Zinc Recovery from Flue Dust

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Abstract

Flue dust from processing of steelmaking dust in cupola furnace was processed hydrometallurgically in order to recover zinc. The flue dust contained 17.8% Zn, 8.14% Si, 4.20% Fe, 2.34% Pb and minor elements. Leaching of the dust in H_2SO_4 enabled achieving almost 100% Zn extraction. Iron was removed from the leach liquors by means of hydrolytic precipitation up to pH = 4.5. Zinc electrowinning was used to obtain metallic zinc of high purity from purified solutions. As an alternative process of winning zinc from the leach liquors, precipitation of basic zinc carbonate was investigated.

Keywords: zinc recovery, flue dust, steelmaking

Introduction

Steelmaking dust arises during steel production in amount about 15–20 kg per ton of steel. On one side it is classified as a hazardous waste, on the other side it represents big material value. The most valuable constituent of the dust is Zn; depending on type of steelmaking process, the dust contains 15–35% Zn. Many processes have been developed in order to recover values from steelmaking dust. Hydrometallurgical processes are less energy consuming and offer interesting alternative for Zn recovery, but they still face the problem of efficient extraction of Zn due to its bonding in zinc ferrite. This is the main reason causing no industrial application of hydrometallurgical processes for steelmaking dust recycling. Overview of hydrometallurgical processes can be found e.g. in the work of Jha, Kumar and Singh (2001). Pyrometallurgical processes, on the other hand, require more energy, but they are capable of processing steelmaking dust economically. Therefore, there are recycling facilities for steelmaking dust based on a pyrometallurgical process in operation worldwide.

Among pyrometallurgical processes, the most spread and best known is Waelz process. In the Waelz kiln, steelmaking dust undergoes reduction using carbon containing reductant. At temperatures 1000–1300°C, elements like Zn, Pb, Cd are volatilized, reoxidised in the vapor phase and recovered as so called Waelz oxide. It is than being processed hydrometallurgically in order to obtain Zn. Iron is concentrated in the slag which has only limited usage. Similar to Waelz process are SDHL process (Mager et al., 2000) or FASTMET process (Doronin and Svyazhin, 2011).

An alternative to Waelz process represents treatment of pelletized Zn containing dust in rotary hearth furnace (Oda, Ibaraki and Abe, 2006). The process produces direct reduced iron and zinc oxide. Another possibility for treatment of steelmaking dust is DK process – modified blast furnace process producing pig iron and zinc oxide (Hillmann and Sassen, 2006). PRIMUS (Roth et al., 2001) is a multistage process suitable for treatment of powder materials containing more than 5% Zn. Products of the process are Fe of similar quality as the Fe produced by blast furnace, ZnO concentrate containing more than 55% Zn and inert slag.

Kursa et al. (2006) deal in their work with dust originating from treatment of steelmaking dust in cupola furnace. The process is based on reduction of initial material, products being cast iron and mixed oxide containing Zn, Pb, Cd. The authors present thermodynamic analysis of processes in cupola furnace and made also some experiments concerning mainly characterization of the Zn-rich dust from cupola furnace.

The aim of this work was to design and verify on a laboratory scale a process for obtaining Zn from a dust originated from processing steelmaking dust in cupola furnace.

Materials and methods

Flue dust used in this work was provided by a company which made an experiment with reprocessing steelmaking dust in cupola furnace. The dust was analyzed for its particle size using laser particle sizer (Fritsch Analysette 22). Concentrations of metals in solutions were established using AAS method (GBC 932plus). The concentration of chlorides was determined by means of standard titration. Composition of solid samples was obtained by X-ray diffraction (PANalytical X´Pert PRO), X-ray fluorescence (THERMO ARL 9400XP) and/or by chemical analyses using stan-

Tab. 1 Content of elements in the flue dust

Tab. 1 Zawartość pierwiastków w pyle stalowniczym

Element	Zn	Fe	Pb	Si	Mn	Ca	Al	Cl
Content (%)	17.8	4.20	2.34	8.14	0.62	0.80	0.73	1.60

