The sample meets several conditions, which are crucial for agglomerate formation. It has a high amount of fines (48 wt. %, particle size less than 5 mm), relatively high amount of potassium (5 – 11 wt. %) and finally a high off gas temperature (730 ^{o}C). Despite all of these factors, the sample is not agglomerated.

From the point of view on natural agglomeration, Sample no. 5 fits all conditions except one, that is, high water content. This demonstrates that only when all three factors meet together, natural agglomeration of the charge can possibly occur. Condensation of 5 wt. % to 10 wt. % of potassium compounds has not resulted in agglomeration of the charge. Therefore, it is possible to conclude that deposition up to 10 wt. % of potassium compounds in the charge mixture does not necessarily lead to agglomeration.

3.2. Slag agglomeration

From table 1 and table 2 it can be seen that slag phase plays an important role in agglomeration of top layers of the charge. Out of 8 investigated samples, 6 samples were significantly contaminated with the slag phase. All slag phases were analysed by XRF. Chemical analyses, table 3, have shown a relatively high variety of compositions. However, it was noticed that some slags contain high amount of potassium and sodium, while the rest are almost free from them. Thus, slags found in different samples were classified as high and low alkali slags. table 3 also shows that most of SiMn and FeMn slags have composition common for the coke bed area.

Table 3: Chemical composition of slag phases found in agglomerated samples. Analyses were made by XRF

Sample№	MnO	FeO	CaO	SiO_2	MgO	Al_2O_3	BaO	Na_2O	K_2O	S	Cl	ZnO	PbO
1	5.2	0.4	9.7	21.6	1.5	4.7	0.5	5.7	19.3	0.3	0.1	0.03	-
4	19.2	5.2	11.0	27.8	3.1	14.9	1.0	0.2	1.4	0.2	1.13	59 ppm	-
6	21.9	1.9	7.3	16.7	1.5	7.1	0.8	0.08	1.69	0.4	2.0	0.02	-
7	37.3	2.8	3.8	4.1	0.2	2.8	0.2	0.9	18.2	0.4	0.1	2.0	-
8	33.5	3.6	9.9	25.7	6.0	5.8	0.6	0.1	0.7	0.3	0.2	76 ppm	-
9	41.1	2.0	3.5	10.8	2.1	3.6	0.3	1.1	13.3	0.3	0.1	4.6	0.6
9	46.4	2.8	3.2	2.2	4.3	5.2	0.3	0.5	15.2	0.2	0.3	3.3	0.5

In order to estimate melting temperature of slags, their composition was compared with the ternary slag diagrams. Table 3 shows, that composition of analysed slag samples has usually more than five main components. The melting point of five or more component systems cannot be found mainly due to the lack of information about alkali containing slags. Therefore, the slag composition

was transformed into three component system. The example of comparison of slag composition with the known ternary diagrams is shown in figure 4.

The comparison of slag composition with the ternary diagrams has shown that melting points of low alkali slags vary between 1200 °C and 1450 °C, while high alkali slags, which contain from 10 wt. % to 26 wt. % of potassium, have melting point in a range from 1000 °C to 1200 °C. Producers assured that the re-melt with the size close to the size of found agglomerates was not charged into the furnace. Thus, a number of factors, such as large size of agglomerates (up to 6 m^2), high melting temperature of slags (1000 °C – 1450 °C), relatively low off-gas temperature at the top of the charge layer (maximum reordered temperature was around 840 °C) and the composition of slag phase, indicate that the slag erupted from the coke bed zone.

Two different mechanisms were proposed with regard to agglomeration of the charge due to eruption of high alkali slags. One mechanism implies eruption of the slag to the top of the charge followed by solidification. During solidification the surface of the slag can be contaminated by alkali compounds from the off-gases. Therefore, a higher potassium concentration can be expected in the slag phase close to the surface of agglomerates. The other mechanism describes the presence of high alkali slags by eruption and boiling through the alkali rich layers.

