1. INTRODUCTION

Continuous reduction of CO₂ emissions to the atmosphere during steel production will increase the use of post-amortisation and shredded scrap in the steel smelting process, increasing its contamination mainly with copper and tin. On the other hand, the continuous increase in steel production will result in an increasing consumption of ores, which will contain less and less Fe and more Sn and As. These elements are harmful in steel due to the deterioration of its hot forming ability and the deterioration of the mechanical properties of steel products. Therefore, industrial methods of removing these elements from ores, as well as from scrap and liquid steel are being sought. The purpose of the study was to investigate the possibility of removing copper, tin and arsenic from iron ore, scrap and liquid steel in the light of the latest state of metallurgical technology, based on the analysis of methods for removing these elements, presented in available publications and on the basis of thermodynamic simulations carried out using the FactSage 7.2 software and original laboratory tests. The paper presents a selection of methods of removing Cu, Sn and As from iron-bearing materials, possible to be carried out in industrial conditions in the nearest time perspective.

The study investigates the ability to remove copper, tin and arsenic from iron ore, scrap and liquid steel based on the literature and thermodynamic calculations using the FactSage 7.2 software. Methods of removing Cu, Sn and As from iron-bearing materials, feasible in industrial conditions in the near term, were selected. Simulation tests with the use of the FactSage 7.2 software showed that under reduced pressure conditions Cu and Sn can be removed from the steel bath, while As evaporation is not possible. Laboratory tests were carried out, including the removal of Sn and Cu in the process of degassing of liquid steel in a deep vacuum in a vacuum induction furnace and the removal of Sn from iron ore in the sintering process. Under conditions of deep vacuum (below 40 Pa), high temperature (1670°C) and a correspondingly long vacuum treatment time (over 30 minutes), the efficiency of removing the copper and tin contents from the liquid steel of approximately 14 and 17% respectively was obtained. The iron ore sintering test with a high Sn content showed the effectiveness of reducing the Sn content during this process, amounting to approx. 30%.

Keywords: steel, vacuum degassing, iron ore, sintering, copper, tin, arsenic
2. REVIEW OF THE LITERATURE ON THE PRIOR ART OF REMOVING CU, SN, AS FROM IRON ORE, SCRAP AND LIQUID STEEL

Copper cannot be removed from scrap-based steel by conventional refining in a steel refining process. Several methods of reducing the Cu content in steel were proposed, namely the improvement of scrap sorting, dilution of contaminated input with directly reduced iron, as well as mechanical or chemical pre-treatment of the scrap [1]. Considerable research efforts have been made to develop pyrometallurgical techniques. On a laboratory scale, it was confirmed that copper can be removed during treating the steel bath with sulphide fluxes, but treatment under decreased vacuum is a more promising method. This method of selective evaporation of copper has been successfully tested on a laboratory scale [2–4]. Research is currently underway to optimise the operation of the shredder in relation to the copper content of scrap. Preliminary results show that copper content can be controlled by changing the way the shredder works. With regard to sorting scrap, copper was found to be most efficiently removed by manual sorting. Portable optical emission spectrometers, image analysis and X-ray fluorescence (XRF) are used for sorting and identifying scrap components. Many already available commercial devices, both portable and hand-held, ensure the selection of scrap with purity above 98% Fe [1].

Tin, as one of the main residual elements in steel, occurs in the form of segregation, which affects the thermoplasticity, tempering brittleness and susceptibility of steel products to heat treatment [5]. Using the FactSage7.2 thermochemical program, the influence of calcium, oxygen and sulphur on the removal of tin was investigated [5], and it was found that under reducing conditions it was possible to remove tin from the liquid steel with calcium, after exceeding its critical content in the steel. This critical calcium content increases as the oxygen and sulphur content of the steel increases. Hence, before starting the removal of tin with calcium, the oxygen and sulphur content of the steel should be reduced as much as possible. The process of removing tin with calcium is facilitated by the lowest possible temperature of the liquid steel. Calcium is introduced into the steel through slag made of calcium compounds: CaO, CaC and CaF₂. A process of removing tin from liquid steel that is promising for the industry is low-pressure treatment [6, 7]. The vapour pressure of Sn at the temperature of liquid steel is several dozen times greater than that of Fe. At a temperature of the liquid steel of 1600°C, pressure of 10 Pa and treatment time of 42 min, the efficiency of Sn removal was above 99% in laboratory conditions. Due to the fact that this process can be difficult to implement in the industry due to the difficult control of its temperature, a more effective and economical sulphide roasting process is considered [10], in which tin phases are transformed mainly into SnS and removed by evaporation.

