THE EFFECT OF POTASSIUM AND ZINC CIRCULATION ON AGGLOMERATION OF A CHARGE IN SAF

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

[1] Norwegian University of Science and Technology/Department of Materials Science and Engineering, Norway; dmitriy.slizovskiy@material.ntnu.no
[2] Norwegian University of Science and Technology/Department of Materials Science and Engineering, Norway; merete.tangstad@material.ntnu.no

ABSTRACT

In ferromanganese production, potassium and zinc compounds are always present in the raw materials and their concentration may increase due to circulation in the submerged arc furnace (SAF). The presence of these compounds in a furnace may lead to disintegration of coke particles, formation of hard bank materials, bridges and as a result irregular flows of the charge. The effect of potassium and zinc circulation on agglomeration of charge materials has been studied for the manganese process. Conditions close to industrial furnaces producing HC FeMn were reproduced in an 15kVA induction furnace. The stability, penetration, formation and flow of potassium and zinc compounds have been discussed based on thermodynamic and experimental data.

1 INTRODUCTION

High concentration of zinc, potassium and sodium in manganese furnace is believed to be one of the reasons for unsteady operation of SAF (submerged arc furnace). The presence and circulation of alkali and zinc in SAF cannot be avoided, as they are present in the raw materials. It is believed that recirculation and accumulation of alkali can be a problem in following ways:

- Alkali vapour causes catastrophic swelling and disintegration of pellets and coke [1 – 3].
- The presence of alkali compounds have an unfavorable influence on the Boudouard reaction [1,2,3,4].
- The alkalis have a damaging effect on the lining refractories of the furnace walls [1,3,5].
- Alkali compounds cause erratic performance of the furnace resulting in hangings and slippings and causing scaffolds to appear on the furnace walls [1 – 3].

Accumulation of Zn may also have an unwanted effect on furnace operation. Y. Lee and D.S. Kozak [6] examined the influence of Zn accumulation through the excavation of Elkem's submerged arc furnace. They found, that zinc accumulation inside the smelting furnace caused the formation of hard bank materials, which encouraged the formation of bridges and irregular flows of the charge mix. It was suggested that when the bridge collapses, some of the unreacted raw material fall into the superheated zones and undergo gas forming reactions. The rapidly expanding gases can produce a shock wave with a considerable destructive force.

Formation of hard bank materials or bridges and uneven gas distribution can be caused by agglomeration of raw materials in colder zones of the furnace. Thus, this work is focused on the reduction of potassium and zinc compounds in a temperature range from 1000 ^{o}C to 1200 ^{o}C, deposition of their vapours in colder zones and investigation of deposition effect on agglomeration properties of a charge.

1.1 Thermodynamics of potassium behaviour in SAF

The potassium enters the furnace as constituents of the ore, the agglomerates, the flux and the coke. It comes in the form of oxide, carbonates or complex silicates [1 – 4], or even as constituents of the manganese minerals; e.g. Cryptomelane - KMn_8O_{16}, Birenssite – $(Ca,Na,K)(Mn,Mg)\ Mn_6O_{14}$-$5H_2O$, Todorokite – $(Ca,Na,K)(Mg,Mn)Mn_5O_{12}$-$H_2O$, Vernadite – $(Ba,K)MnO_2\ H_2O$ or Romanechite – $(Ba,K,Mn)Mn_5O_{10}$-H_2O [7].

For simplicity carbonates and silicates are represented by K_2CO_3 and K_2SiO_3 respectively. The calculated equilibrium vapour pressure of potassium for some potassium compounds in the temperature range of 400 – 1600 °C in equilibrium with solid carbon is shown in Figure 1. This is in accordance with similar calculations by Turkogan [8].

