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# OKREŚLENIE WARUNKÓW MAKSYMALNEGO ODCYNKOWANIA MIESZANKI MATERIAŁÓW ŻELAZONOŚNYCH W PROCESIE SPIEKANIA NA PODSTAWIE OBLICZEŃ NUMERYCZNYCH Z WYKORZYSTANIEM PROGRAMU TERMOCHEMICZNEGO FactSage

## DETERMINATION OF CONDITIONS FOR MAXIMUM DEZINCIFICATION OF A MIXTURE OF FERROUS MATERIALS IN THE SINTERING PROCESS BASED ON NUMERICAL CALCULATIONS USING THE FactSage THERMOCHEMICAL PROGRAM

Multi-million tons of sludge produced as a result of wet dedusting of blast furnace and converter gases have been deposited in landfills across the country. These materials are also created on an ongoing basis. Due to the high iron content, their potential as a ferrous raw material is significant. Unfortunately, in addition to components which are desirable from the point of view of metallurgical processes such as Fe, C and CO, they also contain many harmful elements such as Zn, Pb, Na and K. The article describes the sources and form of Zn found in post-production waste of steelworks and the methods of removing zinc from ferrous waste materials. The optimal conditions for zinc removal during the sintering process of galvanised ferrous materials were identified using thermochemical calculations carried out with the FactSage computer program.

**Keywords:** zinc, ferrous sludge, sinter, blast furnace, numerical simulations, dezincification

Na terenie kraju na składowiskach zdeponowano wielomilionowe ilości ton szlamów powstałych w wyniku mokrego odpylania gazów wielkopieczowych i konwertorowych. Materiały te powstają także na bieżąco. Z uwagi na dużą zawartość żelaza ich potencjał jako surowca żelazonośnego jest znaczący. Niestety oprócz pożądanych składników z punktu widzenia procesów metalurgicznych Fe, C, CO, zawierają one także wiele pierwiastków szkodliwych takich jak: Zn, Pb, Na, K. W artykule opisano źródła pochodzenia i postać Zn występującego w odpadach poprodukcyjnych hut oraz metody usuwania cynku z odpadowych materiałów żelazonośnych. Dokonano identyfikacji optymalnych warunków usuwania cynku w czasie procesu spiekania zacynkowanych materiałów żelazonośnych, dokonując obliczeń termochemicznych przy użyciu programu komputerowego FactSage.

**Słowa kluczowe:** cynk, szlam żelazonośny, spiek, wielki piec, symulacje numeryczne, odcynkowanie

### 1. INTRODUCTION

Circular economy is one of the three pillars of the sustainable economy philosophy [1]. Its goal is to eliminate waste and minimise the use of natural resources of the earth. Circular systems promote reuse, use, repair, regeneration and recycling to reduce the consumption of natural resources, waste generation

and carbon emissions [2]. The waste should become an input material for other industrial processes.

The need to dispose of sludge and dust from steelworks is a particularly urgent problem in Poland, as many millions of tons of this material have been deposited in landfills, and several hundred thousand tons are added each year. Sludge is formed as a result of wet dedusting of blast furnace and converter gases.

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Due to the high content of iron, this waste is a valuable ferrous raw material. In addition to components that are desirable from the point of view of metallurgical processes, such as: Fe, C and CaO, this sludge also contains metals whose presence in the blast furnace (BF) (the basic device for the production of pig iron in the world) is harmful. These are: Zn, Pb, Na and K, with zinc being particularly harmful, as it significantly reduces the efficiency of the blast furnace process as a result of causing the charge to hang, and also destroying the BF refractory lining.

Sludge produced in integrated steelworks are characterised by too high a content of Zn (2.5–10%), which makes it impossible to use them in the blast furnace process. Blast furnace sinter, which is the main component of ferrous charge in raw material steelworks operating in Poland, must not contain more than 0.015% of zinc. This sludge cannot be used in the zinc production industry due to the Zn content being too low for this application (required above 15%). Therefore, attempts are made at dezincifying this sludge in the process of sintering ore mixtures with its addition. So far, there is no industrial technology in the world to effectively remove Zn in the sintering process.

The article presents the results of numerical simulations performed in order to determine the conditions for the maximum dezincification of a mixture of ores and waste ferrous materials using the FactSage computer program. In addition, the sources of origin and the form of Zn found in post-production waste from steelworks and the methods of removing zinc from ferrous waste materials are described. It is expected that in the next article the results of physical simulations performed with the use of a semi-industrial sintering installation in a sintering pan will be described and the results of both simulations will be compared, and the developed technology of sintering with dezincification will be developed. All results are the result of statutory works carried out at Łukasiewicz – Institute for Ferrous Metallurgy.

## 2. STATE OF KNOWLEDGE IN THE FIELD OF ZINC REMOVAL FROM FERROUS WASTE IN IRON AND STEEL PRODUCTION PROCESSES

The source of zinc in BF or electric arc furnaces (EAF) are charge materials. In the case of BF, these are: iron ores, concentrates, blast furnace sinter, pellets or briquettes produced on the basis of ores and concentrates with the addition of dusts and sludge, and in the case of EAF it is steel scrap – the basic charge for furnaces for steel production. Zinc is an undesirable element in the production of pig iron or steel because when introduced into the BF it deteriorates the efficiency of the furnace and destroys the refractory lining, while in the process of steel production it creates growths in the furnace chamber which detach from the lining and, falling into the metal bath, disturb its final chemical composition. All these adverse effects of the presence of zinc in the processes of smelting pig iron and steel generate an increase in production costs.

### 2.1. SOURCES AND FORM OF ZN OCCURRING IN POST-PRODUCTION WASTE FROM STEELWORKS

#### 2.1.1. Blast furnace process – blast furnace sludge and dusts

Zinc is introduced into BF through input materials such as: iron ores and concentrates, blast furnace sinter or pellets, and steel scrap. In iron ores, Zn occurs mainly in the form of sphalerite (ZnS) and zinc carbonate ( $ZnCO_3$ ), as well as ferrite ( $ZnFe_2O_4$ ) and silicate ( $Zn_2SiO_4$ ). Zinc and the usually accompanying Pb are also found in many other fine-grained minerals and are often located at the edges of Fe oxide grains [3].

In sinters and pellets used for the blast furnace process, Zn is usually present in the form of silicate and spinel ( $ZnFe_2O_4$ ) [4]. In blast furnace dusts, Zn is present in the form of ZnO oxide and  $ZnFe_2O_4$  spinel

**Table 1. Sources and forms of zinc and lead in charge materials for iron production processes – blast furnace process [4, 5]**

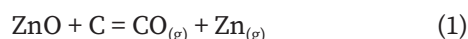
**Tabela 1. Źródła i postać występowania cynku i ołowiu w materiałach wsadowych do procesów wytwarzania żelaza – proces wielkopiecowy [4, 5]**

Source	Ingredient	Specifications
Iron ore	$ZnCO_3$ , ZnS, $ZnFe_2O_4$ and $Zn_2SiO_4$	The content of Zn in BF is minimal, mainly in the form of ZnO and Zn
	PbS, PbO, $PbSO_4$ and $PbCO_3$ or lead silicate	The content of Pb in BF is minimal. Pb occurs mainly in the form of PbO and Pb
Zn in sinter and pellets	ZnO, $Zn_2SiO_4$ , $ZnFe_2O_4$ and small amounts of ZnS	With good desulphurisation the content of $ZnSO_4$ and ZnS is minimal
	$PbO > PbO \cdot SiO_2$ and $2PbO \cdot SiO_2 >$ lead ferrite $> PbSO_4$ ; metallic Pb and PbS	Sintering causes desulphurisation – sulphides turn into oxides
Zn in (blast furnace) dust	Zinc compounds ranked according to their occurrence: $ZnFe_2O_4 > ZnO > Zn_2SiO_4 > ZnS$ and $ZnSO_4$	ZnO is easily leached, ale $ZnFe_2O_4$ is sparingly soluble
	PbO	

or  $Zn_2SiO_4$  zinc silicate, and in small amounts – zinc sulphide.

The sources of Zn and Pb in the iron production process are shown in Table 1.

During the blast furnace process, zinc with a melting point of 419°C and a boiling point of 907°C is first transformed into ZnO, and then it is reduced in the zone with a temperature above 950°C, turning into zinc vapour as a result of the following reaction [6]:



The reaction is endothermic and all its products are gases, therefore the conditions favouring it are: high temperature and low pressure.

### 2.1.2. Oxygen converter, electric furnace – steel sludge and dust

Zinc goes to these aggregates with galvanised steel scrap, e.g. car body plates, bodies of household appliances (refrigerators, washing machines).

