THE ENTIRE REUSE OF THE WASTE WITH ZINC CONTENT

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REZUMAT. Metalele joacă un rol important în societatea modernă şi au fost asociate încă din trecut cu dezvoltarea industrială şi îmbunătăţirea standardelor de viaţă. Metalele pot fi reciclate aproape la infinit. Zincul, la fel ca şi celelalte metale, este pe deplin reciclabil. 80% din zincul disponibil pentru reciclare este reutilizat, reprezentând aproximativ 30% din totalul de zinc de pe piaţă. Valorificarea integrată a deşeurilor cu continut de zinc prezintă importanţă, atât din punct de vedere al protecţiei mediului, cât şi din punct de vedere economic.

Cuvinte cheie: deşeuri, recuperare, valorificare, zinc.

ABSTRACT. The metals play an important role în the modern society and were associated from the past with the industrial development and improving of the life standards. The metals can be recycled almost at the infinity. Zinc like other metals can be fully recycled. 80% from the available zinc for recycle is reused, representing almost 30% from the total zinc from the market. The complete recover and reuse of the wastes with zinc content present importance both from the environmental protection point of view and also from the economical point of view.

Keywords: wastes, recover reuse, zinc.

1. INTRODUCTION

The metals play an important role in the modern society and were associated from the past with the industrial development and improving of the life standards. The society can use like metals sources, the natural ore and also the metals removed after use. The prime materials are transformed (processed) by various technological processes, resulting useful product (finite product). These can be used accordingly or can constitute reused materials in other technological processes. Besides the finite products, in general, from the technological processed are obtained some secondary products with various uses, and also wastes [1-3].

Without any reason or specific purpose the modern industry created a linear model of the resources consume, according to figure 1.

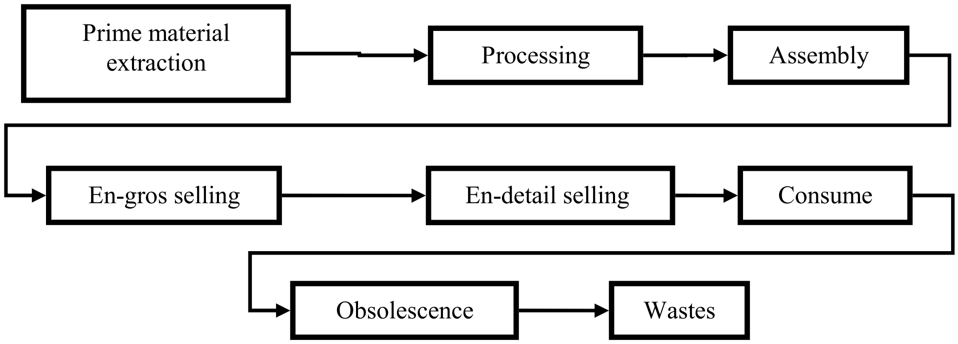

Fig. 1. The linear model of the resources consume.

The solid wastes stored in dump, occupy a large land surface, affecting the environment. Also, because of the rains, the soluble components are being infiltrated in soil and impure the freatic waters. The inefficient recover of the metals from the economy increase the necessity of using primary resources and can have an impact on the nature through increasing the metals dispersion in the ecosystems. The depletion of the reach resources leads to the exploitation and processing of the resources with lower content, which will create higher tensions of the environment. In general, can be said that in the obtaining process of different products is consumed higher energy than when are used natural resources, than when are used some recycled materials.

The model of the ecological industry accentuates the reuse security of the wastes generated by the society as a base line for the environment quality improvement. To realize this model, the industry and society should work together to recover the metals their recycling from secondary sources and to the minimal losses of materials from the industry-society system. In the last years, was outlined a new conception regarding the industry, which have in mind concomitant the wastes, energy preservation, materials recover and recycle. In conclusion, the linear idea of resources consume presented in figure 1 was changed with the cycle preservation of materials according to figure 2.

The metals can be recycled almost to infinity. Beside the plastic and polymers materials the metals properties can be integral returnable, not always with facility, regardless of their chemical and physical form. Though, the ability to recover the metals after their use depends by the way in which it were used initial and by their chemical reactivity. [4-6].

The zinc like the others metals, is completely recyclable. 80% from the available zinc for recycling is reused, representing almost 30% from the total zinc on the market [7, 8].

