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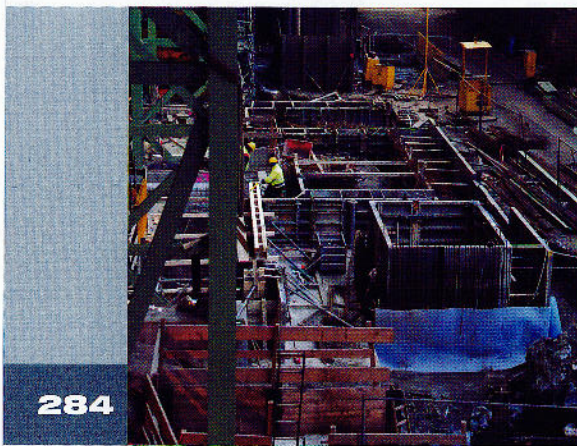
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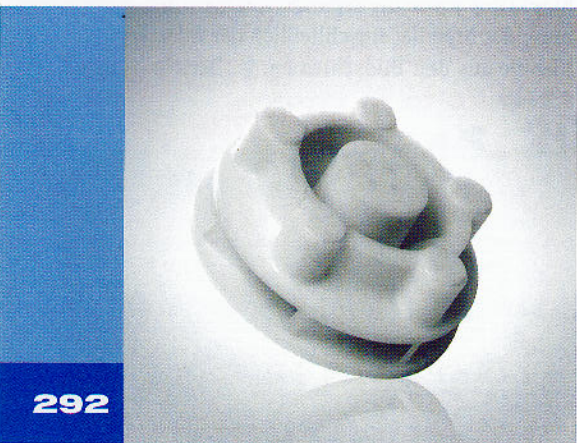
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Acid Leaching of Top Dross Generated During Wet Batch Hot-dip Galvanizing Process

Piroskova, J. (1); Trpcevska, J. (1); Laubertova, M. (1); Holkova, B. (1), Smincakova, E. (2)

Flux skimming is a specific waste which is generated by reaction between the flux and zinc, zinc oxide, and iron. Flux skimming sample containing 46.8% Zn, 22.7% Cl and Al, Fe, Si and Pb below 1%.

The leaching experiments were carried out at the temperatures of 20, 40, 60 and 80°C. HCl solutions of 0.25, 0.5, 1 and 2M were used as a leaching agent, which gives the L:S ratio equal to 80, 40, 20.

The highest extraction of Zn (nearly 100%) was obtained at 20°C in 0.25 M HCl within the first minutes of leaching at ratio of L:S = 40 and in 0.5M HCl at 40°C and at all ratios L:S were almost 100%.

Hot-dip galvanizing (HDG) is the process of dipping fabricated steel into a kettle of molten zinc. While the steel is in the kettle, the iron metallurgical reacts with the molten zinc to form a tightly-bonded alloy coating that provides superior corrosion protection to the steel. In addition to hot-dip galvanizing, there are a number of other zinc coatings applied to steel such as zinc-rich paint, electrostatically applied zinc, metalizing and mechanically applied zinc. Hot-dip galvanizing has been the most commonly used method of protecting steel products from corrosion [1]. It is a metallurgical process typically carried out in steel kettle at temperature from 450 to 470 °C. Hot-dip galvanizing process can be divided according to way of used technology into a continuous and batch [2, 3]. Continuous hot-dip galvanizing process is used for steel sheet, strip and wires. Batch hot-dip galvanizing is used for galvanizing of the steel parts and construction.

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 batch hot-dip galvanizing technology is divided into dry and wet galvanizing [4, 5]. Surface preparation is the most important step in the application of any coating. The surface preparation step in the galvanizing process consists of three steps (see Fig. 1).

- Degreasing – a hot alkaline solution removes dirt, oil, grease, shop oil, and soluble markings.
- Pickling – dilute solutions of either hydrochloric or sulphuric acid removes surface rust and mill scale to provide a chemically clean metallic surface.
- Fluxing – steel is immersed in a zinc ammonium chloride solution to remove oxides and to prevent oxidation prior to dipping into the bath of molten zinc. In the dry galvanizing process, the item is separately dipped in a liquid flux bath, then removed and subsequently dry, and then galvanized. In the wet galvanizing process, the flux floats on top of the molten zinc and the item passes through the flux immediately prior to galvanizing [6, 7]. This paper deals with waste generated only during wet batch hot-dip galvanizing process.