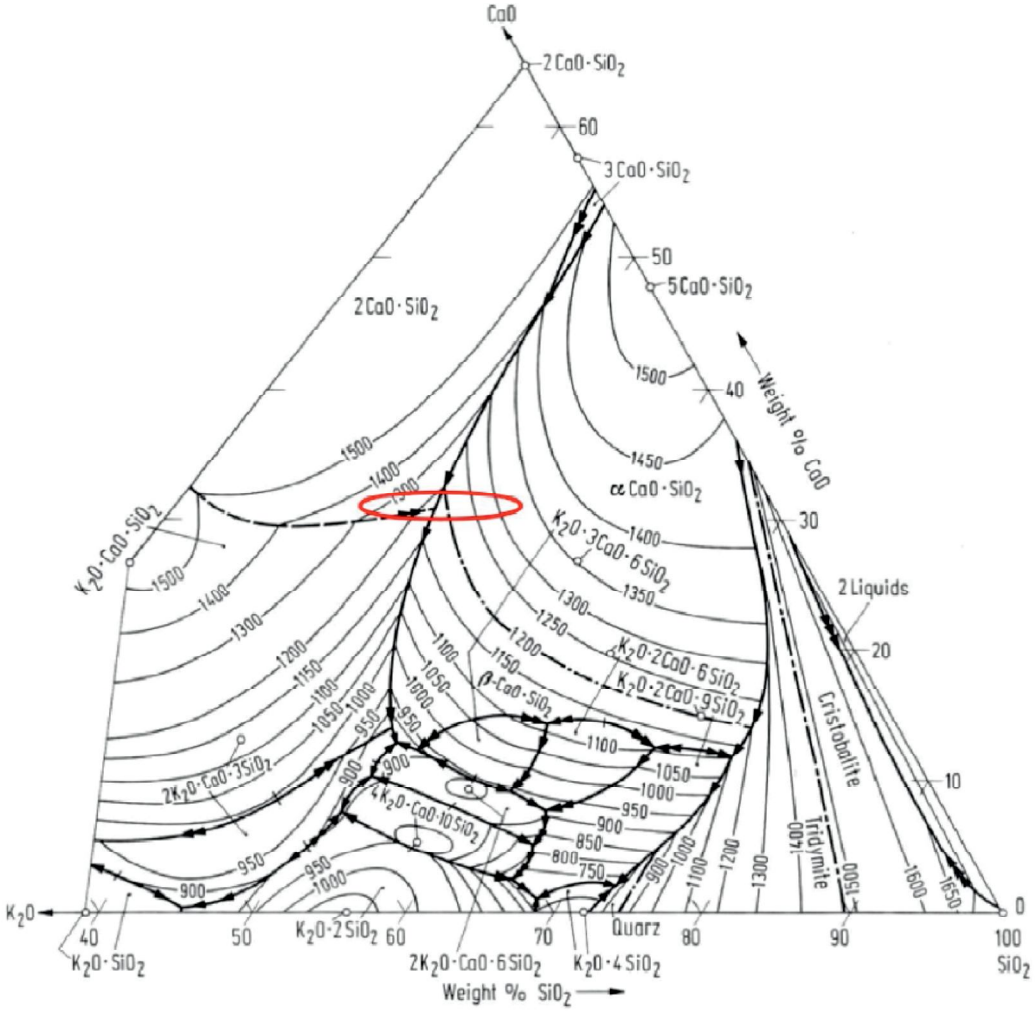


Figure 4: Ternary diagram of the system K_2O-SiO_2-CaO [1].
Composition of the binder slag phase of Sample 1 is indicated by red ellipse

3.3. Condensate agglomeration

Condensate agglomeration of the charge can be seen in sample no. 7-A and sample no. 7-B from furnace no. 1, figure 2. In general, agglomerate has a concrete like structure and the voids between the charge particles are filled with condensed potassium rich phases. Influence of slag eruption was also found in the samples. Several slag phases were seen in the agglomerate, despite no re-melt or slag being added to the charge. The low amount of slag phase and the structure of agglomerate make it possible to propose that condensate agglomeration was dominating in this sample.

Two types of agglomerates were excavated from the furnace no. 1. The light colour sample has a layer structure and contains a high amount of fines and alkali (28.9 wt. %). This sample has a composition, which is very close to the composition of sample no. 5. The major difference between agglomerate from the FeMn furnace and charge sample no. 2 from the SiMn furnace is the alkali content. This difference shows that an increase in amount of deposited potassium compounds from 10 wt. % to 28.9 wt. % can have a crucial effect on the structure of the charge materials. It is also possible to conclude that deposition up to 10 wt. % of potassium compounds in the charge mixture does not necessarily lead to agglomeration.

Alkali deposits were studied by XRD. The typical XRD phase analysis of potassium rich deposits is shown in figure 5. Potassium was found mainly in the form of potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$).

