FLUX SKIMMINGS ORIGINATED DURING HOT-DIP GALVANIZING PROCESS AND ITS HYDROMETALLURGICAL PROCESSING

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Abstract
Flux skimming as the specific waste forms on the surface of molten zinc in a separate section kettle during the wet batch hot-dip galvanizing. After the certain hot dip galvanizing time flux becomes less effective and loses its function. It is hazardous waste containing a significant amount of zinc. This work deals with the hydrometallurgical processing of flux skimming. Flux skimming sample containing 36.9% of Zn was supplied by the Slovak company operating wet batch hot-dip galvanizing.
Flux skimming was hydrometallurgicaly processed by leaching in the distilled water in which the ratio of L:S (4:1, 6:1, 8:1, 10:1, 12:1) and the influence of temperature on zinc extractions at different temperatures, 20°C, 40°C, 60°C, 80°C, were investigated. According to the experimental results optimal L:S ratio and temperature were determined. Leaching of flux skimming in hydrochloric acid media was also carried out. Based on the results it is obvious that Zn leaching in hot water (60°C) proceed fast and the highest efficiency of Zn leaching was reached in the first 5 to 10 minutes. The flux skimming leaching in 0,2M HCl media appears not to have any measurable effect on efficiency of zinc leaching.

Keywords: flux skimming, hydrometallurgy, hot-dip galvanizing

1 Introduction

Hot-dip galvanizing is one of the oldest methods of zinc coating which involves dipping of steel products in molten zinc to provide a corrosion protecting finish. There are some advantages like long life cycle, uniform coating formation and higher resistance to mechanical influences [1-3]. Hot-dip galvanizing can be divided according on using technologies continuous and batch. In the batch galvanizing process the steel article to be galvanized is cleaned, pickled and fluxed prior to dipping [4].
Special operation is flux application whose aim is to clean steel surfaces. According to the flux application hot-dip galvanizing technology is divided into „dry” and „wet” galvanizing [5, 6]. During the hot-dip galvanizing process solid waste containing high amount of zinc is formed. It consists of waste accumulating at the bottom of the zinc kettle (bottom dross) even on the surface of molten zinc (zinc ash, top dross and flux skimming) [6-10].
Flux skimming is the specific waste forming only during the wet batch galvanizing. It mainly forms when a top flux containing NH_4Cl freely floats on the liquid zinc surface [8-17].
The primary purpose of flux is to dissolve oxides that are forming on the steel after the pickling operation. During wet batch hot-dip galvanizing steel articles input into the molten zinc bath still

wet and flux freely floating on the surface of molten zinc bath reduces splattering of molten zinc into the environment [12, 15]. The important function of flux is to clean the surface of the steel articles and molten zinc so that the zinc and iron could react each other. Flux contributes to the production of thinner coatings and reduces oxidation of the molten zinc surface and thus reduces ash formation [13]. Flux mainly consists of NH_4Cl (ammonium chloride) or zinc ammonium chloride. Sometimes, Na_3AlF_6 (cryolite) is added for higher Al contents [13]. Based on the literature [16] the flux is prepared by putting a mixture of zinc ash (zinc oxide), sal ammoniac powder (ammonium chloride) and some glycerine or glycol. The choice of flux depends on the steel cleanliness, throughput rate and amount of fuming that can be tolerated.

After the certain galvanizing time kettle flux becomes less active and less effective. Its melting point increases in consequence of increasing of contaminants.

The dead flux is skimmed from the surface of zinc melting periodically. It should be skimmed off carefully to minimize the amount of zinc entrained with the skimming [17].

According to the Ministry of Environment Decree No. 284/2001 Z.z., which defines Catalog waste flux skimming is placed in the category "hazardous waste". Flux skimming is formed by oxides, sulphides, ammonium chloride etc. In addition to the original salt, NH_4Cl, $ZnCl_2$, $ZnCl_2.NH_4Cl$ it also contains 18 – 22 % of metallic zinc, 30 – 35 % of ZnO and other contaminants as Fe_2O_3 [8, 18]. According to the literature [19] flux skimming consists of 48.1 % $ZnCl_2$, 27.4 % ZnO, 5.6 % metallic zinc, 3.1 % aluminum chlorides and other chlorides and oxides of Fe, Cd and Al.

Kovotvar Kúty, v.d. is the only company in Slovakia that operates wet batch hot-dip galvanizing. Flux skimming is not processed in Slovak Republic. It is very necessary to deal with this issue since flux skimming being hazardous waste contains valuable metallic zinc. Based on the literature [8, 18] flux skimming can be processed as follows.