In the batch hot-dip galvanizing process a lot of wastes originate in liquid, solid and gaseous forms. Gaseous and liquid wastes are generated in the pre-cleaning treatment processes e.g.: waste waters, alkaline solutions, exhausted solution of HCl and fumes of HCl, NH₄Cl, etc.. Solid wastes are

accumulated during batch hot-dip galvanizing process at the bottom of zinc bath such as bottom dross and on the surface of zinc bath such as zinc ashes and flux skimmings (top dross) [9]. These wastes due to high zinc content represent valuable secondary raw materials.

Function of flux

The primary purpose of galvanizing flux is to dissolve surface layer that form 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 [10, 11]. The important function of this 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 [12]. Flux mainly consists of NH₄Cl (ammonium chloride) or zinc ammonium chloride. Based on [13] the flux is prepared by putting a mixture of zinc ash (zinc oxide), salt ammoniac powder (ammonium chloride) and some glycerol. 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. During galvanizing main constituent fluxes (NH₄Cl) is lost by evaporation but also by reactions between Fe, Zn and ZnO. With use, top flux becomes rich in zinc chloride butter of zinc lacking in ammonium chloride [12]. Cross section of the kettle flux shown in Fig. 2 illustrates the effect of temperature on ammonium chloride content. A foamed kettle flux will have a temperature at the zinc metal interface of (454 °C) but the insulating foam blanket will drop the temperature to as low as (343 °C) at the outer surface. Diagram shows the equilibrium concentrations of ammonium chloride for each temperature. This ranges from 2 to more than 30% [14]. A flux system should contain 10% to 15% dissolved ammonium chloride to function effectively. This concentration can be achieved by reducing the flux temperature, moving along the equilibrium line toward higher ammonium chloride content in solution in the liquid flux [14].

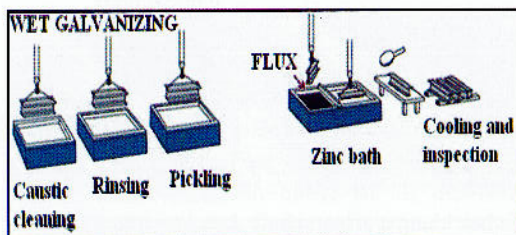


Fig. 1: Flowsheet of wet batch HDG [8]

Characterization of top dross / flux skimming

Top dross – flux skimming is generated in separate parts of kettle due to the reaction of molten zinc with fluxes. This waste contains except original salts NH_4Cl , $ZnCl_2$, also $ZnCl_2 \cdot 2NH_4Cl$ and 18–22% metallic zinc, ZnO 30–35% and 10–20% the other impurities, mainly Fe_2O_3 [15, 16]. Typical phase composition of flux skimming according to (M. K. Jha) is as follows: 5.6% metallic Zn, 48.1% $ZnCl_2$, 27.4% ZnO 3.1% aluminium chloride and other chlorides and oxides, especially Fe, Cd and Al [9, 17]. According to The European Waste Catalogue & Hazardous Waste List – Valid from 1 January 2002 flux skimming is placed in the category „hazardous waste“. The spent

composition. The samples have been previously homogenized before their characterization. The treatment of flux skimming samples consisted of drying-up, crushing and grinding. In order to obtain a representative sample quartering followed. The sample was subjected to AAS analysis to determine the chemical composition using VARIAN Spectra AA – 20 plus. The result of chemical composition is shown in Table 1.

The phase composition was analysed by means of X-Ray Diffraction method (XRD) using diffractometer Seifert 3003 PTS with Co radiation. Parameters of measurement are shown in Table 2. The XRD pattern of flux skimming is shown in Fig. 4.

The analysis proved the presence of phases of zinc chloride hydroxide - $Zn(OH)Cl$ and



Fig. 3: Skimming the spent flux and flux skimming sample

flux is skimmed from the surface of zinc melt periodically. It should be skimmed off carefully to minimize the amount of zinc entrained with the skimming. The flux

sal ammoniac - NH_4Cl . Quantitative XRD analysis shows that the sample consists of 96.43% $Zn(OH)Cl$ and from 3.57% NH_4Cl . The sample has a crystalline fraction

Sample of flux skimming	Element [%]				
	Zn	Fe	Al	Cl-	Residue
Content	46.8	0.03	0.12	22.7	30.55

Tab. 1: Chemical composition of flux skimming sample

skimming sample is shown in Fig. 3. 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.