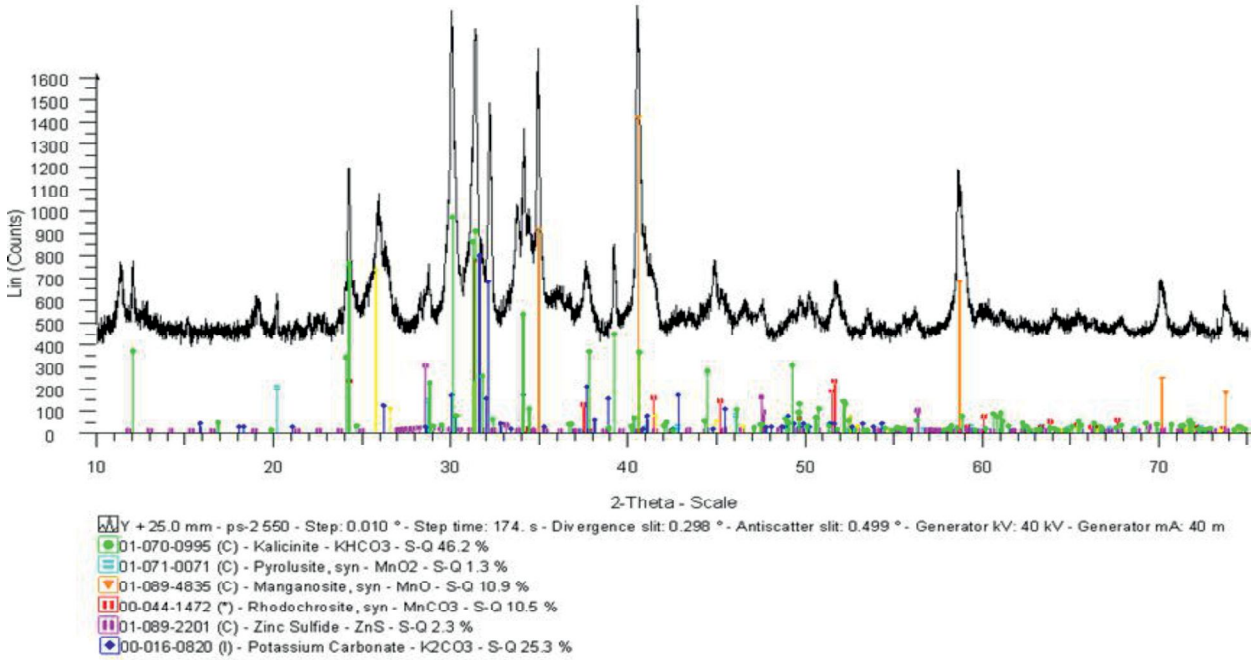


Figure 5: Typical XRD pattern and corresponded phases of potassium condensed phase

Sample no. 9 is the only sample with a significant effect of zinc deposition on agglomeration of the charge. The agglomerated sample contains around 3.6 wt. % of Zn. The phase analyses have shown that metallic zinc and zinc oxide are mainly presented in the binder phase, which covers the surface of raw materials, figure 6. Despite the fact, that Norwegian producers set the limits on average zinc load for all ferromanganese and silicomanganese furnaces at a level of 0.7 wt. % [2], zinc deposition can have a strong effect on formation of agglomerates.

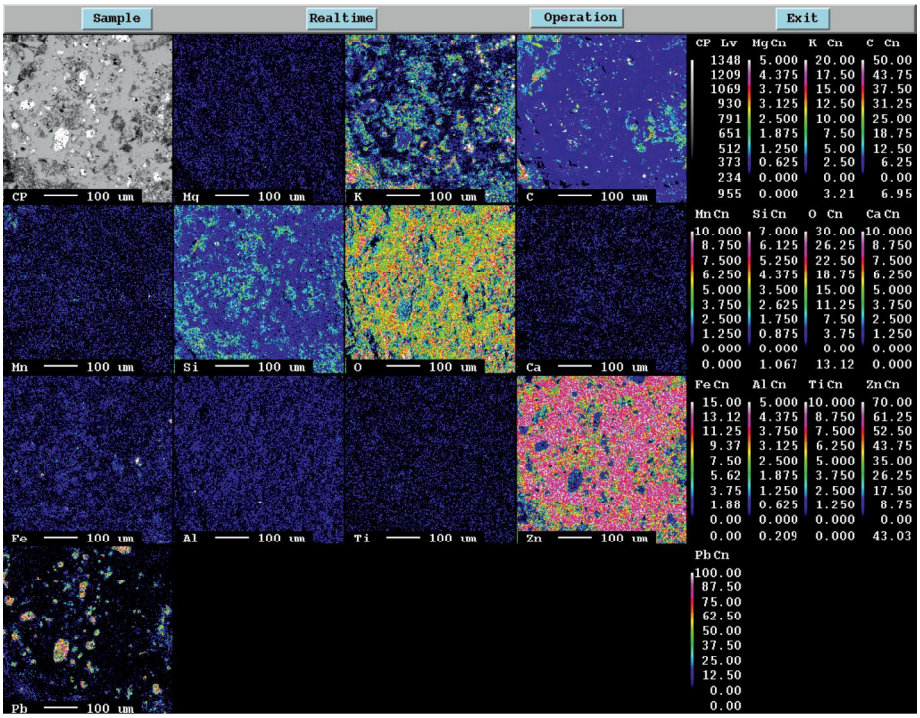


Figure 6: Mapping of the surface of agglomerated Sample № 9

3.4. Compressive tests of the samples

A number of compressive strength tests were performed with obtained agglomerates. The procedure, equipment and the way of processing of agglomerated samples were previously described by Slizovskiy (2012) [3]. The strength of all agglomerates found in FeMn and SiMn furnaces have been tested at room temperature. The cumulative results of the test are shown in figure 7. The red coloured columns represent the strength of agglomerates which contain a high amount of slag and relatively low amount of potassium. The dark columns correspond to the strength of agglomerates filled with potassium.