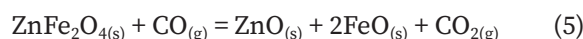
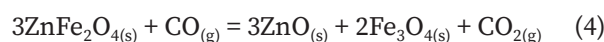
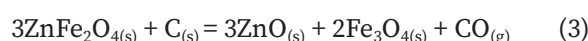
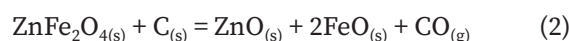
Practically the entire amount of zinc coming with the scrap charge to the oxygen converter (BOF) leaves it in the form of its vapours through the process gas extraction and purification system. Zinc compounds present in BOF dusts are characterised by high vapour pressure at steelmaking temperatures (<1600°C). The efficient evaporation of zinc is also favoured by the high production rate of the process gas. The final levels of zinc content in steel and slag are below 50 ppm [7, 8]. The grain and phase composition of the dust varies depending on the melting period in the BOF converter [9]. Dust with the largest particle size is formed before the blowing period, the finest during the blowing period, and medium-sized – after this period. Converter dust stored outside for many years undergoes significant iron oxidation to  $Fe_3O_4$  and  $Fe_2O_3$  [10, 11].

Dusts from electric arc furnaces (EAF) usually contain a dozen or so percent of Zn. This is due to the fact that the process is based on scrap of increasingly galvanised steel products. In addition, the ability to recycle the dust increases its Zn content. This makes it possible to obtain its content at the level of twenty percent and higher, which guarantees economical processing of the dust with zinc recovery in the Walz process.

## 2.2. REDUCTION OF MINERALS CONTAINING ZINC

From the processes used in the zinc metallurgy, it is known that obtaining zinc from its sulphide minerals (ZnS) is carried out by oxidative roasting, followed by CO or C and CO reduction to Zn vapour [4, 12, 13], in the presence of CaO and C or CO at a temperature in the range of 900–1000°C. At temperatures above 1167°C, Fe replaces Zn in ZnS and Zn becomes vaporised. During oxidative roasting, ZnS turns into ZnO at 750°C and forms  $ZnFe_2O_4$  with  $Fe_2O_3$  [14]. The reduction of  $ZnFe_2O_4$  is not simple and takes place with

C and CO to ZnO. Typical reactions are given by the following formulas:



$ZnFe_2O_4$  decomposes into  $Fe_3O_4$  and ZnO at 650°C according to reaction (3) or (4). The share of ZnO on the surface of  $ZnFe_2O_4$  particles gradually increases with increasing temperature. At temperatures above 850°C, reactions (2) and (5) occur. The produced FeO will be partially reduced to the original Fe. At 950°C,  $ZnFe_2O_4$  can be completely reduced to Fe [4].

The decomposition temperature of  $ZnSO_4$  into ZnO and  $SO_2$  is 921°C, and  $ZnSO_4$  can also be reduced to ZnS using C or CO [12].

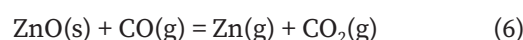
At 700–950°C,  $Zn_2SiO_4$  decomposes in two stages.

In the first stage,  $Zn_2SiO_4$  decomposes into ZnO and  $SiO_2$ , and in the second stage, Zn is released from ZnO in the form of vapour [15]. ZnO decomposes to form zinc vapours in the temperature range of 700–950°C.

$ZnCO_3$  can thermally decompose completely to ZnO at relatively low temperatures (~300°C) [16].

C, CO,  $CH_4$ ,  $H_2$  and Fe can be ZnO reducers, with C and CO being the main reducers [17].

Oxidation, reduction and decomposition are the main reactions in the pyrometallurgical Zn smelting process. Similarly, zinc can be recovered from its compounds contained in blast furnace and steelmaking dusts by reduction with carbon or with the use of CO.



Using high-temperature chlorination and reductive roasting, ZnO is converted into  $ZnCl_2$  with a low boiling point and high volatility, and thus Zn can be removed and  $ZnCl_2$  vapours recovered [14].

## 2.3. METHODS OF REMOVING ZINC FROM WASTE FERROUS MATERIALS

A number of studies are being carried out to develop effective and economically viable dust treatment methods to recover metallic Zn, Pb, Cd and Fe. These methods include pyrometallurgical as well as hydrometallurgical and hybrid processes.

Various processes are known to remove Zn from blast furnace sludge, such as:

- separation of coarse-grained dusts from fine-grained ones, i.e. those with a lower content of zinc from those rich in zinc, using the mechanical or magnetic method,
- leaching: with acid or alkaline (microwave-assisted leaching was also tested),

- roasting,
- chlorinating.

These processes may be combined into ‘hybrid processes’.

So far, the removal of Zn from blast furnace dusts and sludge in chemical or thermal processes is uneconomical due to the large mass of waste. Currently, in the era of striving for a sustainable economy, economic issues become less important, and the use of all waste becomes obligatory. The pursuit of zero CO<sub>2</sub> emissions is an obstacle to the use of some methods.

In 2006, dust treatment processes were mainly pyrometallurgical [18] and accounted for over 99% of their recycling capacity. Most of them are based on the following processes: in rotary kilns, plasma and flame reactors. In order to concentrate the zinc content to levels that justify the economics of processing, dust recycling is used in the BOF and EAF steel-making processes.

**Reduction roasting or sintering** are known processes for removing zinc from materials. Carrying out the reduction of ZnO and increasing the rate of removal of zinc vapours requires controlling the atmosphere and temperature in the range of thermodynamic stability of FeO and Zn [15]. The dezincification stage in the reduction roasting process requires a reducing atmosphere, usually CO–CO<sub>2</sub>, and the use of a (solid) carbon reducer, as well as the use of iron oxide (FeO). The tests showed that the dezincification process was intensified when the share of coke was 9.0 wt% of the amount of raw material, and the CO content in the gases reached 20 vol%. Iron oxide played an important role in the reduction of ZnO: when the CO content was less than 20 vol%, ZnO and Fe<sub>3</sub>O<sub>4</sub> reacted to form ZnFe<sub>2</sub>O<sub>4</sub>, CO<sub>2</sub> was the oxidant that promoted the conversion of Fe<sup>2+</sup> to Fe<sup>3+</sup>. Increasing the temperature also favoured the formation of ZnFe<sub>2</sub>O<sub>4</sub>. The influence of iron oxide on the reduction of ZnO gradually weakened with the increase of the CO content above 20 vol%.

Another possible zinc extraction technology is **chlorination**. The possibility of using chlorination to extract metals from waste was determined by the fact that chlorine shows high reactivity towards many compounds at relatively low temperatures. Chlorination is the reaction of the starting material (mineral concentrate or industrial waste) with chlorine to produce volatile chlorides, which can then be separated. The most desirable chloride is purified and then used as a raw material for the production of pure metal or its oxide (by oxidation of the chloride). As a result, roasting chlorination is a pyrometallurgical technique that can be used to recover metals. It is economical to use for the recovery of metals from various industrial wastes: by-products [19], spent catalysts [20], slags [21] and fly ashes [22]. Chlorination processes require appropriate safeguards to protect equipment and the environment, e.g. it is important

to remember about the need to purify the exhaust gases, e.g. using an aqueous NaOH solution, before releasing them into the atmosphere.

The knowledge of the influence of different variables on the reactivity of the system is the basis for the development of metal recovery technology by **roasting with the use of chlorides**.

The mechanism of extraction of iron and zinc with chlorination results from their thermodynamic properties: transition temperatures and Gibbs free energy at 727 °C (1000 °K) of iron and zinc.

Pure oxides can be converted to chlorides as a result of metal oxide reacting with a chlorinating agent, which are more readily reduced to metals. The metal chloride obtained at sufficiently high temperatures evaporates and can be recovered from the gas phase by condensation. The advantage of the chlorination process is the low melting and boiling points of the produced chlorides and the difference in their vapour pressure in the chlorination temperature range. Selective separation of valuable metal chlorides (CuCl<sub>2</sub>, PbCl<sub>2</sub> and ZnCl<sub>2</sub>) from iron and sulphur chlorides is possible due to the difference in vapour pressure between these two groups of chlorides at relatively low temperatures, e.g. 300 °C [11, 23].