Experimental material and methods

For experimental purposes a flux skimming sample was provided by Slovak company. Supplied flux skimming sample had an irregular shape and heterogeneous

(83.7%) and amorphous content (16.3%). Subsequently the flux skimming was observed by light microscope type Leica Wild M3Z. Observation was realised at temperature 25 °C, standard atmospheric pressure of 0,1 MPa and 60% air humidity. As can be seen in Fig. 5 it supplied material is characterized by high hygroscopic properties, because in within 16 seconds flux skimming absorbed air humidity. High hygroscopic property is related to presence of chloride compounds in flux skimming. This experiment confirmed theoretical

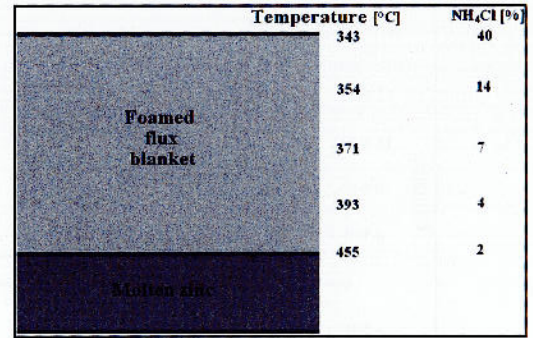


Fig. 2: Foam blanket cross section [14]

knowledge about chloride compounds properties [18 - 20].

Leaching of flux skimming samples

Experiments were carried out in the apparatus consisting from a thermostat, a modified sealed glass reactor with the volume of 800 ml with the holes for temperature measurements and sample taking. The reactor was placed in the water thermostat. The leached experiments were carried out at temperature 20, 40, 60 and 80°C. Hydrochloric acid solution 0.25M, 0.5M, 1M and 2M HCl were used as a leaching medium. Time of leaching was 90 minutes. The different L:S ratio (liquid to solid) 80, 40, 20 was chosen in these experiments. The samples were analyzed by AAS method for zinc contents. The liquid samples were taken according to given time schedule at 1, 5, 10, 15, 20, 25, 30, 60 and 90 minutes.

The samples were filtrated and analyzed for zinc content by atomic absorption spectrometry (Varian SpectrometerAA20+). After leaching, the remaining solution was subjected to filtration. The final volume was measured for the purpose of correction values in zinc as a result of sampling and evaporation.

Generator	35 kV, 40 mA
X-ray radiation	Co -line focus
Filter	Fe
Scan step	0.02 theta
Range of measuring	10 - 130° 2theta
Input slits	3 mm, 2 mm
PSD Detector	Meteor1D

Tab. 2: The parameters of XRD measurement flux skimmings (supplementation of XRD)

Results and discussion

The objective of the experimental part was both to prove the leachability of flux skim-

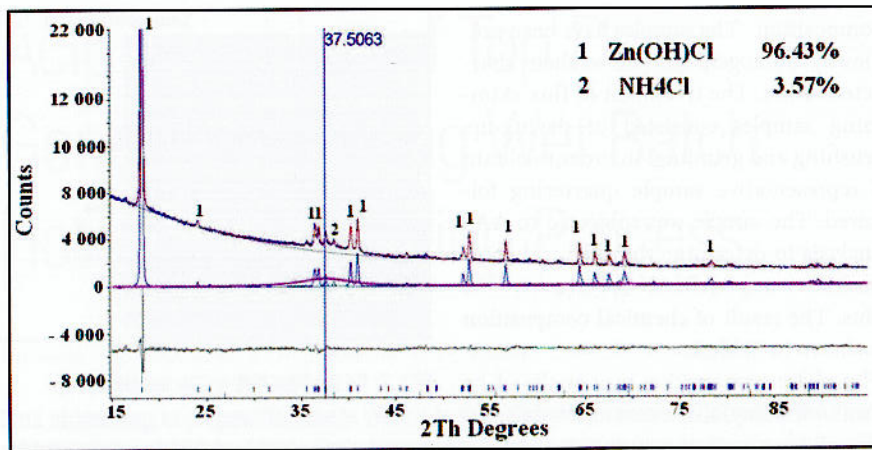


Fig. 4: XRD pattern of flux skimming sample

ming in hydrochloric acid, and to achieve the highest extraction of zinc into the solution. The influence of the temperature (20, 40, 60 and 80°C) and ratio L:S to convert