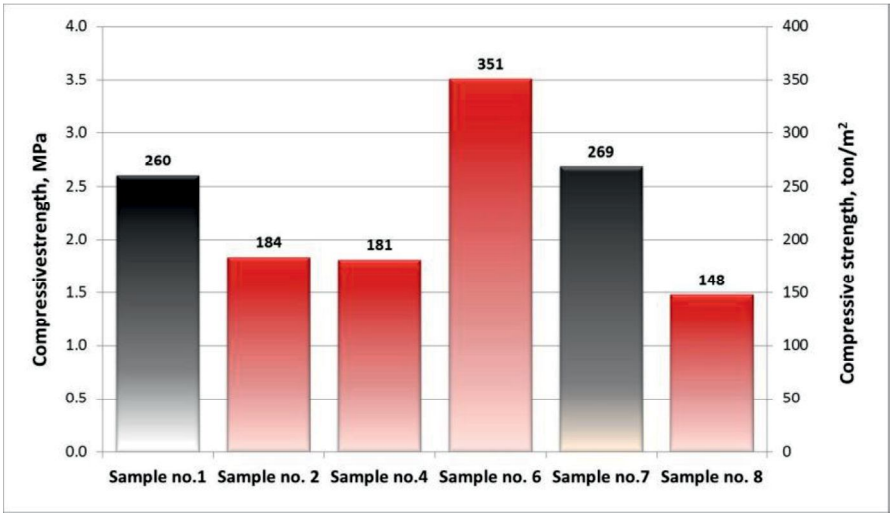


Figure 7: The mean strength of agglomerates excavated from SiMn and FeMn furnaces. [Black – high alkali agglomerates. Red – high amount of slag]

The strength of the slag based agglomerates varies in a wide range from 148 ton/m^2 to 351 ton/m^2. The porous slag with a low amount of charge materials showed the lowest strength. The high amount of pores in the sample, which is acting as seats of tension, reflects the strength. The strength of the alkali based agglomerate (sample no. 7), alkali based agglomerate (sample no. 1) and slag based samples are in the same range.

It can be concluded that strength of industrial agglomerates is relatively high. As an example, the load needed for breaking industrial agglomerates is equivalent to approximately a 50 m high column of charge materials. The strength of agglomerates can be significantly reduced during heating in the furnace. However, it is believed that agglomerates can resist the pressure of the charge materials and in some cases reach the coke bed zone.

4. CONCLUSIONS OF AGGLOMERATION IN INDUSTRIAL FURNACES

During the investigation of industrial samples, the high importance of slag eruption for agglomeration of the charge was shown. In five agglomerated samples out of nine the slag phase was acting as a binder phase. Both high and low alkali slags were found in the samples. The following conclusions have been made for high and low alkali slag:

- The low alkali slag, in general, has a typical composition for the coke bed zone area;
- The melting point of low alkali slag varies from 1200 ^{o}C to 1450 ^{o}C;
- The high alkali slag usually contain from 10 wt. % to 26 wt. % of potassium. Thus, the melting point of high alkali slag is lower, 1000 ^{o}C – 1200 ^{o}C.

The following mechanism of slag type agglomeration has been proposed:

- Formation of slag agglomeration starts with eruption of liquid slag from the coke bed zone to the surface of the charge with further solidification.
- During solidification the surface of the slag can be contaminated by alkali compounds from the off-gases. Therefore, a higher potassium concentration can be expected in the slag phase close to the surface of agglomerates.
- The high alkali slag can also be formed when the liquid slag boils up through the alkali rich layers.

The following conclusions can be drawn regarding the effect of potassium deposition on agglomeration of the charge in industrial furnaces:

- Potassium is depositing in FeMn furnaces mainly in the form of potassium carbonate and potassium bicarbonate.
- The extremely high amount of potassium, approximately 33 wt. %, depositing in the charge mixture can lead to the formation of strong agglomerates.
- The high amount of fines, high temperature and concentration of potassium in the charge below 11 wt. % will not necessarily lead to agglomeration.

The effect of zinc deposition on agglomeration of the charge in industrial furnaces can be concluded as shown below:

- Despite the limits which were set by Norwegian producers to the average amount of zinc load with the raw materials, the deposition of zinc compounds can lead to agglomeration of the charge.
- Deposition of approximately 3.6 wt. % of zinc compounds can result in formation of agglomerates.

All investigated agglomerates have a very high strength. At room temperature agglomerates can resist pressure many times higher than can be formed by the weight of charge.

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