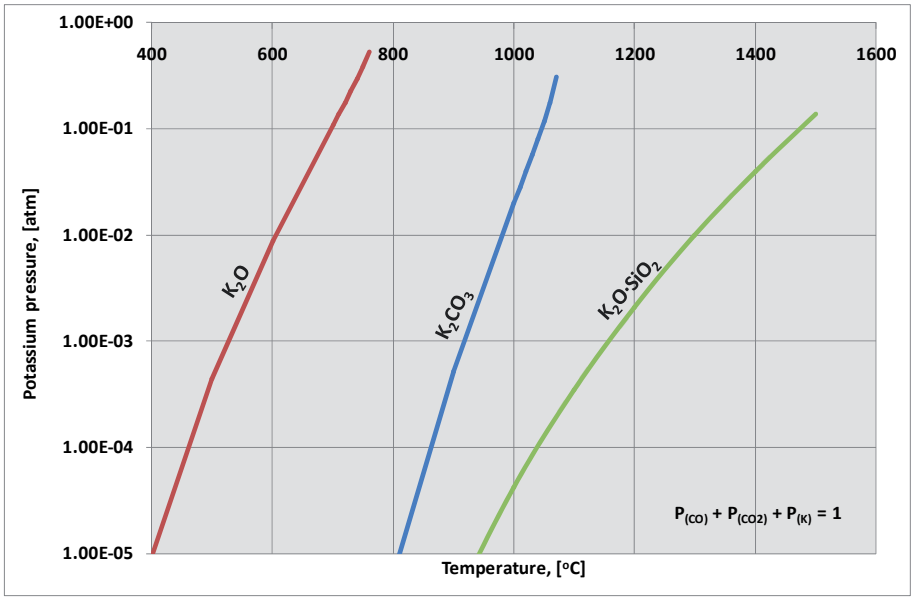

Figure 1: Vapour pressure of potassium for some pure potassium salts in equilibrium with solid carbon.

As can be seen in Figure 1, silicates are more stable than carbonates and potassium oxide. The potassium oxide will be reduced to $K_{(g)}$ at a temperature range between 600 °C and 770 °C. The carbonates and silicates are reduced to $K_{(g)}$ at temperatures around 1000 °C and 1300 °C, respectively.

1.2 Thermodynamics of Zn behaviour in SAF

Zinc enters ferroalloy furnaces with manganese and iron ores, alloy fines and sinter [9]. In manganese ores Zn appears to exist as ZnO [6]. Zinc oxide may be reduced by C or CO. ZnO has a high melting point, 1975 °C, and is not fluxed easily by most basic and acidic oxides. However, calculations of zinc vapour pressure for ZnO in equilibrium with solid carbon have shown, that zinc oxide is stable under reduction conditions only up to 900 °C, see Figure 2.

The Zn released by the reduction is partly distributed between the slag and metal phases, and the rest exists as zinc vapour. The Zn vapour ascends with the gas to the colder zones higher up in the furnace, where it oxidizes to ZnO or condenses as liquid metal.

2 EXPERIMENTAL SETUP

The reduction of potassium and zinc compounds and effect of their deposition in a charge was simulated in an 15 kVA induction furnace. Carbon crucible with the inner diameter around 12 cm was used as a charge container. Comilog ore and SSAB coke were used as charge materials. The ore and coke were preliminarily sieved to a size of 8 – 15 mm.

The scheme of crucible with the height of 40 cm is shown in Figure 3. The mixture of potassium carbonate with coke or zinc oxide with coke were placed at the bottom of the crucible as shown in Figure 3-A. The mixture at the bottom of crucible consisted of approximately 400 g of zinc or potassium carbonate with approximately 300 g of coke. Position of these layers was chosen due to the features of the induction furnace. The highest temperature in the furnace was at the bottom of the crucible, the lowest at the top of the charge as shown on Figure 3-C.