From the results of leaching flux skimming in a 1M HCl solution (Fig.8) it can be stated that the optimum ratio L:S = 80. The highest Zn extraction into a solution

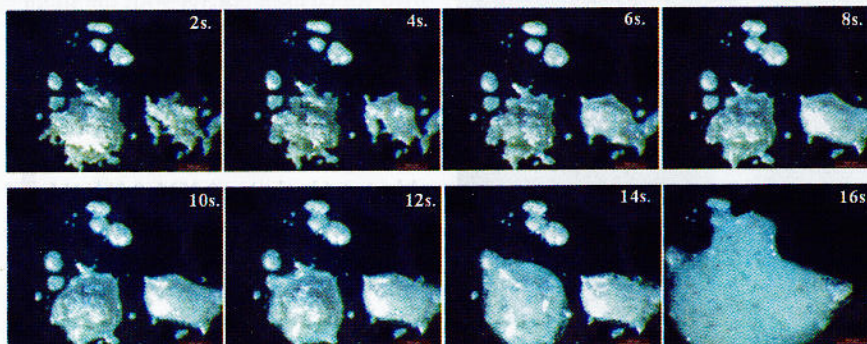


Fig. 5: Change tracking of humidity absorption at the time (scale 200 μ m)

the zinc into the solution was observed. Kinetic curves of zinc extraction in 0.25M; 0.5M; 1M and 2M HCl at temperature 20°C are shown in Fig. 6-9.

Almost 100% extraction of zinc in a 0.25M HCl and ratio L:S = 40 in the first 5 minutes of leaching was already obtained. With increasing leaching time, the zinc extraction slightly decreased. During the leaching in 0.5M HCl solution (Fig. 7) and at L:S = 20, in the first minutes of leaching 82% extraction of zinc was already achieved.

(almost 100%) was already achieved with in 1-5 minutes of leaching at a given ratio L:S = 80.

The kinetic curves of zinc extraction in 2M HCl solution are shown in Fig.9. From these curves it follows that the highest zinc extraction into solution (almost 100%) was achieved at a ratio of L:S = 80 in the first minute. With increasing duration of leaching zinc extraction slightly decreased. Kinetic curves of zinc extractions in 0.25M; 0.5M; 1M and 2M HCl, at temperature 40 °C are shown in Fig. 10 – 13.

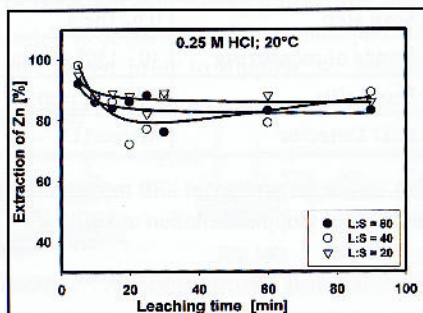


Fig. 6: Kinetic curves of Zn extraction in 0.25M HCl, 20°C and various L:S

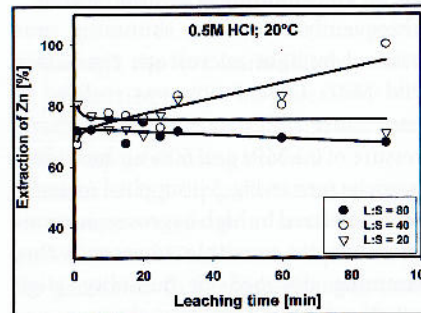


Fig. 7: Kinetic curves of Zn extraction in 0.5M HCl, 20°C and various L:S

Fluctuations in of zinc extraction in the process of leaching are probably due to the leaching of zinc into the solution and its subsequent precipitation from solution in the form of colloidal solutions.

Fig. 10 and Fig. 11 show the kinetic curves of zinc extraction into solution in 0.25M and 0.5M HCl, at temperature 40 °C. Already in the first minutes of leaching at the ratios L:S = 40 and L:S = 80 there was a nearly 100% zinc extraction into the solution. With increasing leaching time, the process has stabilized.

During the leaching of flux skimming in 1M HCl solution (Fig. 12) was observed almost 100% extraction of zinc already in the first minutes of leaching. This zinc extraction was achieved at the ratio L:S = 80. Fig. 13 shows kinetic leaching curves of flux skimming in 2M HCl. The highest zinc recovery was achieved at the ratio L:S = 80, 83% zinc extraction was achieved in the first minute. With increasing leaching time, zinc extraction into the solution increased to almost 100% from 30 up to 90 minutes of leaching. The lowest zinc extraction was achieved at the ratio L:S = 20. Kinetic curves of zinc extraction show that with increasing leaching time zinc extraction decreased from 80% Zn in the first minute to 63% at 90 min of leaching.

