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ANALYTICAL STUDY OF ZINC RECOVERY FROM SPENT SOLUTIONS RESULTING AFTER GALVANIZATION PROCESS

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Abstract

Galvanization is a widely employed process in metallurgical practice for the protection of steel products against corrosion. The spent, hydrochloric acid solutions generated from this process contain considerable amounts of valuable metals, such as zinc (40–60 g/L) and manganese (1–2 g/L). The recovery of these metals is not only economically advantageous but also environmentally sustainable. The fundamental difficulty in the treatment of such solutions lies in their high acidity and the high concentration of iron (160–190 g/L).

Based on a comprehensive literature review, the following scheme can be proposed for the recovery of zinc in the form of zinc sulfate. The processes include removal of iron through precipitation as iron hydroxide; the precipitation of zinc and manganese hydroxides; dissolution of these precipitates in sulfuric acid to generate a sulfate solution.

The objective of the present study is to carry out a detailed thermodynamic evaluation of the possible chemical interactions at each stage using the HSC Chemistry software, version 10.5, specifically the modules: Reaction Equations and Eh–pH Diagrams.

***Keywords**: Thermodynamic; Galvanic waste solutions; Iron removal, Zinc and manganese recovery.*

1. INTRODUCTION

Worldwide, more than 50 % of zinc is used for galvanizing each year. Due to the high consumption of zinc, ore reserves of this metal are decreasing [1]. This necessitates the recovery of zinc from secondary products, including the recycling of waste solutions from hot-dip galvanizing facilities. They represent hazardous waste due to the high concentration of heavy non-ferrous metals (mainly zinc and manganese) and the high concentration of hydrochloric acid. The concentration of zinc in the spent solutions may reach up to 130 g/L, that of iron up to 190 g/L, and of hydrochloric acid up to 10% [2,3].

Typical methods for the treatment of these solutions include precipitation with alkaline reagents, most often with $Ca(OH)_2$. As a result, large amounts of precipitates containing iron, calcium, and relatively low zinc content (<20 %) are formed. Alternative methods for separating iron from zinc include ion exchange, solvent extraction and chemical precipitation [4,5].

The present work proposes an analytical study of the processes of separation of iron from zinc and manganese based on chemical interactions in the multi-component systems: Fe-Zn-Mn-Ca-Cl-H_2O; Zn-Cl-Mn-Na-H_2O and Zn-Mn-S-H_2O. Combined Eh-pH diagrams for each system gives visual information about the existence of ionic and non-ionic forms of the substances as a function of redox potential (Eh) and pH at given temperature.

2. THERMODYNAMICAL ANALYSIS

The analytical study was focused on the three multicomponent water systems: **Fe-Zn-Mn-Ca-Cl-H_2O**, **Zn-Cl-Mn-Na-H_2O** и **Zn-Mn-S-H_2**O. The thermodynamic estimation of possible chemical interactions in the three studied systems was made based on the calculated values of the free Gibbs energy and the equilibrium constant. The calculations were made using the professional software program HSC Chemistry, ver. 10.5, module Equation Reaction.

Combined Eh-pH diagrams were calculated for the following waste solution, in g/L: 165 Fe, 43 Zn, 1.5 Mn and 75 HCl. The quantities of: $Ca(OH)_2$, NaOH and H_2SO_4 were determined based on chemical reactions. For the calculation of the Eh-pH diagrams relevant elements in mol/kg_{H2O} (Table 1) and types of ionic and non-ionic species are given in Table 1 and 2 respectively.