Arsenic also has a detrimental effect on the properties of steel, namely it increases the hot surface brittleness, lowers plasticity and impact strength [11, 12]. The chemical affinity of arsenic to oxygen is lower than that of iron to oxygen [12] and therefore it is difficult to remove by oxidation in the steelmaking process. Theoretically, it is possible to remove As from liquid iron by means of high consumption of O₂ and Fe-Ca alloys or rare earth metals, but it also requires prior deep deoxidation and desulphurisation, which makes the costs of removing As in industrial conditions very high [12]. Arsenic can be removed from arsenic-bearing ore in the process of roasting or sintering using the volatility of arsenic and its compounds [12]. It is also important to recover arsenic from dusts from these processes, preventing further As accumulation and environmental contamination. Previous studies [12, 13] showed that arsenic can be economically removed from iron ores containing arsenopyrite by roasting in air or in a slightly reducing atmosphere containing nitrogen. Arsenic is removed in the roasting process in the form of gaseous As₂O₃ and residual arsenic reacts in the ore with oxides to form arsenates (FeAsO₄, Al₂AsO₆, Ca₃(AsO₄)₂), which can only be removed during roasting in a reducing atmosphere. Arsenic removal in an oxygen atmosphere occurs mainly according to the following reaction (3) [12]:

\[
2\text{FeAsS} + 5\text{O}_2(g) = \text{Fe}_2\text{O}_3 + 3\text{As}_2\text{O}_3(g) + 2\text{SO}_2(g)
\] (3)

The rate of arsenic removal increases with increasing temperature from 700 to 1000°C and is slower with roasting in air compared to roasting in nitrogen atmosphere.
3. THERMODYNAMIC CALCULATIONS OF CU, Sn AND AS REMOVAL USING THE FACTSAGE 7.2 SOFTWARE

Numerical simulations of tin, copper and arsenic removal from liquid steel under reduced pressure conditions were performed using the Equilib module of the FactSage 7.2 thermochemical program.

Input data for the numerical simulation are shown in Table 1.

Due to the fact that the post-amortisation, shredded scrap contains both Cu and Sn, the simulations were performed in two variants:
- removal of tin and copper that occur together in a steel bath
- arsenic removal.

The results of the calculations are presented in the graph of the content of elements in the steel bath as a function of the pressure above the bath (Fig. 1), as well as in the summary table with the values of pressure necessary to achieve the assumed final level of tin and copper (Table 2).

Table 1. Input data for thermochemical calculations
Tabela 1. Dane wyjściowe do obliczeń termochemicznych

| Variant | Chemical composition [%] | Pressure [Pa] |
|---------|--------------------------|--------------|
| As      | C=0.40–1.00, Si=0.20–0.60, O=0.002, S=0.06, Al=0.02, Sn=0.02, As=0.04, Cu=0.08 | 15 |
| Cu+Sn   | C=0.40–1.00, Si=0.20–0.60, O=0.002, S=0.06, Al=0.02, Sn=0.02, As=0.04, Cu=0.08 | 1600, 1680 |