Fig. 14 shows the leaching of flux skimming at temperature 60°C, 0.25M HCl solution and various ratios L:S. Almost 100% extraction of Zn into solution was achieved at ratio L:S = 80 in first minutes of leaching and the achieved Zn extraction remained constant over time. Increasing of HCl concentration up to 0.5M at identical ratio S:L, Zn extraction was unchanged, reaching almost 100% during the whole period of leaching Fig. 15.

Fig. 16 shows kinetic curves of zinc extraction in 1M HCl solution. It was achieved 98% zinc extraction at ratio L:S = 80 in the first minute, then zinc extraction fallen to 78% in 90 minutes. Kinetic curves of zinc

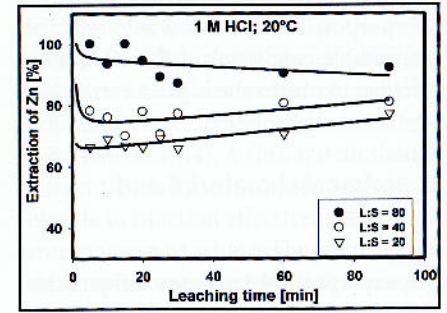


Fig. 8: Kinetic curves of Zn extraction in 1M HCl, 20°C and various L:S

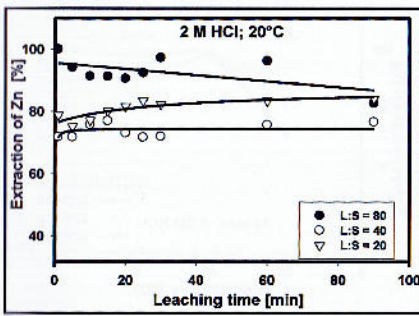


Fig. 9: Kinetic curves of Zn extraction in 2M HCl, 20°C and various L:S

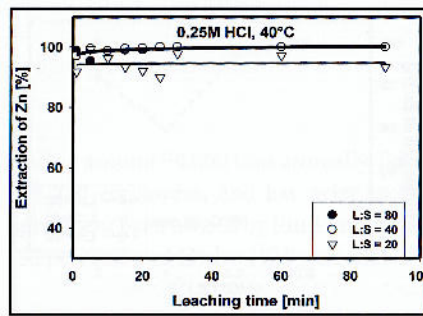


Fig. 10: Kinetic curves of Zn extraction in 0.25M HCl, 40°C and various L:S

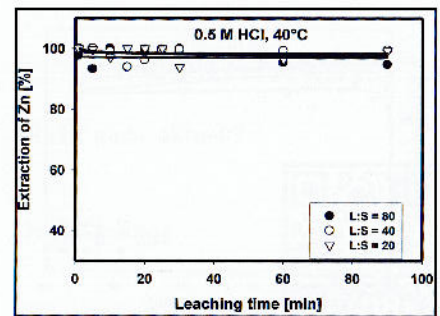


Fig. 11: Kinetic curves of Zn extraction in 0.5M HCl, 40°C and various L:S

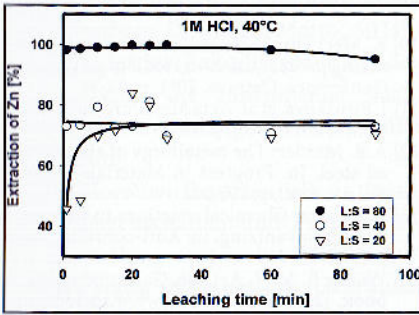


Fig. 12: Kinetic curves of Zn extraction in 1M HCl, 40°C and various L:S