Table 1. Concentrations of elements used in calculation of diagrams in mol/kg_{H2O}

	Fe	Zn	Mn	Ca	Cl	Na	S
Stage I	2.95	0.66	0.03	4.67	7.97	-	-
Stage II	-	0.66	0.03	-	-	0.68	-
Stage III	-	0.66	0.03	-	-	-	0.68

Table 2. Type of ionic and nonionic forms in the investigated systems and theirs free Gibbs energy of formation at T = 25 ºC and T = 60 ºC

Species	ΔG, kJ/mol		Species	ΔG, kJ/mol		Species	ΔG, kJ/mol	
	T = 25 ºC	T = 60 ºC		T = 25 ºC	T = 60 ºC		T = 25 ºC	T = 60 ºC
Fe			**Zn**			**Ca**		
Fe(+2a)	-91.52	-91.36	**Zn(+2a)**	-147.25	-146.50	**Ca(+2a)**	-552.80	-553.89
Fe(+3a)	-17.18	-13.28	**$Zn(OH)_2$**	-555.92	-545.39	**$CaCl_2$**	-748.78	-743.34
Fe_3O_4	-1012.3	-1000.28	**ZnCl(+a)**	-279.65	-280.05	**CaCl(+a)**	-684.89	-682.56
$Fe(OH)_2$	-486.97	-477.36	**ZnCl3(-a)**	-531.56	-519.91	**$Ca(OH)_2$**	-898.24	-887.96
$Fe(OH)_3$	-703.28	-688.38	**ZnCl4(-2a)**	-669.94	-655.59			
FeCl(+2a)	-156.89	-150.35	**Cl**					
Mn			**Cl(-a)**	-131.26	-126.76	**S**		
Mn(+2a)	-229.97	-231.06	**ClO_4(-a)**	-7.89	-6.41	**H_2S(a)**	-115.66	-111.25
Mn2O3	-880.97	-871.84	**Na**			**HS(-a)**	52.07	67.20
Mn3O4	-1281.2	-1269.2	**Na(+a)**	-261.90	-264.49	**HSO_4(-a)**	-3161.74	3096.36
MnCl(+a)	-360.95	-360.10	**NaOH(a)**	-379.65	-374.24	**SO_4(-2a)**	-3115.90	3031.85
Mn(OH)2	-617.68	-608.18	**NaCl(a)**	-384.07	-380.91			

3. RESULTS AND DISCUSSION

Table 3 shows the calculated values of the Gibbs energy and equilibrium constants for the three systems at two temperatures: 25ºC и 60 ºC.

It can be shown that in stage-I, the most thermodynamically possible reaction is precipitation of iron as $Fe(OH)_3$ in the presence of oxygen. The second reaction is of hydrochloric acid with $Ca(OH)_2$. From the other reactions only the reaction of $MnCl_2$ with $Ca(OH)_2$ is almost thermodynamically impossible. At the neutralization with NaOH (stage-II), the most thermodynamically possible reaction is precipitation of zinc as $Zn(OH)_2$. In the third stage (stage III), gypsum will be formed followed by the reactions of the formation of zinc and manganese sulfate.

Combined Eh-pH diagrams of the system **Fe-Zn-Mn-Ca-Cl-H_2O are shown on the Figure 1 and 2**

Table 3. Computed values of the free Gibbs energy and equilibrium constant of the possible chemical interactions during each stage of separation of the metals

Reactions	T = 25ºC		T = 60ºC	
	ΔG, kJ/mol	LogKp	ΔG, kJ/mol	LogKp
I-stage Neutralization with calcium hydroxide				
$2HCl(a) + Ca(OH)_2 = CaCl_2(a) + 2H_2O$	-133.27	23.35	-135.10	21.18
$FeCl_2(a)+Ca(OH)_2=Fe(OH)_2+CaCl_2(a)$	-92.98	16.29	-87.75	13.76
$4FeCl_2(a)+4Ca(OH)_2+O_2(g)+2H_2O=4Fe(OH)_3+4CaCl_2(a)$	-190.72	33.42	-183.03	28.67
$ZnCl_2(a) + Ca(OH)_2 = Zn(OH)_2 + CaCl_2(a)$	-58.14	10.19	-54.79	8.59
$MnCl_2 + Ca(OH)_2 = Mn(OH)_2 + CaCl_2$	-27.81	4.87	-27.92	4.38
II-stage Neutralization with sodium hydroxide				
$ZnCl_2 + 2NaOH = Zn(OH)_2+2NaCI$	-81.85	14.27	-82.54	12.94
$MnCl_2 + 2NaOH = Mn(OH)_2 +2NaCl$	-59.49	10.42	-61.74	9.68
$CaCl_2 + 2NaOH = Ca(OH)_2 + 2NaCl$	-14.15	2.48	-17.76	2.78
III-stage Resulting of $ZnSO_4.7H_2O$ and MnO_2				
$Zn(OH)_2 + H_2SO_4 + 5\ H_2O = ZnSO_4.7H_2O$	-131.77	23.09	-124.53	19.53
$Mn(OH)_2 + H_2SO_4 = MnSO_4 + 2H_2O$	-123.85	21.70	-123.86	19.42
$Ca(OH)_2 + H_2SO_4 = CaSO_4.2H_2O$	-208.96	36.61	-207.27	32.50

