

PROCESSING OF SOLUTION AFTER LEACHING OF STEELMAKING DUST BY CEMENTATION

Marek Palenčár ¹⁾, František Kukurugya ¹⁾, Andrea Miškufová ¹⁾

¹⁾Technical University of Kosice, Faculty of Metallurgy, Department of Non-ferrous Metals and Waste Treatment, Slovakia

Received: 09.01.2015

Accepted: 04.05.2015

*Corresponding author: e-mail: marek.palencar@tuke.sk, Tel.: +421 55 602 2426, Department of Non-ferrous Metals and Waste Treatment, Faculty of Metallurgy, Technical University of Kosice, Letná 9, 04200 Kosice, Slovakia

Abstract

The work includes a description of a hydrometallurgical processing of steelmaking dust a waste product of steel production from electric arc furnace (EAF). Most attention is paid to cementation. The aim is to study purification of solution by cementation of impurities that could cause problems in zinc electrowinning process. Most attention is focused on removal of cadmium and lead from the sulphate and chloride solutions. The highest efficiency of cadmium removal was achieved in the sulphate solution, at 25, 50, 80 °C and at pH = 4, 5, 6. The highest efficiency of lead removal from sulphate solution (87.61 %) was achieved at pH = 6 and temperature of 80 °C. In chloride solution, the highest efficiency of lead removal (99.94 %), at the same pH but at a lower temperature of 50 °C was achieved.

Keywords: Steelmaking dust, hydrometallurgy, cementation, lead, cadmium, zinc powder, purification

1 Introduction

Steelmaking production is accompanied by generation of different kinds of waste. Except a slag and emission, sludge and steelmaking dust, which consist of mainly iron oxides, are generated. When a scrap is melted, volatile elements like zinc, cadmium and lead, get into a steelmaking dust [1].

Input material in EAF varies by its composition, what leads to variable composition of EAF dust. The contents of the main elements vary in a certain range. The example of composition of EAF dust is shown in **Table 1**.

Table 1 The example of composition of EAF dust [2]

Element	Content [%]	Element	Content [%]
Zn	2-35	Al	0.0-1
Fe	30-45	Mg	0.1-3
Pb	0.5-2	Na	0.1-1
Cd	0.1-0.3	Si	0.1-2
Ca	1-7	Cl	0.5-3
Cu	0.01-0.2	F	0.05-0.1

EAF dust is, due the content of heavy metals (**Table 1**), classified as hazardous waste (according to European legislative). Due to the interesting content of zinc it is also potential secondary raw material for production of zinc and /or its compounds.

There are three possible ways of processing EAF dust: hydrometallurgical, pyrometallurgical and combined [1].

Pyrometallurgical methods of processing steelmaking dust require high temperature and reduction agent, whereby product is crude zinc oxide of low commercial value.

By hydrometallurgical methods, zinc can be recovered at lower energy consumption by various procedures [2].

The main part of hydrometallurgical treatment includes a purification of solution after leaching in order to decrease concentration of ineligible elements to the level of allowable limits (Tab.2), which do not cause problems in the further electrolytical recovery of zinc. Impurities present in the unpurified neutral solution coming from iron precipitation step, can lead to:

- lower current efficiency of zinc electrolysis,
- deposition of impurities on the cathode together with zinc,
- reverse reaction on the cathode and anode.

Table 2 The example of suitable composition of electrolyte before electrolysis [mg.l⁻¹][4]

Zn	Cu	Cd	Co	Ni	As	Sb	Ge	Fe
140- 170	< 0.2	< 1.0	< 1.0	< 1.0	< 0.24	< 0.3	< 0.05	< 20

Basically, following purification processes can be applied in order to remove ipurities from a solution: chemical precipitation, electrochemical deposition, ion exchange, cementation with zinc powder and solvent extraction. In industrial practice, mainly cementation with zinc powder in a continuous multi-step proces, is used for purification of solutions [3].

The aim of this paper is to study purification of sulphate and chloride solutions coming from leaching of steelmaking dust. The attention was paid to removal of cadmium, lead and iron from the solution and comparison of conditions, at which the process reaches the highest efficiency.

2 Theoretical part

Cementation belongs to physico- chemical methods of extracting the metals from a solution, based on the electrochemical reaction between the cementing metal and the ion of the precipitated metal.

Thermodynamic feasibility of cementation is determined from the ratio of the values of the electrode potential. The electrode potential of the displacing metal E_M must be more negative than that of the displaced metal E_{Me} ($E_M < E_{Me}$). The cementation of the metal is accompanied obviously by a change of its concentration in the solution, and consequently, of its potential. When the equilibrium values are reached ($E_M = E_{Me}$), the process stops. On the basis of the difference in the electrode potentials, it can be determined the electrode pairs of the cementing and cemented metal [5]. The cementation process can be described by the equation (1) [5]:



n_1, n_2 - ion charge; Me - cementated metal; M – cementing metal (element)

Cementation is heterogenous process between the solid and the liquid phase. On the surface of the reducing metal is fomrmed a stationary layer of the solution- Nernst layer [6-8].