Table 2. Required temperatures and pressures to remove Cu and Sn to final contents
Tabela 2. Wymagane temperatury i ciśnienia do usunięcia Cu i Sn do końcowych zawartości

| Temperature [°C] | Beginning of rapid Cu evaporation | End of Cu evaporation (total Cu removal) | Required for achieving final content Cu=0.1% | Required for achieving final content Sn=0.02% |
|------------------|----------------------------------|------------------------------------------|---------------------------------------------|---------------------------------------------|
| Steel bath composition | 98.878% Fe, 0.4% C, 0.2% Si, 0.06% S, 0.02% Al, 0.002% O, 0.4% Cu and 0.04% Sn |
| 1600             | ~14                              | ~9.3                                     | ~11                                        |                                              |
| 1680             | ~32                              | 23                                       | 25                                         |                                              |
| Steel bath composition | 98.878% Fe, 0.1% C, 0.6% Si, 0.12% S, 0.08% Al, 0.02% O, 0.8% Cu and 0.08% Sn |
| 1600             | 24                               | 6                                        | ~11                                        |                                              |
| 1680             | 50                               | 17.5                                     | ~24                                        | 22                                          |

Fig. 1. Change of the content of Cu, Sn and S in steel bath with the above-mentioned chemical composition as a function of pressure above the bath at a constant temperature of 1600°C and 1680°C
Rys. 1. Zmiana udziału Cu, Sn i S w kąpieli stalowej o podanym wyżej składzie chemicznym w funkcji ciśnienia nad kąpielą w stałej temperaturze 1600°C i 1680°C
The graphs also take sulphur into account, as it is an important element increasing the activity of Cu and Sn in liquid metal in a vacuum, as well as steel contamination that can be removed under reduced pressure.

In order to compare the evaporation parameters for copper and tin depending on the bath composition, Table 2 summarises the pressure values at which the assumed final level of copper and tin will be achieved, i.e. 0.1 and 0.02 weight %, respectively.

The following observations result from the numerical simulations and the analysis of the results presented in Fig. 1 and Table 2:

- Under reduced pressure conditions, both Cu and Sn can be removed from a steel bath with the composition: 0.40–1.00% C; 0.20–0.60% Si; 0.06–0.12% S and 0.02–0.08% Al, but it is not possible to evaporate As.
- The higher the temperature of the liquid steel, the lower the required negative pressure and the greater the dynamics (rate) of evaporation of Cu and Sn from the steel bath.
- Obtaining the content of 0.1% Cu in the steel bath with the above-mentioned chemical composition at 1600°C requires reducing the pressure above the bath to approximately 9.5 Pa, and at 1680°C to approximately 24 Pa.
- Obtaining the content of 0.02% Sn in the steel bath with the above-mentioned chemical composition at 1600°C requires reducing the pressure above the bath to approximately 7–8 Pa, and at 1680°C to approximately 20–22 Pa.
- No influence of the chemical composition of the steel bath within the analysed limits (including: 0.002 to 0.02% O and 0.02 to 0.08% S) on the evaporation of Cu and Sn from it was found.

4. COURSE AND DISCUSSION OF LABORATORY TEST RESULTS

Laboratory tests included laboratory smelting of steel in a vacuum induction furnace with a crucible capacity of 30 kg of liquid metal for simultaneous removal of Cu and Sn from liquid steel and a sintering test of a mixture containing tin dioxide in a laboratory sintering pot.

4.1. LABORATORY TEST OF CU AND SN REMOVAL FROM LIQUID STEEL UNDER REDUCED PRESSURE

Sample material. In the test, armco iron was used as input to the induction furnace, with the following chemical composition in weight %: C – 0.020; Mn – 0.11; Si – 0.06; P – 0.004; S – 0.005; Cu – 0.04; Al – 0.059, in the form of bars, dimensions 40×60×500 (mm) and the following alloying additives of metallic or elemental purity, in weight %: Si (99.5), Mn (99.8), C (98.0), S (99.9), Cu (99.9), Sn (99.9), Al (99.99).

Methodology. The test was carried out in a VIM 30 vacuum induction furnace, shown in Fig. 2, with a crucible capacity of 30 kg of liquid metal. The crucible was made of a refractory spinel (MgO-Al₂O₃) material. After melting the input and supplementing the additives, the bath was heated to 1660°C and subjected to vacuum degassing at the pressure maintained at 27 Pa, for 30 minutes, with continuous heating of the metal bath. The temperature was then adjusted to the casting temperature (1612°C) and an ingot weighing 24 kg was poured from which samples were taken for chemical analysis.