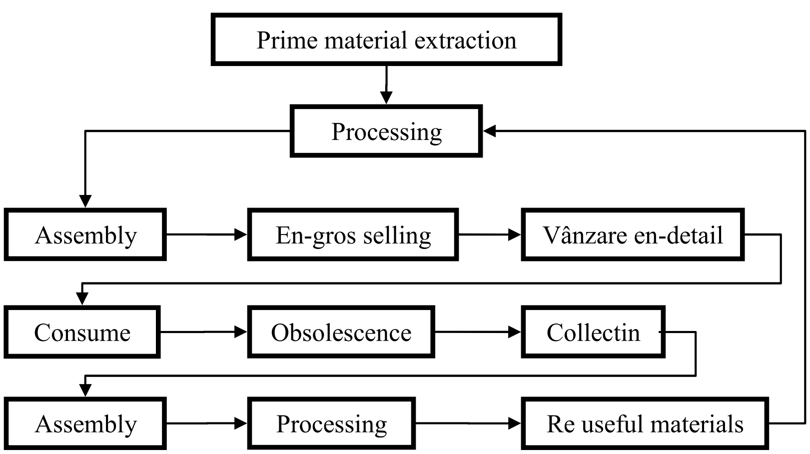

Fig. 2. The cycle model of the materials preservation.

Is used in many industries: to the alloy obtaining, to the with dyes obtaining in ceramics, to wood preservation, to fertilizers obtaining, in pharmaceutical and medicine obtaining, in the automotive industry, in foundry and constructions. Also the sinc present a large use in advances industries like the obtaining of the combustion fuels based on zinc and in water purification.

The most important use of zinc is the steel protection against corrosion, both from the quantity of used zinc, and also from the economical profits for the society. From the most used methods the most commune in the hot-dip galvanizing.

The hot-dip galvanizing is an industrial process, which was called a dirty industry because of the high quantities and varieties of wastes which results from the process [9-12].

The recover and reuse of the metals ions from these wastes present importance, both from environmental protection and economical point of view. So in the present paper, were made studies regarding the recover and reuse of the metals ions from wastes resulted from the hot-dip galvanizing process of the steals parts [13-22].

2. EXPERIMENTAL

The hot-dip galvanizing process has a negative impact on the environment from the solids and liquid emissions in atmosphere.

The residual solutions, resulted from the preparing process of the surfaces of the parts which will be coated, have a higher content of the metals ions and represent the higher quantity of wastes resulted in the hot-dip galvanizing process. So these solutions can not be discharged directly in the sewerage because they not fulfill the requirements of the NTPA 0002 normative, regarding the quality of the waste waters discharged in the municipal sewerage.

In this purpose were made studies regarding the establishment of the optimum conditions of the metals ions elimination from the residual waters, so this to be discharged and the metals ions to be recovered and reused. The metals ions (iron, zinc and lead) elimination from residual solutions was made by treatment using as neutralization agent: 30% NaOH solution, 10% Na_2CO_3 solution and CaO under suspension and solid form, the successive use of NaOH and Na_2CO_3.

Through the neutralization process take place the elimination of the metals ions, so these can be discharged in the sewerage, without any risk on the environment. The problem of the waste waters was resolved, but appears the question what happened with the sludge resulted after the neutralization process.

This disposal attitude leads to serious disadvantages, as it contributes to a great build up of environmentally hazardous materials on the earth's crust; on the other side, it does not consider the recovery of the heavy metals for re-use, which might represent an economy of raw materials and potential profit.

The heavy metal from the sludge resulted during thermal zinc coating can be extracted applying pyrometallurgical and hydrometallurgical procedure. In this purpose the optimum conditions of heavy metals removal from sludge by extraction with sulphuric acid and sodium hydroxide solution were established.

The zinc ash results at the surface of the coated batch and contains almost 80 % zinc. In spite of this the zinc ash is considered a waste. In this paper was made studies regarding the recover of zinc from zinc ash resulted during thermal zinc coating by extraction with hydrochloric acid, sulphuric and acetic acid solutions.

3. RESULTS AND DISCUSSION

The experimental data regarding the chemical composition of the wastes resulted from the hot-dip galvanizing are presented in table 1.

Table 1. **The chemical composition of the wastes resulted from the hot-dip galvanizing**

Residual solution			
Acidity	**Fe, g/L**	**Zn, g/L**	**Pb, mg/L**
52,7	28,6	2,84	4,95
Sludge			
Ca, %	**Fe, %**	**Zn, %**	**Pb, %**
1,35	51,8	4,05	0,11
Ash			
Ca, %	**Fe, %**	**Zn, %**	**Pb, %**
0,07	0,51	78,0	1,25

From the experimental data can be observed that the resulted wastes have a higher content of the metals ions, so these can be treated in the view of the metals ions recover and reuse.