Whereas, cementation is preferred environmental and economic refining operations, several results of metal cementation from the solutions have been published in the literature. The review

of conditions, under which the cementation was carried out is included in the **Table 3**. Some of these works deal with the cementation from the synthetic solutions [7-10] and some deal with cementation from a solution after leaching of steelmaking dust [11-12].

Table 3 The review of works and conditions of Cd and Pb cementation

Solution	Cemented metal	Cementing metal	Temperature [°C]	pH	Literature
CdSO ₄	Cd	Zn metal	25-30	5.2	[9]
CdSO ₄	Cd	Zn dust	15 a 45	5.7-6	[10]
ZnSO ₄	Cd	Zn dust	25 a 45	-	[11]
ZnSO ₄	Cd	Zn dust	20	5.2-5.4	[12]
NaOH	Pb, Cd	Zn dust	20	8-10	[13]
NaOH	Pb, Cd	Zn dust	-	10	[14]

From this review, it is clear, that cadmium and lead cementation was carried out in both acidic and alkaline media, where zinc dust was used as cementing metal in the most of the experiments. It also follows from the literature review, that cementation was realized at temperatures in the range of 25- 45 °C, from pH 5.2 to 6. This work provides a comparison of purification sulphate and chloride solution by cementation from impurities (Cd, Pb, Fe), which can cause problems in zinc electrowinning process. This work deals also with a phase analysis of solid residues formed during cementation.

3 Experimental part

3.1. Material and methods

For experimental studies of cementation process, solutions coming from leaching steelmaking dust in sulfuric and hydrochloric acid were used. Before starting experiments these solutions were analyzed by AAS (atomic absorption spectrometry) for concentration of Cd, Pb, Fe and Zn. The concentration of analyzed metals are shown in the **Table 4**. In this table, also values of pH before cementation are given.

Both solutions (sulphate and chloride) were used for studying the cementation. Contents of Cd, Pb, Fe and Zn were analyzed in this solutions. The influence of temperature and pH on cementation efficiency was monitored in these experiments. Following experimental conditions were chosen: time of the experiments 60 minutes, temperatures 25, 50 and 80 °C, 0.5g of zinc powder (purity of 99.99 %) added into 250 ml of the solution.

All the experiments were realized in the glass reactor. This reactor was placed into a thermostatically controled water bath (**Fig. 1**). The solution was stirred by glass propeller with constant speed (300 rpm) during all experiments. For adjusting the pH values to 4,5 and 6 the solution of 6M NaOH was used.

The pH was adjusted before starting a cementation. Also experiments at temperature 50 °C for 60 minutes, without adjusting pH was carried out in order to compare the cementation efficiency. After experiments, a solution was filtered. Liquid samples (volume of 15 ml) were taken after filtration. These samples were analyzed by AAS (atomic absorption spectrometry Varian AA240+) for concentration of Cd, Pb, Fe and Zn.

The resulting filter cake was washed by distilled water to the neutral pH and dried at temperature 80 °C per 24 hours. After drying, the filter cake was weighted and analyzed by XRD diffraction phase analysis with diffractometer Panalytical X-Pert Pro.

Concentrations of monitored metals in the solutions after cementation were compared with the concentrations of metals in the solutions before cementation and the results are shown in **Fig. 2 - 9**. Efficiency of the cementation and purity of the solution were monitored parameters after cementation.

Table 4 Concentration of metals and pH in solutions before cementation

Medium	Concentration of metals [mg.l^{-1}]				pH
	Cd	Pb	Fe	Zn	
H_2SO_4	18.9	5.1	3308.8	5310	0.64
HCl	13	302.4	1835.2	4570	0.81

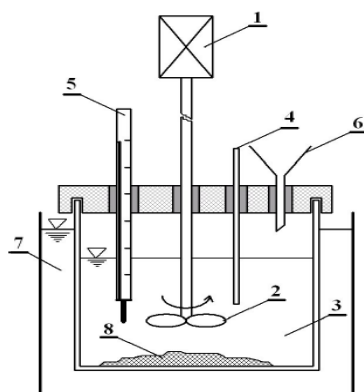


Fig. 1 Apparatus used for the cementation: 1- mechanical stirrer, 2- propeller, 3- pulp, 4- sampler, 5- thermometer, 6- feeder, 7- water thermostat, 8- cementing metal (Zn dust) [1]