A. Leaching of flux skimmings in the hot water. The leachate consists of NH_4, $ZnCl_2$. Insoluble leach residue consists of Zn, ZnO and Fe_2O_3 as an impurity.
B. Treatment of the leachate, it is thickening in the evaporation equipment, the final product is solution containing $ZnCl_2$, subsequently, this solution is subjected to crystallization and the last product is NH_4Cl;
C. Treatment of leach residue consists of drying, crushing and separation of coarse-grained fractions containing metallic zinc which is a final product of this processing step while fine-grained fractions with zinc ash are proceed to the additional treatment.

The purpose of this work was to establish the suitable conditions of flux skimming leaching to obtain the highest extractions of zinc into the solution.

2 Experimental material and methods

For experimental purposes a flux skimming sample was supplied by Kovotvar Kúty, v.d.. As supplied flux skimming sample had an irregular shape and heterogeneous composition it was needed to treat it, to homogenize. The treatment of flux skimming consisted of drying-up, crushing and grinding. In order to obtain a representative sample quartering followed. For determination of quantitative amounts of elements the sample was chemically analyzed by AAS method using VARIAN Spectra AA – 20 plus. The result of chemical composition is shown in **Table 1**.

Table 1 Chemical composition of flux skimming sample

Element	Content [%]
Zn	36.9
Cl^-	30.14
Fe	0.68

Presence of $Zn_2OCl_2.2H_2O$ and ZnO.HCl phase was identified with X-Ray diffraction analysis (XRD) using diffractometer BRUKER ADVANCE 8 with Cu radiation. The result of analysis is shown **Fig. 1**.

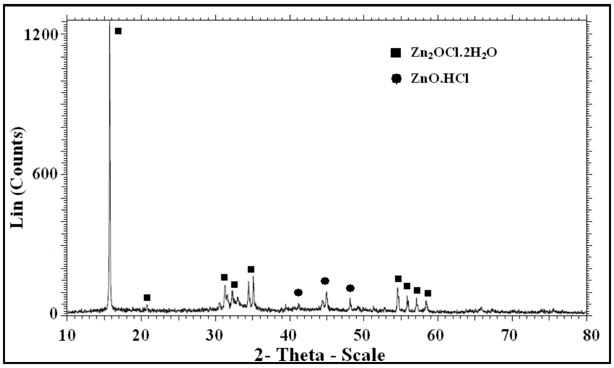

Fig. 1 EDX diffraction analysis of flux skimming sample

2.1 Leaching of flux skimming sample

For leaching experiments apparatus outlined on **Fig. 2** was used. Experiments were carried out in glass beaker immersed in water bath at temperatures: 20, 40, 60 and 80°C with constant stirring. Distilled water was used as a leaching medium. Time of leaching was 120 minutes. The different L:S ratio (liquid to solid) 4:1, 6:1, 8:1, 10:1, 12:1 was chosen in this experimental program. The samples were analyzed by AAS method for zinc, iron and chlorine contents. The liquid samples were taken according to given time schedule at 5, 10, 30, 60 and 120 minutes. Leaching of flux skimming in 0.2M HCl was also included in experimental program.

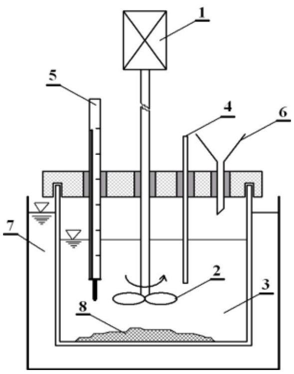

Fig. 2 The scheme of the leaching apparatus (1- stirrer engine, 2-propeller, 3-leaching pulp, 4- sampler, 5- thermometer, 6- feeder, 7- water thermostat, 8- flux skimming) [20]

3 Results

Kinetic curves of zinc extractions in distilled water at 20°C are shown in **Fig. 3**. The following L:S ratios 4:1, 6:1, 8:1, 10:1, 12:1 were observed to determine the optimal ones.