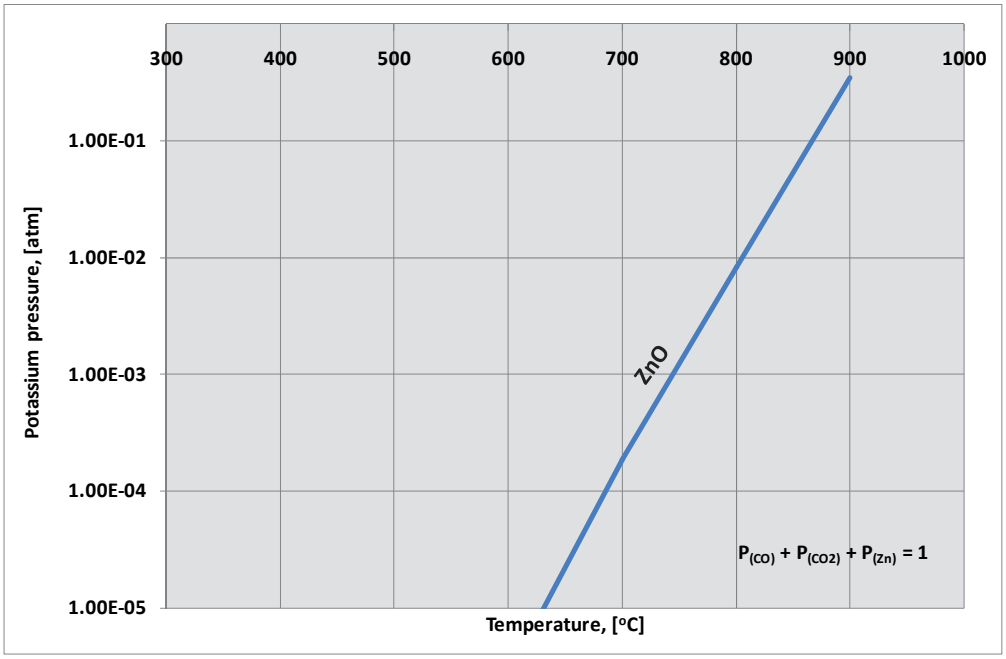

Figure 2: Vapour pressure of zinc for ZnO in equilibrium with solid carbon.

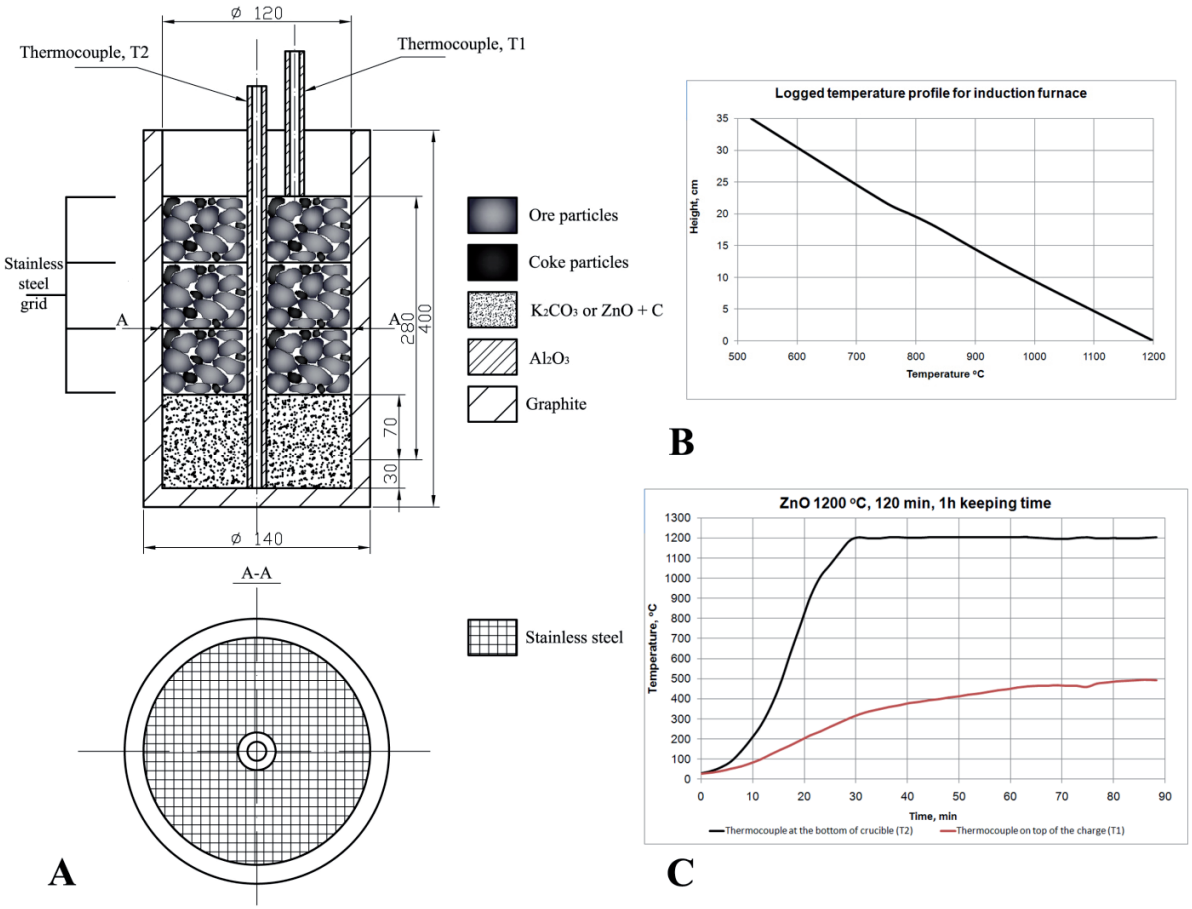

Figure 3: A) The scheme of the crucible used for reduction and deposition of zinc and potassium. B) Temperature profile of crucible logged after 40 min of keeping time. C) Typical temperature profile from thermocouple T1 and T2.