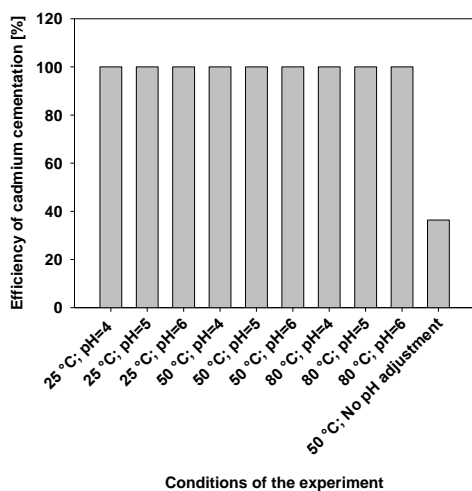
4 Results and discussion

4.1 Cementation from sulphate solutions

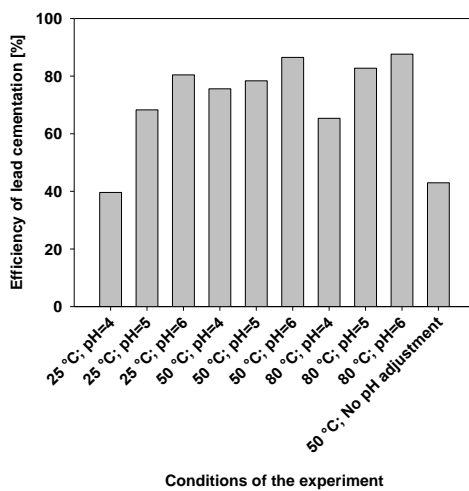
Efficiency of cadmium and lead removal by cementation from sulphate solution at different temperature and pH are shown in **Fig. 2**. From the results, it is clear that cadmium is removed from the sulphate solution at pH 4, 5 and 6 at all temperatures (**Fig. 2a**). According to the E – pH diagram of Cd-S- H_2O system (**Fig. 3a**), cadmium is in the solution in the form of Cd^{2+} at temperatures 25, 50 and 80 °C at pH 4, 5 and 6. Phase analysis (**Table 6**) confirmed the presence of cadmium in the solid residue after cementation at pH 4 and 5 and temperature 25, 50 and 80 °C. It follows from **Fig. 2** that pH value about 1 leads to lower efficiency of removal cadmium comparing to higher value of pH ($\text{pH} > 4$). This was also confirmed by another literature where pH value higher than 1.5 is required for cementation of cadmium from a solution [15]. At cementation of lead (**Fig. 2b**) the highest efficiency, 87.61 % at temperature 80 °C and pH = 6 was achieved. The lowest efficiency of lead cementation (39.6 %) was achieved at 25 °C and pH = 4. It is clean, from **Fig. 2b** that efficiency of lead cementation raises with increasing pH. **Table 5** shows calculated ΔG°_T of the cementation of cadmium and lead from sulphate solution at temperatures 25, 50 and 80 °C. Calculation have been performed by use of program HSC 6.1. The reactions (2 and 3) have tendency to proceed spontaneously in direction of products formation.

Table 5 Calculated ΔG°_T of the cementation of kadmium and lead from sulphate solution at temperatures 25, 50 and 80 °C.

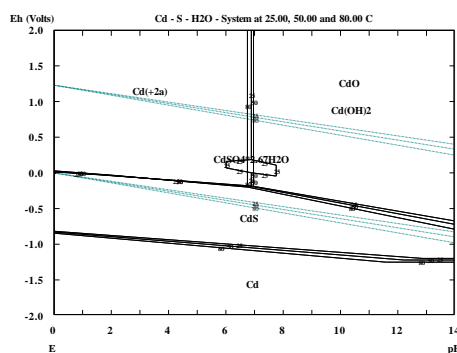
Reaction	ΔG°_T [kJ]		
	25	50	80
(2) $\text{CdSO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{Cd}$	-45.952	-45.908	-45.983
(3) $\text{PbSO}_4 + \text{Zn} = \text{ZnSO}_4 + \text{Pb}$	-55.711	-55.353	-54.956



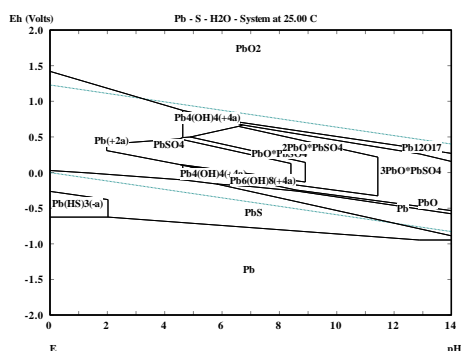
a.)



b.)