Roasting with chlorination of BOF (basic oxygen furnace) dust under laboratory conditions showed promising results. More than 80% of the zinc was removed at the roasting temperature of 1000 °C, with a CaCl<sub>2</sub>:BOF dust ratio of 1:10 [24]. The key factors of chlorination selectivity were found to be: reaction temperature, time and partial pressure. In addition, it was shown that unroasted material has a higher reaction rate than roasted samples, and that increasing the process temperature increases the chlorination effect. Chlorinating agents can be added in gaseous, liquid or solid form. Solid chlorinating agents include: CaCl<sub>2</sub>, MgCl<sub>2</sub>, NaCl, AlCl<sub>3</sub>, NH<sub>4</sub>Cl [25]. Examples of gaseous agents that can be used in the chlorination technology are: chlorine and hydrogen chloride. The liquid agents are carbon tetrachloride (CCl<sub>4</sub>) and sulphur chloride (S<sub>2</sub>Cl<sub>2</sub>). Both are sometimes used in their gaseous state. Temperature is an important factor in chlorination. The chlorides of the extracted metals evaporate in the temperature range of 600–1000 °C. It was found that with increasing temperature there is a noticeable increase in the rate of reaction [26].

The use of gaseous chlorine is restricted due to the hazards associated with it. Chlorine gas is toxic, corrosive and known to cause severe irritation to the respiratory system, skin and eyes. Therefore, it is preferable to use liquids and solids that release gaseous hydrogen chloride as the chlorinating agent. The most commonly used solid reagents are: NaCl and CaCl<sub>2</sub>.

### 3. IDENTIFICATION OF OPTIMAL CONDITIONS FOR ZINC REMOVAL DURING THE SINTERING PROCESS OF GALVANISED FERROUS MATERIALS – THERMOCHEMICAL CALCULATIONS USING THE FACTSAGE COMPUTER PROGRAM

#### 3.1. NUMERICAL SIMULATIONS OF DEZINCIFICATION DURING SINTERING PROCESS

The simulations were performed using the FactSage 7.2 thermochemical program using the FactPS and FToxid databases and the Equilib calculation module. The aim of the simulation was to identify the optimal conditions for zinc removal during the sintering process of galvanised ferrous materials.

#### 3.2. SCOPE OF NUMERICAL SIMULATIONS

The scope of the calculations included:

- behaviour of ZnO zincite during heating in the following atmosphere conditions: oxidising (oxygen) and reducing (CO),
- determination of the dependence of the degree of dezincification of the ore mixture with the participation of galvanised sludge in the sintering process as a function of: pressure and temperature of the sintering process, alkalinity of the mixture (% CaO / % SiO<sub>2</sub>) and the share of the dezincification agent in the form of: NaCl and/or CaCl<sub>2</sub>, in two variants: in the oxidising and reducing atmosphere.

#### Assumptions adopted for the calculations:

- Constant parameters:
  - basic composition of the ore mix: 40 % Kryvbas + 50 % Kryvyi Rih + 10 % converter sludge,

- form of zinc in the sintered material: mainly ZnO,
- type of fluxes: quicklime + limestone + dolomite,
- simulation temperature range: from 500 °C to 1400 °C.
- Variable parameters:
  - alkalinity resulting from the addition of quicklime and limestone, and consequently the ratio of the share of CaO to SiO<sub>2</sub> contained in the ore components ( $B = \%CaO / \%SiO_2$ ): in the range of 0.8 to 1.6,
  - pressure: 1 atm, 0.1 atm, 0.05 atm, 0.01 atm,  $1 \cdot 10^{-3}$  atm,  $1 \cdot 10^{-4}$  atm,  $1 \cdot 10^{-5}$  atm.

The negative pressure in the sintered layer is the result of air being drawn through the ore mix on the sinter belt. According to literature data [28], the oxygen pressure is between  $10^{-5}$  and  $10^{-6}$  atm in the zone with a temperature of 1350 °C.

In the zone corresponding to the temperature range from 600 to 1000 °C, the oxygen pressure increases to the level of  $10^{-4}$  atm.

The measurement of the negative pressure under the sintering pan of the semi-industrial sintering line at Łukasiewicz – IMŻ, depending on the fan sequence used to draw air through the sintered layer in a given sintering test, shows negative pressures in the following range: from 3,500 Pa to 18,000 Pa (from ~0.035 atm to ~0.178 atm).

#### 3.2.1. Behaviour of zincite ZnO during heating in the conditions of an oxidising atmosphere (oxygen)

Under atmospheric pressure, zincite (ZnO) sublimates at 1800 °C [20]:

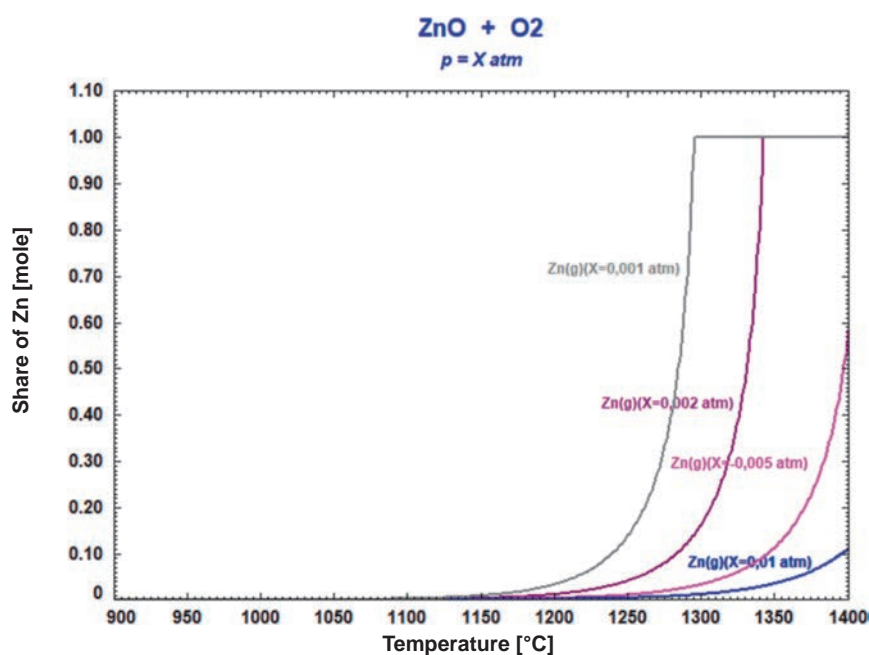
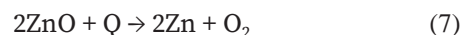


Fig. 1a. Change in the share of Zn in the gas phase as a function of temperature, at different pressures (from 0.001 to 0.01 atm) in an oxidising atmosphere

Rys. 1a. Zmiana udziału Zn w fazie gazowej w funkcji temperatury, przy różnych wartościach ciśnienia (od 0,001 do 0,01 atm) w atmosferze utleniającej

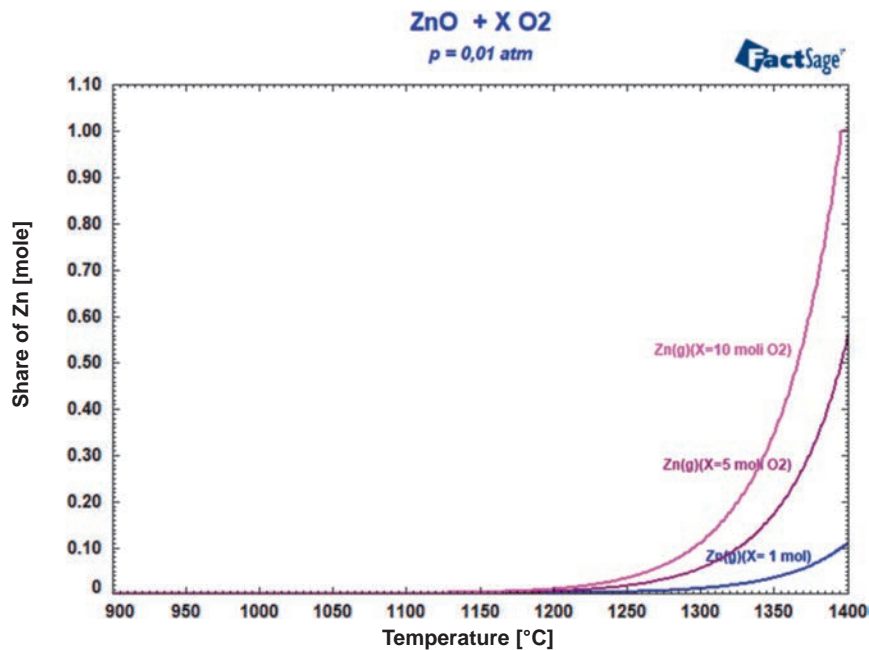


Fig. 1b. Change in the share of Zn in the gas phase as a function of temperature at a pressure of  $p = 0.01$  atm in an oxidising atmosphere, with different share of oxygen in the system ( $X = 1; 5$  and  $10$  moles)

Rys. 1b. Zmiana udziału Zn w fazie gazowej w funkcji temperatury przy ciśnieniu  $p = 0,01$  atm w atmosferze utleniającej, przy różnym udziale tlenu w układzie ( $X = 1; 5$  i  $10$  moli)

The calculations show that zincite heated in an oxidising atmosphere goes directly from solid to gaseous state (sublimation), enriching the gaseous phase of the system with oxygen and zinc.