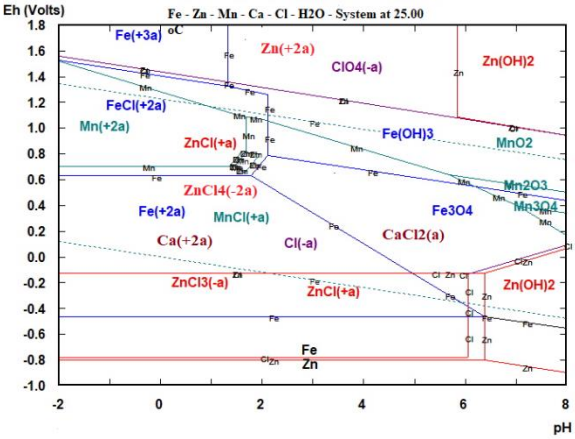

Figure 1 - Combined Eh-PH diagram of the system Fe-Zn-Mn-Cl-H_2O

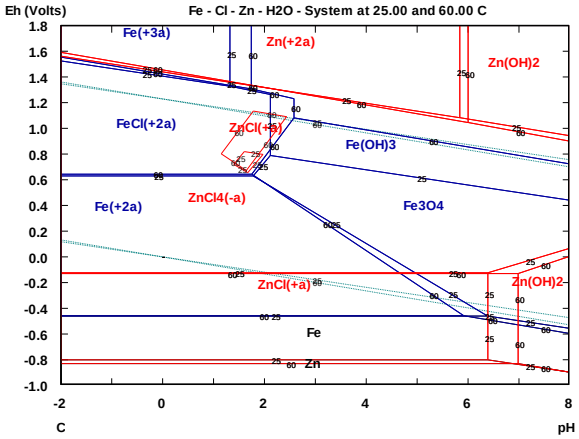

Figure 2 - Impact of the temperature on the stability regions of ionic and non-ionic species in the system Fe-Cl-Zn-H_2O.

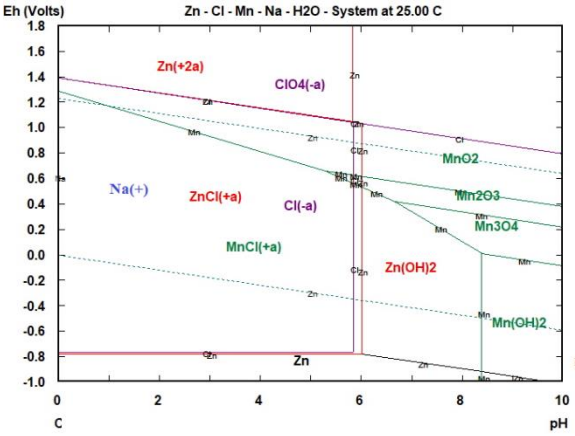

Figure 3 - Combined Eh-PH diagram of the system Zn-Cl-Mn-Na-H_2O

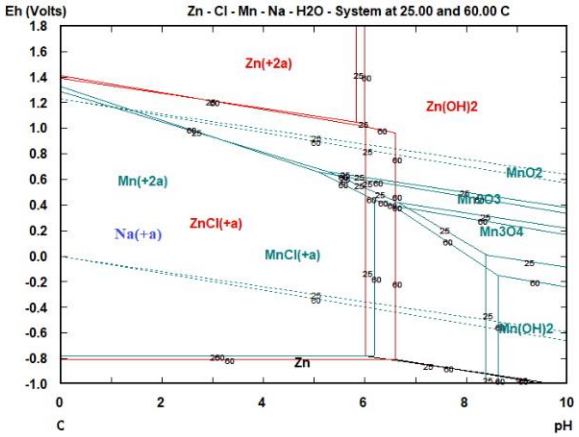

Figure 4 - Impact of the temperature on the stability regions of ionic and non-ionic species in the system Zn-Cl-Mn-Na-H_2O