Fig. 2 Cementation efficiency from sulphate solution a.) cadmium ; b.) lead

a.)



b.)

Fig. 3 Combined E-pH diagrams of the systems a.) Cd-S-H₂O and b.) Pb-S-H₂O at temperatures 25, 50 a 80 °C.

Fig. 4a show the efficiency of iron removal from sulphate solution. It can be seen from E – pH diagram of the Fe-S-H₂O system, that when pH is adjusted by adding NaOH solution, iron starts to precipitate as iron hydroxide before cementation at all studied temperatures. Phase analysis of

filter cake after cementation (**Table 6**) confirmed the presence of iron in the form of Fe_2O_3 and $\text{FeO}(\text{OH})$. At the experiment without adjusting pH at $50\text{ }^\circ\text{C}$, iron was only partially precipitated, i.e. there is still iron remaining in the solution after cementation.

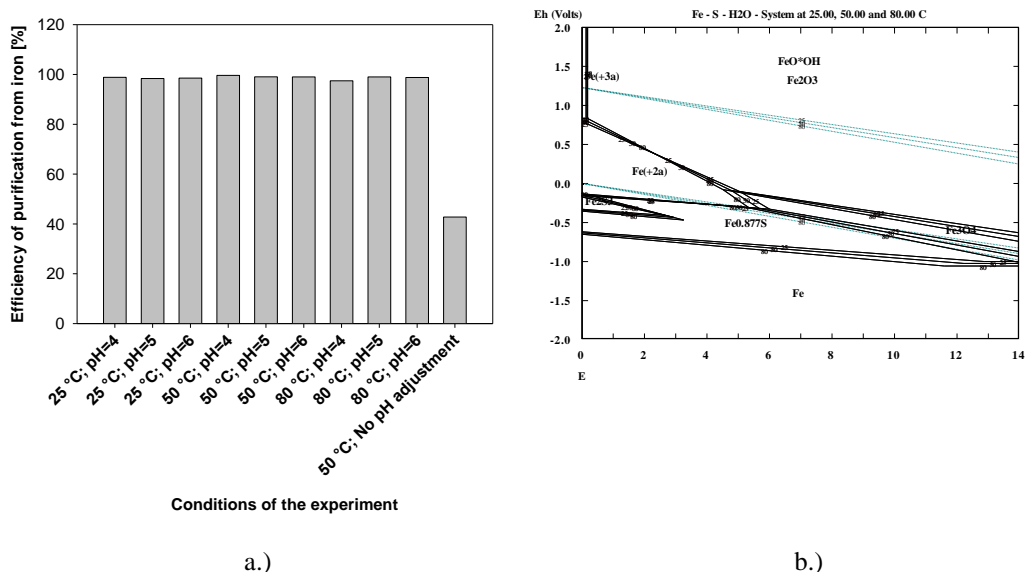


Fig. 4 a) Efficiency of iron removal from sulphate solution b) E-pH diagram of the Fe-S- H₂O system at temperatures 25, 50 and 80 °C

Fig. 5a graphically shows a comparison of zinc content in the sulphate solution before and after cementation at selected conditions. Adding of zinc powder as cementing metal into the solution led to increasing its concentration at all selected temperatures and at pH = 4 and 5. However, at pH = 6 part of zinc, present in the solution, precipitated as it is evident in **Fig. 4b** what caused lower concentration of zinc in the solution after cementation in comparison to zinc concentration before cementation.

Fig. 5b shows E – pH diagram of the Zn-S-H₂O system at temperatures 25, 50 and 80 °C.

From **Fig. 5b** it can be seen, that zinc starts to precipitate from the solution at pH = 6. At pH lower than 6 zinc remains in the solution in the form of Zn^{2+} .

Precipitation of zinc was confirmed by phase analysis, where phases ZnO and $\text{Zn}(\text{OH})_2$ was identified in solid residue coming from cementation carried out at pH = 6 and 80 °C (**Table 6**).

Table 6 Phase composition of selected solid residues after cementation from sulphate solution

Conditions of the experiment		Phases							
Temperature [°C]	pH	Cd	CdO	Pb	Zn	ZnO	$\text{Zn}(\text{OH})_2$	Fe_2O_3	$\text{FeO}(\text{OH})$
25	5	+	+	+	+	+	+	+	+
50	5	-	+	-	+	+	+	+	+
80	4	+	+	+	+	+	+	-	+
80	6	+	-	+	+	+	+	+	+