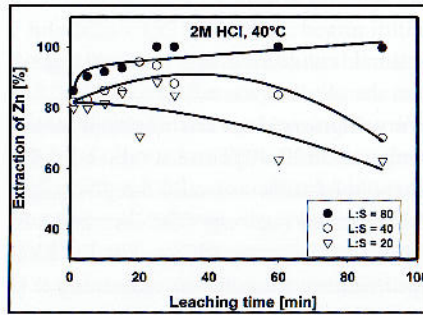


Fig. 13: Kinetic curves of Zn extraction in 2M HCl, 40°C and various L:S

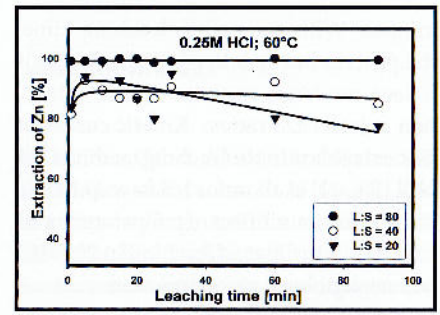


Fig. 14: Kinetic curves of Zn extraction in 0.25M HCl, 60°C and various L:S

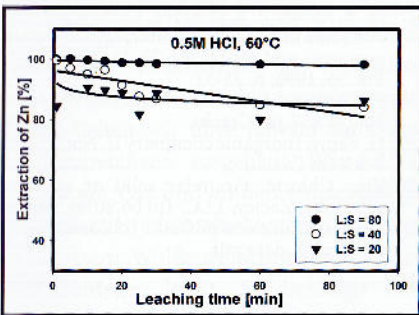


Fig. 15: Kinetic curves of Zn extraction in 0.5M HCl, 60°C and various L:S

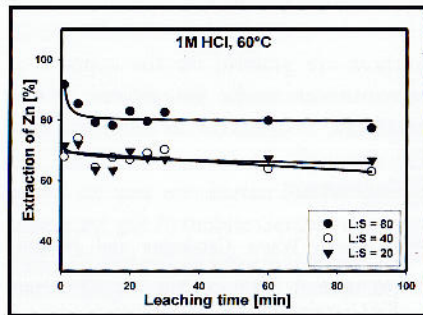


Fig. 16: Kinetic curves of Zn extraction in 1M HCl, 60°C and various L:S

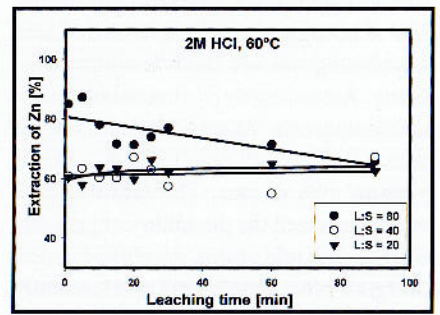


Fig. 17: Kinetic curves of Zn extraction in 2M HCl, 60°C and various L:S

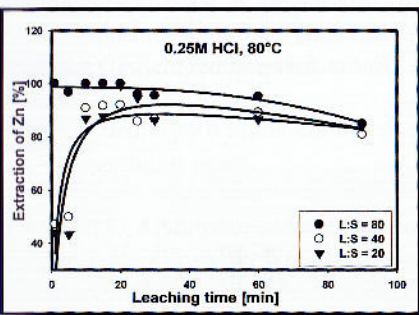


Fig. 18: Kinetic curves of Zn extraction in 0.25M HCl, 80°C and various L:S

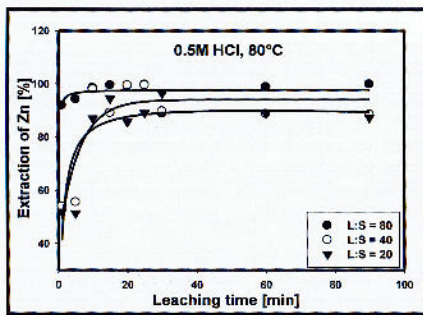


Fig. 19: Kinetic curves of Zn extraction in 0.5M HCl, 80°C and various L:S

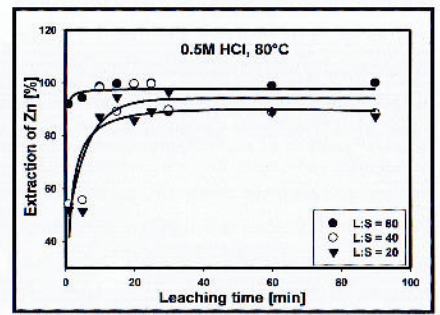


Fig. 20: Kinetic curves of Zn extraction in 1M HCl, 80°C and various L:S

extraction at other ratios were approximately the same. Increasing the duration of leaching zinc extraction slightly decreased. Increasing concentrations of HCl solution (Fig.17) has no significant effect on zinc extraction into the solution. The flux skimming was also leached at 80°C, at the above-mentioned ratios S:L and the con-