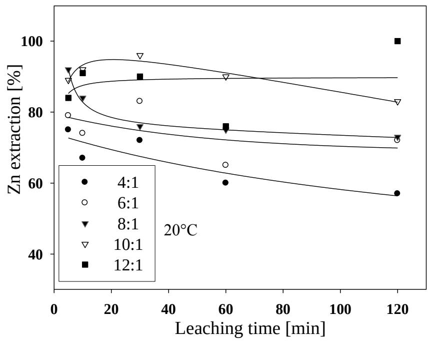

Fig. 3 Kinetic curves of zinc extractions at various L:S

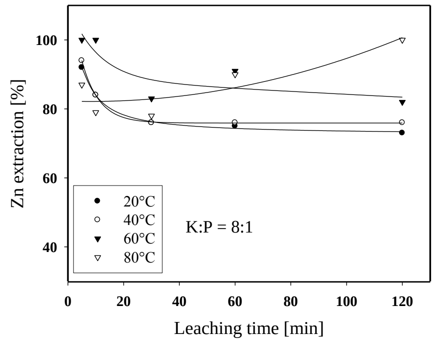

Fig. 4 Kinetic curves of zinc extractions at various temperature

Kinetic curves of zinc extractions in distilled water at different temperatures 20°C, 40°C, 60°C and 80°C are shown in **Fig. 4**. During these experiments constant ratio L:S = 8:1 was used.

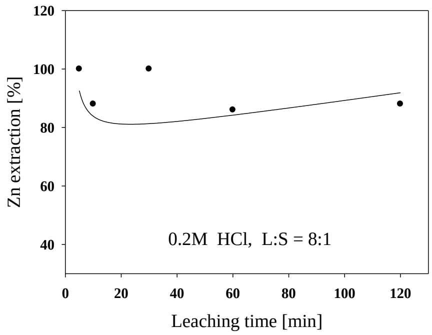

Fig. 5 Kinetic curves zinc extraction at 0.2M HCl

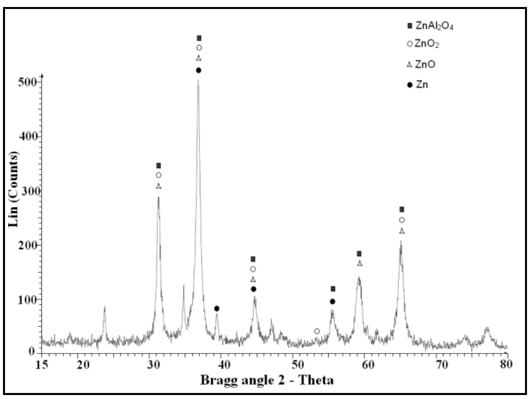

Fig. 6 XRD pattern of leaching residuum

Skimming was also leached in the solution of 0.2M HCl, at temperature of 20°C, the leaching time was 120 minutes at constant ratio of L:S = 8:1. Zinc extraction in the solution of 0.2M HCl was also almost 100%, which is seen in **Fig. 5**.

XRD diffraction analysis of residuum after the flux skimming leaching process was performed with the aim to determine the phase composition in **Fig. 6**. Based on the XRD analysis, $ZnAl_2O_4$, ZnO_2, ZnO and metallic zinc as a possible phases are supposed to be present in the pattern.

4 Discussion

The aim of the experiments was found out the ratio L:S and temperature dependence of zinc extraction and to determine the ratio L:S and temperature at which zinc extractions is the highest. On the base of the zinc extraction results **Fig.3**, the optimal ratio for subsequent experiments was L:S = 8:1. Zinc recovery reached 92% at this value of L:S. The highest zinc extraction almost 100% was reached at 60°C and ratio L:S = 8:1 during the first 5 – 10 minutes of leaching **Fig .4**. Skimming was also leached in the solution of 0.2M HCl, at temperature of 20°C, the leaching time was 120 minutes at constant ratio of L:S = 8:1.

Zinc extraction in the solution of 0.2M HCl was also almost 100%, which is seen in Fig. 5. This behavior is comparable with zinc extraction in distilled water. During the first five minutes zinc extraction reached approximately 100%. With the increasing of leaching time zinc extraction slightly decreased. The use of 0.2M HCl had no significant influence on zinc extraction.

5 Conclusion

In this paper the hydrometallurgical treatment of flux skimming forming during the wet batch hot-dip galvanizing was studied. The results suggest that distilled water is sufficient for zinc extraction into the solution at ambient temperature. The highest amount of zinc 92% was reached after five minutes of leaching at a ratio of L:S = 8:1 and at temperature of 20°C. Almost 100% zinc recovery was reached at temperature of 60°C during the first five to ten minutes. Similarly almost 100% zinc recovery was reached at temperature of 80°C after 120 minutes of leaching process. Flux skimming leaching at medium of 0.2M HCl at temperature of 20°C has achieved almost 100% zinc recovery after 5 minutes of the process.

The purpose of this work was to establish the suitable conditions of flux skimming leaching to obtain the highest extractions of zinc into the solution.

Acknowledgements

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