The obtained results of the simulations show that this transformation is influenced by the pressure and oxygen content. The lower the pressure, i.e. the higher the negative pressure, the lower the temperature of and the faster the zincite sublimation process (Fig. 1a). Increasing the share of oxygen in the system increases the rate of zinc sublimation (Fig. 1b). It should be noted that for the defined system this process occurs intensively in the temperature range of  $\sim 1300$ – $1350^\circ\text{C}$ , at a pressure not higher than  $2 \cdot 10^{-3}$  atm.

### 3.2.2. Behaviour of zincite ZnO during heating in CO reducing atmosphere

The sinter mix contains solid fuel, usually in the form of coke breeze (fine coke). In the process of coke breeze combustion, CO is formed, which is then burnt to  $\text{CO}_2$  as a result of excess oxygen from the air sucked through the sintered layer. In certain areas of the sintered layer, CO, which can act as a reducing agent, is present during the process.

Fig. 2 shows a graph of changes in the composition of process gases (flue gases) collected during the iron ore sintering process.

Zincite heated in a reducing atmosphere of carbon monoxide is reduced by carbon monoxide according to the following reaction:



This process is strongly dependent on temperature and, above all, on pressure. The lower the pressure (higher negative pressure), the more intensive the reduction process takes place at lower temperatures. As a result of the Boudouard reaction ( $2 \text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ ), carbon in the form of graphite, CO and  $\text{CO}_2$  are present in the system.

Figure 3 shows the influence of pressure on the process of carbothermic reduction of ZnO.

### 3.2.3. Carbothermic reduction of ZnO with CO deficiency

The results of the numerical simulation of the ZnO reduction process in the CO reducing atmosphere, with a reducer deficiency, in comparison with the stoichiometric amount, showed full carbothermic reduction under atmospheric and reduced pressure (the calculations were made for the following pressures: 1 atm, 0.1 atm, 0.05 atm 0.001 atm). The process takes place in two stages (Fig. 4), the first occurring at lower temperatures is most likely the result of reduction with carbon monoxide, while the second, occurring at higher temperatures, is the result of thermal decomposition.

The lower the process pressure, the lower the temperature required for the transition of zinc from ZnO to gaseous Zn.

### 3.2.4. Dependence of the dezincification of the sinter mixture with the use of dry blast furnace sludge on the negative pressure

Simulations were performed in two variants: in an oxidising (oxygen) and reducing (carbon monoxide) atmosphere. The chemical composition of the sintered

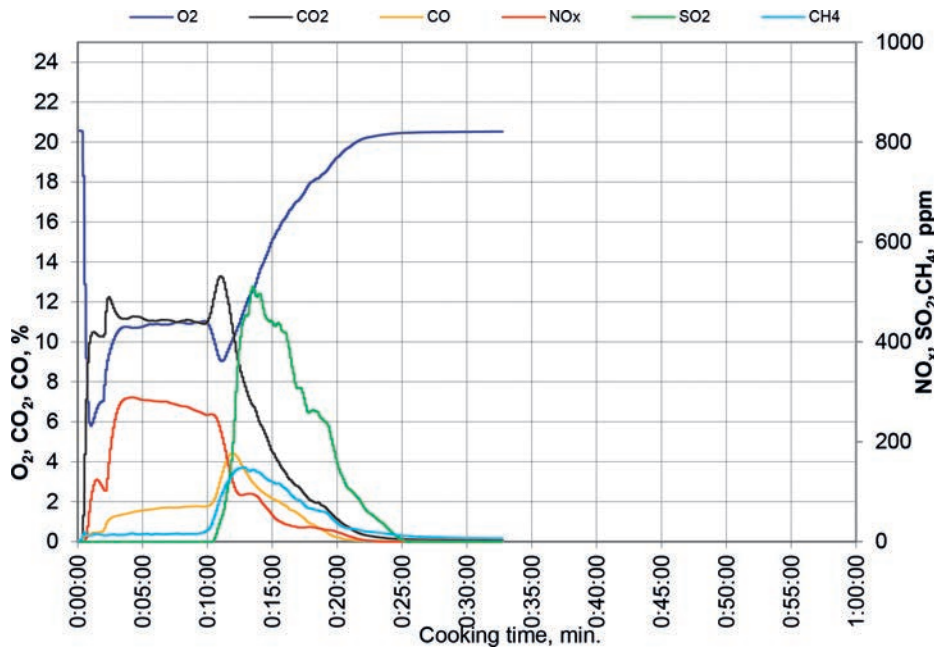


Fig. 2. Change in the composition of gases in the flue gas – an analysis was performed during one of the sintering tests with the participation of galvanised sludge, at the pressure under the pan 3500 Pa = 0.034542 atm

Rys. 2. Zmiana składu gazów w spalinach – przykładowa analiza wykonano w trakcie jednej z prób spiekania z udziałem cynkowego szlamu, przy ciśnieniu pod misą 3500 Pa = 0,034542 atm

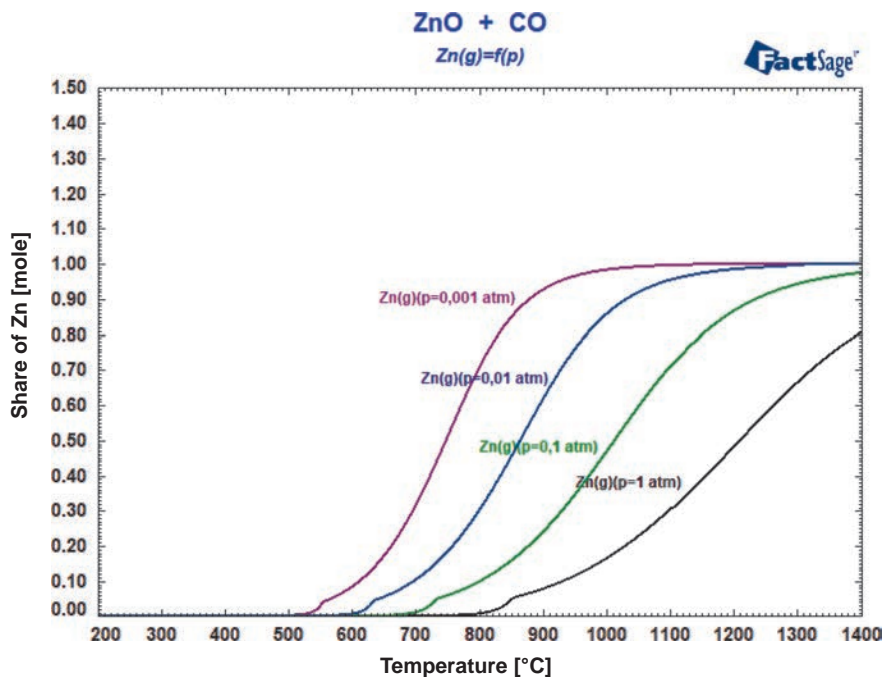


Fig. 3. Change in the share of ZnO as a result of carbothermic reduction at different pressures (0.001; 0.01; 0.1 and 1.0 atm) in the range up to 1400°C

Rys. 3. Zmiana udziału ZnO w wyniku redukcji węglotermicznej przy różnym ciśnieniu (0,001; 0,01; 0,1 i 1,0 atm) w zakresie do 1400°C

mixture and the oxygen content adopted for the calculations are presented in Table 2. The performed calculations include the change in the phase composition of the sintered mixture and the change in the zinc content in the solid phases, liquid slag phase and gas phase.

On the basis of the oxide composition of the mixture of iron ores, dry sludge from converters and blast furnaces, and used fluxes in the form of quicklime, limestone and dolomite in the atmosphere of

oxygen from the air, changes in the phase composition under equilibrium conditions were simulated. Figures 5 and 6 show the transition of zinc from solid to gaseous state depending on temperature and pressure.

The transition of zinc from a solid to gaseous state depends on temperature and pressure.