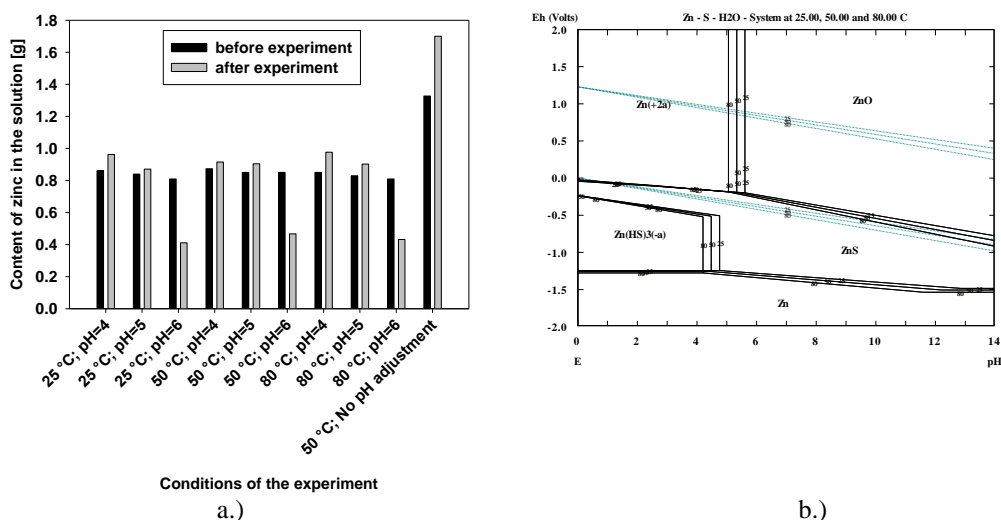


Fig. 5 a.) Content of zinc in the sulphate solution before and after cementation b.) E-pH diagrams of the Zn-S-H₂O system at temperatures 25, 50 a 80 °C

4.2 Cementation from chloride solution

Efficiencies of cadmium cementation in chloride solution are illustrated in **Fig. 6a**. These results show that cadmium cementation from chloride solution reached 100 %. It means, that cadmium in chloride solution (as in the case of sulphate solution) was completely cemented without any influence of temperature and pH. **Fig. 7a** shows a combined E-pH diagram of the Cd-Cl-H₂O system at temperatures 25, 50 and 80 °C. According to this diagram, cadmium is in the region of water stability in the form of CdCl₃(-a) at studied conditions.

In the case of experiments without pH adjusting, cementation efficiencies of cadmium and lead were very low, 19.1 % and 4.28 % respectively. Thermodynamic study of cadmium and lead cementation from chloride solution at temperatures 25, 50 and 80 °C is listed in **Table 7**. It results from thermodynamic study that the reactions will proceed in the direction of product formation at all studied temperatures.

Table 7 Calculated ΔG°_T of the cementation of cadmium and lead from the chloride solution at temperatures 25, 50 and 80 °C

Reaction	ΔG°_T [kJ]		
	25	50	80
(4) $\text{CdCl}_2 + \text{Zn} = \text{ZnCl}_2 + \text{H}_2$	-36.224	-26.337	-26.558
(5) $\text{PbCl}_2 + \text{Zn} = \text{Pb} + \text{ZnCl}_2$	-56.204	-56.167	-56.111

Efficiencies of lead cementation in chloride solution are illustrated in **Fig. 6b**. The highest efficiency of lead cementation, 99.94 %, was achieved at pH = 6 and temperature 50 °C. **Fig. 7** shows a combined E-pH diagram of the Pb-Cl-H₂O system at temperatures 25, 50 and 80 °C. It results from the E-pH diagram, that lead is in the region of water stability in the form of PbCl₄(-a) at all studied temperatures.

As can be seen from achieved efficiencies, in chloride solution unlike sulphate solution, 100 % cementation of efficiencies were reached at all studied conditions. Achieving higher cementation efficiency in the sulphate solution was probably inhibited by formation of $PbSO_4$.

