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## Improving the Attractiveness of Waste Steel Cans for Steel Mills by Removing Tin

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### Abstract

The ever-increasing amount of municipal waste due to the rising demand for consumer goods presents a significant challenge in finding new, effective methods for material recovery and recycling. A considerable proportion of these materials are steel cans made of tin-coated steel sheets. Tin, being a metal with broad applications and limited natural resources, should be recovered from waste materials. Recovering/removing tin from waste steel cans would make them a more attractive raw material for steel mills. Processes for recovering tin from the surface of steel sheets in used cans mainly rely on hydrometallurgical methods. This paper presents the results of tin recovery from steel sheets using leaching with a 1M NaOH solution at 90°C. Tests were conducted on the removal of paint and varnish layers that inhibit the tin removal process. The results show that it is possible to improve the efficiency of tin recovery from cans through chemical treatment, which will significantly increase steel mills' interest in this type of waste as a valuable input for metallurgical processes and a source of iron. Closing the loop in a closed circuit involved the electrolysis of tin from the leaching solution.

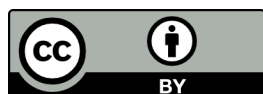
**Keywords:** tin, steel waste, recovery leaching process

### 1. Introduction

Metal packaging, mainly various types of cans, constitutes a significant group of municipal waste. In metal recovery processes from such waste, particular attention is paid to steel and aluminium, regardless of the protective coatings used in their production. For steel packaging, tin is of particular importance. This metal has a relatively low tendency to oxidise and does not undergo corrosion processes. For these reasons, tin is widely used as an anti-corrosion protection for steel sheets used in the production of food cans. Currently, the typical coating amounts to 2.8/2.8 g/m<sup>2</sup> on the outer and inner sides of the steel sheet, respectively. Tin is considered a contaminant in various grades of steel, and its content should not exceed 0.05-0.08%. It lowers the yield strength of steel, reducing the material's load-bearing capacity. Tin also increases the brittleness of steel and its

tendency to crack during hot plastic processing. One of the largest sources of tin contamination in steel is ferrous scrap. The development of modern steelmaking equipment, such as electric arc furnaces (EAF), increases the demand for steel scrap. In these furnaces, steel scrap constitutes the majority of the charge [1,2]. This necessitates careful control of tin content in the scrap. Due to the continuously growing amount of waste, recent years have seen research on metal recovery from various waste streams, such as batteries [3], LCD panels [4,5,6], NdFeB magnets [7], slags [8], electronic waste [9,10], including printed circuit boards [11,12], and anodic sludge [13]. Chen et al. investigated tin recovery from tin-coated steel wire using pyrite as a sulphurising agent [14].

The amount of currently estimated tin reserves on earth - established at the current level of its consumption, is determined according to various sources - as sufficient for the next 25-50



years. This fact determines that tin is classified as a potentially critical metal – a scarce one [15].

Globally, 14 raw materials are classified as critical or rare. This forms the basis for increasingly extensive research aimed at recovering these metals from residual waste. Grimes et al. [16] investigated the recovery of indium from solutions containing tin and lead, which are typical components of solutions generated by the leaching process of the metallic fractions of electronic waste.

The relatively large proportion of waste in the form of used cans in the municipal waste fraction makes the recovery of the tin they contain economically viable. Tin recovery/removal from the surface of waste steel tin sheet mainly relies on hydrometallurgical methods using aqueous alkaline solutions [17,18]. The application of the leaching process for metal recovery from various types of waste has been the subject of numerous publications [3-14, 16].

The use of tin in the aforementioned areas necessitates its recovery from waste raw materials, such as steel cans, while its removal from waste will make waste steel cans "more attractive raw materials for steel mills". Proper processing of these wastes, preceded by tin recovery, enables their utilisation in steelmaking. Developing new efficient methods for recovering tin from waste steel cans requires precise determination of its content level in the waste stream. For further processing of waste containing large amounts of tin-coated steel cans, it is crucial to properly prepare the scrap for use in steelmaking. This means the additional necessity of reducing the tin content in the feedstock material, as its presence as a non-ferrous metal in steels produced in electric arc furnaces with a high proportion of steel scrap causes numerous material defects in the products. The costs of tin removal processes could be offset by the sale of the recovered metal, especially since the price of tin on global markets is approximately 33,000 USD per ton [19]. The negative effect of tin on the properties of steel is due not only to its separation at grain boundaries or the formation of low-melting intermetallic compounds during solidification of continuous steel ingots, but also to its interaction with other harmful elements from scrap—in particular copper. The maximum allowable tin content in structural steels generally amounts to about 0.015%.