For the elimination of the metals ions from the residual solution was followed the dependences of the metals ions residual concentration respective of the separation degree versus the reaction mass pH, stirring time, the ratio neutralization agent-residual solution and versus the nature of the neutralization agent.

The lime is the most efficient neutralisation agent because this have a low cost price, but is inefficient because the obtained separation degree of the metals ions are very small. From all the used neutralisation agents the most efficient is NaOH, but this is the most expensive too. Using Na_2CO_3 is obtained also good efficaciousness, but this present the disadvantage of an abundant frothing of the mass reaction. To eliminate these two disadvantages was use a mixed of NaOH and Na_2CO_3. In the case of solutions neutralisation with NaOH and aeration is obtained satisfactory results but only after 24 hours of aeration. In conclusions the optimum conditions of the heavy metals elimination from the waste waters resulted from thermal zinc coating are: the neutralisation agent the mixed of NaOH with Na_2CO_3 at a pH range in a interval 7 - 8, at an stirring time of 30 minute. In this case is obtained a residual concentration of the metals ions under the maximum admitted value (1 mg/L) by the legislation.

In case of the metals ions extraction from sludge with sulphuric acid can be observed that the metals ions extraction concentration, respective the extraction degree increase with the sulphuric acid concentration and are not influenced by the increase of the ratio S:L.

The obtained solution after extraction of metals ions from sludge with sulphuric acid can be used to the obtaining of products with zinc and iron. By treatment of sludge with ammonium solutions is realised a selective extraction of zinc ions and the resulted solution, which contain ammonium complex with zinc, can be used at the obtaining of liquid and solid fertilizers with zinc microelement. The resulted sludge after the extraction of zinc ions with ammonium solution can be used after decay at 400ºC as iron red pigment

From the experimental data can be observed that in the case of the extraction of metals ions from zinc ash, the metals ions extraction concentration and extraction degree is influenced by the studied parameters, these decrease with the increasing of ash fraction, and of the ratio Zn^{2+}: acid solution, and increase with the increasing of the acid concentration and with the increasing of the contact time..

It can be observed that are obtained almost 100% extraction degree in case oif use for extraction of the sulphuric and hydrochloric acid., in case of use for extraction of the acetic acid is obtained a extraction degree of zinc ions of almost 50%.

The obtained solution of zinc chlorine, zinc sulphate and zinc acetate, were purified to remove the iron ions. The chlorine solution contain 200 g/L Zn^{2+} and can be re-entered in the process to the obtaining of the flux solution, or can be used to the obtaining of other zinc compounds.

From the zinc sulphate and zinc acetate solution were obtained the respective salts, and after these annealing is obtained the zinc oxide.

4. CONCLUSIONS

Was established that the wastes resulted from the hot-dip galvanizing process, the metals ions (Fe, Zn) can be recovered and reused under useful products, avoiding the negative impact of these wastes on the environment, and in the same time these wastes represent a valuable secondary sources of zinc and iron.

The optimum condition of elimination, respective extraction of the metals ions from the resulted wastes in the process of hot-dip galvanizing are presented in table 2.

Table 2. **The optimum condition of elimination, respective extraction of the metals ions from the resulted wastes**

Waste	Optimum condition of recover and reuse	Results
Residual solution resulted after the preparing process of the steal parts in the view of coating	Succsevi neutralisaiton with sodium hydroxide and sodium carbonate at a stirring time of 30 minutes	Residual concentration of the metals ions under the maximum admitted value by the legislation The solutions can be discharged in the sewerage.
Sludge	Extraction with sulphuric acid: - stirring time 60 minute; - ratio L:S = 3:1; - sulphuric acid concentration 50%.	The obtained solution after an advanced purification can be used in the obtaining process of compounds with zinc and iron
Sludge	Extraction with ammoniac solution: - stirring time 5 minute; - ratio L:S = 3:1; - ammoniac solution concentration 25%.	The obtained solution can be used at the obtaining of the liquid fertilizers with the zinc microelements. The resulted sludge with iron content can be used at the obtaining of the iron red pigment.
Ash	- ash fraction < 0,315 mm; - acid concentration 20%; - contact time between ash and acid solution 30 minute; - ratio L:S = 1:1.	HCl- The chlorine solution of high purity can be re-entered in the process to the obtaining of the flux solution, or can be used to the obtaining of other zinc compounds. H_2SO_4 – obtaining of the zinc sulphate, respective of the zinc oxide CH_3COOH – obtaining of the zinc acetate, respective of the zinc oxide

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