Comparing Figures 5 and 6, it can be concluded that in the process of sintering in a reducing atmos-

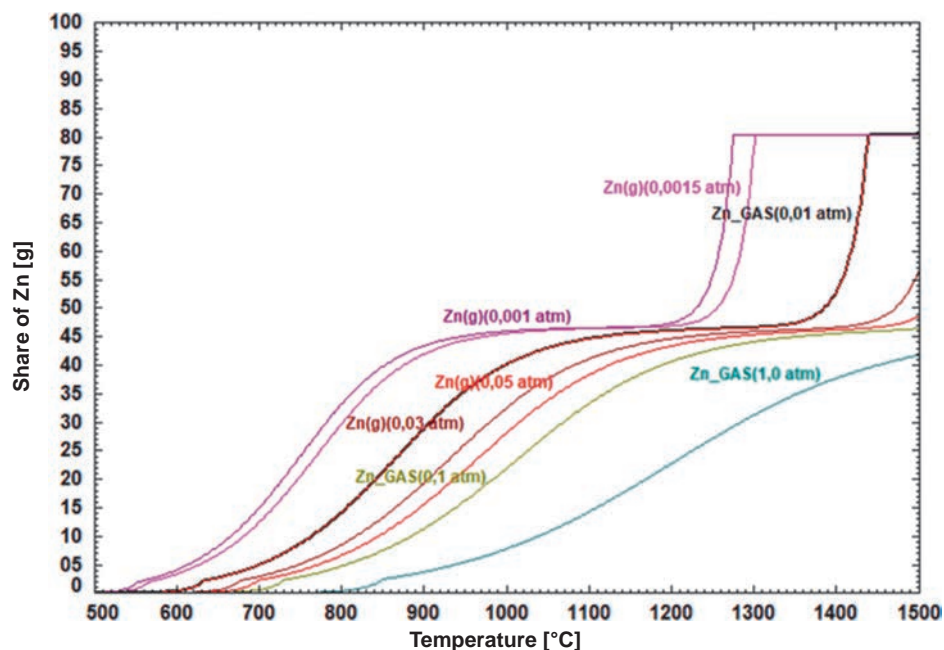


Fig. 4. Change in the gaseous content of zinc in the 100ZnO+20CO system as a function of temperature at different pressures  
 Rys. 4. Zmiana udziału gazowego cynku w układzie 100ZnO+20CO w funkcji temperatury przy różnym ciśnieniu

Table 2. Chemical composition of a system composed of a sintered mixture and oxygen from the accompanying atmosphere  
 Tabela 2. Skład chemiczny układu złożonego ze spiekanej mieszanki i tlenu z towarzyszącej atmosfery

Ores + sludge	Content [weight %]								B = CaO/SiO <sub>2</sub>
	FeO	Fe <sub>3</sub> O <sub>4</sub>	SiO <sub>2</sub>	CaO	Al <sub>2</sub> O <sub>3</sub>	MgO	ZnO	O	
32.84%K+ 41.05 KR+ 8.21S+1.5Q+14.4L+2.0Dol)	17.15	55.34	6.94	11.11	0.74	0.64	0.2044	7.8	1.6

K – Kryvbas sinter ore, KR – Kryvvi Rih concentrate, S – sludge from converters and blast furnaces, Q – quicklime, L – limestone, Dol – dolomite

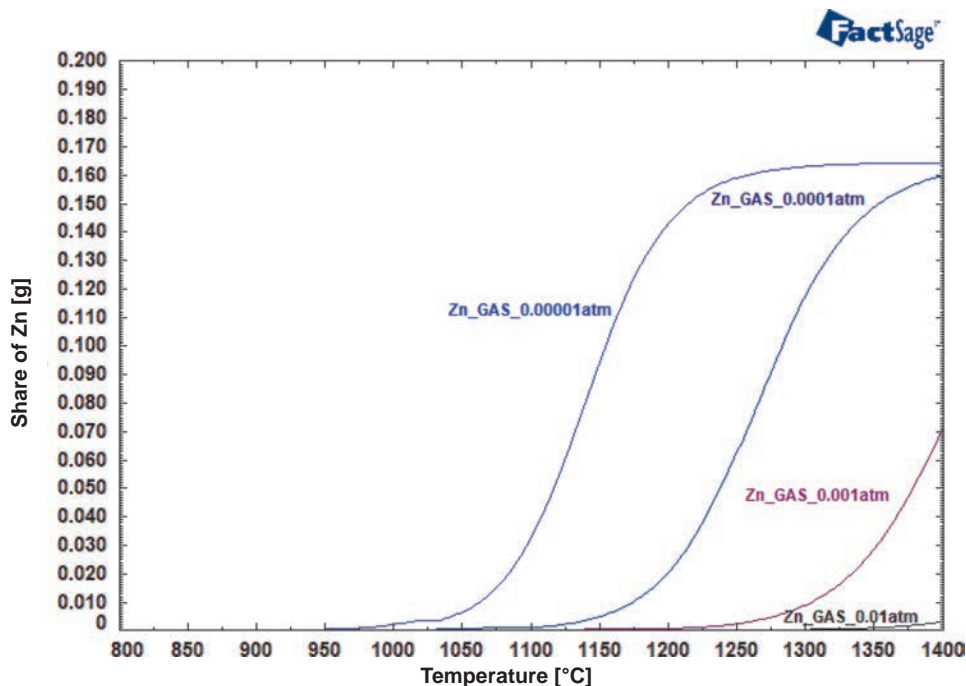


Fig. 5. Share of zinc in the gas phase as a function of temperature – the process of dezincification of the mixture during sintering at different negative pressure for the system: sinter mix: 17.2 % FeO; 55.34 % Fe<sub>3</sub>O<sub>4</sub>; 6.94 % SiO<sub>2</sub>; 11.11 % CaO; 0.74 % Al<sub>2</sub>O<sub>3</sub>; 0.64 % MgO; 0.2044 % ZnO; oxidising atmosphere – oxygen

Rys. 5. Udział cynku w fazie gazowej w funkcji temperatury - proces odcynkowania mieszanki w czasie spiekania przy różnym podciśnieniu dla układu: mieszanka spiekalnicza: 17,2 % FeO; 55,34 % Fe<sub>3</sub>O<sub>4</sub>; 6,94 % SiO<sub>2</sub>; 11,11 % CaO; 0,74 % Al<sub>2</sub>O<sub>3</sub>; 0,64 % MgO; 0,2044 % ZnO; atmosfera utleniająca – tlen



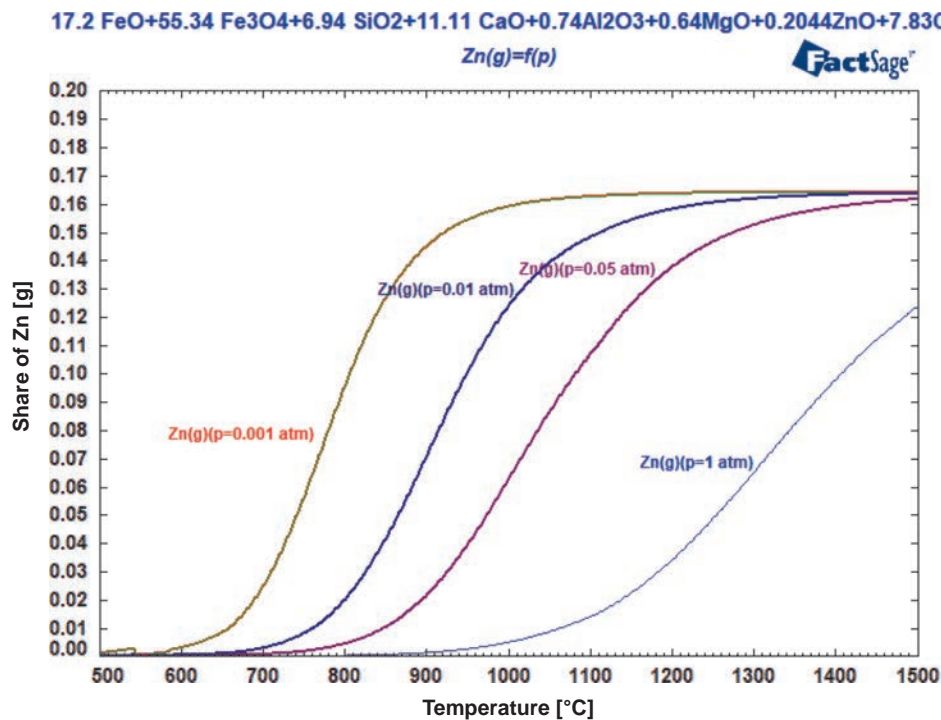


Fig. 6. Course of zinc sublimation during heating of the sinter mix with the above-mentioned chemical composition at different pressure values:  $p = 0.001$  atm,  $p = 0.01$  atm,  $p = 0.05$  atm,  $p = 1$  atm; reducing atmosphere – CO

Rys. 6. Przebieg sublimacji cynku w czasie ogrzewania mieszanki spiekalniczej o podanym wyżej składzie chemicznym przy różnej wartości ciśnienia:  $p = 0,001$  atm,  $p = 0,01$  atm,  $p = 0,05$  atm,  $p = 1$  atm; atmosfera redukcyjna – CO

phere, zinc will be removed much faster, i.e. at lower temperatures and higher pressure.