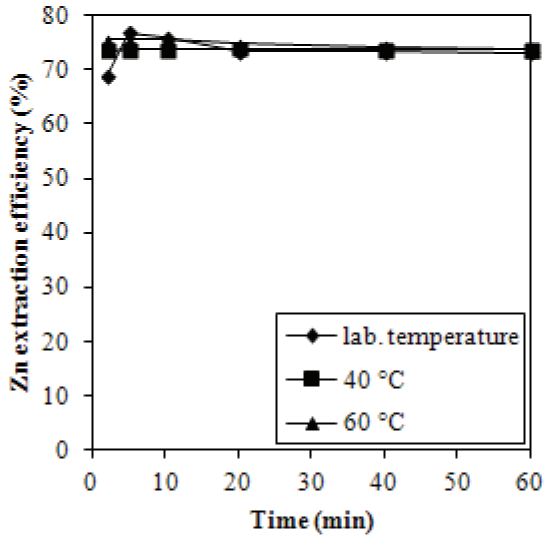


Fig. 1 Zn extraction efficiency at different temperatures in 0.5 mol/L H_2SO_4, L:S=5:1

Rys. 1 Skuteczność ekstrakcji cynku w różnych temperaturach w roztworze 0,5 mol/L H2SO4, L:S=5:1

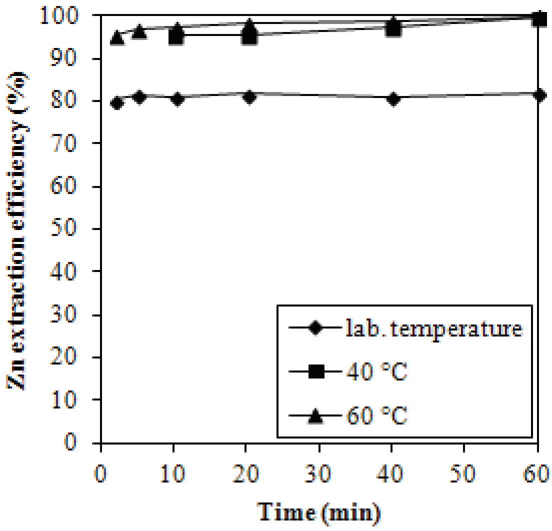


Fig. 2 Zn extraction efficiency at different temperatures in 1 mol/L H_2SO_4, L:S=5:1

Rys. 2 Skuteczność ekstrakcji cynku w różnych temperaturach w roztworze 1 mol/L H2SO4, L:S=5:1

dard methods (acid dissolution, alkali or acid fusion). Element composition of the dust is given in table 1.

According to X-ray diffraction, the flue dust consisted of ZnO, $Zn_{1.7}SiO_4$, Fe_3O_4, SiO_2, $CaFeSi_2O_6$.The size of majority of particles was less than 10 µm.

Leaching experiments were carried out in a closed, thermostated, stirred 1L glass reaction vessel provided with temperature control and a water cooler. Mixing was accomplished by means of an impeller at agitation speed of 400 rpm. Leaching conditions were as follows: concentration of H_2SO_4 solution 0.5 or 1 mol/L, liquid-to-solid ratio (L:S) of 5:1 or 10:1, laboratory temperature, 40 and 60°C, reaction time 60 min. During leaching, samples were withdrawn at selected time intervals to determine the reaction rates of zinc and impurity dissolution, their concentrations in the filtrates were established using the AAS method. After the completion of leaching tests, leach residues were filtered, water-washed and dried. Composition of leach residues was determined by X-ray diffraction and X-ray fluorescence analysis.

Iron was precipitated from leach liquors by adding flue dust to pH = 4.0–4.5. During precipitation process, pH was continuously measured using pH electrode connected to a laboratory pH meter. Precipitation was performed in a beaker at laboratory temperature or in the same type of vessel as leaching at 40°C. After completion of precipitation, the resulted precipitate was water-washed, dried and analyzed.

Zinc electrowinning was performed in a laboratory electrolytic cell from both model solution and purified leach liquor. The model solution was prepared from pure chemicals and its composition corresponded to the composition of leach liquor. Zinc electrowinning was performed at the current density of 400 A/m^2, at 37°C, 120 or 180 min.

Zinc carbonate was precipitated from purified leach liquors by adding Na_2CO_3 up to pH = 7.5 at laboratory temperature. The precipitates were analysed for their mineralogical and chemical composition.