Table 1: Chemical composition of ore

Ore	Al_2O_3	CO_2	CaO	XH_2O	Fe_2O_3	MgO	MnO_2	MnO	K_2O	SiO_2	BaO	FeO	Total (dry)	H_2O
Comilog ore	5.3	0.1	0.1	3.7	3.6	0.1	78.2	2.9	0.8	4.4	–	–	99.2	8.7

Table 2: Chemical composition of coke

Coke	H2O (wt. %)	Ash (wt. %)	Volatile (wt. %)	C – Fix (wt. %)	K_2O
SSAB coke	0.63	12.43	1.13	86.44	0.19

The mixture of raw materials (ore and coke) was placed on top of the potassium or zinc mixture. Chemical composition of ore and coke is presented in Table 1 and Table 2 respectively. For better excavation of crucibles after experiments, the ore-coke charge was separated by stainless steel grid. In order to control temperature during experiment, two S thermocouples were installed at the bottom and at the top of the charge.

The graphite crucible with the mixture of potassium carbonate and coke was heated up to 1000 ^oC, 1100 ^oC and 1200 ^oC and kept for 1 h or 2 h. The experiments with ZnO and C mixture were conducted at 1100 ^oC and 1200 ^oC with holding time 1h and 2h. The experimental plan is shown in Table 3.

When the temperature at the bottom of the crucible reached 1000 ^oC, 1100 ^oC or 1200 ^oC, the temperature on top of the charge was sufficiently low, from 350 ^oC to 500 ^oC. The goals of experiments were:

- to simulate reduction conditions at the bottom of the crucible and deposition of potassium and zinc vapours in a colder regions of the crucible.
- to determine the form of alkali and zinc depositions.
- to study the charge agglomerate due to alkali and zinc condensation.

Table 3: Experimental plan and results after visual investigation of the charge

Experiment	Bottom composition	Temperature ^oC	Holding time, min	Agglomeration strength	Type of agglomeration
S1E1	K_2CO_3 + coke	1100	60	3	P
S1E2		1200	120	3	P
S1E3		1100	120	3	P
S1E4		1000	120	3	P
S2E1	ZnO + coke	1100	60	2	L
S2E2		1200	120	3	L
S3E1	K_2CO_3 + ZnO + coke	1200	120	3	L + P

After experiments, crucibles were cooled down in air and excavated. The charge was then visually studied. Position of deposited layers was compared with the temperature profile of the crucible during experiment, Figure 3-B. Samples from different layers of the charge were studied by EPMA (electron probe micro-analyzer).

3 RESULTS AND DISCUSSION

Three series of experiments were performed. First series was conducted to study effect of potassium deposition on a charge. The second series was performed to investigate effect of zinc deposition on agglomeration of the charge. The experiment from the third series was focused on deposition of potassium and zinc mixture in a charge.

3.1 Experimental results and discussion from experiments with potassium carbonate reduction

Four experiments with the different temperatures at the bottom of the crucible and with the different keeping time were performed for the first series, see Table 3. To protect the graphite crucible from potassium and avoid intercalation effect, a crucible made from stainless steel was placed at the bottom.

For better description of alkali or zinc agglomeration in the charge, the strength and type of agglomeration were classified. The agglomeration strength was expressed through the numbers from 0 to 5 (five is the highest strength of agglomerate, 0 – no agglomeration). The type of agglomeration was divided on particle (P) and layer type (L). Particle agglomeration is defined here as agglomeration between two or more ore and coke particles. Layer agglomeration is agglomeration when almost all ore and coke particles are coalesced together at some level across the graphite crucible.

The results of visual investigation of experiments with potassium carbonate are shown in the Table 3. Excavations of the experiments with potassium have shown that approximately 50 % of the bottom material was left after heating. Agglomerated layers were not found in the charge. However, a few agglomerated particles were found in the middle of ore-coke mixture.