### 3.2.5. Dependence of the dezincification of the sinter mix with dry blast sludge from converters and blast furnaces on its alkalinity

The alkalinity of the sinter mix is expressed as % aO / % SiO<sub>2</sub>. In order to study the influence of this parameter on the dezincification process during sintering, a number of simulations were performed for three values of this index: 1.3, 1.0 and 0.8, and the required alkalinity of the mixture was obtained by appropriately reducing the share of CaO, while maintaining all its other components. Like all previous simulations, the simulations were performed in oxidising and reducing atmospheres. Figures 7 and 8 show changes in the share of Zn in the gas phase with increasing temperature for different alkalinities of the sinter mixture.

Based on the comparison of Fig. 7 and Fig. 8, it can be concluded that, in contrast to the case of sintering in an oxidising atmosphere, the alkalinity has some effect on the dezincification process of the sinter mix in the case of a reducing atmosphere. The higher alkalinity of the mixture favours its dezincification as a result of the formation of Zn vapours. The process takes place in the same temperature range under the conditions of a given negative pressure, but it is faster – more intensive for the case of higher alkalinity.

### 3.2.6. Dependence of the dezincification of the sinter mix with the use of dry sludge from converters and blast furnaces on the share of sodium chloride or calcium chloride in the mix

The factor intensifying the dezincification process of the iron ore sinter mix and zinc-coated waste (sludge, dust) is chlorine added to the mix in the form of NaCl or CaCl<sub>2</sub>, and the dezincification mechanism consists in the formation of ZnCl<sub>2</sub> and PbCl<sub>2</sub> chlorides, whose evaporation temperatures are low and amount to: 732°C and 954°C. Unfortunately, the disadvantage of using chlorides is their destructive effect on the structural components of devices. They destroy refractory materials of BF's refractory linings and disturb the operation of the furnace. Simulations were carried out for the basicity of the mixture  $B = 0.8$  and 1.6 and for the pressure  $p = 1$  atm, 0.01 atm and 0.05 atm. The addition of chloride in the amount of 2% of the mass of the sinter mix was assumed for the calculations.

Based on the calculations, it can be concluded that the higher the negative pressure, the faster (i.e. in the range of lower temperatures and more intensive) the dezincification process will take place. In the case of heating a mixture containing sodium chloride, zinc, at the appropriate temperatures for a given pressure value, will exist as an independent gas phase and/or in the gas phase of zinc chloride (ZnCl<sub>2</sub>) and complex sodium and zinc chloride (NaZnCl<sub>3</sub>).

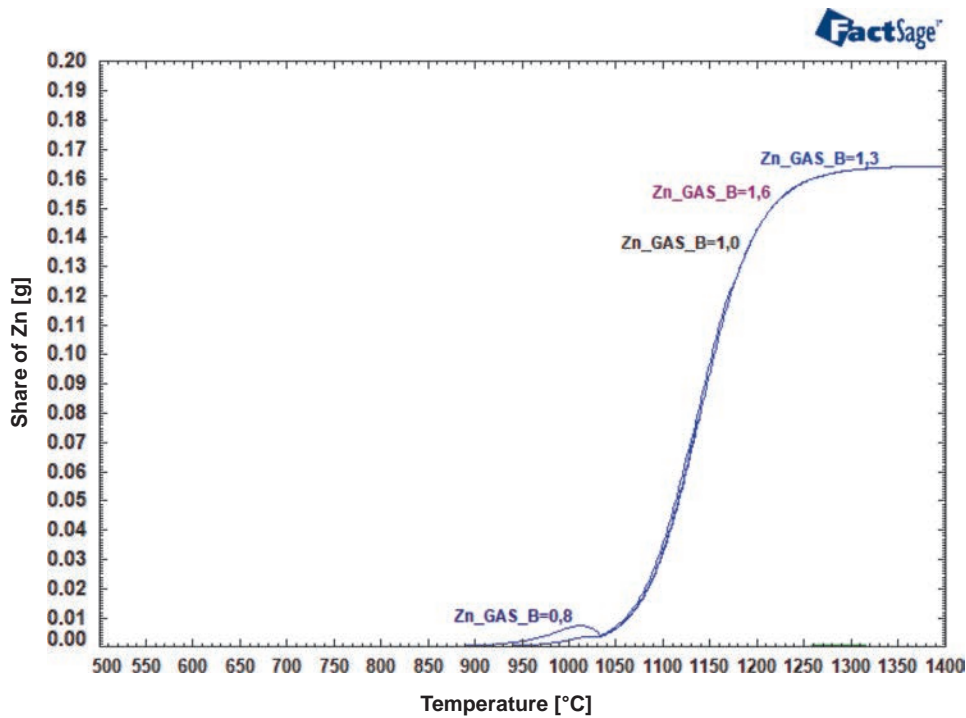


Fig. 7. Increase in the share of Zn in the gas phase with the increase in temperature – course of the dezincification process of the sintered material with different alkalinity  $B = \%CaO/\%SiO_2$  0,8, is 1,0; 1,3 and 1,6, respectively; at negative pressure  $p = 0.00001$  atm; oxidising atmosphere

Rys. 7. Przyrost udziału Zn w fazie gazowej w raz ze wzrostem temperatury – przebieg procesu odcynkowania materiału spiekane go o różnej zasadowości  $B = \%CaO/\%SiO_2$  odpowiednio 0,8; 1,0; 1,3 i 1,6; przy podciśnieniu  $p = 0,00001$  atm; atmosfera utleniająca

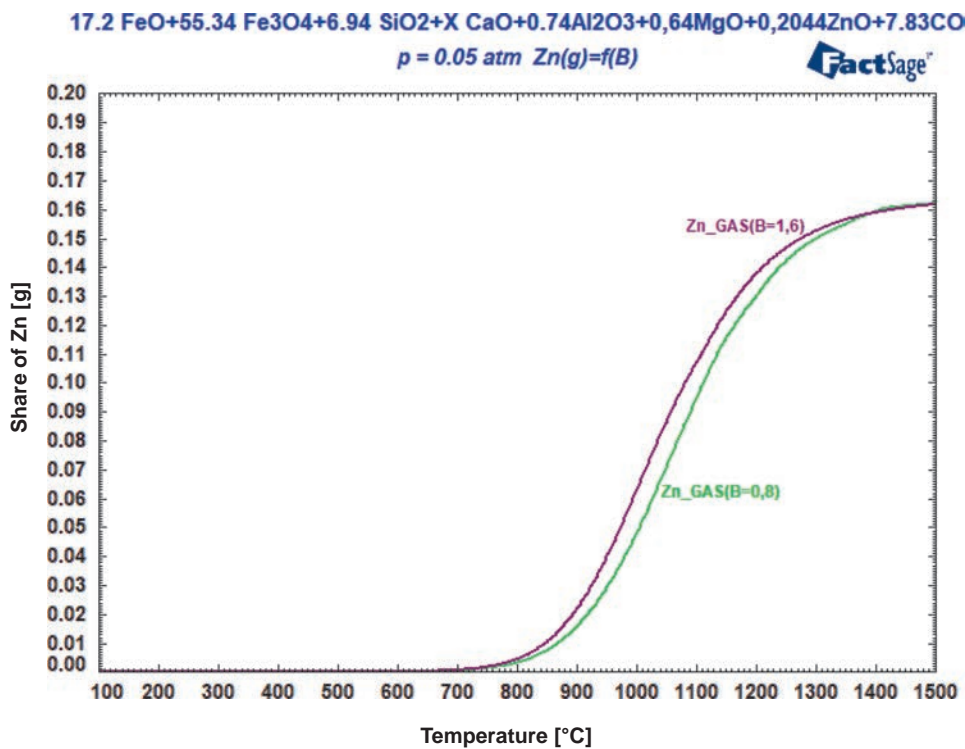


Fig. 8. Change in the gaseous content of zinc as a function of temperature in a system with the above-mentioned oxide composition at a negative pressure of 0.05 atm: reducing atmosphere; violet curve: alkalinity  $B = \%CaO/\%SiO_2 = 1.6$ ; green curve: alkalinity  $B = \%CaO/\%SiO_2 = 0.8$