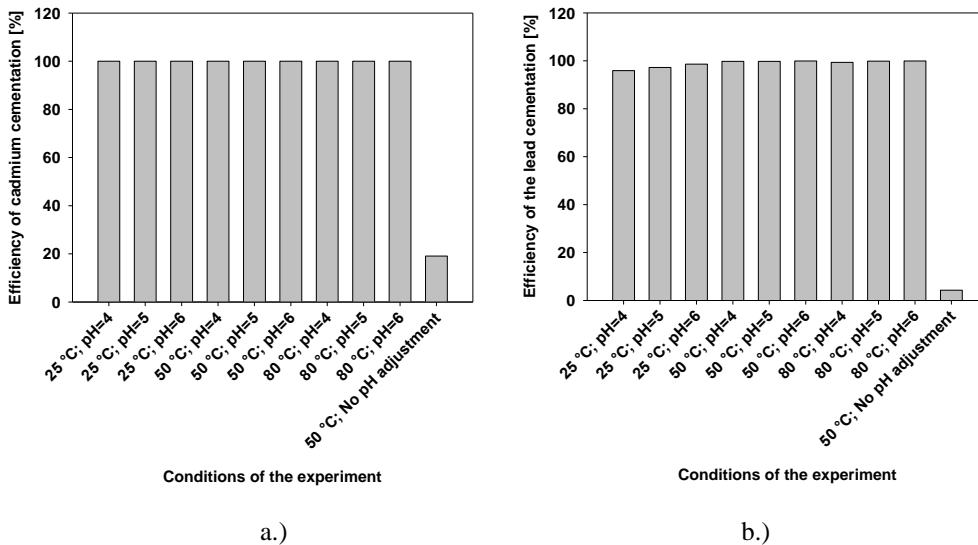


Fig. 6 Cementation efficiency from chloride solution: a.) cadmium; b.) lead

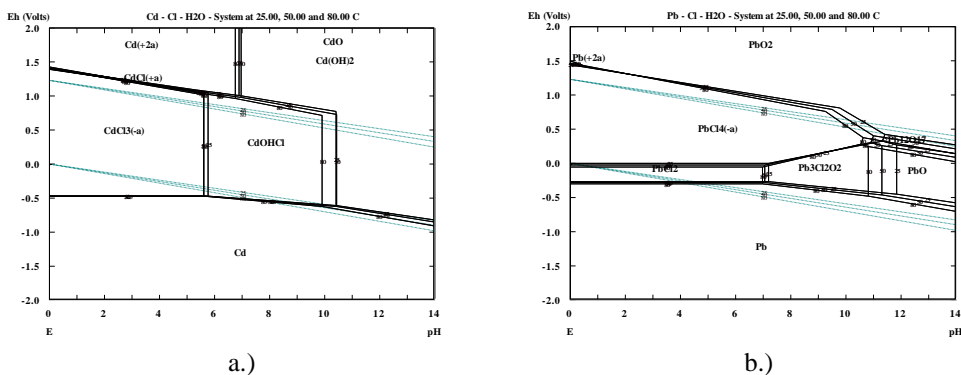


Fig. 7 Combined E-pH diagrams of the systems a.) Cd-Cl-H₂O , b.) Pb-Cl-H₂O at temperature 25, 50 and 80 °C

Efficiencies of iron cementation from chloride solution is illustrated in **Fig. 8a**. As it results from combined E-pH diagram of the Fe-Cl-H₂O system at temperatures 25, 50 and 80 °C (**Fig. 8b**), iron is present in the chloride solution in the form of $FeCl_2^-$ to pH = 5. At pH > 5, iron starts to precipitate. Efficiency of iron cementation at pH = 4 was 96 % at all selected temperatures. Iron was precipitated from the solution by adjusting the pH solution to values 5 and 6 by adding a hydroxide sodium solution. XRD phase analysis confirmed the presence of iron in the form of FeO(OH) in the solid residue after filtration (**Table 8**).

In the case of the experiment without adjusting pH (pH about 1) iron was cemented with lower efficiency (13.13 %) comparing to higher values of pH.

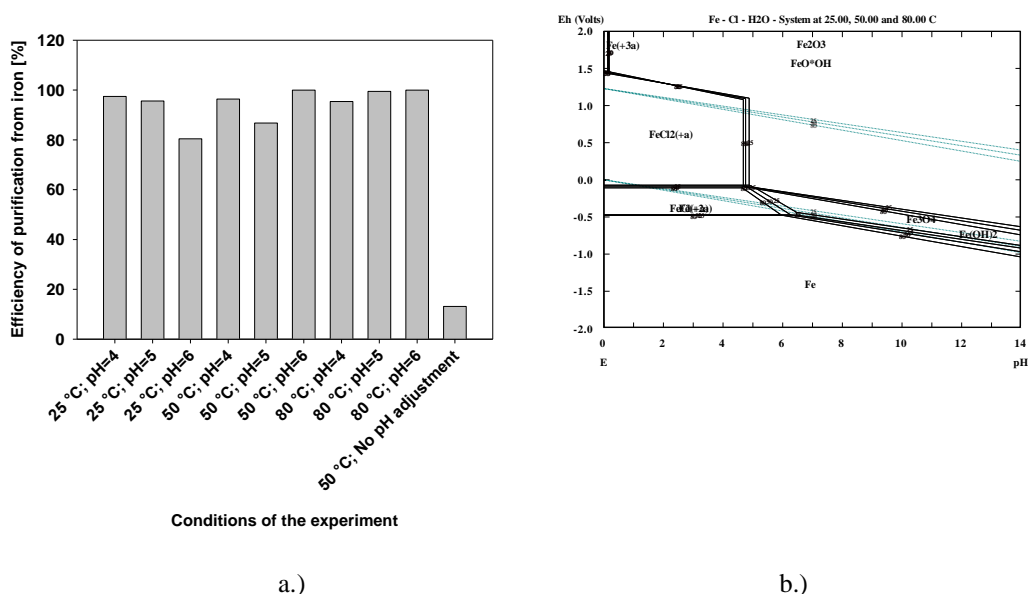


Fig. 8 a.) Efficiency of iron removal from chloride solution b.) E-pH diagram of the Fe-Cl-H₂O system at temperatures 25, 50 a 80 °C