Four sample groups (two ore and two coke particles from each layer) were taken for EPMA analyses from the experiment conducted at 1100 ^{o}C and holding time 120 min. It was found that some ore and coke particles from each layer were covered with potassium. Some of coke particles were also filled with potassium as seen in Figure 4. The uneven distribution of particles covered or filled with potassium and particles free from potassium within the same layers can be result of uneven distribution of potassium vapour flow rate in a crucible.

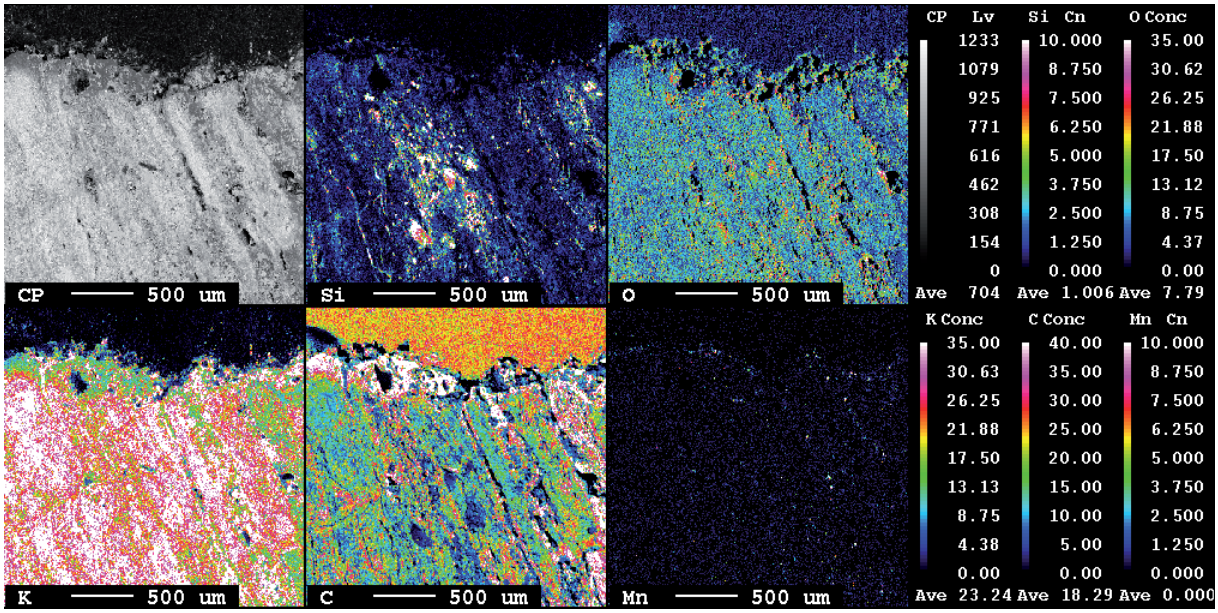

Figure 4: The EPMA analyses of ore particle from experiment conducted at 1100 ^{o}C and 2h keeping time. The coke particle was taken at a level 7 cm above the K_2CO_3-C layer. Potassium compounds were found on the surface and inside the coke particle.

In order to study the potassium distribution along the height of the crucible, the coke and ore particles were studied by XRF (X-ray fluorescence) analyses. The XRF analyses have shown slight increase of potassium concentration in the ore particles, from 0.8 wt.% to 1.09 wt.%. The concentration of potassium in coke increased from 0.19 wt.% to 0.70 wt.%, as it is shown in Table 4. The highest concentration of potassium in a charge was found at the bottom of ore-coke layer, which was right above the potassium-coke layer. Thus, the slight increase of potassium concentration can be explained with contamination from the potassium carbonate layer. Based on this, most of the potassium has gone to the off-gas.

Table 4: XRF analyses of ore-coke layers from the experiment performed at 1100 °C with 2h keeping time.