Rys. 8. Zmiana udziału gazowego cynku w funkcji temperatury w układzie o podanym wyżej składzie tlenkowym przy podciśnieniu równym 0,05 atm: atmosfera redukcyjna; krzywa fioletowa: zasadowość  $B = \%CaO/\%SiO_2 = 1,6$  ; krzywa zielona: zasadowość  $B = \%CaO/\%SiO_2 = 0,8$

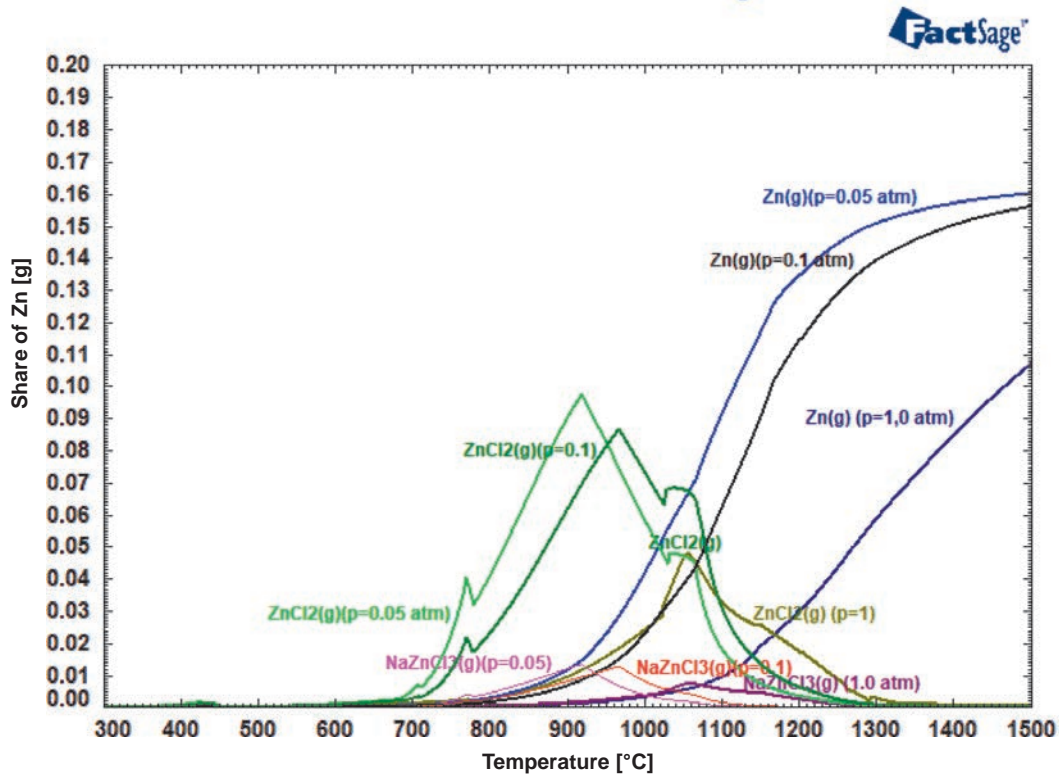


Fig. 9a. Share of Zn in individual gas phases in a system with the above-mentioned chemical composition as a function of temperature – summary drawing for pressure  $p = 1.0$  atm;  $0.1$  atm and  $0.05$  atm

Rys. 9a. Udział Zn w poszczególnych fazach gazowych w układzie o podanym wyżej składzie chemicznym w funkcji temperatury – rysunek zbiorczy dla ciśnienia  $p = 1,0$  atm;  $0,1$  atm i  $0,05$  atm

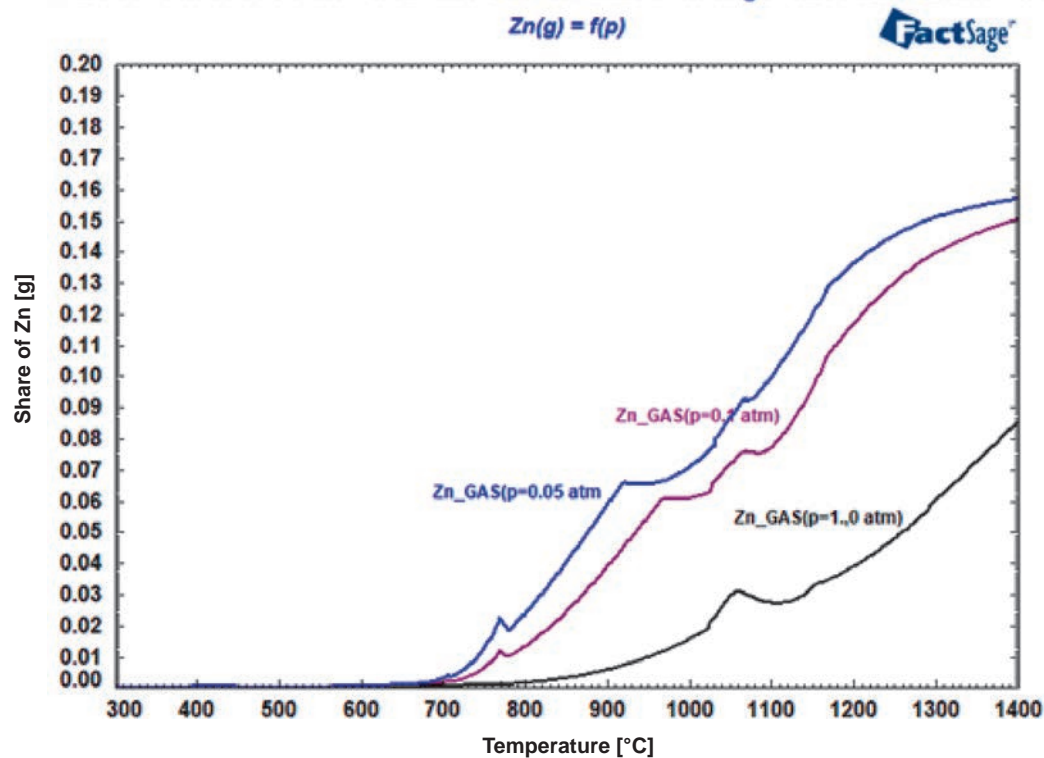


Fig. 9b. Change in the gas share of Zn as a function of temperature for different pressures:  $p = 1$  atm,  $0.1$  atm and  $0.05$  atm

Rys. 9b. Zmiana udziału gazowego Zn w funkcji temperatury dla różnej wielkości ciśnienia:  $p = 1$  atm,  $0,1$  atm i  $0,05$  atm

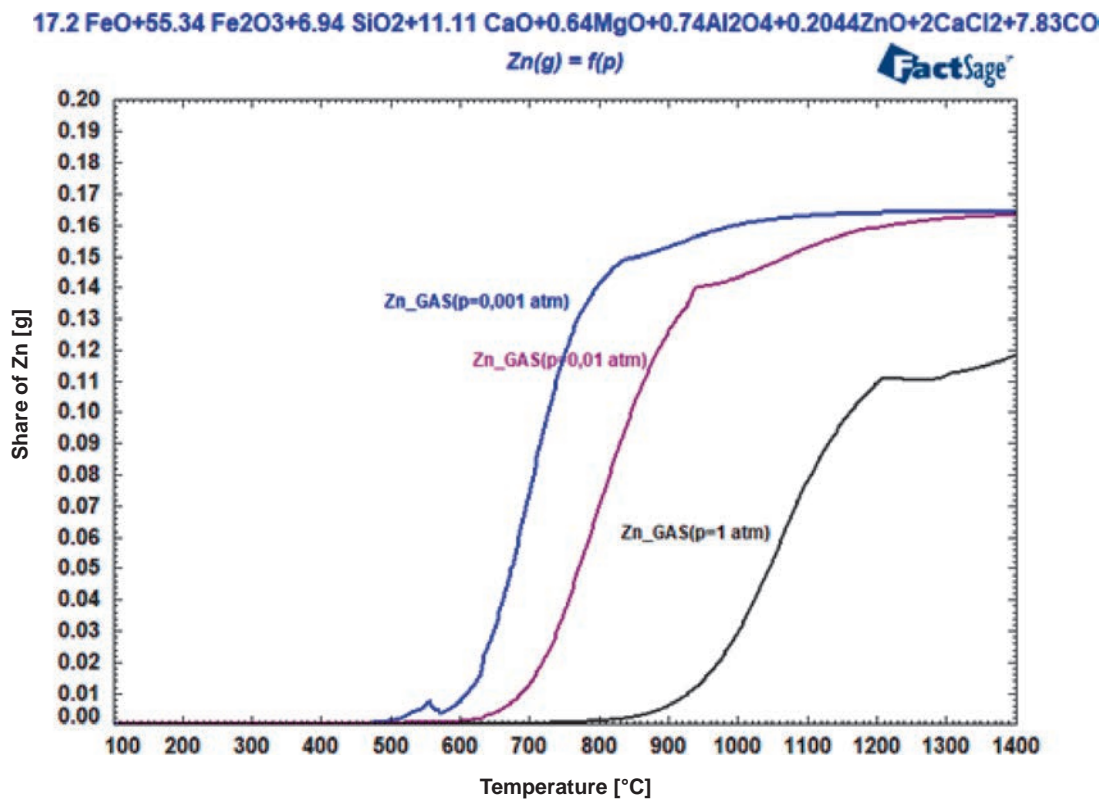


Fig. 10. Change of the gas share of Zn as a function of temperature for different pressures:  $p = 1$  atm, 0.01 atm and 0.001 atm  
 Rys. 10. Zmiana udziału gazowego Zn w funkcji temperatury dla różnej wielkości ciśnienia:  $p = 1$  atm, 0,01 atm i 0,001 atm