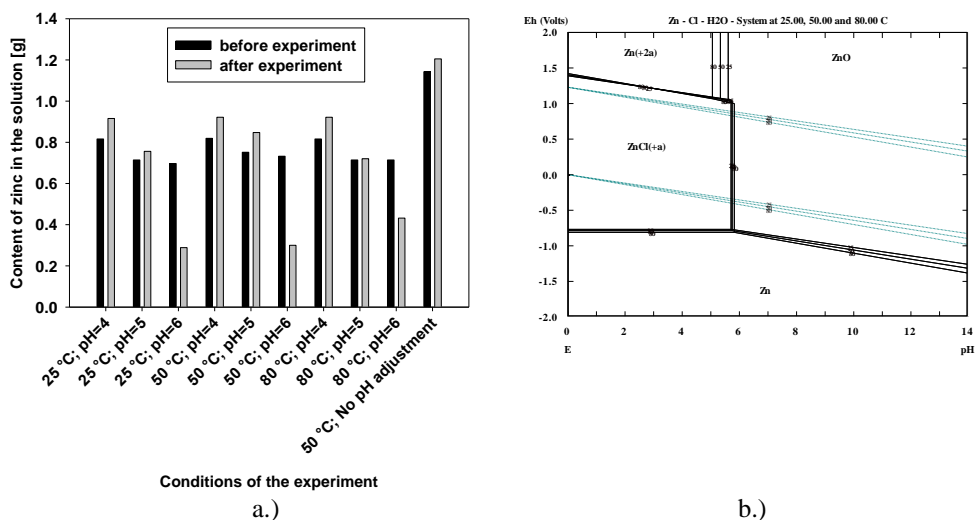


Fig. 9 a.) Content of zinc in the chloride solution before and after cementation b.) E-pH diagram of the Zn-Cl-H₂O system at temperatures 25, 50 a 80 °C

Fig. 9a graphically shows comparison of zinc content in the chloride solution before and after cementation at selected conditions. It results from **Fig. 9a**, that using zinc as cementing metal

increases its concentration in the solution at pH = 4 and 5 and at all studied temperatures. Similarly, as in the case of sulphate solution, zinc starts to precipitate at pH = 6.

This fact is confirmed by E-pH diagram of the Zn-S-H₂O system at 25, 50 and 80 °C, where zinc is in the soluble form till pH = 6, but over this value zinc starts to precipitate. Phase analysis of the solid residue after cementation confirmed the presence of phases ZnO and Zn(OH)₂ (**Table 6**). In the case of the experiment without adjusting pH, zinc concentration raised too, what could be caused by its dissolution due to the presence of free acid in the solution.

Table 8 Phase composition of selected solid residues after cementation from chloride solution

Conditions of the experiment		Phases							
Temperature [°C]	pH	Cd	CdO	Pb	Zn	ZnO	Zn(OH) ₂	NaCl	FeO(OH)
25	6	-	-	+	+	-	+	+	+
50	6	+	+	+	+	+	+	+	+
80	4	+	+	+	+	+	+	+	-

Experimental results show the possibility of using cementation as way of removing metals (mainly Cd, Pb and Fe) from solutions to the acceptable limits. The most effective conditions of cementation found out in this work are listed in **Table 9**. However, it is obvious that at pH 6 except of cementation occur also precipitation, what contribute to improvement overall refining process.