Therefore, it seems appropriate and necessary to seek new methods for recovering and removing tin present in the composition of steel sheets from waste cans.

The main goal of this work was to remove the layers of paint and varnish that hinder the process of recovering/removing tin from steel sheets. Removing tin from waste steel cans can increase their attractiveness as secondary raw materials for steel mills, thus boosting the recycling of such waste. This will have a positive impact on the natural environment.

## 2. Methodology

The primary goal of the research was to determine the basic parameters of the processes involved in the preliminary preparation of galvanised steel sheets for tin removal via leaching in a 1 M NaOH solution. The samples used in the study were

galvanised steel sheets obtained from a leading industrial producer of cans for food packaging. The steel sheet, with a thickness of 0.15 mm, was coated on both sides with tin layers weighing 2.8/2.8 g/m<sup>2</sup> each (outer/inner) and covered with epoxy-phenolic and polyester varnish coatings. The steel sheets were cut into discs with a diameter of 6 mm using a pneumatic press. The prepared material is shown in Figure 1.

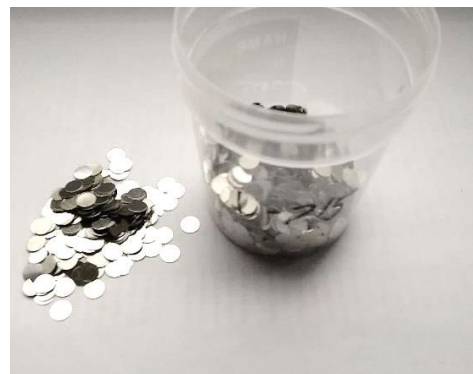


Fig. 1. Samples of steel sheets cut into discs

### 2.1. Removal of varnish and paint layers

Preliminary tests on tin leaching from tin-coated steel sheets showed that the layer of paints and varnishes effectively inhibits this process. Therefore, a 50 g sample of steel sheet discs was subjected to mechanical treatment to remove the varnish layer using a laboratory roller mill. This method enabled the removal of approximately 70% of the varnish and paint layers but also resulted in tin losses [20,21].



Fig. 2. Laboratory roller mill

The next step was to use an innovative chemical method for removing varnish layers. This method, besides effectively preparing the tin-coated sheets (after paint removal) for further tin recovery through hydrometallurgical methods, also ensures environmentally safe handling of the waste containing bisphenol A (BPA) from the removed varnish.

The leaching process was conducted in a laboratory chemical reactor produced by HEL (Figure 3). The leaching solution was a mixture of 10% NaOH and 10% ethylene glycol. The process was carried out for 30 minutes at a temperature of 95°C [21]. The

volume of the reaction liquid was 0.45 L, and the mass of the steel sheet sample was 100 g. Additionally, to ensure proper mixing of the reactor contents, a mechanical stirrer rotating at a constant speed of 600 rpm was used. The test sample was a tin-coated sheet with a tin coating weight of 2.8/2.8 g Sn/m<sup>2</sup>.



Fig. 3. Chemical removal of varnish and paint layers in a reactor. State after 1 minute of the process

Due to the possibility of tin losses during the leaching process, the absence of any visible damage to the tin coating structure was confirmed through studies conducted using an X-ray fluorescence device type Fischerscope® XRAY XDL manufactured by HELMUT FISCHER GmbH.

## 2.2. Tin Leaching

After the chemical removal of the protective layer, the steel sheet samples were subjected to tin leaching. The leaching was conducted in a 1 M NaOH solution for 180 minutes at a temperature of 90°C. The concentration of tin in the tested solution was determined using atomic emission spectroscopy (Agilent spectrometer MP-AES 4200).