Table 3 summarises the results of a laboratory test of Cu and Sn removal from liquid steel in a vacuum induction furnace.

The analysis of the results collected in Table 3 shows that under the conditions of deep vacuum (about 30 Pa), high temperature (1670°C), during vacuum treatment (for 30 minutes), the contents of copper and tin in the liquid steel decreased by 14 and 16.6%, respectively. In order to effectively lower the content of these elements to trace values, a vacuum of less than 20 Pa is required, which is difficult to achieve under laboratory furnace conditions.

4.2. LABORATORY TEST OF Sn REMOVAL FROM ORE IN THE SINTERING PROCESS

The following materials were used in the sintering test:

- iron ore concentrate, with the composition given in Table 4, in the amount of 78% of the weight of the input mixture

Table 4. Chemical composition of iron ore, [weight %]

|        | Fe<sup>Total</sup> | Fe<sup>++</sup> | SiO<sub>2</sub> | CaO | Al₂O₃ | MgO | S  |
|--------|-------------------|--------------|-------------|-----|-------|-----|---|
| wt %   | 65.57             | 26.69        | 7.99        | 0.15 | 0.18  | 0.37 | 0.035 |

The analysis of the results collected in Table 3 shows that under the conditions of deep vacuum (about 30 Pa), high temperature (1670°C), during vacuum treatment (for 30 minutes), the contents of copper and tin in the liquid steel decreased by 14 and 16.6%, respectively. In order to effectively lower the content of these elements to trace values, a vacuum of less than 20 Pa is required, which is difficult to achieve under laboratory furnace conditions.

Table 3. Chemical compositions of samples from laboratory steel smelting with Cu and Sn removal and the degree of Cu and Sn removal

| Analysis  | C        | Mn      | Si       | S        | Cu      | Sn      | Al<sub>Total</sub> |
|-----------|----------|---------|----------|----------|---------|---------|---------------------|
| – computational  | 0.45    | 0.23    | 0.20     | 0.065    | 0.40    | 0.13    |
| – prior to treatment in deep vacuum | 0.26    | 0.16    | 0.17     | 0.062    | 0.5     | 0.12    | 0.004  |
| – after vacuum, from ingot  | 0.43    | 0.10    |
| Degree of removal  | Stopień usunięcia, [%] | 14      | 16.6    |
• tin carrier – cassiterite (SnO₂ – 99.99%), in the amount of 0.27% of Sn in the weight of the input mixture,
• limestone, with the composition given in Table 5, in the amount of 5.7% of the weight of the input mixture,

| Table 5. Chemical composition of limestone, [weight %] |
|-----------------------------------------------|
| CaO   | SiO₂ | Al₂O₃ | MgO  | S    | Fe_total |
| 53.92 | 0.94 | 0.34  | 0.59 | 0.15 | 1.25     |

• burnt lime, with the composition given in Table 6, in the amount of 0.5% of the weight of the input mixture

| Table 6. Chemical composition of burnt lime, [weight %] |
|--------------------------------------------------------|
| CaO   | SiO₂ | Al₂O₃ | MgO  | Fe_total |
| 95.40 | 0.50 | 0.07  | 0.30 | 0.63     |

• coke breeze containing 83.3% C and 11.80% ash with the composition given in Table 7, in the amount of 7.5% of the weight of the input mixture

| Table 7. Chemical composition of coke breeze ash, [weight %] |
|-------------------------------------------------------------|
| Fe_total | Fe³⁺ | SiO₂ | CaO  | Al₂O₃ | MgO | S   |
| 6.5      | 0.35 | 36.14| 4.54 | 18.76 | 2.04| 0.61|

• sinter return in the amount of 8% of the input weight. The graining of all materials was from 0.05 to 0.5 mm.