Table 9 The most effective conditions of cementation Cd, Pb and Fe

Metals	Cd		Pb		Fe	
Concentration [mg.l ⁻¹]						
Medium/ most effective conditions	Before	After	Before	After	Before	After
Sulphate solution / pH 6; 80 °C	18.9	0	5.1	9 x10 ⁻⁵	3.31	6 x10 ⁻³
Chloride solution / pH 6; 50 °C	13	0	0.3	4.4 x10 ⁻⁵	1.84	1.8 x10 ⁻⁴

5 Conclusion

From experimental study of cadmium and lead cementation from solutions coming from leaching of steelmaking dust, following conclusions can be stated:

- Cementation of cadmium was carried out under selected conditions (pH = 4, 5 and 6 and at temperatures 25, 50 and 80 °C) with 100 % efficiency in both sulphate and chloride solution. Cadmium was completely cemented at all selected conditions without any influence of temperature and pH. Phase analysis of solid residue after cementation confirmed the presence of cadmium as Cd and CdO, which probably formed by oxidation of Cd in solid residue.
- The highest efficiency of lead cementation in sulphate solution, 87.61 %, was reached at pH = 6 and temperature 80 °C. In chloride solution the efficiency of 99.94 % was achieved at pH 6 and 80 °C. Lead was present in solid residues in the form of Pb in both sulphate and chloride solution, what confirms its cementation.

- Phase analysis of solid residues after cementation confirmed, that iron precipitates from sulphate solution by increasing pH above 4 as Fe_2O_3 and $\text{FeO}(\text{OH})$.
- Adjusting pH to the value of 6 caused partial precipitation of zinc from sulphate solution. Phase analysis of solid residue confirmed its presence in the form of Zn, ZnO and $\text{Zn}(\text{OH})_2$. The same phases were identified also in solid residues coming from chloride solution.
- It results from comparison of experiments with and without adjusting pH in both sulphate and chloride solutions, that increasing pH value has a positive effect on efficiency of cementation cadmium and lead from the solution. However, adjusting pH to the value of 6 causes precipitation of iron and partial precipitation of zinc, which stays in solid residues.

References

- [1] T. Havlík, B. Vidor e Souza, M. Brnardes, I. Schneider, A. Miškufová: Acta Metallurgica Slovaca, Vol. 12, 2006, No.1, p. 42- 53
- [2] G. Graf: Zinc, *Ullmann's Encyclopedia of Industrial Chemistry*, first ed., Wiley- VCH Verlag GmbH a Co., 2005
- [3] Z. Sedláková, D. Oráč, T. Havlík: Acta Metallurgica Slovaca, Vol. 12, 2006, No.1, p. 338 - 345
- [4] M. Wua, J.H. She, M. Nakano: Engineering Applications of Artificial Intelligence, Vol.14, 2001, No.5, p. 589–598, doi: 10.1016/S0952-1976(01)00019-7
- [5] T. Havlík: *Hydrometallurgy, Principles and application*, first ed., Košice: Emilena, 2005, ISBN 80-8073-337-6
- [6] M. Štofko, M. Štofková: *Non-ferrous metals*, first. ed., Košice: Emilena 2000, ISBN 80-7099-527-0
- [7] R. Lacko, M. Štofko, M. Škrobán: *Activation cementation of metal by current pulse*, Waste recycling, VŠB-TU, Ostrava, 2007, p. 191- 196
- [8] R. Lacko, J. Kaduková: Proceedings of the workshop held on the occasion of the anniversary of prof. Štofko, Herľany, EQUILIBRIA, 2008, p. 61-66
- [9] N.K. Amin, Z. El-Ashtoukhy, O. Abdelwaha: Hydrometallurgy, Vol. 89, 2007, No.3, p. 224–232, doi: 10.1016/j.hydromet.2007.07.007
- [10] M. Arousseau, N.T. Pham, P. Ozil: Ultrasonics Sonochemistry, Vol. 11, 2004, No. 1, p. 23–26, doi: 10.1016/S1350-4177(03)00130-5
- [11] M. S. Safarzadeh, D. Moradkhani, M. Ilkhchi: Chemical Engineering and Processing, Vol. 46, 2007, No.12, p. 1332–1340, doi: 10.1016/j.cep.2006.10.014
- [12] S.R. Younesi, H. Alimadadi, E. Alamdari: Hydrometallurgy, Vol. 84, 2006, No.3-4, p. 155-164, doi: 10.1016/j.hydromet.2006.05.005
- [13] O. Ruiz, C. Clemente, M. Alonso, F.J. Alguancil: Journal of Hazardous materials, Vol. 141, 2007, No.1, p. 33-36, doi: 10.1016/j.hazmat.2006.06.079
- [14] G. Orhan: Hydrometallurgy, Vol. 78, 2005, No. 3, p. 236–245, doi: 10.1016/j.hydromet.2005.03.002
- [15] R. Ligiane: Minerals Engineering, Vol. 20, 2007, No. 9, p. 956-958, doi:10.1016/j.mineng.2007.04.016

Acknowledgements

This work was supported by Ministry of Education of the Slovak Republic under grant MŠ SR 1/0293/14. Article is the result of the Project implementation: University Science Park

TECHNICOM for Innovation Applications Supported by Knowledge Technology, ITMS: 26220220182, supported by the Research & Development Operational Programme funded by the ERDF.