## 2.3. Electrowinning

To complete the tin recovery/removal cycle, electrolysis was carried out using the solution obtained after leaching the steel sheet. Studies on tin electrowinning from the leaching solutions were conducted on a sample solution derived from leaching the steel sheet after the chemical removal of the protective paint and varnish layer, achieving a tin leaching level of 97%. The tin electrowinning test was carried out using an ELECTROLYSER MLW Labortechnik Ilmenau ELYN 1 electrolyser in a glass vessel with a volume of 0.1 dm<sup>3</sup>, filled with the test electrolyte in the amount of 0.06 dm<sup>3</sup>. Graphite rods with a diameter of 6 mm were used as electrodes inside the vessel. The distance between the electrodes, measured along their axes of symmetry, was 20 mm. The active height of the electrodes was 50 mm, and the active surface area was 970.26 mm<sup>2</sup>. The parameters of the electric current used were: current intensity  $I = 0.15$  A, current density  $J = 1$ , and voltage  $U = 3.5$  V. The tin electrowinning process was conducted at a temperature of 90°C, using an integrated stirrer and laboratory heater type MS 11HS. Before starting the experiment,

the cathodes were weighed. The mass measurement was carried out twice during the first phase of the process, lasting 30 minutes, at intervals of 15 minutes.

The collected sponge deposit was analysed using an X-ray diffraction device (D8 Advance) produced by Bruker, equipped with a copper lamp (CuK $\alpha$ ) and a semiconductor detector LynxEye. Phase analysis of the obtained diffractogram was conducted using Bruker AXS Eva software in collaboration with the ICDD PDF-2 database.

## 3. Research results

### 3.1. Leaching

Previous studies presented in [20] demonstrated the effective blocking of the tin leaching process by the paint and varnish layer. Therefore, the efficiency of tin leaching was compared for different steel sheet samples: (1) without the protective layer, (2) covered with a protective varnish layer, (3) after removing the layer mechanically in a roller mill, and (4) after removing the layer using the chemical method described in the study (Figure 4). The tin concentrations in the solution after leaching with 1 M NaOH at 90°C for 3 hours were 425, 56, 348, and 408 mg/dm<sup>3</sup>, respectively, for samples without the protective layer, with the layer of paint and varnish, and sheets subjected to mechanical and chemical treatment.

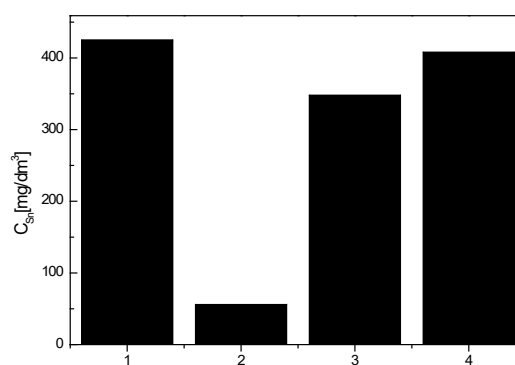


Fig. 4. Tin concentrations in a 1M NaOH solution after 3 hours of leaching for steel sheet samples: 1 – uncoated, 2 – coated on both sides with varnish, 3 – coated on both sides with varnish and mechanically treated, 4 – coated on both sides with varnish and chemically treated

The obtained results indicate the inhibitory role of the paint and varnish layer and the partial loss of tin from the sheet subjected to mechanical treatment. While mechanical treatment improved the leaching effect, it also caused tin loss, which ended up in the dust generated during hammering. For this reason, in subsequent stages of the presented work, a chemical method was used to remove the paint and varnish layer.

The results confirmed the possibility of completely removing the protective varnish layer within 30 minutes. The solution remaining after the process contained a suspension of solid particles derived from the varnishes removed from the surface of the sheets, as shown in Figure 5.



Fig. 5. Reaction mixture after the chemical removal of varnish layers from the tested steel sheet samples

The contaminated reaction liquid was subjected to gravitational filtration using laboratory filter paper (Figure 6). This resulted in a clear leaching solution. Additional tests confirmed that the reaction solution used for chemically removing varnish layers could be employed in a closed-loop technological system. This method of conducting the process requires periodic regeneration using integrated sedimentation and gravitational microfiltration equipment. Depending on the intensity of the process and the thickness of the removed varnish layers, the reaction solution should also be periodically replenished with its basic components, which precipitate as sediment and evaporate as volatile constituents.



Fig. 6. Reaction mixture after filtering the sediment on filter paper

Based on literature studies [22], it was determined that the sediment in the form of solid particles from the removed varnish layers (polyester, epoxy-phenolic) could be utilised as a filler for epoxy resins or as an additive for adhesive or plaster mortars used in construction after appropriate physicochemical testing.