Results and discussion

Results of leaching experiments in the form of time dependences of Zn concentrations are illustrated in figures 1–2. Final metal content in acid liquors is given in table 2.

According to X-ray diffraction analysis, the leach residues contained SiO_2, $PbSO_4$, $ZnFe_2O_4$.

From the results of leaching tests, figures 1–2, it is obvious that extraction efficiency of Zn increas-

Tab. 2 Concentrations of metals in leach liquors [n … not determined]

Tab. 2 Stężenia metali w cieczach ługowych [n … nie określone]

H_2SO_4 concentration	L:S	Temperature (°C)	Metal concentration (mg/L)	
			Zn	Fe
0.5 mol/L	5:1	laboratory	26.0	n
		40	26.2	n
		60	26.3	n
1 mol/L	5:1	laboratory	29.1	3.02
		40	38.3	3.88
		60	38.7	n
1 mol/L	10:1	laboratory	17.7	4.55

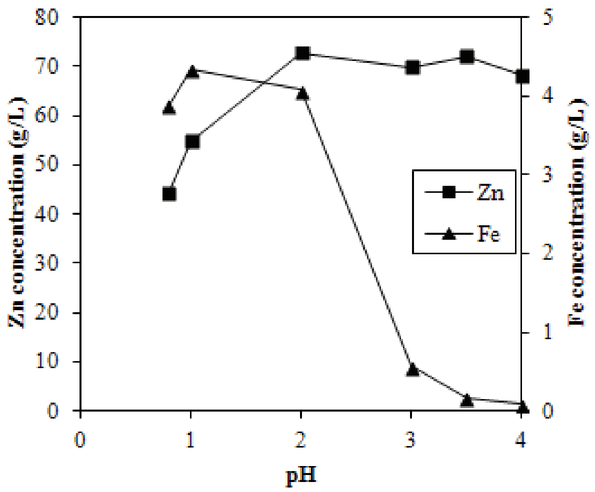


Fig. 3 Dependency of Zn and Fe concentration on pH (original liquor: from leaching in 1 mol/L H_2SO_4, L:S = 5:1, 40°C)

Rys. 3 Zależność stężenia Zn i Fe of pH (oryginalna ciecz: z ługowania w 1 mol/L H2SO4, L:S = 5:1, 40°C)

es with increasing temperature. By using 0.5 mol/L H_2SO_4, L:S = 5:1, at all investigated temperatures, Zn extraction efficiency reached only slightly more than 73%. Zinc extraction efficiencies by leaching in 1 mol/L H_2SO_4, L:S = 5:1, reached at laboratory temperature only 81.7%. Leaching temperatures 40 and 60°C increased these values to almost 100%. When using 1 mol/L H_2SO_4, L:S = 10:1, 99.2% Zn was extracted even at laboratory temperature, but the Zn concentration in the leach liquor was less than half of the best results achieved at L:S = 5:1. The optimum leaching conditions are therefore 1 mol/L H_2SO_4, L:S = 5:1, 40°C or 1 mol/L H_2SO_4, L:S = 10:1, laboratory temperature.

Hydrolytic precipitation provided practically complete removal of Fe. Using the flue dust as a precipitating agent enabled increasing of Zn concentration in leach liquors, in case of leach liquors from leaching at L:S = 5:1 of about 20 g/L. Reaching the equilibrium by precipitation at laboratory temperature lasted very long time and even after several hours, there were still tens of mg/L Fe remaining in the solutions. Therefore, the temperature of precipitation was increased to 40°C which was sufficient for Fe removal in reasonable time. The course of dependency of Zn and Fe concentration on pH during precipitation is illustrated in figure 3.

As there was only small amount of purified liquor for Zn electrowinning, the first attempt was done with model solution. It was found out that even relatively high concentration of Cl^- in the solution did not negatively influence the electrowinning. Similar results were obtained also by Zn electrowinning from purified leach liquor. After 3h of electrowinning, the current efficiency reached 94%, table 5.

The quality of obtained Zn was not affected as well, as it could be seen from figure 4. The purity of Zn obtained from purified leach liquor reached > 99%, the amount of impurities in the Zn is given in table 6.