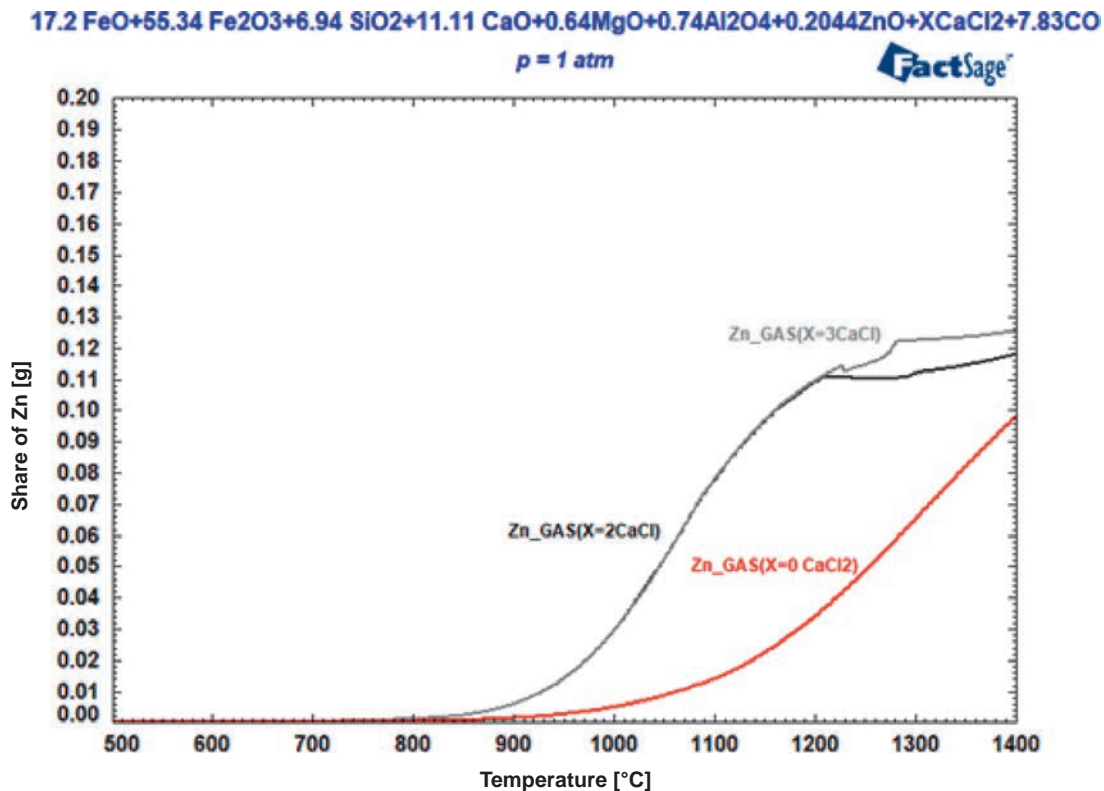


Fig. 11. Change in the share of gaseous zinc in the system defined above as a function of temperature for different shares of  $\text{CaCl}_2$ : 0, about 2% and 3% of the mixture mass, respectively

Rys. 11. Zmiana udziału cynku gazowego w układzie zdefiniowanym powyżej w funkcji temperatury dla różnego udziału  $\text{CaCl}_2$ : odpowiednio 0%, około 2% i 3% masy mieszanki

Fig. 9a shows the share of Zn in individual gas phases as a function of temperature, using sodium chloride (NaCl) for dezincification of the sinter mix with the addition of blast furnace sludge in a reducing atmosphere. In turn, Fig. 9b shows the course of changes in the share of zinc in the gaseous state (the sum of zinc present in various gas phases) as a function of temperature, at different pressures: 1.0 atm, 0.1 atm and 0.05 atm.

Fig. 10 shows the results of the simulation of dezincification of the sinter mix using calcium chloride  $\text{CaCl}_2$  (in the amount of 2% of the mix mass). The result of the calculations showed that the lower the pressure, the faster the dezincification process using  $\text{CaCl}_2$  at lower temperatures.

Fig. 11 presents the results of the simulation of the dezincification process during sintering of the mix without chlorides and with calcium chloride ( $\text{CaCl}_2$ ) at the level of 2% and 3% of the mass of the sinter mix. The following were assumed: pressure of 1 atm; alkalinity of 1.6, and mixture composition analogous to previous simulations. The chart shows that:

- the addition of calcium chloride favours the dezincification of the mixture, significantly increasing its degree, and the process itself takes place at lower temperatures,
- increasing the share of  $\text{CaCl}_2$  from 2 to 3% slightly increased the degree of dezincification in the temperature range above 1200°C.

#### 4. SUMMARY AND CONCLUSIONS

The article presents the results of numerical simulations performed in order to determine the conditions of maximum dezincification of a mixture of ferrous materials in the sintering process.

The first part presents information on the sources, forms and amounts of Zn found in waste from black metallurgy processes: in sludge and dusts from blast furnaces and steelworks. In addition, the processes of zinc reduction from zinc-containing minerals and methods of zinc removal from ferrous waste materials were characterised.

The second part presents the results of thermochemical simulations of the sintering process with dezincification of materials containing iron and zinc in an oxidising (oxygen) and reducing (CO) atmosphere. They included the determination of the influence of: temperature, pressure, oxidising and reducing atmospheres, alkalinity and the content of chlorides, on the dezincification process of the sinter mix with a specific chemical composition.

The results of the numerical simulations carried out allow the following conclusions to be drawn:

1. The dezincification process takes place at lower temperatures in a reducing atmosphere compared to an oxidising atmosphere, which is probably related to the mechanism of the process, because in

the case of an oxidising atmosphere thermal decomposition of ZnO occurs, and in the case of a CO atmosphere ZnO reduction occurs.

2. Pressure has the strongest effect on the dezincification process. The greater the negative pressure, the faster and to a greater extent the dezincification at lower temperatures.
3. Chlorides introduced into the mixture significantly intensify the process of its dezincification.
4. The effect of the alkalinity of the sinter mix on the process of its dezincification was not unequivocally observed. Simulations in an oxidising atmosphere showed no effect of alkalinity on the course of dezincification. On the other hand, in a reducing atmosphere, there is an increase in the degree of dezincification with an increase in alkalinity, while simulations of sintering in a reducing atmosphere in the presence of chlorides showed an intensification of the dezincification process with a decrease in alkalinity. Further calculations and analyses are needed to explain these relationships.
5. There is a limit amount of chlorine in the system, and when it is exceeded it does not cause intensification of dezincification.

The results of the numerical simulations should be verified on the basis of physical simulations. It should be noted that the kinetics of the dezincification processes have a large impact on the course of the process of sintering and removing zinc from the sintered material. The preparation of the mixture, as well as its homogenisation and granulation are of importance. The degree of dezincification in the sintering process depends on the duration of the process, reaction area, transport of substrates to reaction sites and reaction products from these sites.

The use of the technology of sintering of ferrous materials on a sinter belt for dezincification of sludge and/or dusts from blast furnaces and steelworks is supported by the high efficiency of this process, as well as the possibility of their processing at the site of generation. The carbon necessary for the process can and should be replaced to the maximum extent possible with materials of biomass origin. The required share of total carbon in the technology developed in the next stage of R&D works will be determined by the demand for CO for reduction with carbon monoxide. On the other hand, the share of carbon will be limited so as not to exceed the temperature that could cause excessive melting of the material.

Physical simulations of the sintering process with dezincification will be the subject of further research, the results of which will be published in another article.

***The article contains some of the research results obtained in the following works: SO-1037 and SW-0088/BS/2021.***

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