To confirm the effectiveness of the chemical method for removing organic layers, steel sheets not coated with an organic layer and sheets after chemical removal of the varnish layer were subjected to the leaching process. As shown in Figure 7, both curves representing the tin ion concentration in the solution over time are very similar, indicating the high efficiency of the chemical method and confirming the integrity of the tin layer on the steel sheet. The chemical method and the composition of the

mixture have been refined and published in patents No. 238149 and 238150 [23,24].

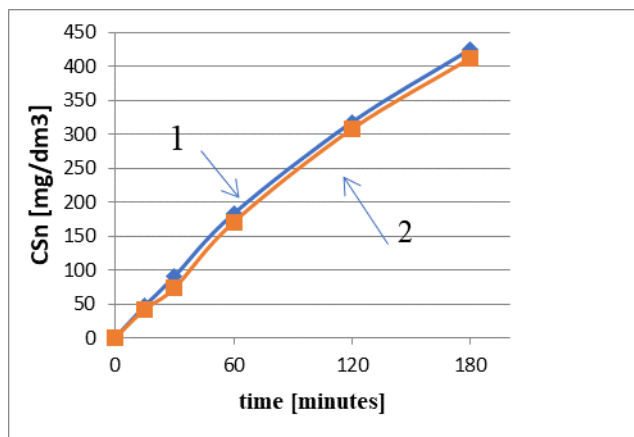


Fig. 7. Kinetics of tin leaching from steel sheet samples: 1 - not coated with paint, and 2 - sheets after chemical removal of the varnish layer using 1.0 M NaOH solution

### 3.2. Electrolytic tin deposition from the leaching solution

To close the loop of tin removal/recovery from steel sheets, the leaching solution was used in the electrolysis process. The cathode deposit formed during the tests, in the form of tin sponge, was observed using a NIKON SMZ 1500 microscope with 100x magnification. The results showed that it has a dendritic, highly branched structure, grey in colour (Figure 8).



Fig. 8. Microscopic photograph of the deposited tin sponge. Image magnified 100 times

The collected sponge deposit was analysed using an X-ray diffraction device. The diffraction spectrum is shown in Figure 9.

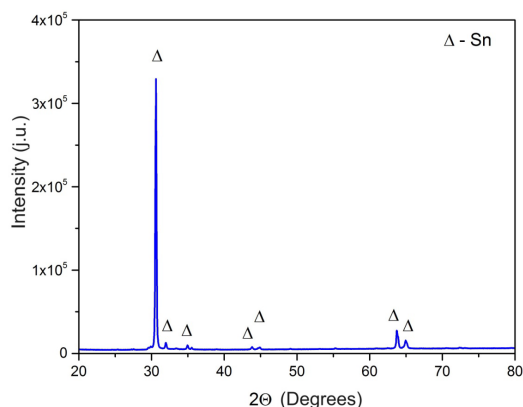


Fig. 9. X-ray diffraction spectrum of the tin sponge sample

According to the above graph, the results of the substance identification test of the examined deposit using the X-ray diffraction device showed that it is tin in metallic form, as evidenced by the characteristic peak indicating the intensity of reflections at the level of  $3.25 \times 10^5$ . This may indicate a high level of purity of the deposited tin.

## 4. Conclusions

In industrial recovery installations, tin in dusty form is partially retained on filters. However, some of the tin dust penetrates the environment in an unorganised manner during the operation of the installation, constituting what is known as workplace emissions. Along with these dusts, protective varnish dust from the surfaces of processed tin sheets also penetrates the environment. These varnishes are a source of bisphenol A (BPA), which is harmful to human health and often a component of these varnishes. Considering the value of tin losses during mechanical removal of varnish layers and the resulting emissions, it seems reasonable to use processes that effectively remove these varnish layers while eliminating unorganised emissions of contaminants into the environment. One method that combines both features is the chemical removal of varnish layers as a process preceding further treatment of sheets for tin recovery/removal. The studies demonstrated the high effectiveness of this method and its lack of impact on the tin layer covering the steel.

After removing the paint and varnish layer that inhibits the tin leaching process, this metal can be effectively removed or recovered. To close the loop, tin recovery through electrolysis is proposed. Given the high prices of this metal and limited natural resources, this process can offset its operational costs. Tin-free sheets can serve as more valuable and attractive raw materials in steel mills.

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