Obtaining Zn from solutions by alternative method – basic Zn carbonate precipitation – was also investigated. This method is generally suitable for solutions containing high concentrations of Cl^-. The resulting precipitate contained negligible amount of Cl^-, but also > 1% Mn. This amount of Mn makes the use of precipitate for pure ZnO production impossible. In such case, another purification step for Mn removal would be necessary.

Tab. 3 Cathode current efficiency and electric energy consumption during Zn electrowinning

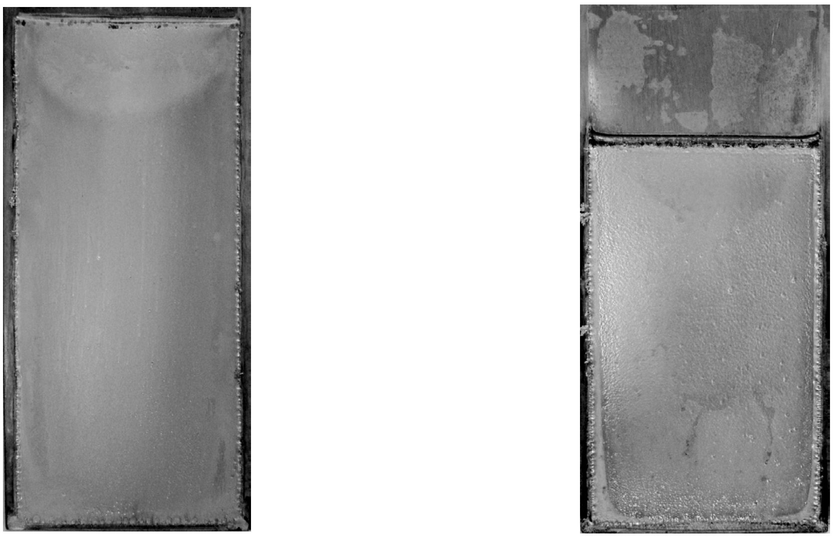
Tab. 3 Skuteczność prądu katody i zużycia energii podczas elektrolizy Zn

solution	Time (min)	Cathode current efficiency (%)	Electric energy consumption (kWh/kg)
model	60	98.9	3.50
	120	98.6	3.32
purified leach liquor	60	97.7	3.29
	120	95.8	3.25
	180	94.0	3.18

Tab. 4 Composition of obtained Zn

Tab. 4 Skład otrzymanego Zn

Element	Zn	Pb	Mg	S
Content (%)	> 99	0.13	0.13	0.13



model solution after 2 h   purified leach liquor after 3 h

Fig. 4 Photographs of Zn obtained by electrowinning

Rys. 4 Fotografie Zn otrzymanego z elektrolizy

Conclusion

Hydrometallurgical processing of the dust originating from reprocessing steelmaking dust in cupola furnace was proposed and verified on a laboratory scale. Optimum leaching conditions are as follows: 1 mol/L H_2SO_4, L:S = 5:1, 40°C or 1 mol/L H_2SO_4, L:S = 10:1, laboratory temperature. Subsequent hydrolytic precipitation up to pH = 4.0 – 4.5 enabled almost complete removal of Fe from leach liquors. Metallic Zn was obtained by electrowinning; its purity was > 99%. Precipitation of basic $ZnCO_3$ can be seen as an alternative, but in that case, a refining step for Mn removal would be necessary.

Acknowledgements

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Odzysk cynku z pyłów stalowniczych

Pyły lotne z przetwarzania pyłów stalowniczych w piecu żeliwnym zostały przetworzone za pomocą hydrometalurgii w celu odzysku cynku. Pył ten zawierał 17,8% Zn, 8,14% Si, 4,20% Fe, 2,34% Pb oraz śladowe ilości innych pierwiastków. Ługowanie pyłu w H_2SO_4 umożliwiło uzyskanie niemal 100% Zn. Żelazo zostało usunięte z cieczy za pomocą precypitacji hydrolitycznej przy wartości pH = 4,5. Elektroliza cynku została zastosowana do otrzymania cynku metalicznego o dużej czystości z oczyszczanych roztworów. Jako alternatywny proces otrzymania cynku z cieczy ługowniczych, zbadano precypitację bazowego węglanu cynku.

Słowa kluczowe: odzysk cynku, pyły lotne, produkcja stali