**Sintering test methodology.** After pelletising, the input mixture weighing about 70 kg was loaded into the sintering pot onto the sinter return base. At 1150°C and a vacuum of 5 kPa, the mixture in the pot ignited and sintering proceeded at a suction of 10 kPa. After the end of sintering, the sinter was cooled for 3 minutes under a suction pressure of 5 kPa. After cooling, the sinter was discharged from the sintering pot, crushed, and samples were taken for chemical analysis corresponding to the upper, middle and lower sinter layers in the pot. The laboratory sintering installation with a sinter in the sintering pot is shown in Fig. 3.

Table 8 summarises the results of the analysis of Sn, Fe, Fe³⁺ and Fe²⁺ content in the sinter. Fe_total and FeO were determined using the titration method, Fe₂O₃/Fe met using the titration and conversion method, and Sn using the OES ICP spectrometric method, Agilent 5100 ICP-OES.

The performed laboratory test of sintering iron ore with high Sn content (Table 8) showed a reduction of Sn content in the sinter by an average of 26.9%, and therefore the possibility of effective reduction of Sn content in this process. It can be assumed that the increase in the degree of tin removal from the ore will be achieved by selecting the appropriate sintering parameters, namely the composition of the mixture, the amount of reducing agent and the process temperature.

Fig. 3. Laboratory sintering installation with a sinter in the sintering pot

Rys. 3. Widok laboratoryjnej instalacji spiekalniczej ze spiekiem w misie spiekalniczej

| Table 8. Analysis of Sn, Fe, Fe³⁺ and Fe²⁺ content in sinter in various places along the height of the sintered layer |
|---------------------------------------------------------------|
| Substance content = Zawartość substancji, [wt %] | Sn | Fe | Fe₂O₃³⁺ | FeO |
| – computational in input = obliczeniowa we sadzie      | 0.36 |    |        |     |
| – in sinter sample from the top = w próbie spieku z góry | 0.26 | 61.85| 32.90  | 37.23 |
| – in sinter sample from 1/2 of layer’s height = w próbie spieku z 1/2 wysokości warstwy | 0.28 | 60.74| 34.37  | 35.19 |
| – in sinter sample from the bottom = w próbce spieku z dołu | 0.25 | 60.04| 39.37  | 26.57 |

**Degree of Sn removal = Stopień usunięcia Sn³⁺, [%]**

26.9

Notes: ³⁺ – other iron forms, including Fe₂O₃ and metallic Fe; ³⁺⁺ – mean value
5. CONCLUSIONS

Based on the research performed, the following conclusions can be drawn:

1. Numerical simulations with the use of the FactSage 7.2 software showed that under reduced pressure conditions both Cu and Sn can be removed from the steel bath, while As evaporation is not possible, whereas:
   - the higher the temperature of the liquid steel, the lower the required negative pressure and the greater the dynamics (rate) of evaporation of copper and tin from the steel bath,
   - effective reduction of the content of these elements to trace values: Cu<0.10%; Sn<0.02% requires a vacuum of less than 20 Pa at 1670°C.

2. Under the conditions of laboratory recasting in a vacuum induction furnace during a 30-minute vacuum treatment with a minimum pressure over the bath of 27 Pa and a maximum temperature of 1670°C, a decrease in Cu content by 14% and Sn by approximately 17% was obtained.

3. The iron ore sintering test with a high Sn content showed that it was possible to effectively reduce its content in this process. It is assumed that the obtained tin removal result of 28% can be improved by selecting the optimal sintering conditions, including the composition of the sintering mixture, the amount of reducing agent and the sintering temperature.

4. The conducted attempts to remove tin and copper from the steel bath, as well as to remove tin in the sintering process, do not yet provide grounds for the development of assumptions for industrial tests for the removal of Sn and Cu. It can only be stated that these processes can be used in industrial conditions in the future, as nowadays industrial devices for vacuum treatment of liquid steel in a ladle are manufactured with a vacuum production capacity below 20 Pa. The extracted and captured Sn, SnO and Cu vapours are deposited on the walls of the vacuum chamber and on the filter, and can be recycled in non-ferrous metallurgy for the recovery of Sn and Cu.

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