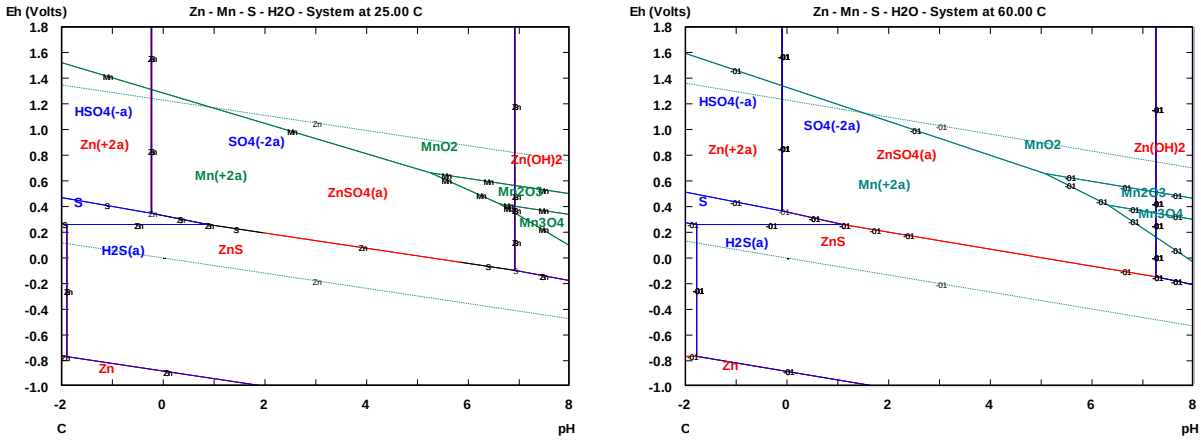

Figure 5 - Combined Eh-pH diagram of the system Zn-Mn-S-H_2O at temperature 25°C and 60°C

In the first system (Figure 1) Fe^{2+} ions present in solution are oxidized to Fe^{3+} under controlled conditions (Eh > 1.3V), leading to hydrolysis and subsequent precipitation as amorphous $Fe(OH)_3$ (pH > 1.8). Effect of the temperature on the stability of ionic and non-ionic forms is insignificant. In the system, **Zn-Cl-Mn-Na-H_2O,** the focus shifts to the **selective precipitation of zinc and manganese hydroxides (Figures 3 and 4). It can be shown that $Zn(OH)_2$ and $Mn(OH)_2$ are precipitated at pH > 6 and > 8.5 respectively and relatively low potential of the systems.** An increase of temperature reduces the area of stability of the formed hydroxides. The third system, **Zn-Mn-S-H_2O (Figure 5),** describes the final stage, involving the **formation of $ZnSO_4$ and $MnSO_4$** sulfates. Manganese can be removed from solution by oxidation with peroxide to insoluble MnO_2.

4. CONCLUSIONS

Based on the thermodynamic analysis and computed of combined Eh-pH diagrams it has been established that iron removal in the form $Fe(OH)_3$ is thermodynamically possible at high oxidation potential and pH > 2 with using of $Ca(OH)_2$. From the resulting filtrate zinc and manganese are precipitated with NaOH, selectively in the form of hydroxides at pH above 6 and 8 respectively. Further, resulting precipitations are dissolved in sulfuric acid. The processes are thermodynamically possible and with an increase of the temperature, an expansion of the stability of zinc sulfate is observed. Manganese can be removed in the form of MnO_2 at a higher oxidation potential.

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