centration of HCl. Kinetic curves of zinc extraction are shown in Fig. 18 – 21. The kinetic curves of zinc extraction in a 0.25M HCl and at temperature 80 °C are shown in Fig.18. The highest extraction Zn (100%) was already achieved in the first minute at a ratio L:S = 80. Increasing leaching time has caused decreasing zinc

extraction to approximately 90% for all three ratios. Similar character of kinetic curves of zinc extraction can be observed in a 0.5M HCl Fig. 19. During the leaching of flux skimming in 1M HCl solution at temperature 80 °C was achieved the highest zinc extraction (almost 100%) at ratio L:S = 80 in 20

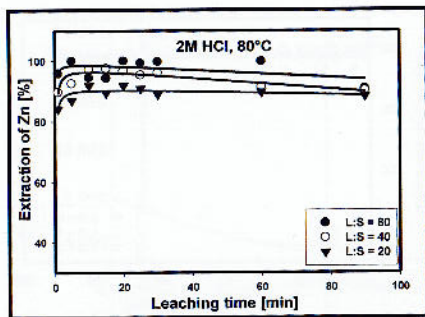


Fig. 21: Kinetic curves of Zn extraction in 2M HCl, 80°C and various L:S

minute. With increasing leaching time, the process has stabilized. From Fig. 20 it is seen moderate increase of zinc extraction at lower L:S ratios. Kinetic curves of zinc extraction in the leaching medium 2M HCl (Fig. 21) at all ratios L:S have quite the same behaviour. Effect of temperature and L:S ratio in the case of leaching in 2M HCl was negligible on zinc extraction.

Conclusions

The presented work briefly describes the flux skimming formation, which forms only during the wet batch hot-dip galvanizing. According to [1] flux skimming is hazardous waste. At present the skimming flux ends at landfill despite the fact that it contains 40% of zinc. The results of the work confirmed the possibility of processing flux skimming using simple hydrometallurgical processes. It was experimentally confirmed that the zinc leaching process is very fast and takes only a few minutes. The amount of leached zinc is affected by the hydrochloric acid concentration and temperature of process. The results of the zinc extractions show that higher temperatures and higher concentrations of HCl have no significant effect on maximum conversion of zinc into the solution. The optimum leaching time on zinc extraction into a solution is 30 min. The highest rate of zinc extraction (almost 100%) was achieved at temperature of 20°C, in 0.25M HCl and at ratio L:S = 40 during the first five minutes. shows, that on the leaching of flux skimming At temperature 40°C 0.5M concentration of HCl is sufficient for all ratios L:S (Fig.22) in term of the highest zinc extraction. Using less concentrated acid satisfies economic demands, reducing the process costs. It was also confirmed (Fig. 23) that the leaching of flux skimming at a lower temperature to 40°C is sufficient. Temperature increase has not positive effect on the zinc extraction. The

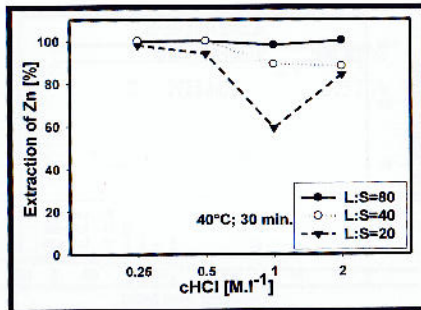


Fig. 22: The effect of HCl concentration on the extraction of Zn in 30 minutes at various leaching of L:S

optimal conditions for zinc extraction into the solution was achieved using 0.5M hydrochloric acid as a leaching agent, at the temperature 20-40°C and at ratio L:S = 80. These conditions are valid for given flux skimming owing to specific chemical and mineralogical composition. For leaching optimization of each flux skimming it is recommended to examine the processing conditions separately.

Acknowledgements

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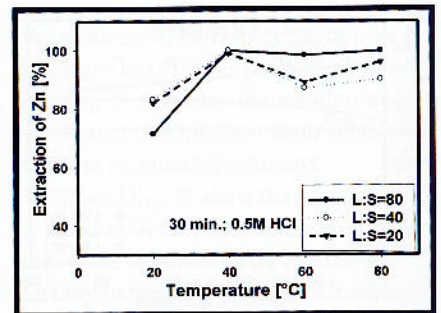


Fig. 23: The effect of temperature on extraction zinc in 30 minutes at various leaching L:S

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