Formula	Manganese ore, 10 – 17 cm from the bottom of the crucible [wt.%]	Manganese ore, 17 – 24 cm from the bottom of the crucible [wt.%]	Manganese ore, top layer [wt.%]	Coke, 10 – 17 cm from the bottom of the crucible [wt.%]	Coke, 17 – 24 cm from the bottom of the crucible [wt.%]	Coke, top layer of the crucible [wt.%]
MnO	59.32	53.23	54.96	7.26	3.88	1.11
Al_2O_3	6.16	7.35	6.86	3.91	4.20	3.45
Fe_2O_3	4.17	7.11	5.26	7.90	9.03	6.73
SiO_2	3.66	4.88	4.89	8.99	10.11	8.93
K_2O	**1.08**	**1.02**	**0.90**	**0.70**	**0.51**	**0.48**

* - The concentrations are given in weight percent.

It is possible, that residence time of $K_{(g)}$ in the crucible is too low for deposition or that the flow rate of the potassium vapour is too high, and that it as a result passes through the charge without deposition. The other possibility is that temperature at the top of the charge was too high for deposition. The temperature at the top of the charge was around 450 °C.

3.2 Experimental results and discussion from experiments with reduction of zinc oxide

Two experiments were performed with the mixture of ZnO and coke at the bottom of the crucible, see Table 3. Around 40 g of solidified metal layer was found at the bottom of the crucibles during excavation. For both experiments, a dense agglomerated layer of manganese ore with the coke covered by white powder and metal droplets were found in the middle of the charge, see Figure 5. The agglomerated layer was wider in the experiment with longer holding time and higher temperature. The height of the agglomerated layers were measured and compared with the temperature profile.

To study composition of deposited compounds, two samples of agglomerate from each experiment have been analyzed by EPMA. It can be seen in Figure 6 that both Zn and ZnO are covering the surface of ore particle. It was found through the EPMA analyses that ZnO can penetrate from the surface of the particles to the center through the big cracks or pores. However, no zinc oxide was found in a middle of the manganese ore particles.

Figure 5: The layer of charge materials filled with metallic Zn and ZnO. The experiment was performed at 1100 °C and 1 h of keeping time.

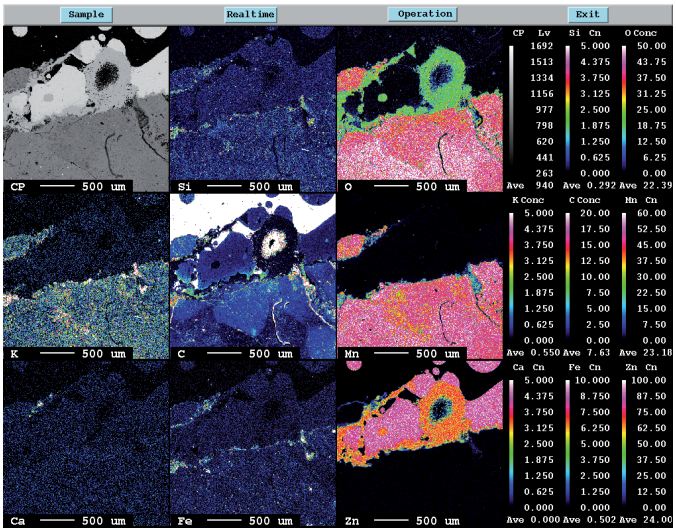

Figure 6: The EPMA analyses of ore particle from experiment conducted at 1100 °C with 1 h keeping time. Zn and ZnO covering the surface of ore particle.

The strength and type of agglomerate is presented in Table 3. The type of agglomerate was classified as layer agglomeration. The strength of agglomerate was classified as number 2 and 3. The higher number was given to the agglomerate from experiment with longer keeping time and temperature at the bottom. At the same time, the amount of metallic zinc at the bottom of the crucible was higher for the experiment with lower temperature and keeping time. As expected for the experiment with longer holding time and higher temperature, more zinc oxide reduces from the bottom and deposits in the charge, which leads to an increase of agglomerate strength.

The temperature range of deposition for the first experiment is 744 – 862 °C. For the second experiment, agglomerate layer was found between 685 – 833 °C. The difference can be explained on the one hand by difference in amount of reduced and deposited ZnO and on the other hand by the slight increase of the charge temperature during longer holding time.

It was seen from experiments with potassium that charge level was decreasing due to reduction and melting of the potassium carbonate. In experiments with zinc vapour deposition, charge layer was stable. Obtained agglomerate in both experiments was strong enough to keep the rest of the charge at the same level. The same effect is expected in industrial furnaces, so-called bridging effect.

Metallic zinc particles have a spherical form and can easily be removed from the surface of the ore particles. This is explained by low wetting of ore and coke particles by metallic zinc. However, wetting properties may vary with increase of the temperature.

3.3 Experimental results and discussion from experiments with simultaneous reduction of potassium carbonate and zinc oxide

One experiment was made with a mixture of zinc oxide and potassium carbonate at the bottom of the crucible. The results of that experiment are very similar to the results from the experiments with reduction of zinc oxide. Agglomerate was found in the middle of the ore/coke mixture. Manganese ore and coke were covered with white powder and metallic droplets. Some very strong bounded particles covered by white-yellow powder were also found during the excavation. The agglomerate was classified as number 3. In Table 3, the type of agglomerate was determined as L and P simultaneously.

During the experiment the charge level was stable, which shows a high strength of the agglomerate at experimental temperature. The temperature range for deposited powder and metal was determined.

The samples from deposition layers have been studied by EPMA. The analyses have shown that the white powder which covers manganese ore and coke particles is ZnO. Metallic zinc was also found in the charge. In this experiment two different layer were found within the agglomerated layer. One layer consists of ZnO and has a temperature range from 641 °C to 890 °C, and as shown in Figure 7. The second layer consists of ZnO and metallic Zn and has a temperature range from 685 °C to 729 °C. In previous experiments with zinc deposition, metallic zinc and zinc oxide were mixed up across the whole agglomerated layer.

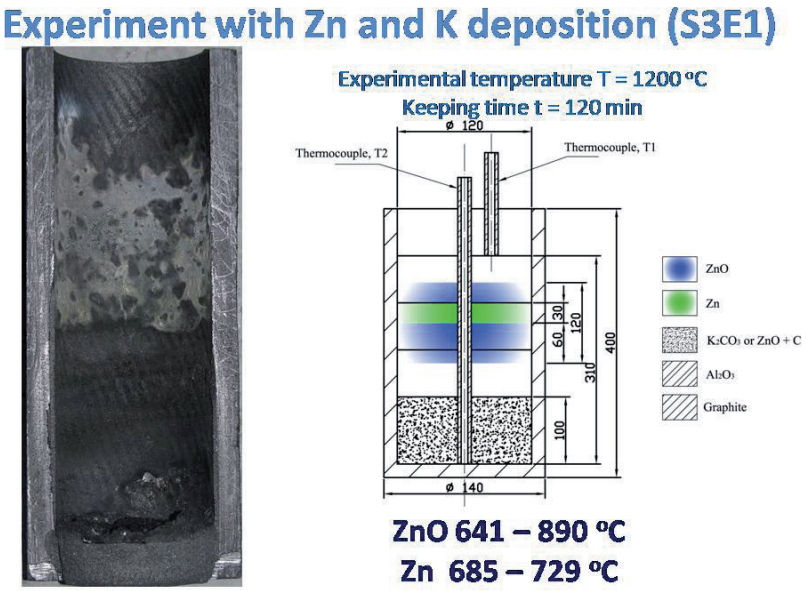

Figure 7: The height of deposited layers and temperature of deposition.

The presence of potassium was detected on the surface and in the middle of only one of the sampled ore particle. The detected value of potassium lies in the range 1.2 – 1.5 wt. %, which is 0.4 – 0.7 wt.% higher than the initial concentration of potassium in ore. However, it is hard to say if this concentration was reached due to potassium deposition, or if it is a random distribution of potassium in ore particles.

Some of the particles that were found inside the agglomerated layer were covered with white-yellow powder. The same type of particles was found in experiments with potassium deposition and has not been seen in experiments with zinc deposition.

4 CONCLUSIONS

To simulate the behaviour of Zn and K vapours in HC FeMn charge mixture, experiments in an 15 kVA induction furnace has been performed.

It was found that zinc vapour ascends to the colder zones and deposits on a charge in a form of metallic zinc and zinc oxide. The deposition of zinc oxide and metallic zinc is leads to agglomeration of charge and occurs at a temperature range around 650 °C to 900 °C. Agglomerate has average strength. The strength and height of the agglomerated layers are depended on the amount of deposited zinc vapour.

Any significant amount of potassium depositions was not found in a temperature range 350 – 1200 °C. Only a few strong bonded particles were found. However, the temperature range of potassium deposition and its effect on agglomeration of the charge is unclear yet.

5 ACKNOWLEDGEMENTS

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